Infrared Intensities as a Quantitative Measure of Intramolecular Interactions. Part XXV.[1] Interactions between Substituents in *para*-Disubstituted Benzenes

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The relation of ν_8 i.r. intensities (including previously unpublished data) for *para*-disubstituted benzenes to σ°_R constants is considered in the light of: (i) statistic analysis assuming no interaction between substituents of the same electronic nature; (ii) differences between ^{19}F n.m.r.- and i.r.-determined σ°_R values; (iii) rotational barriers; (iv) theoretical analysis including measurement of deuteriated derivatives; and (v) the variable demand interaction approach developed by Blagdon. Through-conjugation in *para*-disubstituted benzenes is treated quantitatively in terms of interaction between donor and acceptor groups. Previous work is reassessed. Mixing occurs between ν_8 and ν_{NO_2} in *para*-substituted nitrobenzenes.

ADDITIONAL interaction (through-conjugation) occurs when one resonance donor and one resonance acceptor substituents are attached *para* to each other on a benzene ring. The estimation of such 'through-conjugation' and also of interactions between a π-electron donor and a *d*-orbital acceptor placed *para* to one another in a benzene ring has attraced much attention over the past decade. In particular, the utility of many methods of measuring substituent effects, such as n.m.r. and reactivity measurements, depend on such interactions being either of known magnitude or absent.

Some years ago, we reported [2] a method for estimating such interactions from i.r. intensities. The i.r. method depended on the empirical observation that the measured intensity of the ν_8 (ν_{16} in Herzberg's notation) vibrations of mono- and di-substituted benzenes could be related to the σ°_R value of the substituent. The relations reported were equations (1) and (2), where the constants

$$\text{mono}^3 : A = 17{,}600\,(\sigma^\circ_R)^2 + 100 \qquad (1)$$

$$para\text{-di}^2: \quad A = 11{,}800\,[\sigma^\circ_R(1) - \sigma^\circ_R(2) + \lambda]^2 + 170 \qquad (2)$$

100 and 170 were suggested to arise from overtone absorptions known to occur in the region. The proportionality constant in equation (1) was obtained [3] by plotting A (in l mol^{-1} cm^{-2}) against $(\sigma^\circ_R)^2$ values derived from n.m.r. and reactivity measurements. The form of equation (2) for the *para*-disubstituted compounds derives from the supposition that in addition to the interactions of each substituent separately with the benzene ring [terms in $\sigma^\circ_R(1)$ and $\sigma^\circ_R(2)$], allowance has to be made for the interactions between the substituents referred to above (term λ). The *para*-series proportionality constant of 11,800 was derived empirically using compounds with either two donor or two acceptor substituents, for which compounds the through-conjugation (λ) was assumed to be zero. Values of λ were then obtained for donor–acceptor-substituted compounds by fitting to the equation; this treatment was applied [2,4,5] to both π- and *d*-orbital acceptor groups and was also extended to *para*-disubstituted alkylbenzenes.[6]

The i.r. method thus offers an independent and direct approach for the investigation of through-conjugation. We [2,4-8] and other workers [9] have employed it to look at interactions in a variety of substituted benzenes and have, for example, established that certain substituents show π-electron interactions proportional to the electron demand of the attached aromatic system. Clearly, the magnitudes of λ and hence quantitative estimates of through-conjugation necessarily depend on the value of the proportionality constant of equation (2). The value of 11,800 adopted in 1968 was emphasised [2] as tentative and was based on the assumption that $\lambda = 0$ for donor–donor and acceptor–acceptor compounds; compounds for which only limited data were then available.

Reanalysis of the original,[2] subsequently published,[4-8] and further data reported have now indicated a constant of 15,000 ± 1000 [equation (3)]. This paper shows how

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

several independent approaches are consistent with these values, and comments on the implication of the revision as regards the earlier conclusions on qualitative and quantitative estimates of through-conjugation and other interactions in *para*-disubstituted benzenes. We also clear up the discrepancy which remained in the earlier work regarding nitro-compound intensities.

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† On leave from the University of Rostov-on-Don.

[1] Part XXIV, R. T. C. Brownlee, D. G. Cameron, R. D. Topsom, A. R. Katritzky, and A. J. Sparrow, *J. Mol. Structure*, 1973, **16**, 365.

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

[3] R. T. C. Brownlee, A. R. Katritzky, T. T. Tidwell, and R. D. Topsom, *J. Amer. Chem. Soc.*, 1968, **90**, 1757.

[4] J. M. Angelelli, R. T. C. Brownlee, A. R. Katritzky, R. D. Topsom, and L. Yakhontov, *J. Amer. Chem. Soc.*, 1969, **91**, 4500.

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

[6] T. J. Broxton, L. W. Deady, A. R. Katritzky, A. Liu, and R. D. Topsom, *J. Amer. Chem. Soc.*, 1970, **92**, 6845.

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

[8] N. C. Cutress, T. B. Grindley, A. R. Katritzky, M. V. Sinnott, and R. D. Topsom, *J.C.S. Perkin II*, 1972, 2255.

[9] See, for example, D. Martin, and W. M. Brause, *Chem. Ber.*, 1969, **102**, 2508; I. W. Serfaty, T. Hodgins, and E. T. McBee, *J. Org. Chem.*, 1972, **37**, 2651; A. Soumia, Thesis, University of Science and Technology of Languedoc, 1972.

TABLE 1

Intensities (A/l mol^{-1} cm^{-2}) for the ν_8 vibrations of some *para*-disubstituted benzenes

Substituents		ν/cm^{-1}	(A − 170) ν_8	M.p. (°C)	Lit. m.p. (°C)	Ref. to prep.
CN	CO_2Me	1612, 1565	273	65—66	62[a]	*a*
CN	SO_2Me	1597, 1570	0[b]	142—143	141[c] 142[d]	*c*
CN	CF_3	1623, 1580	180			*e*
COMe	CO_2Me	1610, 1570	480[b]	94—95	93—94[f]	*f*
COMe	SO_2Me	1595, 1573	286[b]	127—128	127—128	*g*
COMe	CF_3	1617, 1579	263			*e*
COMe	CN	1608, 1567	371			*e*
CHO	CO_2Me	1610, 1578	437[b]	58—59	60[a]	*a*
CHO	SO_2Me	1599, 1578	648[b]	156—157	157[c]	*c*
CO_2Me	SO_2Me	1600, 1576	125	118—119	118—119[h] 119[d]	*h*
CO_2Me	CF_3	1602, 1586	145	B.p. 89—90 (18 mmHg)	B.p. 94—95° (21 mmHg)	*j*
F	$N[CH_2]_4$	1613, 1586	950	28	*k*	*l*
OAc	$N[CH_2]_4$	1609, 1582	3444	69	*m*	*n*

[a] K. H. Slottag and R. Kethur, *Ber.*, 1938, **71**, 335. [b] In $CHCl_3$ solvent; all others in CCl_4. [c] A. T. Fuller, I. M. Tonkin, and J. Walker, *J. Chem. Soc.*, 1945, 633. [d] O. Manasck, O. Exner, and P. Zuman, *Coll. Czech. Chem. Comm.*, 1968, **33**, 3988. [e] Commercial sample, recrystallised before use. [f] E. D. Bergmann and J. Blum, *J. Org. Chem.*, 1959, **24**, 549. [g] G. B. Backman and C. L. Carlsen, *J. Amer. Chem. Soc.*, 1951, **73**, 2857. [h] H. S. Forrest, A. T. Fuller, and J. Walker, *J. Chem. Soc.*, 1948, 1501. [j] Y. Okamoto, T. Inukai, and H. C. Brown, *J. Amer. Chem. Soc.*, 1958, **80**, 4969. [k] Found: C, 73·0; H, 7·2; N, 7·8. $C_{10}H_{12}FN$ requires C, 72·7; H, 7·3; N, 8·5%. [l] From reaction of *para*-fluoroaniline with 1,4-dibromobutane (A. H. Sommers, *J. Amer. Chem. Soc.*, 1956, **78**, 2439). [m] Found: C, 69·6; H, 7·3; N, 6·6. $C_{12}H_{15}NO_2$ requires C, 70·2; H, 7·4; N, 6·8%. [n] From reaction of *para*-acetoxyaniline with 1,4-dibromobutane.

TABLE 2

Intensity values (A − 170) (in l mol^{-1} cm^{-2}) for the ν_8 bands of resonance donor–donor and acceptor–acceptor *para*-disubstituted benzenes (C_6H_4XY)

X	Y	A − 170	[$\sigma^\circ_R(1) - \sigma^\circ_R(2)$]	$\left(\frac{A-170}{15,000}\right)^{\frac{1}{2}}$	Δ†
$N[CH_2]_4$	OAc	3444[a]	0·39	0·48	0·09
	F	950[a]	0·29	0·25	−0·04
NMe_2	OMe	0[b]	0·10	0·00	−0·10
	F	210[b]	0·19	0·12	−0·07
	Bu^t	2829[c]	0·41	0·44	0·03
	Pr^i	2480[c]	0·42	0·41	−0·01
	Et	2777[c]	0·43	0·43	0·00
	Me	2030[c]	0·43	0·37	−0·06
NHMe	F	240[b]	0·18	0·13	−0·05
	Me	2560[b]	0·42	0·42	0·00
ND_2	OMe	0[b]	0·04	0·00	−0·04
	F	250[b]	0·13	0·13	0·00
OMe	F	72[b]	0·09	0·07	−0·02
	ND_3^+	730[b]	0·24	0·22	−0·02
	Bu^t	1628[c]	0·30	0·33	0·03
	Pr^i	1568[c]	0·31	0·33	0·02
	Et	1573	0·32	0·33	0·01
	Me	1360[c]	0·33	0·30	−0·03
	$CH[CH_2]_2$	1235[c]	0·25	0·29	0·04
	CH_2Cl	2590[d]	0·40	0·42	0·02
OH	Me	1290[b]	0·30	0·30	0·00
F	ND_3^+	210[b]	0·15	0·12	−0·03
	Me	580[b]	0·24	0·20	−0·04
Me	ND_3^+	0[b]	0·08	0·00	−0·08
	CH_2Cl	87[b]	0·07	0·08	0·01
SO_2Me	CN	0[a]	0·02	0·00	−0·02
	CO_2Me	125[a]	0·10	0·09	−0·01
	COMe	286[a]	0·16	0·14	−0·02
	CHO	648[a]	0·18	0·21	0·03
CN	CF_3	180[a]	0·02	0·11	0·09
	CO_2Me	273[a]	0·07	0·14	0·07
	CO_2Et	160[b]	0·09	0·10	0·01
	COMe	371[a]	0·13	0·16	0·03
CF_3	CO_2Me	145[a]	0·05	0·10	0·05
	COMe	263[a]	0·11	0·13	0·02
CO_2Me	COMe	480[a]	0·06	0·18	0·12
	CHO	437[a]	0·09	0·17	0·08

[a] This paper. [b] Ref. 2. [c] Ref. 6. [d] Ref. 25.

† $\Delta = [(A - 170)/15,000]^{\frac{1}{2}} - [\sigma^\circ_R(1) - \sigma^\circ_R(2)]$.

EXPERIMENTAL, CALCULATIONS, AND RESULTS

The methods of preparation and physical constants of *para*-disubstituted benzenes for which intensities for the ν_8 bands are first reported here are given in Table 1. The intensities (A) were measured for dilute solutions in carbon tetrachloride or chloroform in the manner previously described.[10]

We have previously[2] demonstrated that the ν_8 intensities of most *para*-disubstituted benzenes are virtually independent of solvent, although those of compounds having both a strong donor and strong acceptor group increase in intensity with increase in polarity of the solvent. This is not a problem for the results reported here, since the solvents are of similar and relatively low polarity.

The intensities of the ν_8 vibrations of the *para*-deuterio-substituted benzenes were of magnitude similar to those of the corresponding mono-compounds. The intensities of both series were therefore measured[1] by an improved method involving[11] separating the spectral trace into component peaks of variable Gaussian–Lorentzian type. This method has been shown[11] to be highly reproducible; the intensity values obtained are somewhat higher than those from the manual integration method mainly since proper allowance is made for the wings. A comparison of the measured intensities for the series C_6H_5Y and p-DC_6H_4Y is given in Table 6.

(1) *Evidence for Through-conjugation in* para-*Disubstituted Benzenes*

Procedure and Summary.—Evidence regarding the magnitude of the proportionality constant in equation (3) is obtained by the following means: (i) by the assumption that donor–donor and acceptor–acceptor compounds do not experience substituent–substituent interactions (as previously); (ii) by estimation of through-conjugation in *para*-substituted fluorobenzenes by comparison of σ°_R values determined by the ^{19}F n.m.r. and i.r. methods; (iii) from rotation barriers; (iv) from theoretical calculations including a study of deuterio-derivatives; and (v) from the variable demand interaction approach developed by Blagdon.[12]

All these approaches are consistent with a constant of 15,000 ± 1000 for equation (3).

(i) *Reanalysis of Results for Donor–Donor and Acceptor–Acceptor* para-*Disubstituted Benzenes.*—In Table 2 we list ν_8 intensity values ($A - 170$) for such compounds together with the substituent constant difference $\sigma^\circ_R(1) - \sigma^\circ_R(2)$. Figure 1 shows a plot of ($A - 170$) against $[\sigma^\circ_R(1) - \sigma^\circ_R(2)]^2$ from these results. The small correction for asymmetry[2] has not been applied, since this requires a knowledge of the proportionality constant being investigated. The line shown is the least squares plot through origin. Equation (4) is obtained with a standard deviation of 290. The previous value of 11,800 was adopted on the basis of results then available for twenty-one donor–donor and two acceptor–acceptor *para*-disubstituted benzenes. Of these only ten had ($A - 170$) values of greater than 340 units, that is twice the value of the overtone. (Results from symmetrically *para*-disubstituted benzenes indicated[2] a variation of between 100 and 220 units in the overtone intensity.)

$$A - 170 = 15{,}150\,[\sigma^\circ_R(1) - \sigma^\circ_R(2)]^2 \qquad (4)$$

(ii) ^{19}F *Shielding Parameters in* para-*Substituted Fluorobenzenes.*—In a *para*-disubstituted benzene with one resonance-acceptor substituent (A) and one resonance-donor substituent (D) then if a and d are the corresponding σ°_R values obtained from the monosubstituted benzenes, through-conjugation involves additional charge transfer as in (I) and results in effective σ°_R values of $a + \delta$ and $d - \delta$, respectively. Hence in the i.r. method, $\lambda = 2\delta$.

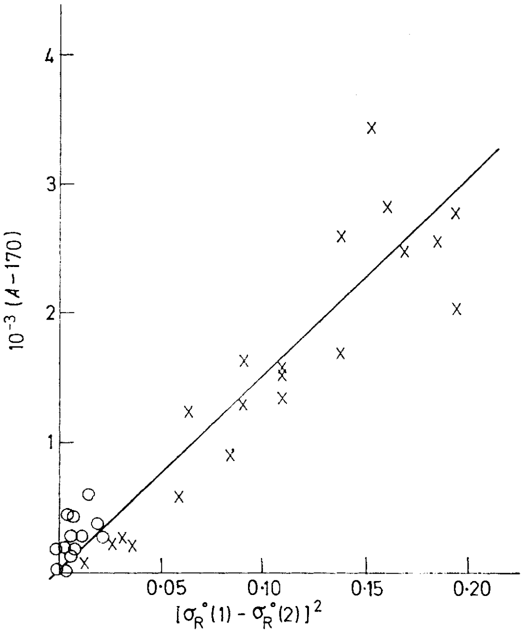
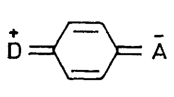


FIGURE 1 Plot of ($A - 170$) against $[\sigma^\circ_R(1) - \sigma^\circ_R(2)]^2$ for donor–donor (×) and acceptor–acceptor (○) *para*-disubstituted benzenes



(I)

The difference between the ^{19}F n.m.r. shifts in correspondingly *meta*- and *para*-substituted fluorobenzenes is proportional[13] to σ°_R. On the reasoning above, we had earlier believed that the ^{19}F shifts observed in *para*-resonance-acceptor-substituted fluorobenzenes reflected only half the amount measured by the i.r. method (that is δ). As explained below we now appreciate that

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

[11] R. T. C. Brownlee, D. G. Cameron, B. Ternai, and R. D. Topsom, *Appl. Spectroscopy*, 1971, **25**, 564; R. T. C. Brownlee, D. G. Cameron, and R. D. Topsom, in preparation.

[12] D. Blagdon, submitted for publication.

[13] 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.

the ^{19}F shifts are also enhanced by *ca.* 2δ in these cases and can therefore be directly compared with i.r. results for *para*-substituted fluorobenzenes.

The change of π-density at the carbon atom adjacent to fluorine caused by attaching a substituent at the *para*-position is close to the change caused at the 1-position carbon atom of benzene itself by similarly attaching a 4-substituent. This change of π-density at the α carbon atom is [14,15] linearly related both to the total change of π-density in a benzene ring brought about by the attachment of a substituent and to the σ°_{R} value of the substituent. The fluorine π-densities for π-electron acceptor substituents follow a linear relationship of about one seventh of the change at the α carbon; however, the ratio is about one fourteenth for π-electron donors. This was interpreted [14] as evidence for through-conjugation in *para*-electron-acceptor-substituted fluorobenzenes leading to additional π-charge removal from the fluorine orbitals without any important effect at the adjacent carbon atom. The ^{19}F shift is thus apparently determined both by the density at the fluorine and by that at the neighbouring carbon atom, since a plot of the shifts against σ°_{R} would not be linear for both electron-accepting and electron-donating substituents if they were determined solely by the density at the fluorine. The ^{19}F values should therefore include a contribution of *ca.* 2δ relating to through-conjugation and should lead to σ°_{R} values for resonance-accepting substituents which are enhanced compared with those obtained by i.r. studies on monosubstituted benzenes. To this approximation equation (5) follows for a series of *para*-substituted fluorobenzenes. Comparison of equation (5) with equation (2) for *para*-disubstituted benzenes leads to equation (6), where c is a constant reflecting the value of σ°_{R} for the fluorine substituent.

$$\sigma^{\circ}_{R}\ (\text{n.m.r.}) - \sigma^{\circ}_{R}\ (\text{i.r.}) = 2\delta = \lambda \qquad (5)$$

$$(A - 170)^{\frac{1}{2}} = b^{\frac{1}{2}}\,[\sigma^{\circ}_{R}\ (\text{n.m.r.}) - \text{c}] \qquad (6)$$

Figure 2 shows a plot of $(A - 170)^{\frac{1}{2}}$ *versus* σ°_{R} (n.m.r.) for the *para*-substituted fluorobenzenes listed in part A of Table 3. These are substituents for which adequate n.m.r. data are available [16] for non-polar solvents since the analysis depends on small differences and therefore on accurate data. The least squares plot is given by equation (7)

$$(A - 170)^{\frac{1}{2}} = 117\,[\sigma^{\circ}_{R}\ (\text{n.m.r.}) + 0{\cdot}38] \qquad (7)$$

with a standard deviation of 0·046 in σ°_{R}. This gives a constant of 13,780.

If the plot is constrained to a c value of 0·34 (σ°_{R} for fluorine [3]), the standard deviation is 0·054 and the constant is 16,600. An argument could be made for this approach since the shift data are taken relative to fluorobenzene. Taken together, the data are best covered by a value of about 15,000 rather than the 11,800 earlier adopted. Values for certain other substituents for which comparisons of σ°_{R} values determined from i.r. and ^{19}F n.m.r. methods have been made in Parts IV [3] and IX [4] of this series are also given in part B of Table 3. These values fall reasonably well on the line in the Figure.

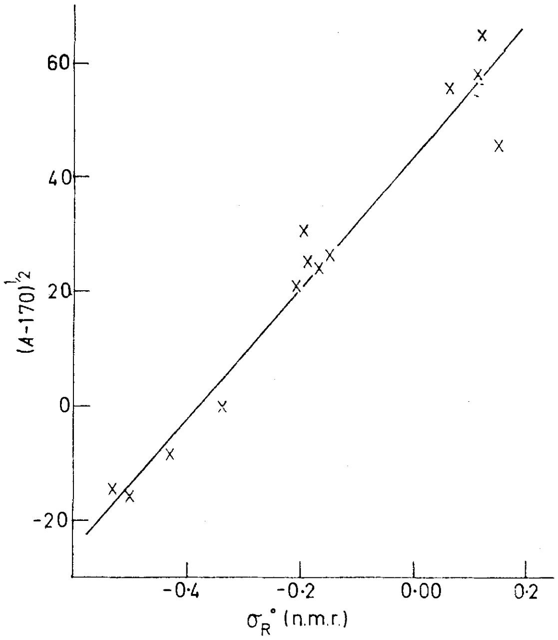

FIGURE 2 Plot of $(A - 170)^{\frac{1}{2}}$ against $\sigma^{\circ}_{R}(^{19}\text{F})$ for *para*-disubstituted fluorobenzenes

TABLE 3

I.r. and n.m.r. data for *para*-substituted fluorobenzenes

Substituent	σ°_{R} (i.r. [b])	σ°_{R} (n.m.r.)	$A - 170$
Part A [a]			
NMe_2	−0·54	−0·53 [e]	210
ND_2	−0·47	−0·50 [e]	250
OMe	−0·43	−0·44 [e]	70
F	−0·34	−0·34 [e]	20
SMe	−0·25	−0·20 [e]	950
Cl	−0·22	−0·21 [e]	440
Br	−0·23	−0·19 [e]	630
I	−0·22	−0·15 [e]	690
Me	−0·10	−0·17 [e]	580
CN	0·09	0·15 [e]	2090
CF_3	0·11	0·06 [e]	3110
CO_2Et	0·18	0·12 [e]	3450
COMe	0·22	0·13 [e]	4220
Part B			
$SnMe_2C_6H_4F$	−0·19	0·02 [c]	2517
$SnEt_2C_6H_4F$	−0·19 [c]	0·01 [c]	2496
$SnEt_3$	−0·13 [c]	0·01 [c]	2672
$SnMe_3$	−0·10 [c]	0·01 [c]	2552
$SiMe_3$	0·02 [d]	0·04 [d]	2527
CHO	0·24	0·27	5340

[a] Data used for least square plots; see text. [b] Ref. 3 unless otherwise shown. [c] Ref. 4. [d] Ref. 7. [e] Values are $(\int_{H}^{pX} + 7{\cdot}3\sigma_{I})/30{\cdot}8$; $\int_{H}^{pX}$ taken from ref. 16 and σ_{I} from C. D. Ritchie and W. F. Sager, *Progr. Phys. Org. Chem.*, 1964, **2**, 323.

(iii) *Evidence from Rotational Barriers.*—We recently

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[14] R. T. C. Brownlee and R. W. Taft, *J. Amer. Chem. Soc.*, 1970, **92**, 7007.

[15] R. T. C. Brownlee and R. W. Taft, *J. Amer. Chem. Soc.*, 1968, **90**, 6537.

[16] R. T. C. Brownlee, S. Ehrenson, and R. W. Taft, *Progr. Phys. Org. Chem.*, 1973, **10**, 1.

reported[17] that the barrier to rotation of a group around an attached benzene ring is related to its σ°_R values in the conjugated (σ°_R) and orthogonal conformers $(\sigma^\circ_R)_{tw}$ and the steric strain (S) in the conjugated conformer by equation (8). This treatment was successfully

$$\Delta G^\ddagger_{mono} = 33\,[\sigma^\circ_R - (\sigma^\circ_R)_{tw}] - S \qquad (8)$$

extended[17,18] to *para*-disubstituted benzenes by the incorporation of a term to allow for the additional energy (δ) involved in through-conjugation. Thus we can contrast the barrier to rotation for a given group in a *para*-disubstituted benzene with that for the same group in the corresponding monosubstituted case, making the assumption that $(\sigma^\circ_R)_{tw}$ and S for the group are equal in the mono- and di-substituted benzenes. This leads to equation (9), where δ is in σ°_R units and $\Delta G^\ddagger$ values are in

$$\Delta G^\ddagger_{para} - \Delta G^\ddagger_{mono} = 33\delta \qquad (9)$$

kcal mol^{-1}. This treatment assumes no through-conjugation in the orthogonal form.

The δ values so obtained should be the same as $\lambda/2$, the factor 2 arising as discussed above. Equation (10) thus follows. The results of such calculations are shown in

$$(A - 170)^{\frac{1}{2}} = b^{\frac{1}{2}}\,[\sigma^\circ_R\,(\text{acceptor}) - \sigma^\circ_R\,(\text{donor}) + 2(\Delta G^\ddagger_{para} - \Delta G^\ddagger_{mono})/33] \qquad (10)$$

Table 4. The average b value obtained is 18,200. Any residual through-conjugation in the twisted forms of the *para*-disubstituted compounds would decrease this value. As the method relies on rotational barrier differences, which are subject to relatively large errors, it is concluded that the results are compatible with the constant of 15,000 as expressed in equation (3).

TABLE 4

Rotational barriers for formyl and acetyl groups in substituted benzenes

Substituents		$\Delta G^\ddagger$/kcal mol^{-1}	Ref.	b
CHO	H	7·9	†	
CHO	OMe	9·3	18	18,000
CHO	F	8·3	18	14,400
CHO	NMe_2	10·7	17	19,700
COMe	H	6·3	17	
COMe	NH_2	8·5	‡	20·600

† F. A. L. Anet and M. Ahmad, *J. Amer. Chem. Soc.*, 1967, **86**, 119. ‡ R. K. McKenzie and D. D. MacNicol, *Chem. Comm.*, 1970, 1299.

(iv) *Theoretical Calculations.*—We have previously[1,19] reported CNDO/2 calculations of the ν_8 intensities of both mono- and *para*-di-substituted benzenes. A good linear relation was found[1,19] for the monosubstituted benzenes between the observed intensity values and those calculated with a proportionality constant close to unity.[1]

A satisfactory linear relationship was not found[19] for *para*-disubstituted benzenes and the intensities for *para*-donor–acceptor-substituted benzenes were greater than calculated. Calculated dipole transition moments[19] for the ν_{8a} vibration of *para*-donor–donor-substituted compounds (Table 5) are all higher than those observed for the total ν_8 intensity. The figures calculated for the *para*-disubstituted compounds were also slightly higher on the average than the sum of the dipole derivatives calculated for the corresponding monosubstituted benzenes. We investigated this further by calculating the dipole transition moment for the ν_{8a} vibration of fluorobenzene using alternatively the co-ordinates[19,20] for monosubstituted benzenes (based on chlorobenzene) and those for *para*-disubstituted benzenes (based on *para*-dichlorobenzene).

TABLE 5

Calculated and observed dipole transition moments for the ν_8 vibration of *para*-disubstituted benzenes (C_6H_4YZ)

Substituents Y	Z	$\frac{\partial\mu}{\partial Q}$(*para*)	$\frac{\partial\mu}{\partial Q}$(Y)	$\frac{\partial\mu}{\partial Q}$(Z)	$\Sigma\frac{\partial\mu}{\partial Q}$(mono)	$\frac{\partial\mu}{\partial Q}$(obs)
F	Me	51·7	73·2	26·6	46·6	43·5
F	OH	21·7	73·2	95·2	22·0	15·4
F	NH_2	35·9	73·2	118·8	45·6	28·6
NH_2	Me	111·9	118·8	26·6	92·2	74·5
NH_2	OH	15·7	118·8	95·2	23·6	0·0
Me	OH	81·8	26·6	95·2	68·6	65·1

The A values predicted were 1589 and 1689, respectively. However, in the later calculation the movement of the *para*-hydrogen atom relative to the attached carbon was kept as in the monosubstituted benzenes. Heavier substituents do not move appreciably in the vibrations and when the hydrogen was likewise restrained by using the full co-ordinates for a *para*-disubstituted benzene, the predicted A value dropped to 1292. Thus while the differences in carbon skeletal displacements would lead to a small increase in gradient of *para*-disubstituted benzenes as compared with monosubstituted ones, as suggested above, the *para*-hydrogen atom makes a considerable contribution to the intensity in the latter. The calculation shows that this results from both a reduction in the rate of change of substituent-ring interaction and a C–H induced dipole acting in the opposite direction to the main induced dipole. The replacement of a hydrogen atom in a monosubstituted benzene by a *para*-substituent should thus lead to a decrease in the gradient b. The single calculation above gives 14,300 (17,600 × 1292/1589).

Small changes in bond lengths are known to occur in some *para*-disubstituted benzenes as compared with monosubstituted compounds. Lengthening the bond from 1·32 to 1·37 Å led to an 18% decrease in predicted intensity, showing the importance of these changes.

The ν_8 intensities for *para*-deuterio-substituted benzenes should be similar to those for the corresponding monosubstituted benzenes since the D atom moves less

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[17] T. B. Grindley, A. R. Katritzky, and R. D. Topsom, *Tetrahedron Letters*, 1972, 2643.

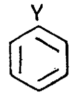
[18] T. B. Grindley, A. R. Katritzky, and R. D. Topsom, submitted to *J.C.S. Perkin II*.

[19] R. T. C. Brownlee, A. R. Katritzky, M. V. Sinnott, M. Szafran, R. D. Topsom, and L. Yakhontov, *J. Amer. Chem. Soc.*, 1970, **92**, 6850.

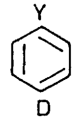
[20] J. A. Scherer, 'Planar Vibrations of Chlorinated Benzenes,' The Dow Chemical Company, Midland, Michigan. We thank Dr. Scherer for making available to us the Cartesian displacement matrix used for calculating the normal co-ordinates.

than H. The intensity values listed[1] in Table 6 (measured by the improved method[11]) for the *para*-deuterio-compounds are generally close to but slightly less than those for the protio-compounds.

Little evidence was found for mass effects in the ν_8 vibrations of monosubstituted benzenes and the normal co-ordinates are little altered for *para*-disubstituted benzenes. Direct evidence for the *para*-disubstituted compounds comes from the series (A)—(D). The effective σ°_R value measured for the substituent Y in each case

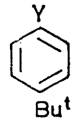


(A)



(B)

(C)



(D)

does not show a continuous change in the series which would be expected if the reduced mass of the second substituent were important. (Frequency values in such series also fail to show changes expected if mass effects were important.) Further, the reduced masses for most of the substituents employed should be fairly similar since the atom attached to the benzene ring is usually C, N, or O.

TABLE 6

Intensities (A/l mol^{-1} cm^{-2}) for the ν_8 bands of C_6H_5Y and p-DC_6H_4Y

Y	C_6H_5Y	p-DC_6H_4Y
NMe_2	6268	6244
OMe	3731	3782
F	2702	2501
Br	1180	1126
Me	401	406

(v) *Analysis of Infrared Intensity Data for* para-*Disubstituted Benzenes in Terms of Variable Demand Interaction.*—The analysis in (i) assumes that $\lambda = 0$ in equation (2), that is that the effect of two resonance-donating or two resonance-accepting substituents is additive in *para*-disubstituted benzenes. However, there is some evidence that when two resonance-donating or two resonance-accepting substituents are attached *para* to each other in a benzene ring, their resonance contributions are reduced. For example, this was apparent in an extensive analysis[16] of Hammett constants in series such as *para*-substituted phenols. Some other recent evidence includes a microwave spectroscopic study which suggests[21] that the NH_2 group is further out-of-plane with respect to the benzene ring in *para*-fluoroaniline than it is in aniline itself; theoretical calculations[14] on *para*-donor-substituted fluorobenzenes likewise imply some reduction of the fluorine π-donation to the ring; dipole moment and molecular Kerr constant measurements suggest[22] a similar reduction in individual substituent resonance contributions in *para*-diacetylbenzene.

Blagdon[12] has recently developed a method of analysing substituent–substituent interactions in *para*-disubstituted benzenes which allows for the polarisation of each substituent by the other and also for the sensitivity of the reaction or property to such effects. The substituent constant varies continuously with the electron demand in the reaction or property. The effective substituent constant ($\bar{\sigma}_R$) is given by an equation of the form (11) * where a represents the ability of the π-system

$$\bar{\sigma}_R = a/(p - d) \qquad (11)$$

of the substituent to overlap the benzene ring orbitals, and p is a measure of the polarisability of the substituent (and is of different sign for donors and acceptors). The d value is a measure of the electron demand in the reaction on the substituent and is derived from the statistics of fit. It can be seen that for $d = 0$ then $a/p = \sigma^\circ_R$.

For the analysis of our i.r. results we used equation (12), which is of the same form as equation (2). We have attempted to estimate the electron demand on one substituent by relating the demand to the total σ value of the other substituent, giving equation (13).

$$(A - 170)^{\frac{1}{2}}_{para\text{-di}} = \text{constant}^{\frac{1}{2}} \left[\frac{a(1)}{p(1) - d(1)} - \frac{a(2)}{p(2) - d(2)}\right] \qquad (12)$$

$$d(1) = D[\sigma_R^\circ(2) + \sigma_I(2)] \qquad (13)$$

We analysed the available data for all *para*-disubstituted benzenes for which substituent a and p values were reported by Blagdon.[12] In practice this meant combinations of the substituents NMe_2, ND_2, SMe, OMe, F, Cl, Br, Me, CF_3, COMe, CO_2R, CN, and SO_2Me except that data for d-orbital acceptors combined with strong resonance donors was omitted. The a and p values used were those listed by Blagdon with a few minor exceptions.†

The best fit obtained was with $D = -0{\cdot}8$, with standard deviation (s.d.) 5·82, for a root mean square of the data of 44·67, and constant 13,200; $D = -0{\cdot}6$ gave s.d. 5·84, constant 14,500; $D = -0{\cdot}4$ or $-1{\cdot}0$ gave s.d. 6·3. Only a small improvement in fit was obtained if a variable blend of inductive and resonance parameters was employed, while correlation with $d = D\sigma^\circ_R$ showed much less discrimination and a considerably worse fit.

The method seems to provide a reasonable way of looking at substituent–substituent interactions. The effect of one substituent on a second in a *para*-position seems best described in terms of both the resonance and the inductive nature of the first substituent. From this

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* Blagdon uses the terms c^2, ε_s, and ε_R respectively for the terms here denoted a, p, and d for simplicity.

† The values adopted for a and p were those listed by Blagdon (c^2 and ε_S, respectively) except that c^2/ε_S values ($= \sigma^\circ_R$) for CN, CO_2R, and Me were adjusted slightly to bring them into line with our preferred (ref. 4) σ°_R values of 0·09, 0·18, and $-0{\cdot}10$ while the values for F and CF_3 were modified to make those substituents somewhat (28%) less polarisable than suggested by Blagdon.

[21] A. Hastie, D. G. Lister, and J. K. Tyler, *Chem. Comm.*, 1970, 108.

[22] P. H. Gore, P. A. Hopkins, R. J. W. Le Fèvre, L. Radom, and G. L. D. Ritchie, *J. Chem. Soc.* (*B*), 1971, 120.

point of view a substituent with $\sigma^{\circ}_{R} = 0$ would still have an effect on the resonance interaction of a *para*-substituent provided that the first group had a significant σ_{I} value. The analysis above suggests that a constant of *ca.* 14,000 would be appropriate.

This approach to treating substituent interactions is different in some respects to that at present preferred for treatment of i.r. data. The Blagdon approach assumes an ' attenuation ' in interaction when both substituents are donors or both are acceptors, and does not differentiate *d*-orbital substituents. Finally the mutual modification substituents are not identical, contrary to the normal valance-bond representation of through-conjugation (I).

Although we cannot now differentiate between these two methods, many of the data at present available cannot be treated by the Blagdon approach because of the lack of knowledge of parameters.

para-*Substituted Nitrobenzenes*.—A discrepancy remaining from our previous treatment was the unexpectedly high intensity observed for the ν_8 band of nitrobenzenes having another resonance electron-withdrawing substituent in the *para*-position. We present evidence below to show that this results from intensity sharing with the $\nu_{NO_2 as}$ band. Data from such compounds are therefore ignored in the analyses reported here.

The asymmetric NO_2 stretching vibration in nitrobenzene occurs at about 1531 cm^{-1}. It is then reasonably close to the ν_8 modes and may share intensity. In *para*-substituted nitrobenzenes, the substituent causes a shift[23] in ν_{NO_2} which varies from 1550 for a nitro-group to 1507 cm^{-1} for an amino-group. We had earlier reported[2] anomalously high ν_8 intensities for *para*-substituted nitrobenzenes containing electron-accepting substituents, that is just those compounds where intensity sharing with the extremely strong ν_{NO_2} vibration might be greatest. In order to check this we measured the ν_8 intensities of pentadeuterionitrobenzene and nitrobenzene itself under identical conditions.[11]

Pentadeuteriation of a monosubstituted benzene usually[1] lowers ν_8 by 25—30 cm^{-1} but has a relatively small effect on the intensity. Here, however, we found a lowering of only 18 cm^{-1} in frequency whereas ν_{NO_2} was lowered by 6 cm^{-1}. This suggests interaction leading to higher ν_8 and lower ν_{NO_2} and this was confirmed by relative ν_8 intensity values of 2344 $l\ mol^{-1}\ cm^{-2}$ for nitrobenzene and 2778 for the pentadeuterio-compound.

We are therefore confident that considerable intensity sharing occurs in substituted nitrobenzenes and, in particular, in those containing resonance-accepting substituents.

Asymmetry Effects.—In an earlier[2] publication we pointed out that asymmetry corrections were required in *para*-disubstituted benzenes containing substituents of less than C_{2v} symmetry. Equation (14) applies to

$$A = b[(\sigma^{\circ}_{R}s - \sigma^{\circ}_{R}as)^2 + 2\sigma^{\circ}_{R}s\,(\sigma^{\circ}_{R}as - \sigma^{\circ}_{R}x)] + 170 \quad (14)$$

a compound containing one substituent *s* of at least C_{2v} symmetry. The constant term in the correction factor, $2(\sigma^{\circ}_{R}as - \sigma^{\circ}_{R}x)$ can be determined[2] for asymmetric substituents from equations (15) and (16), where $\sigma^{\circ}_{R}x$ and

$$A_{\text{mono-}as} = 17{,}600\ (\sigma^{\circ}_{R}X^2 + \sigma^{\circ}_{R}Y^2) + 100 \quad (15)$$

$$A_{para\text{-}as/as} = 2b\ (\sigma^{\circ}_{R}y)^2 + 170 \quad (16)$$

$\sigma^{\circ}_{R}y$ are the vector components of σ°_{R} along the main axis (*x*) and one perpendicular to it, and $A_{para\text{-}as/as}$ refers to the intensity of the *para*-diasymmetrically substituted compound. Use of these equations with $b = 15{,}000$ and the data previously reported[2] gives the values shown in Table 7. The values of $\sigma^{\circ}_{R}y$ and the correction terms $2(\sigma^{\circ}_{R}as - \sigma^{\circ}_{R}x)$ are very small and subject to error from the overtone correction. The asymmetry correction can thus normally be neglected in *para*-disubstituted compounds for all but low intensity measurements but may be important for *meta*-disubstituted compounds.

TABLE 7

Asymmetry corrections for *para*-disubstituted benzenes

	$\sigma^{\circ}_{R}as$	$\sigma^{\circ}_{R}x$	$\sigma^{\circ}_{R}Y$	$2(\sigma^{\circ}_{R}as - \sigma^{\circ}_{R}x)$
OMe	−0·428	−0·425	0·062	−0·006
SMe [a]	−0·250	−0·241	0·068	−0·018
SBu^t [a]	−0·07	−0·07	0	0
COMe	0·219	0·216	0·036	0·006
CO_2Me	0·155	0·140	0·066	0·030
CO_2Et	0·180	0·173	0·045	0·014
CHO	0·244	0·233	0·073	0·022
SO_2Me [b]	0·06	0·06	0	0
SOMe [b]	−0·07	−0·07	0	0

[a] Data from ref. 27. [b] Data from N. C. Cutress, T. B. Grindley, A. R. Katritzky, M. Shome, and R. D. Topsom, *J.C.S. Perkin II*, 1974, 268.

(II) *Quantitative Treatment of Through-conjugation in* para-*Disubstituted Benzenes*

In our first paper on *para*-disubstituted benzenes,[2] we found that the additional interactions could be distributed in terms of the resonance effects of the two substituents. Equation (17) applied for π-acceptor groups,

$$\lambda = K_{A}(\sigma^{+}D - \sigma^{\circ}D) \quad (17)$$

$$\lambda = K_{X}\sigma^{\circ}_{R}D \quad (18)$$

where K_{A} was a constant characteristic of the π-acceptor, and $(\sigma^{+} - \sigma^{\circ})$ represented the ability of the donor group to satisfy further electron demand.

However, for *d*-orbital acceptors, we found a different relation, equation (18), in which K_{X} is characteristic of the *d*-orbital acceptor, but the additional interaction here appeared to be proportional to σ°_{R} for the donor group.

We have now treated the large amount of data at present available with the revised equation (3). We find that equations (17) and (18) still hold for π-acceptors and *d*-orbital acceptors, respectively. The magnitudes of the interactions are less than originally considered, but the qualitative conclusions remain unchanged, as will now be demonstrated.

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[23] R. D. Kross and V. A. Fassel, *J. Amer. Chem. Soc.*, 1956, **78**, 4225.

TABLE 8

K_A and K_X values

K_A Values	Present [a]	Ref.	Lit values	Ref.
N_2^+	0·50 ± 0·03	*b*	0·99	*h*
NSO	0·50 ± 0·04	*c*		
NCO	0·30 ± 0·04	*c*	0·36	*j*
NCS	0·30 ± 0·04	*c*	0·35	*j*
N_3	0·28 ± 0·04	*c*	0·32	*j*
C_2H	0·26 ± 0·04	*d*		
CHO	0·25 ± 0·02	*b*	0·57	*k*
NO	0·20 ± 0·04	*c*	0·43	*j*
4-Aza-*N*-oxide	0·20 ± 0·04	*b*	0·37	*l*
COMe	0·16 ± 0·04	*b*	0·45	*k*
NC	0·15 ± 0·04	*c*	0·17	*j*
CO_2R	0·14 ± 0·04	*b*	0·36	*k*
CN	0·13 ± 0·03	*b*	0·29	*k*
NMe_3^+	0·13 ± 0·04	*b*		
4-Aza	0·12 ± 0·01	*b*	0·50 [n]	*l*
CF_3	0·08 ± 0·01	*e*		
K_X Values				
SMe	0·51 ± 0·02	*f*	0·44	*m*
SO_2Me	0·49 ± 0·03	*g*		
$SiMe_3$	0·43 ± 0·04	*f*	0·62	*k*
I	0·43 ± 0·02	*f*	0·55	*k*
SBu^t	0·40 ± 0·04	*f*		
SOMe	0·35 ± 0·03	*g*		
SH	0·34 ± 0·04	*f*		
Br	0·32 ± 0·02	*f*	0·42	*k*
Cl	0·22 ± 0·01	*f*	0·32	*k*

[a] The error represents the approximate latitude in fitting the results (see text). Not enough results are available to allow a statistical analysis. [b] This paper. [c] Ref. 26. [d] T. B. Grindley, K. F. Johnson, A. R. Katritzky. H. J. Keogh, and R. D. Topsom, *J.C.S. Perkin II*, 1974, 273. [e] Ref. 25. [f] Ref. 27. [g] N. C. Cutress, T. B. Grindley, A. R. Katritzky, M. Shone, and R. D. Topsom, *J.C.S. Perkin II*, 1974, 268. [h] Ref. 8. [j] Ref. 5. [k] Ref. 2. [l] Ref. 24. [m] Ref. 7. [n] K_X Value.

Values of K_A and K_X, determined for the data in this and the accompanying papers, are compared in Table 8 with the values previously accepted. Thus values of K_A and K_X provide quantitative estimates of the ability of acceptor groups to enter into through-conjugation with donors. The K_A and K_X values really refer only to the solvent employed but will be almost constant for the relatively non-polar solvents mostly used.

TABLE 9

para-Substituted pyridines and pyridine *N*-oxides (A values in l mol^{-1} cm^{-2} from ref. 24)

	4-Substituted pyridines			4- Substituted pyridine *N*-oxides		
Substituent	$\left(\frac{A-170}{15{,}000}\right)^{\frac{1}{2}}$	λ [a]	f_p [b]	$\left(\frac{A-170}{15{,}000}\right)^{\frac{1}{2}}$	λ [c]	f_p [b]
NMe_2	0·95	−0·15	0·95	0·59	−0·25	0·57
OMe	0·77	−0·88	0·78	0·33	−0·13	0·35
SMe	0·55	−0·07	0·59			
Cl	0·56	−0·01	0·50	0	−0·02	0·02
Me	0·40	−0·02	0·39	0	−0·03	0·08
$CH{\cdot}CH_2$	0·39	−0·02 [d]	0·34			
CH_2OH	0·37	−0·02 [d]	0·37			
H	0·28	0	0·27	0·22	0	0·21
CN	0·30	0	0·18	0·37	0·08	0·38
CO_2Et	0·27	0	0·09	0·46	0·08	0·47
COMe	0·19	0	0·05	0·54	0·10	0·53

[a] $\lambda = 0{\cdot}12(\sigma^+D - \sigma^\circ D)$. [b] $f_p = |[\sigma^\circ_R(1) - \sigma^\circ_R(2) + \lambda]|$. [c] $\lambda = 0{\cdot}20(\sigma D - \sigma^\circ D)$ for donors or $0{\cdot}60K_A$ for acceptors. [d] Taken as for Me substituent.

We now discuss other results previously interpreted in terms of equation (2).

4-*Substituted pyridines and their* N-*oxides*. The previous conclusions [24] that 4-substituted pyridines exhibit through-conjugation with donor substituents, whereas 4-substituted pyridine 1-oxides display through-conjugation with both donor and acceptor substituents are substantiated (Table 9). K_A Values are given in Table 8, and the intensities for 4-acceptor-substituted pyridine 1-oxides are satisfactorily correlated by assuming $\sigma^+ - \sigma^\circ$ for the 4-aza-*N*-oxide group is 0·60.

Trimethylphenylsilanes. The good correlation found previously [7] for *para*-substituted trimethylphenylsilanes is fully maintained in the present treatment, with the revised K_X value of 0·43 for $SiMe_3$.

Diazonio- and Trimethylammonio-substituents. As we previously concluded,[8] the diazonio-substituent is a strong acceptor (σ°_R +0·29), which is also readily polarised to undergo further acceptance of electrons in situations of high electron availability. A K_A value of 0·50 for N^{2+} correlates with the observed intensities (Table 10). The trimethylammonio-substituent is a resonance donor (σ_R −0·14), but in situations of high electron availability it is polarisable and is constrained to donate less electrons, a behaviour correlated by $K_A = 0{\cdot}13$ for NMe_3^+ (Table 10).

Further para-*substituted compounds*. Additional Parts of this series have been concerned with the treatment of *para*-derivatives by use of the previous equation (2). In each case, reinvestigation indicated that the conclusions stand as described in the place indicated: alkylbenzenes [6] in ref. 25; donor–acceptor substituents [5] in ref. 26; metalloid derivatives [4] in the ^{19}F n.m.r. section of this paper. A discussion of K_X values is given in a following paper.[27]

Summary.—In Figure 3 we show a graph of $(A - 170)^{\frac{1}{2}}$ against $[\sigma^\circ_R\,(1) - \sigma^\circ_R\,(2) + \lambda]$ for all *para*-disubstituted benzenes for which data are available (including refs.

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[24] A. R. Katritzky, C. R. Palmer, F. J. Swinbourne, T. T. Tidwell, and R. D. Topsom, *J. Amer. Chem. Soc.*, 1969, **91**, 636.

[25] T. J. Broxton, G. Butt, A. R. Katritzky, R. Liu, L. H. Teo, and R. D. Topsom, *J.C.S. Perkin II*, in the press.

[26] G. Butt, M. Davis, Y. T. Pang, R. D. Topsom, and A. R. Katritzky, *J.C.S. Perkin II*, 1974, 260.

[27] N. C. Cutress, T. B. Grindley, A. R. Katritzky, and R. D. Topsom, *J.C.S. Perkin II*, 1974, 263.

TABLE 10

para-Substituted benzenediazonium fluoroborates and trimethylanilinium iodides

Substituent	$XC_6H_4{\cdot}N_2{}^+BF_4{}^-$			$XC_6H_4{\cdot}NMe_3{}^+I^-$		
	$\left(\frac{A - 170}{15,000}\right)^{\frac{1}{2}}$	λ [a]	f_p [b]	$\left(\frac{A - 170}{15,000}\right)^{\frac{1}{2}}$	λ [c]	f_p [d]
NMe_2	1·50	−0·63	1·45	0·57	−0·17	0·55
OMe	1·07	−0·33	1·05	0·34	−0·09	0·37
OEt				0·35	−0·09	0·38
F	0·67	−0·12	0·75	0·21	−0·03	0·22
Cl	0·56	−0·05	0·57			
Me	0·50	−0·08	0·47	0	−0·02	0·07
NO_2	0·27	0	0·12	0·30		

[a] $0{\cdot}50\,(\sigma^+D - \sigma^\circ D)$. [b] $|[\sigma^\circ_R(1) - 0{\cdot}29 + \lambda]|$. [c] $0{\cdot}13(\sigma^+D - \sigma^\circ D)$. [d] $|[\sigma^\circ_R(1) - (-\,0{\cdot}15) + \lambda]|$.

26 and 27). The λ values are zero, $(\sigma^\circ_R D)K_X$, or $(\sigma^+ - \sigma^\circ)K_A$ as appropriate and the line shown has slope $(15{,}000)^{\frac{1}{2}}$. The correlation obtained (s.d. = 0·056 for 140 points) provides good evidence for the utility of the approach adopted. The values of $\sigma^\circ_R D$ for a substituent are a measure of its ability to share π-electrons with an attached benzene ring; $(\sigma^+ - \sigma^\circ)$ provides a measure of a substituent's tendency to donate further on demand, K_A a measure of a substituent's tendency to accept further on demand, and K_X a measure of the tendency of a substituent to accept π-electron density into its *d*-orbitals. A summary of such values for common substituents is given in Table 11; the figures should prove useful in characterising the behaviour of the substituents listed.

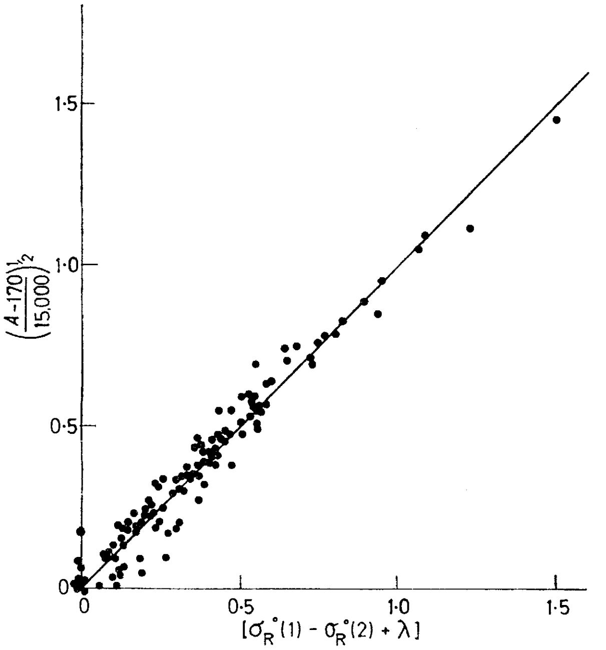

FIGURE 3 Plot of $(A - 170)^{\frac{1}{2}}$ against $[\sigma^\circ_R(1) - \sigma^\circ_R(2) + \lambda]$ for *para*-disubstituted benzenes (the line shown has gradient 15,000)

TABLE 11

Electronic behaviour of common substituents

	σ°_R	$\sigma^+ - \sigma^0$	K_A	K_X
NMe_2	−0·53	−1·26		
ND_2	−0·47	−0·92		
OMe	−0·43	−0·66		
OH	−0·40	−0·79		
F	−0·40	−0·24		
SMe	−0·25	−0·57		0·51
Cl	−0·22	−0·11		0·22
Br	−0·23	−0·16		0·32
I	−0·22	−0·14		0·43
Me	−0·10	−0·16		
Et	−0·10	−0·16		
Pr^i	−0·11	−0·15		
Bu^t	−0·13	−0·06		
$NMe_3{}^+$	−0·15	−0·40	0·13	
CN	0·09		0·13	
CF_3	0·11		0·08	
CO_2Et	0·18		0·14	
COMe	0·22		0·16	
CHO	0·24		0·25	
4-Pyridyl	0·27		0·12	
$SiMe_3$	0·02			0·43
SO_2Me	0·06			0·49
SOMe	−0·07			0·35

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