benzylammonium cation all show total intensities below 100 but above 50, and this was used in setting the intensity of the combination band (eq 5) as 100 ± 50.

Two or more inductive-withdrawing substituents in a methyl group also effectively reduce the $\sigma_R°$ value to zero as is found for the groups $CHBr_2$, $CHCl_2$, $CH(OMe)_2$, and for CCl_3, CBr_3, and $C(OMe)_3$; all these compounds show total intensities in the range 50–100. However, polyfluoro substitution, as in CF_3, C_2F_5, yields electron-acceptor values of $\sigma_R°$ of 0.111 and 0.075.

Phenyl substituents increase somewhat the $\sigma_R°$ value of methyl to 0.117 (CH_2Ph) and 0.113 ($CHPh_2$).

(iii) CC Multiple Bonds. We have recorded values for several vinyl derivatives PhCH=CHX where X = H, CO_2Me, NO_2, and $N(CH_2CH_2)_2CH_2$. These results are less reliable than most because the compounds show the $\nu_{C=C}$ mode at *ca.* 1630 cm^{-1} and intensity sharing could occur between the two modes. We plan to study polysubstituted analogs, both to test the validity of the $\sigma_R°$ values found and to determine their sign.

The acetylenic substituents C≡CH and C≡CPh show $\sigma_R°$ values of 0.072 and 0.152, respectively: again the study of polysubstituted compounds is needed to confirm the direction of the effect.

(iv) Other Unsaturated Compounds. The carbonyl derivatives COY are all strongly electron withdrawing; the effect varies in the series: COOMe (0.155) ≤ COOEt (0.180) < COPh (0.190) < COCl (0.213) ≤ COMe (0.219) < CHO (0.244) < COOH (0.291). The position of OH in this series is undoubtedly affected by the association of benzoic acid to hydrogen-bonded dimers in $CHCl_3$ solution. However, without considering OH, the order in this series is in marked contrast to the corresponding SO_2Y series (see above). Comparison shows that the two series reflect the strong mesomeric interaction of Y with CO, while Y and SO_2 have mainly an inductive interaction.

Acknowledgments. We thank the Research Committee of the New Zealand Universities' Committee for grants and for a Research Fund Fellowship (to R. E. J. H.), the 3M Company (Great Britian) Ltd. for a Studentship (to R. T. C. B.), and the U. S. National Institutes of Health for a Postdoctoral Fellowship (to T. T. T.). Part of this work was carried out during the tenure of a Nuffield Travelling Fellowship (by R. D. T.). We are very grateful to Professor G. Illuminati (Rome) and Dr. W. A. Sheppard (Wilmington) for the gift of compounds.

Infrared Intensities as a Quantitative Measure of Intramolecular Interactions. IV.[1] *para*-Disubstituted Benzenes. The ν_{16} Band near 1600 cm^{-1}

P. J. Q. English,[2] A. R. Katritzky,[2] T. T. Tidwell,[2,3] and R. D. Topsom[4]

Contribution from the School of Chemical Sciences, University of East Anglia, Norwich, England, and the School of Physical Sciences, La Trobe University, Melbourne, Australia. *Received September 5, 1967*

Abstract: The integrated intensities of the ν_{16} vibration for many *para*-disubstituted benzenes are correlated by the relation $A_{para} = 11{,}800\,(\sigma_R°1 - \sigma_R°2)^2 + 170$. Discrepancies from this relation are interpreted as due to direct interactions between the substituents; such interactions between acceptor and donor substituents are proportional to $(\sigma^+ - \sigma)$ values. Halogens other than F act as d-orbital acceptors, and NO_2 is found to interact with strong acceptor groups. The relation enables the sign of the resonance effect to be directly determined; ND_3^+ and NMe_3^+ groups are shown to be resonance donors.

Previous papers in this series[1,5] have been concerned with the quantitative significance of the infrared intensities of the ring-stretching bands of monosubstituted benzenes. In particular a quantitative relation (eq 1) was found between the integrated area, A, of the bands near 1600 and 1585 cm^{-1} and $\sigma_R°$ for the substituent. We have now extended this work to polysubstituted analogs, and the present paper records and discusses the results for *para*-disubstituted benzenes.

$$A_{mono} = 17{,}600(\sigma_R°)^2 + 100 \quad (1)$$

Some years ago, one of us, in connection with a wider investigation into the infrared spectra of heteroaromatic compounds,[6] measured the frequencies and apparent extinction coefficients for the characteristic vibrations of many *para*-disubstituted benzenes.[7] At that time it was pointed out that the intensity variations of the 1600-cm^{-1} band could be qualitatively explained on the basis of the theory earlier developed[8] for monosubstituted

(1) Part III: R. T. C. Brownlee, A. R. Katritzky, T. T. Tidwell, and R. D. Topsom, *J. Amer. Chem. Soc.*, **90**, 1757 (1968).

(2) School of Chemical Sciences, University of East Anglia, Norwich, England.

(3) Department of Chemistry, University of South Carolina, Columbia, S. C.

(4) School of Physical Sciences, La Trobe University, Melbourne, Australia.

(5) (a) R. T. C. Brownlee, A. R. Katritzky, and R. D. Topsom, *J. Amer. Chem. Soc.*, **87**, 3260 (1965); (b) *ibid.*, **88**, 1413 (1966).

(6) For a review see A. R. Katritzky and A. P. Ambler, "Physical Methods in Heterocyclic Chemistry," Vol. II, Academic Press Inc., New York, N. Y., 1963, p 165.

(7) A. R. Katritzky and P. Simmons, *J. Chem. Soc.*, 2051 (1959).

(8) A. R. Katritzky, *ibid.*, 4162 (1958).

benzenes and 4-substituted pyridines, and it was concluded that "the intensity is low when the substituents are of the same type and increases with increasing difference between the substituents."[7] No quantitative relation for infrared ring-stretching band intensities in *para*-disubstituted benzenes has been reported, although Schmid, *et al.*,[9] have shown that the intensity of the C–H stretching modes is quantitatively determined by the σ_I value of the two substituents, and Bobovich[10] has obtained indications of a relation between the logarithm of the Raman intensity of the 1600-cm^{-1} band and Hammett constants for a limited number of compounds. We found no simple relation between the published[10] Raman intensities and $\sigma_R{}^\circ$ values. The additivity of σ constants for correlating the reaction rates and equilibria of disubstituted phenyl compounds is well established;[11] recently this has been found[12] to hold for the formation constants of charge-transfer complexes of *para*-disubstituted benzenes.

A quantitative correlation for the intensity of the ν_{16} infrared band, related to that for the monosubstituted benzenes,[5] might be expected for the summed band intensity ($A\nu_{16a} + A\nu_{16b}$) of *para*-disubstituted benzenes, provided no interaction occurs between the substituents, on the following grounds. Calculations on *p*-dichlorobenzene[13] suggest that ν_{16} for *para*-disubstituted benzenes has normal coordinates similar to those for the monosubstituted analogs. We have described[1] how the interaction of ring and substituent in a monosubstituted benzene gives to ν_{16} an alternating dipole and our deduction that $\partial\mu/\partial Q$ is proportional to $\sigma_R{}^\circ$. If the two substituents in a *para*-disubstituted benzene act independently, then, by using the valence bond approach developed previously,[1] it follows that the stabilization of the dipolar character of the form I of the vibrational transition I $\rightleftharpoons$ II will be the difference (both substituents donors *or* acceptors) or sum (one donor, one acceptor) of the charge stabilization for the corresponding monosubstituted benzenes. If the dipole contributions by the two substituents are added vectorially, then this relation becomes eq 2 for all combinations of substituent types.

$$\partial\mu/\partial Q_{para} = (\partial\mu/\partial Q_1) - (\partial\mu/\partial Q_2) \quad (2)$$

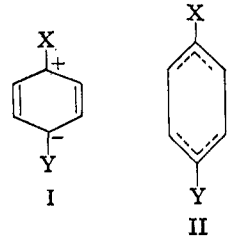
$$A_{para} = b(\sigma_R{}^\circ 1 - \sigma_R{}^\circ 2)^2 + c \quad (3)$$

The intensity of ν_{16} for a *para*-disubstituted benzene should therefore be given by (3) where c represents the contribution from overtone and combination bands and b is a constant. The constant b would be expected to be near that of 17,600 found for monosubstituted benzenes; however, the exact form of the normal vibration is likely to vary somewhat, and for durenes relation 4 was found.[1] The relevant constant for *meta*-disubstituted benzenes is 18,700.[14] The values of b and c in eq 3 are deduced later.

$$A_{\text{durene}} = 11{,}300(\sigma_R{}^\circ)^2 - 30 \quad (4)$$

(9) E. D. Schmid and V. Hoffmann, *Spectrochim. Acta*, 22, 1633 (1966); E. D. Schmid, *ibid.*, 22, 1659 (1966).
(10) Y. S. Bobovich and N. M. Belyaevskaya, *Opt. Spectry.*, 19, 111 (1965); Y. S. Bobovich, *ibid.*, 20, 136 (1966).
(11) H. H. Jaffé, *Chem. Rev.*, 53, 191 (1953).
(12) M. Charton, *J. Org. Chem.*, 31, 2996 (1966).
(13) J. R. Scherer, *Spectrochim. Acta*, 19, 601 (1963); 21, 321 (1965); J. R. Scherer, "Planar Vibrations of Chlorinated Benzenes," Dow Chemical Co., Midland, Mich., 1963.
(14) A. R. Katritzky, M. V. Sinnott, T. T. Tidwell, and R. D. Topsom, unpublished work.

This paper presents evidence for the validity of eq 3 for symmetrical substituents which do not mutually interact and discusses the correlation of discrepancies with substituent interactions. If one or both substituents are of symmetry lower than C_{2v}, a correction must be made to eq 3, as is discussed below. We are presently investigating possible quantitative relations between MO parameters, intensity A, and the $\sigma_R{}^\circ$ values for *para*-disubstituted benzenes.



Experimental Section

Compounds were obtained commercially or prepared by known methods. Purities were checked by gas chromatography or melting point. Anilines were N-deuterated as before.[5b] Spectra were obtained on a Perkin-Elmer 125 spectrophotometer under conditions similar to those previously specified.[5b] Solvents were purified as before. Intensity area A values quoted are averages of four readings, usually on two separate solutions; reproducibility of $A^{1/2}$ was ± 1 unit except where noted. Compounds containing the groups $-ND_3{}^+Cl^-$ and $-NMe_3{}^+Cl^-$ were run in deuterium oxide in Irtran 2 cells, at much slower scan speeds than usual. For these compounds and for the ND_2 derivatives the reproducibility of $A^{1/2}$ drops to *ca.* ± 4 units.

The integrated intensities and the frequencies are recorded in Tables I and II. Frequencies for many of these bands have already been published;[7,15] agreement with present results is usually good. No published values of integrated intensities are available for comparison.

The effect of concentration on the integrated intensity was examined for the following compounds in carbon tetrachloride: *p*-dimethoxybenzene, *p*-chloroanisole, *p*-fluorobenzonitrile, *p*-nitroethyl benzoate, *p*-anisaldehyde, *p*-chlorobenzonitrile, and *p*-chloroacetophenone. In no case was any significant variation of intensity with concentration found.

Compounds were measured where possible in CCl_4 solution; where insufficient solubility or other considerations precluded this, the solvent used is noted in a footnote to Table I. The variation of intensities with change of solvent has been investigated for a selection of *para*-disubstituted compounds. For many of the compounds the variations found were small and hardly above the experimental error. However, compounds with strong donor and acceptor groups mutually *para* show a general increase in intensity with increase in polarity of the solvent; these variations will be discussed in a later paper.

Discussion

Overtone Bands. *para*-Disubstituted benzenes show overtone bands near 1900 and near 1630 cm^{-1}. The species of these bands[16] are A_1 for compounds of C_{2v} symmetry and B_{3u} for symmetrically substituted (V_h) compounds. Hence for compounds of C_{2v} symmetry, mixing is to be expected between the 1630-cm^{-1} band and the bands under discussion. Table III indicates that the intensity of the high-frequency band has an average value of 160 A units (the considerable variations are not correlated in any obvious way with the nature of the substituents). The average value of the low-frequency band for those compounds for which it is not overlapped is 170 A. (For *p*-dimethoxybenzene and *p*-chlorotoluene, both of lower than V_h symmetry, the

(15) C. Garrigou-Lagrange, J. M. Lebas, and M.-L. Josien, *Spectrochim. Acta*, 12, 305 (1958).
(16) D. H. Whiffen, *ibid.*, 7, 253 (1955).

Table I. Measured *A* Values for 1600- and 1630-cm^{-1} Bands in *para*-Disubstituted Benzenes

1 substituent	4 substituent: CHO	COMe	COOEt	NO_2	CN	Me	Cl	I	Br	F	OMe	NMe_2
						σ_R°						
NMe_2	17,900		12,300	18,250[a]	9750	2160	2950	4780[b]	3520[b]	380	80	0[c]
NHMe						2730	2930		3140	410		
ND_2						1860	2020	3220	2620	420	120	
OMe	10,500	8610	6,520	7,360	4690	1530	1624	2464	1864	242	282	
OH						1460						
F	5,510	4390	3,620	4,470	2260	750	610	860	800	190		
Br		3600[b]	2,420	2,950	1625[a]	240	220					
I				2,785[a]		<50						
Cl	4,940[a]	3130	2,490	2,410	1070	280	220					
SMe							<50			895		3107
$ND_3^+Cl^-$						<50	45	<50	40	380	900	
$NMe_3^+Cl^-$				1,500						830	880	
Et				1,740								
Me	2,930	2220	1,720	1,570	890	128						
CH_2Cl				1,200			480					
CN		320	330	1,600[a]	<50							
SO_3Me						550						
SO_2Cl				740		1200	2320			4000	8100	
CF_3				610			2040					6240
NO_2	1,640[a]	1640[a]	1,310	<50[d]								
COOEt			230									
COMe		210[a]										
CHO	330[a]											

[a] In $CHCl_3$. [b] Spread of results. [c] In C_6H_{12}. [d] In CH_3CN.

Table II. Measured Frequencies of Peak Maxima near 1600 cm^{-1} for *para*-Disubstituted Benzenes

1 substituent	4 substituent: CHO	COMe	COOEt	NO_2	CN	Me	Cl	I	Br	F	OMe	NMe_2
NMe_2	1600		1610	1598	1612	1620 1582	1598	1593	1598	1612		
NHMe							1607		1600	1613		
ND_2						1620 1580	1604	1602 1592	1597	1622	1620 1588	
OMe	1602 1582	1603 1577	1609 1583	1612 1594	1608 1576	1615 1588	1596 1583	1590 1576	1596 1581	1604	1594	
OH						1598 1618						
F	1601	1599	1604	1623 1596	1607	1615 1602	1595	1591 1580	(1598) 1590			
Br			1590	1605 1580	1590	1592 1580	1590, 1578 1564					
I				1600 1576		?	1574 1536					
Cl	1598 (1590 s) 1582	1592 1573	1597 1576	1606 1580	1597	1600 1578						
SMe										1590		1594
$ND_3^+Cl^-$							1604	1592	1596	1620 1610	1604 1618	
$NMe_3^+Cl^-$				1622 1598						1606	1610 1598	
Et				1608 1603								
Me	1606 1576	1610 1577	1614 1578	1607 1601	1612							
CH_2Cl				1610			1601 1586					
CN			1612 1570	1603								
SO_3Me						1600						
SO_2Cl				1609		1597	1600 (1580 s)			1594	1598 1580	
CF_3				1615			1612 1584					1620
NO_2	1606	1607	1610 1603 s									
COOEt			1578									
COMe		1570										
CHO	1580											

Table III. C–H Overtones in *para*-Disubstituted Benzenes

	Low-frequency band		High-frequency band[a]	
	A	cm^{-1}	A	cm^{-1}
Me/MeO			100	1860
F/OMe	147	1620		
Cl/OMe	34 s	1620	150	1868
F/SMe	98	1628		
F/F	190	1632	260	1861
F/Cl	155	1632	250	1874
Cl/Cl	222	1635	170	1886
Br/Cl	170	1632		
F/Br	198	1632		
Cl/I	114	1636		
F/I		1630		
Cl/Me	132	1630	150	1888
Br/Me	114	1626		
Br/CN	170	1610		
F/SO_2Cl	s	1620		
Me/Me	128	1630	130	1890
Me/NO_2			110	1921
NO_2/COOEt			120	1944
CN/COOEt	170	1512		
Average[b]	170	1632		

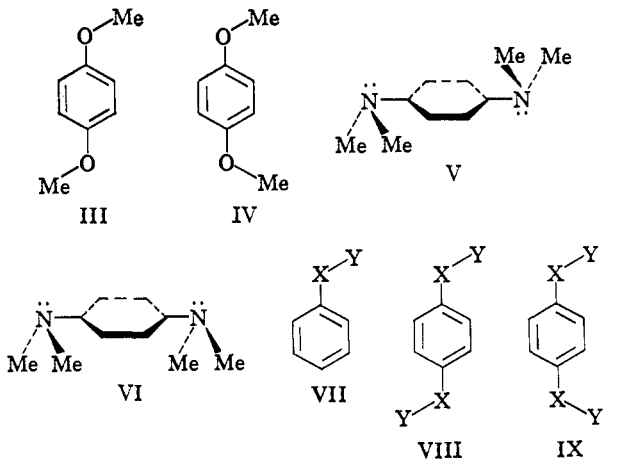
[a] Where measured. [b] Where not overlapped by 1600 band (*i.e.*, symmetrical compounds).

values given are lower limits because mixing could have occurred here.) Therefore an average of 170 A units must be allowed for the overtone contribution to the total area comprising the ν_{16a} and ν_{16b} fundamentals and the overtone band near 1630 cm^{-1}. Hence eq 3 is modified to 5. It may be noted that the overtone con-

$$A_{para} = b(\sigma_R{}^\circ 1 - \sigma_R{}^\circ 2)^2 + 170 \qquad (5)$$

tribution is of little significance except for compounds in which the total intensity is very low. The overtone band is invariably broad, whereas the fundamental band is sharp. Where the intensity of the fundamental is much greater than that of the overtone, the latter is completely overlapped, and the above treatment is used. However, where the intensity of the fundamental is less than, or comparable to, that of the overtone, the two bands can often be differentiated. Where the fundamental is weak, and there is a strong neighboring band (*e.g.*, at 1500 cm^{-1} or the carbonyl frequency), it is not possible to include the overtone band. In Table I, the overtone is included except in the following cases: CHO/CHO, COMe/COMe, CO_2Et/CO_2Et, and all compounds for which the intensity indicated is below 100. In the further treatment of such compounds the factor of 170 is omitted from the relevant equations.

Asymmetry Effects. According to eq 5, *para*-disubstituted benzenes with two identical substituents should show only the intensity of the overtone band just discussed. Correspondingly low intensity is found (Table I) for a group of substituents (i) with at least C_{2v} symmetry (F, Cl, Me, NO_2, and CN). However, marked discrepancies are noted for a group of substituents (ii) with lower symmetry (OMe, OCOMe, COMe, CHO, and CO_2Et). These deviations are a direct consequence of the low symmetry. For *p*-dimethoxybenzene, III and IV are both favored rotational conformers allowing resonance between the substituents and ring;[17] however, although in III the contributions of the two substituents to $\partial\mu/\partial Q$ will clearly cancel, this does not apply to IV. This interpretation is supported by the zero intensity found for the ν_{16} band of crystalline *p*-dimethoxybenzene (in Nujol); in the crystal the compound has been shown by X-ray analysis[18] to exist exclusively in the *trans*-planar conformation III.



No measurable deviation was found for *p*-bis(dimethylamino)- or *p*-bis(chloromethyl)benzene. Ultraviolet spectra indicate[19] that the NMe_2 group in dimethylaniline is bent out of the ring plane in the sense shown in V.[20] Hence, for *p*-bis(dimethylamino)benzene the favored rotamers are V and VI; in neither of these do the substituents cause any dipole change during vibration ν_{16}. Evidently, the direction of the $\partial\mu/\partial Q$ caused by the CH_2Cl group lies close to the axis of the substituent ring bond.

It is necessary to make a correction for all compounds containing a substituent of class ii above. Although in many cases the corrections are very small, in others a significant alteration is made. We assume that for the asymmetrically monosubstituted benzene VII the over-all σ value ($\sigma_R{}^\circ as$) is the vector addition of components ($\sigma_R{}^\circ x$ and $\sigma_R{}^\circ y$) in the x and y directions. Hence $(\sigma_R{}^\circ as)^2 = (\sigma_R{}^\circ x)^2 + (\sigma_R{}^\circ y)^2$, and the intensity of the monosubstituted benzene is given by eq 6 where the terms in x and y deal with the contributions of ν_{16a} and ν_{16b}, respectively.

$$A_{\text{mono-}as} = 17{,}600\{(\sigma_R{}^\circ x)^2 + (\sigma_R{}^\circ y)^2\} + 100 \qquad (6)$$

The corresponding *para*-disubstituted derivatives exist as mixtures of the *cis* and *trans* forms VIII and IX. Rough values for the *cis*/*trans* ratios may be found by dipole moment measurements,[21] provided there is no interaction between the group moments. The values of Table IV, calculated from the data shown, all indicate more than 50% *cis*. However, it is difficult to see why the *cis* form should be favored in this equilibrium be-

(17) The barrier to rotation about the C–O bond in phenol is 3.61 kcal according to P. Delorme, *J. Chim. Phys.*, 61, 1439 (1964); see also T. Kojima, *J. Phys. Soc. Jap.* 15, 284 (1960). For a discussion of OMe barriers see L. A. Wiles, *Chem. Rev.*, 56, 329 (1956); *cf.* also H. Lumbroso, *Bull. Soc. Chim. Fr.*, 812 (1950); J. Dale, *Tetrahedron*, 22, 3373 (1966).

(18) T. H. Goodwin, M. Przybylska, and J. M. Robertson, *Acta Cryst.*, 3, 279 (1950).

(19) J. Burgers, M. A. Hoefnagel, P. E. Verkade, H. Visser, and B. M. Wepster, *Rec. Trav. Chim.*, 77, 491 (1958); B. M. Wepster, *ibid.*, 76, 357 (1957).

(20) The dipole moment of 1,4-diphenylpiperazine has been reported as 3.2 D by J. Raynaud and A. Lattes, *Compt. Rend.*, 254, 4054 (1962); although this seems very high, any nonzero value for this moment indicates nonplanarity at the nitrogen atoms in the sense of V.

(21) By comparing the dipole moment of, for example, chlorobenzene, anisole, and *p*-chloroanisole, the angle of the dipole of the OMe group may be found (assuming no interaction). This enables the dipole of the *cis* form to be calculated, and the *trans* form has zero moment. Hence the apparent moment gives the fraction in each form.

cause dipole–dipole interactions should if anything favor the *trans* form, and we therefore assume equal amounts of *cis* and *trans* conformers although there is evidence that a corresponding assumption does not hold for *meta*-disubstituted benzenes.[14,22]

Table IV. *cis/trans* Ratios for *para*-Disubstituted Benzenes from Dipole Moments

Substituents X	Measured dipole moments, D[a] C_6H_5X	p-$C_6H_4X_2$	p-ClC_6H_4X	Calcd % *cis* in p-$C_6H_4X_2$
OMe	1.25	1.70	2.26	70
CHO	2.8	2.37	2.05	59
COMe	2.9	2.7	2.3	59
COOEt	1.9	2.0	2.5	70

[a] A. L. McClellan, "Tables of Experimental Dipole Moments," W. H. Freeman and Co., San Francisco, Calif., 1963; values are means where a range is quoted.

The x components to $\partial\mu/\partial Q$ cancel for both VIII and IX; the y components cancel for VIII but are additive for IX. Hence it follows that the observed intensity for the *para*-diasymmetrically substituted compounds ($A_{para\text{-}as/as}$) is given by eq 7.

$$A_{para\text{-}as/as} = {}^1/_2 b\{2(\sigma_R{}^\circ y)\}^2 + 170 = 2b(\sigma_R{}^\circ y)^2 + 170 \quad (7)$$

Now consider the *para*-disubstituted compound X, where substituent S is of at least C_{2v} symmetry and $\sigma_R{}^\circ s$ relates to PhS. The expected total intensity is given by eq 8, which reduces to eq 9. Comparison with

$$A_{para\text{-}as/s} = b\{(\sigma_R{}^\circ s - \sigma_R{}^\circ x)^2 + (\sigma_R{}^\circ y)^2\} + 170 \quad (8)$$

$$A_{para\text{-}as/y} = b\,\{(\sigma_R{}^\circ s - \sigma_R{}^\circ as)^2 + 2\sigma_R{}^\circ s(\sigma_R{}^\circ as - \sigma_R{}^\circ x)\} + 170 \quad (9)$$

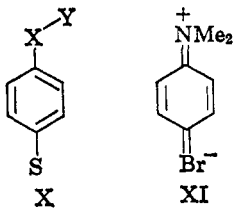
eq 5 shows that the second term in the brace on the right-hand side of eq 9 is the correction factor arising from the substituent asymmetry. The values of the factor $2(\sigma_R{}^\circ as - \sigma_R{}^\circ x)$, which form that part of the correction factor invariant with the asymmetric substituent, are calculated using eq 6 and 7 and a value of 11,800 for the constant in eq 7 (see below). The values found are comparatively small, being 0.061, 0.043, 0.058, and 0.010 for the groups CHO, COMe, CO_2Et, and OMe, respectively. The actual corrections made to the areas are given in Table V.

Table V. Calculated Values of A_{para} from Eq 5[a]

4 substituent	CHO A	CHO B	COMe A	COMe B	COOEt A	COOEt B	OMe A	OMe B
NMe_2	7115	6737			5994	5628	129	200
ND_2							11	82
OMe	5321	5020	4932	4720	4354	4059		
F	4036	3787	3693	3528	3197	2961	82	130
Br			2383	2265	1982	1829	450	480
I							495	530
Cl	2501	2348	2242	2124	1852	1711	519	554
Me	1380	1309	1191	1132	908	849	1274	1286
CN			200	247	106	153	3103	3091
NO_2	47	177	23	106	0	118	4271	4248

[a] A, without correction for asymmetry; B, with correction for asymmetry (from eq 9).

(22) F. A. Miller, W. G. Fateley, and R. E. Witkowski, *Spectrochim. Acta*, **23A**, 891 (1967).



X XI

Comparison of Experimental and Predicted Intensities. To test eq 5, we plotted $\sqrt{A_{obsd} - 170}$ against the modulus of $(\sigma_R{}^\circ 1 - \sigma_R{}^\circ 2)$, making the necessary correction from eq 9 for asymmetric substituents. In the plot (Figure 1), the following subclasses of *para*-disubstituted benzenes are differentiated: (i) two donor substituents paired (except for group iv below), (ii) two acceptor substituents paired (except for group v below), (iii) donor substituent paired with acceptor, (iv) a strong donor, $\sigma_R{}^\circ < -0.3$ (*i.e.*, NMe_2, NHMe, ND_2, OMe, F) paired with a substituent possessing a vacant d orbital next to the ring (*i.e.*, Cl, Br, I, SMe), (v) nitro paired with another acceptor group.

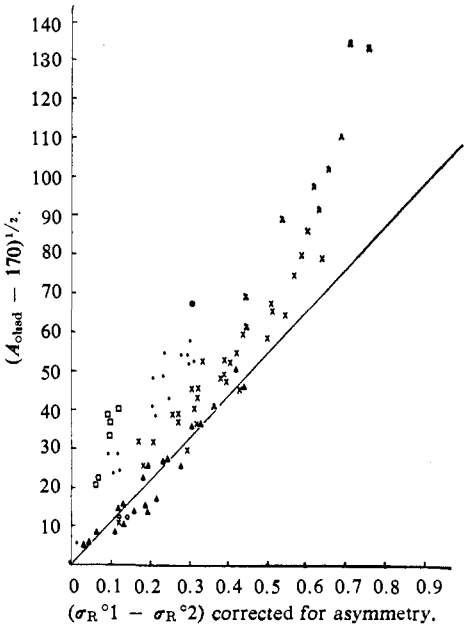


Figure 1. Square root of $(A_{obsd} - 170)$ plotted against the modulus of $(\sigma_R{}^\circ 1 - \sigma_R{}^\circ 2)$ with correction for asymmetry effect as in eq 9: ●, strong donor paired with d-orbital acceptor; ▲, other donor–donor compounds; □, nitro paired with another strong acceptor; O, other acceptor–acceptor compounds; ×, donor–acceptor compounds. The line shown is that found by a least-squares plot of the points of type ▲.

Figure 1 indicates that, even for substituents in any given class, a spread in results is observed, possibly due to variation in the form of the normal modes, as mentioned above. After some consideration as to the best value for the constant b in eq 5, we have taken the classes i and ii above as defining a line from which deviations occur as discussed in the other sections, and calculate from these points a value for b of 11,800. The calculation was initially done omitting the value for the compounds with an asymmetric substituent, which gave b as 11,600; when the values for asymmetrically substituted compounds were included, b became 11,800. Although the deviations of classes iii and iv are later quantitatively interpreted in terms of direct mesomeric

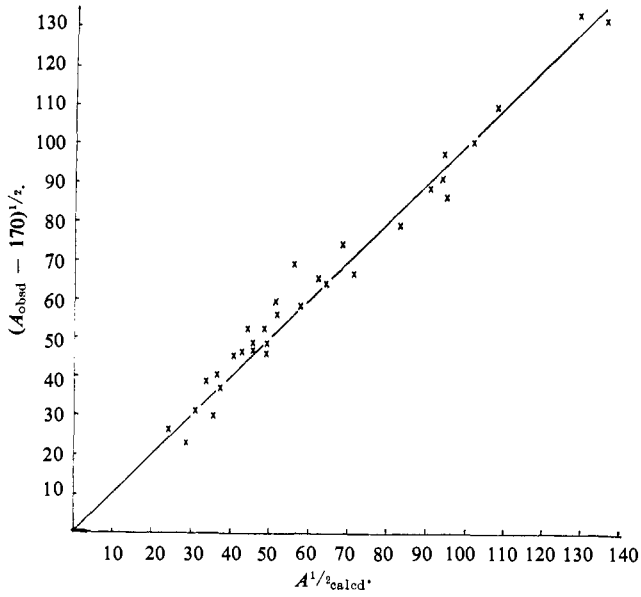


Figure 2. Square root of (A_{obsd} − 170) plotted against 108.7·{σ_R°D − σ_R°A + $K_A(\sigma^+D - \sigma D)$} for donor–acceptor compounds (*cf.* eq 11). The line shown has unit slope.

interaction between the substituents, it is emphasized that the slope of the line is tentative and may have to be revised in the light of further work.

Donor–Acceptor Compounds. From Figure 1 it is evident that the positive discrepancies shown by donor–acceptor compounds roughly increase as the total intensity increases, *i.e.*, as the magnitudes of the individual σ_R° values increase. We ascribe these discrepancies to direct resonance interaction between the two substituents; qualitatively such interactions would be expected to increase with the sizes of the individual σ_R° values. Quantitatively we searched for a relation of type 10 in which K_DK_A represents the substituent–substituent interaction. The values K_D and K_A should be related to the corresponding ($\sigma^+ - \sigma$) and ($\sigma^- - \sigma$) values, respectively, as these differences are measures

$$A_{para\text{-}A/D} = 11{,}800 \times \{\sigma_R°D - \sigma_R°A + K_DK_A\}^2 + 170 \quad (10)$$

of ability of a substituent to conjugate directly with a reaction site.[23] We find that K_D can indeed be replaced by ($\sigma^+D - \sigma D$) and that eq 11 with values of K_A = 0.36 (CO_2Me and CO_2Et), 0.57 (CHO), 0.45 (COMe), 0.55 (NO_2), and 0.29 (CN) provides a close correlation for $A_{para\text{-}A/D}$ as demonstrated in Figure 2.

$$A_{para\text{-}A/D} = 11{,}800 \times \{\sigma_R°D - \sigma_R°A + K_A(\sigma^+D - \sigma D)\}^2 + 170 \quad (11)$$

The values of K_A do not correlate with ($\sigma^- - \sigma$) but are roughly proportional to σ_R° for the acceptor groups. Conversely, ($\sigma^+ - \sigma$) is not proportional to σ_R° for the donor groups; the former quantity increases more rapidly, and is more nearly proportional to $(\sigma_R°D)^2$. Indeed, a fair correlation can be obtained by using $6.5\sigma_R°A\,(\sigma_R°D)^2$ for the discrepancy term in eq 10, but we have not done this because the physical significance is not clear. The differences between the discrepancy

(23) C. D. Ritchie and W. F. Sager, *Progr. Phys. Org. Chem.*, **2**, 323 (1964).

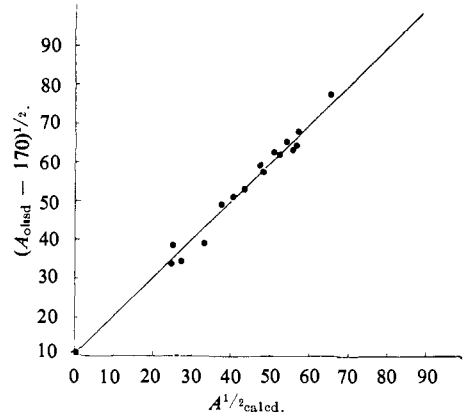


Figure 3. Square root of (A_{obsd} − 170) plotted against 108.7·(σ_R°D − σ_R°X + $K_x\sigma_R$°D) for strong donor–d-orbital acceptor compounds (*cf.* eq 12). The line shown has unit slope.

term in eq 11 and 12 presumably result from differences in ability to enter into π- and d-orbital conjugation.

The infrared results provide some evidence for significant direct resonance interaction between fluorine and *para* strong acceptor substituents; this finding indicates that the σ_R° values for strong acceptors by the Taft ^{19}F nmr method[24] are less reliable than those for other types of substituents. However, because of the small value for fluorine of ($\sigma^+ - \sigma$), −0.11, such resonance interaction is small and would not be expected to increase the observed σ_R° value by more than 0.03 unit. Previous evidence for resonance interaction between the substituent in methyl *p*-dimethylaminobenzoate comes from ^{13}C nmr measurements,[25] though other *para*-substituted methyl benzoates did not show any large effects. We plan to study solvent intensity variations which we believe will depend on variation of the direct interaction between the substituents with the medium.

d-Orbital Interactions. The halogens normally behave as resonance donor groups with negative σ_R° values. However, for compounds where Cl, Br, I (but not F), or SMe is placed *para* to a strong donor substituent the observed intensity is significantly greater than that expected from eq 5. We believe that this is due to direct resonance interaction between the *para* substituents which involves the d orbitals of the heavier halogens and of sulfur.

The effect is greater in the series I > Br ~ SMe > Cl for the d-orbital acceptor, and NMe_2 ≥ NHMe > ND_2 > OMe > F for the donor group. The discrepancies are fitted by introducing into eq 5 the correction term given in eq 12, in which D refers to the donor group

$$A_{para\text{-}X-D} = 11{,}800 \times \{\sigma_R°D - \sigma_R°X + K_x\sigma_R°D\}^2 + 170 \quad (12)$$

and X to the d-orbital acceptor, K_x is a constant for each d-orbital acceptor with the values 0.44 (SMe), 0.32 (Cl), 0.42 (Br), 0.55 (I). Observed *A* values are plotted in Figure 3 against those calculated using eq 12; the correlation coefficient for the line is 0.989.

Interaction of this type between fluorine (as donor) and the heavier halogens (d acceptors) would be ex-

(24) R. W. Taft, E. Price, I. R. Fox, I. C. Lewis, K. K. Andersen, and G. T. Davis, *J. Amer. Chem. Soc.*, **85**, 3146 (1963).
(25) K. S. Dhami and J. B. Stothers, *Can. J. Chem.*, **45**, 233 (1967).

pected to decrease the $\sigma_R°$ values obtained for the heavier halogens by the ^{19}F nmr method. The direct interaction is $K_x\sigma_R°(F)$ in $\sigma_R°$ units from eq 12; such exaltation is due to the fluorine atom behaving as a stronger donor, and the heavier halogen as a weaker donor. On the reasonable assumption that the two last mentioned effects are of equal magnitude, the alteration in $\sigma_R°$ for the heavier halogen should be $^1/_2K_x \cdot \sigma_R°(F)$. Such values are compared with those experimentally found in Table VI, and show good agreement.

Table VI

		Substituent			
		Cl	Br	I	SMe
$\sigma_R°$ (ir)		0.22	0.23	0.22	0.25
$\sigma_R°$ (^{19}F nmr)		0.18	0.16	0.14	0.17
Effect of direct resonance in p-FC_6H_4X	found	0.04	0.07	0.08	0.08
	calcd	0.05	0.07	0.09	0.08

Previous evidence is available for the participation of d orbitals in π bonding. In particular, ultraviolet spectra clearly indicate d-orbital acceptance in phenyl–halogen[26–28] and phenyl–thioalkyl[29] compounds. Schubert and his coworkers invoke such conjugation in their quantitative discussions[30,31] of solvent shifts in ultraviolet spectra. Taft and Rakshys[32] show that π–d interactions influence F chemical shifts. However, we are not aware of a previous quantitative measure of the extent of electron delocalization corresponding to that now afforded by the parameters K_x. These K_x values can be used to correlate a number of other properties, *e.g.*, C–halogen bond polarizability.[33]

Nitro Group Interaction with Acceptor Substituents. All compounds in which a nitro group is paired with a π acceptor show enhanced intensities. The NO_2 asymmetric stretch occurs near 1530 cm^{-1} in these compounds but the enhancement is probably not due to mixing with this substituent vibration, for other nitro compounds give consistent results (*e.g.*, p-iodonitrobenzene, in which the ring frequency is actually nearer to the nitro mode). Apparently the nitro group can interact strongly with other π-acceptor substituents. The ultraviolet spectra of such compounds also disclose anomalous bathochromic shifts;[34] this behavior has been discussed by Murrell[35] who considers that the nitro group can behave as a donor in the excited state, but not in the ground state because the highest filled molecular orbital of the nitro group has a node at the nitrogen atom. However, the dipole moments of ethyl

(26) W. M. Schubert, J. M. Craven, and H. Steadly, *J. Amer. Chem. Soc.*, 81, 2695 (1959).
(27) L. Goodman and L. J. Frolen, *J. Chem. Phys.*, 30, 1361 (1959).
(28) J. R. Hoyland and L. Goodman, *J. Phys. Chem.*, 64, 1816 (1960).
(29) L. Goodman and R. W. Taft, *J. Amer. Chem. Soc.*, 87, 4385 (1965).
(30) W. M. Schubert, H. Steadly, and J. M. Craven, *ibid.*, 82, 1353 (1960).
(31) W. M. Schubert and H. Steadly, *ibid.*, 82, 1357 (1960).
(32) R. W. Taft and J. W. Rakshys, Jr., *ibid.*, 87, 4387 (1965).
(33) A. Vogel, W. T. Cresswell, G. T. Jeffery, and J. Leicester, *Chem. Ind.* (London), 358 (1950).
(34) W. H. Schubert, J. M. Craven, H. Steadly, and J. Robins, *J. Org. Chem.*, 22, 1285 (1957).
(35) J. N. Murrell "Theory of Electronic Spectra of Organic Molecules," John Wiley and Sons, Inc., New York, N. Y., 1963, pp 212–213.

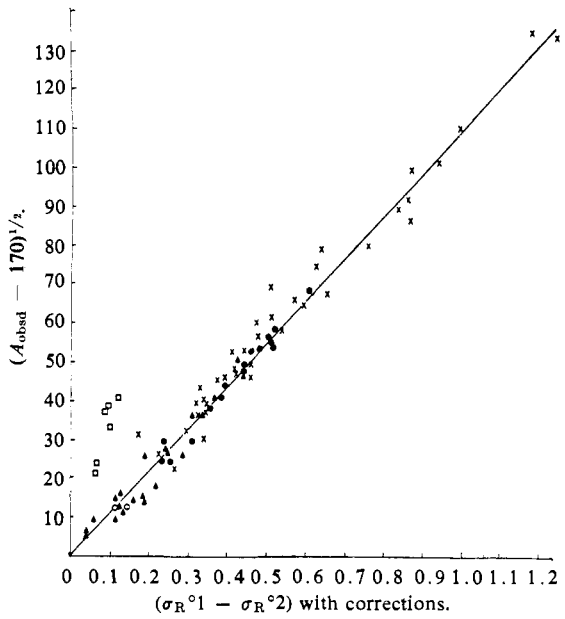


Figure 4. Square root of $(A_{obsd} - 170)$ plotted against $(\sigma_R°1 - \sigma_R°2)$ with corrections for asymmetry effects (eq 9) for donor–acceptor compounds (eq 11) and for donor–d-orbital acceptor compounds (eq 12). Symbols as in Figure 1. The line shown has the same slope as in Figure 1.

p-nitrobenzoate and p-nitroacetophenone are in fair agreement with the vectorially added calculated values.[36]

Taft[37] has shown by fluorine nmr that nitro compounds tend to associate, but this effect can hardly account for the discrepancies now noted, which remain for the present unexplained. We plan to study a wider range of acceptor–acceptor compounds to determine whether such deviations are general in this class of derivative.

Conclusions and Applications. Figure 4 shows a combined plot of $\sqrt{A_{obsd} - 170}$ against $\sqrt{A_{para} - 170}$ in which standard corrections for interaction between donors and both π-bond and d-orbital electron acceptor substituents have been incorporated according to eq 11 and 12. No corrections have been made for substituent–substituent interactions involving ND_3^+, NMe_3^+, of CH_2Cl groups as donors, or SO_2Cl, SO_3Me, or CF_3 groups as acceptors, because insufficient data are available to calculate the relevant constants. Such corrections would improve the correlation. The over-all agreement is impressive, except for the anomalous nitro acceptor derivatives. Discrepancies between A_{para} (corr) and A_{obsd} are given in Table VII, in terms of $\sigma_R°$ units (see footnote to Table VII for calculation).

An important consequence of this good over-all agreement is the ability to determine directly the *sign* of the resonance interaction of any substituent with a benzene ring; we have now applied this to the NMe_3^+ group and we plan to test the direction of resonance interaction in groups such as azo, nitroso, and ethynyl.

Ammonio Substituents. Eight compounds containing the groups NMe_3^+ or ND_3^+ have been investigated, and the results show clearly that these groups are resonance *donors*, with $\sigma_R°$ values of −0.15 and −0.18,

(36) For data and a full discussion see P. J. Q. English, Ph.D. Thesis, University of East Anglia, 1967.
(37) R. W. Taft, G. B. Klingensmith, and S. Ehrenson, *J. Amer. Chem. Soc.*, 87, 3620 (1965).

Table VII. Discrepancies[a] Remaining after Corrections

	CHO	COMe	COOEt	NO_2	CN	Me	Cl	I	Br	F	OMe	NMe_2
NMe_2	−0.033		+0.003	+0.052	+0.031	−0.023	−0.002	+0.020	+0.006	−0.059	+0.008	0.000
NHMe						+0.043	+0.011		−0.010	−0.039		
ND_2						+0.008	−0.006	+0.001	+0.021	+0.017	+0.086	
OMe	−0.014	−0.021	−0.039	−0.104	−0.043	+0.012	+0.007	+0.017	+0.005	+0.013		
OH						+0.029						
F	+0.028	−0.011	−0.011	+0.015	−0.044	−0.026	−0.038	−0.067	−0.022			
Br		+0.061	+0.010	+0.035	+0.011	−0.055	+0.051					
I				−0.002		−0.122						
Cl	+0.121	−0.069	+0.020	−0.017	−0.059	−0.023						
SMe							0.000			+0.006		+0.159
$ND_3^+Cl^-$						−0.084	−0.034		−0.048	−0.023	+0.008	
$NMe_3^+Cl^-$				+0.013						+0.044	−0.030	
Et				−0.013								
Me	+0.066	+0.041	+0.041	−0.006	+0.022							
CH_2Cl				+0.121			−0.055					
CN		−0.125	−0.003	+0.259								
SO_3Me						−0.010						
SO_2Cl				+0.146		+0.088						
CF_3				+0.130			+0.096					+0.073
NO_2	+0.267	+0.297	+0.288									

[a] Discrepancy = $\{[(A_{obsd} - 170)/11{,}800] - \chi\}^{1/2} - \{\sigma_R{}^\circ 1 - \sigma_R{}^\circ 2 + \lambda\}$ where χ is the correction term for asymmetric substituents from eq 9, and λ is the correction term for donor interactions with π or d orbitals from eq 11 or 12.

respectively. There is other evidence in this direction: pK_a measurements indicate[38] σ_R of −0.11 for NMe_3^+; ^{19}F nmr data[39] from *p*-fluorotrimethylanilinium chloride indicate a $\sigma_R{}^\circ$ of −0.08 for the group NMe_3^+. pK values of substituted phenols[40] and the equation $\sigma_R = 1.5(\sigma_p - \sigma_m)$ give $\sigma_R = -0.12$ for NMe_3^+ (*cf.* +0.25 for SMe_2^+).

Kinetic study of the nitration of the anilinium ion[41] and N-methylanilinum ion[42] has shown that for NH_3^+ the partial rate factor for nitration is somewhat *greater* at the *para* than at the *meta* position. The authors tentatively suggested[42] hyperconjugative electron release from the N–H bonds to account for this; the greater reactivity at both the *ortho* and *para* positions of the NH_3^+ derivative over the NMe_3^+ analog was ascribed to solvation effects. Other reactivity evidence is surveyed in this paper.[42] Recently, the effect of NR_3^+ groups on benzenoid chemical shifts[43] was shown to indicate a somewhat higher electron density at the *para* than the *meta* position to NR_3^+; however this was ascribed to the weakening of the inductive effect with distance; resonance interactions between the ring and substituent were not considered.

Acknowledgments. R. D. T. is grateful for the award of a Nuffield Travelling Fellowship. P. J. Q. E. thanks the Science Research Council for a Research Studentship and T. T. T. is grateful for the award of the Public Health Service Fellowship. We thank Professor R. W. Taft for helpful discussions.

(38) W. A. Sheppard, unpublished results privately communicated.
(39) R. W. Taft, personal communication; see also ref 32.
(40) S. Oae and C. C. Price, *J. Amer. Chem. Soc.*, 80, 3425 (1958).
(41) M. Brickman and J. H. Ridd, *J. Chem. Soc.*, 6845 (1965).
(42) M. Brickman, J. H. P. Utley, and J. H. Ridd, *J. Chem. Soc.*, 6851 (1965).
(43) G. Fraenkel and J. P. Kim, *J. Amer. Chem. Soc.*, **88**, 4203 (1966).