Infrared Intensities as a Quantitative Measure of Intramolecular Interactions. Part XXVII.[1] Substituents with Donor–Acceptor Character: the NSO Group

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It is shown that the NSO group has little resonance interaction with a benzene ring in the ground state but that it is capable of resonance donation or acceptance in the presence of a second substituent, depending on the electron demand. This variable interaction is compared with that of related groups.

CONSIDERABLE recent interest has been shown in the properties and reactions of *N*-sulphinylamines, particularly *N*-sulphinylanilines. Reports have been made of theoretical[2] and *X*-ray emission spectrographic[3] studies of electron densities, of dipole moments,[4,5] and of i.r.[6-8] and u.v. spectra. Analysis of the i.r. and Raman spectra of *N*-sulphinylaniline suggested[8] that the NSO group was coplanar with the benzene ring but was not collinear with the axis through the nitrogen atom and C-1 and C-4 of the benzene ring.†

Certain related substituents such as NCO and NCS show[9] variable electronic interaction with a benzene ring, dependent on the demand produced by a second substituent, particularly if this is attached in the conjugated *para*-position. It was possible to reverse the behaviour of such a substituent from resonance-donating to resonance-accepting by introducing a group such as NMe_2 in the *para*-position. Failure to appreciate that some substituents can display such variable π-interaction can lead to confusion, although some workers[4] have appreciated the possibility of such variable interaction

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† *Note added after submission.* Recent evidence (J. S. Bonham, C. L. Cheng, R. J. W. Le Fèvre, and G. L. D. Ritchie, *Austral. J. Chem.*, 1973, **26**, 421) indicates that the planar *trans*-form may be the preferred conformation rather than the planar *cis*-form represented in the diagrams in this paper. However, none of the conclusions are thereby affected.

[1] Part XXVI, T. J. Broxton, D. G. Cameron, R. D. Topsom, and A. R. Katritzky, preceding paper.

[2] V. V. Plemenkov and E. G. Kataev, *Str. Mol. Kvantoveya Khim.*, 1970, 146 (*Chem. Abs.*, 1971, **74**, 87,103).

[3] Y. Takahashi, K. Yabe, and T. Sato, *Bull. Chem. Soc. Japan*, 1969, **42**, 2707; Y. Tkahashi and K. Yabe, *ibid.*, p. 3064.

[4] G. Kresze and H. Smalla, *Chem. Ber.*, 1959, **92**, 1042.

[5] L. Janelli, U. Lamanna, and H. Lumbroso, *Bull. Soc. chim. France*, 1966, 3626.

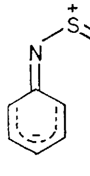
[6] G. Kresze and A. Maschke, *Chem. Ber.*, 1961, **94**, 450.

[7] G. Kresze, U. Uhlich, E. Ropte, and B. Schrader, *Z. analyt. Chem.*, 1963, **197**, 283.

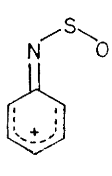
[8] C. V. Stephenson, W. C. Coburn, and W. S. Wildox, *Spectrochim. Acta*, 1961, **17**, 933.

[9] A. R. Katritzky, H. J. Keogh, S. Ohlenrott, and R. D. Topsom, *J. Amer. Chem. Soc.*, 1970, **92**, 6855.

in substituted N-sulphinylanilines [(I) and (II) represent the relevant canonical forms].



(I)



(II)

We have previously[10] measured the intensity of the ν_8 (ν_{16} in Herzberg's nomenclature) absorption of N-sulphinylaniline itself and thereby derived a σ°_R value of $\pm 0{\cdot}09$. A value of $+0{\cdot}13$ has been obtained[11] from ^{19}F shift measurements on *meta-* and *para*-fluoro-N-sulphinylanilines but this may be enhanced[9] by through-conjugation. Other reported i.r. work appears to be limited to general studies[8] or correlation[6,7] of ν_{NSO} frequencies and extinction coefficients with σ values for a series of substituted N-sulphinylanilines. We now report the intensities of ν_8 near 1600 cm^{-1} for a series of *meta-* and *para*-substituted N-sulphinylbenzenes; the results illuminate the resonance effects of the NSO group

EXPERIMENTAL AND RESULTS

The N-sulphinylanilines prepared are listed in Table 1. Two compounds not previously reported are 4-*fluoro*-N-*sulphinylaniline*, prepared from p-fluoroaniline by the general method[12] used for substituted N-sulphinylanilines, as a yellow oil, b.p. 107° at 16 mmHg (Found: C, 45·6; H, 2·7; N, 8·8. C_6H_4FNOS requires C, 45·9; H, 2·6; N, 8·9%); and 4-*cyano*-N-*sulphinylaniline*, similarly obtained from p-cyanoaniline as light yellow needles, m.p. 62—63° (Found: C, 51·4; H, 2·8; N, 16·8. $C_7H_4N_2OS$ requires C, 51·2; H, 2·5; N, 17·1%). The i.r. intensities (A in l mol^{-1} cm^{-2}) were measured for dilute solutions in carbon tetrachloride as previously described.[10] The reproducibility in $(A - 170)^{\frac{1}{2}}$ values is ± 1 except for the value for the di-N-sulphinyl-p-phenylenediamine (± 2). Care was taken to exclude moisture, which leads to hydrolysis of the N-sulphinyl group; this was found to be particularly necessary with the di-N-sulphinyl-p-phenylenediamine (studied in benzene because of low solubility in carbon tetrachloride).

TABLE 1

Intensities (A/l mol^{-1} cm^{-2}) for the ν_8 vibrations of *meta-* and *para*-substituted N-sulphinylanilines ($YC_6H_4{\cdot}NSO$)

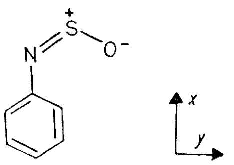
Y	ν/cm^{-1}	$A - 170$	M.p.[B.p.](°C)	Lit. m.p.[b.p.](°C)
para-Series				
NMe_2	1599	22661	72—73	72 [a]
MeO	1596, 1569	8002	25	26 [b]
F	1598, 1587	3325	[107 at 16 mmHg]	
Cl	1585, 1564	1219	32—33	36 [c]
Br	1589, 1575, 1561	1439	61	60—61 [c]
Me	1602, 1578, 1564	530	9	9 [c]
CN	1623, 1607	865	62—63	
NO_2	1621, 1601, 1588	2331	69	70 [c]
NSO	1585	336	111—112	113·5—114·5 [c]
meta-Series		$A - 340$		
MeO	1595, 1589, 1575	5268	[138—139 at 25 mmHg]	[98 at 2 mmHg]
Cl	1583, 1565	1952	[122—124 at 25 mmHg] [e]	[126—127 at 16 mmHg] [c]
Me	1603, 1594, 1573	887	[110—112 at 25 mmHg]	[220 at 760 mmHg] [c]

[a] A. Francke, *Ber.*, 1898, **31**, 2179. [b] Ref. 4. [c] Ref. 12. [d] Ref. 6. [e] Found: C, 41·3; H, 2·5; N, 8·1. Calc. for C_6H_4ClNOS: C, 41·5; H, 2·3; N, 8·1%.

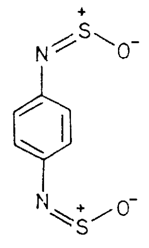
DISCUSSION

Asymmetry.—Monosubstituted benzenes of less than C_{2v} symmetry, such as N-sulphinylaniline (III), have ν_8 intensities made up of contributions in both x and y directions. The σ°_R value previously[10] obtained from equation (1) applicable to monosubstituted benzenes was $\pm 0{\cdot}09$. The A value reported here for di-N-sulphinyl-p-phenylenediamine allows[13,14] the calculation of $\sigma^\circ_R y$ as 0·11 from equation (2).

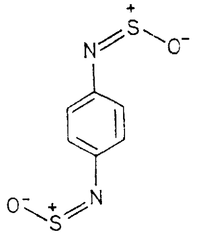
$$A = 17{,}600\,(\sigma^\circ_R)^2 + 100 \qquad (1)$$



(III)



(IV)



(V)

This assumes that the *cis-* (IV) and *trans-* (V) forms occur in equal amounts.

$$A = 15{,}000\,(\sigma^\circ_R y)^2 + 170 \qquad (2)$$

Within this assumption and the accuracy of the overtone contributions of 100 and 170 above it appears that $\sigma^\circ_R x$, equivalent to the normally described resonance interaction of the substituent with the ring, is close to zero.

para-*Substituted* N-*Sulphinylanilines*.—Earlier work[13] showed that the resonance interactions in *para*-disubstituted benzenes could be described by equation (3),

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

where λ represents the change in interaction in addition to that expected for additivity of substituent effects. Equation (4) is applicable where one of the substituents,

$$A - 170 = 15{,}000\,[(\sigma^\circ_R s - \sigma^\circ_R x + \lambda)^2 + (\sigma^\circ_R y)^2] \qquad (4)$$

such as NSO, has lower than C_{2v} symmetry. An analysis[13] of many earlier results had led to the adoption of

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[10] 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.

[11] R. W. Taft and W. A. Sheppard, reported in ref. 10.

[12] A. Michaelis, *Annalen*, 1893, **274**, 173.

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

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

15,000 instead of 11,800[14] for the constant in equations (2)—(4) and we therefore also briefly reconsider some results reported[9] earlier for related substituents, and demonstrate that the conclusions made still hold.

TABLE 2

Electronic interactions in *para*-substituted *N*-sulphinylanilines, phenyl isocyanates, phenyl isothiocyanates, phenyl azides, phenyl isocyanates, and nitrosobenzenes

Substituents		$\left(\frac{A - 170}{15,000}\right)^{\frac{1}{2}}$ [a]	$[\sigma^\circ_R(1) - \sigma^\circ_R(2)]$ [b]	λ [c]	f_p [d]
NSO	NMe_2	1·22	0·54	0·63	1·17
	MeO	0·72	0·43	0·33	0·76
	F	0·46	0·34	0·12	0·46
	Cl	0·26	0·22	0·05	0·27
	Br	0·29	0·23	0·08	0·31
	Me	0·16	0·10	0·88	0·18
	CN	0·21	−0·09	*e*	
	NO_2	0·38 [f]	−0·17	*e*	
NCO	NMe_2	0·50	0·13	0·38	0·51
	F	0·11	0·06	0·07	0·01
	Cl	0·23	−0·19	−0·05	0·24
	Me	0·22	−0·30	0·05	0·25
	NO_2	0·68 [f]	−0·58	*e*	
NCS	NMe_2	0·54	0·18	0·38	0·56
	F	0·13	0·01	0·07	0·06
	Cl	0·17	−0·13	−0·04	0·17
	Me	0·15	−0·25	0·05	0·20
	NO_2	0·66 [f]	−0·52	*e*	
N_3	NMe_2	0·51	0·19	0·35	0·54
	F	0·07	0·00	0·06	0·06
	Cl	0·16	−0·13	−0·05	0·18
	Me	0·17	−0·25	0·04	0·21
	NO_2	0·63 [f]	−0·52	*e*	
NC	NMe_2	0·54	0·39	0·21	0·60
	F	0·17	0·19	0·04	0·23
	Cl	0·12	0·07	0·01	0·08
	Me	0·10	−0·05	0·02	0·03
NO	NMe_2	0·94	0·60	0·25	0·85
	OMe	0·59	0·50	0·13	0·63
	F	0·42	0·41	0·05	0·46
	Cl	0·24	0·29	0·02	0·31
	Br	0·26	0·30	0·03	0·33
	Me	0·25	0·17	0·03	0·20
	NO_2	0·19 [f]	−0·10	*e*	
	COMe	0·12	−0·15	*e*	
	CO_2Me	0·09	−0·11	*e*	
	CN	0	−0·02	*e*	

[a] *A* Values (in l mol^{-1} cm^{-2}) from ref. 9 or this paper. Values for substituted *N*-sulphinylanilines or phenyl azides are corrected for asymmetry. [b] $\sigma^\circ_{R}x$ used instead of $\sigma^\circ_R(1)$ for NSO and N_3. [c] $\lambda = (\sigma^+ - \sigma^\circ)_D K_X$ for donor–acceptor pairs, and the difference between this and $(\sigma^\circ_R)_D K_X$ for cases where both substituents are subject to interactions into *d*-orbitals in the opposite direction. [d] $f_p = |[\sigma^\circ_R(1) - \sigma^\circ_R(2) + \lambda)|$. [e] $(\sigma^+ - \sigma^\circ)$ Values for NSO, NCO, NCS, N_3, and NO are not available. [f] Values for *para*-substituted nitrobenzenes are enhanced by interaction with ν_{NO_2} (see ref. 13).

Table 2 lists values of $[(A - 170)/15,000]^{\frac{1}{2}}$ and of $[\sigma^\circ_R(1) - \sigma^\circ_R(2)]$. It can be seen that considerable discrepancies (Δ) * exist between these quantities for all the classes of substituents studied, demonstrating the existence of strong substituent–substituent interactions of NSO, NCO, NCS, N_3, NC, and NO groups with both donor and acceptor substituents. These discrepancies may be treated quantitatively. Where the substituent acts as an electron acceptor the appropriate equation is (5),[13,14] where $(\sigma^+ - \sigma^\circ)$ values were taken from ref. 13.

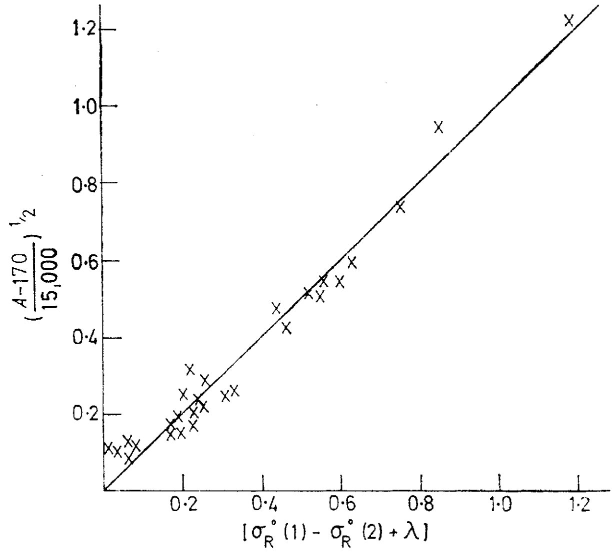
$$\lambda = K_A(\sigma^+D - \sigma^\circ D) \qquad (5)$$

The K_A values calculated from plots of Δ *vs.* $(\sigma^+D - \sigma^\circ D)$ are as follows:

Group:	NSO	NCO	NCS	N_3	NO	NC
K_A	0·50	0·30	0·30	0·28	0·20	0·15

The error in fitting best lines was ±0·04. The values for the groups other than NSO are of smaller magnitude than previously reported,[9] because of the improved form of the equation used, but the previous conclusions are maintained (see below).

The magnitude of K_A for NSO may well result from the ability of the sulphur to accept electrons into its *d*-orbitals.



Plot of $[(A - 170)/15,000]^{\frac{1}{2}}$ *vs.* $[\sigma^\circ_R(1) - \sigma^\circ_R(2) + \lambda]$ for *para*-substituted *N*-sulphinylanilines, phenyl isocyanates, phenyl isothiocyanates, phenyl azides, phenyl isocyanides, and nitrosobenzenes; the line shown has unit slope.

For interaction with the *d*-orbital acceptors chlorine and bromine, in which the foregoing groups act as electron donors, λ is given by equation (6), in which $K_X = 0·21$ for chlorine and 0·32 for bromine.[13]

$$\lambda = K_X\sigma^\circ_R D \qquad (6)$$

Table 2 includes values of λ calculated by equations (5) and (6) and of $f_p = [\sigma^\circ_R(1) - \sigma^\circ_R(2) + \lambda]$. There is satisfactory agreement between $[(A - 170)/15,000]^{\frac{1}{2}}$ and f_p as indicated in the Figure.

The discrepancies for cases where the second substituent is a resonance acceptor indicate increased donor tendency in all the substituents studied. It is clear that NCO, NCS, N_3, NSO, and NC groups can change from donor to acceptor or near acceptor behaviour under conditions of strong electron excess. On the other hand they show increased donor behaviour when placed *para* to electron acceptors or *d*-orbital acceptors. Thus certain substituents not only show continuously variable

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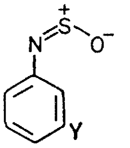
* We use Δ to denote the experimental difference between $[(A - 170/15,000]^{\frac{1}{2}}$ and $[\sigma^\circ_R(1) - \sigma^\circ_R(2)]$ and use λ to denote the calculated correction term.

π-interaction, depending on the electron demand, but may also, at an extreme, change the direction of their effect.

meta-*Substituted* N-*Sulphinylanilines*.—Equation (7) was previously developed[15] to relate the combined intensity of the 1600 and 1585 cm^{-1} bands of *meta*-disubstituted benzenes to σ°_{R} terms where one of the substituents (1) was of lower than C_{2v} symmetry.

$$A - 340 = 19{,}000\,\{[\sigma^{\circ}_{R}(1)]^2 + [\sigma^{\circ}_{R}(2)]^2 + \sigma^{\circ}_{R}(2)\,(\sigma^{\circ}_{R}x \pm \sqrt{3}\sigma^{\circ}_{R}y)\} \quad (7)$$

Application of this equation to *m*-methoxy-, chloro-, and methyl-*N*-sulphinylanilines leads to alternative *A* values of 5620 or 2520, 2270 or 680, and 1100 or 380, respectively. Comparison of these values with those reported in Table 1 shows that one of the two possible conformations (VI) or (VII) [corresponding to the choice of sign in equation (7)], is much preferred. In the absence of knowledge of the direction of $\sigma^{\circ}_{R}y$ this form cannot be assigned.



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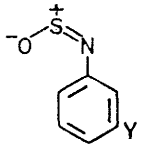

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[3/1196 *Received*, 8*th June*, 1973]

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