this paper we have disproven assumption 2. *Thus the Taft σ_o* constants do not represent an intrinsic general ortho-electrical effect.* They are a combination of the electrical effect in acidic hydrolysis, largely resonance in character, and the electrical effect in basic hydrolysis, largely localized in character. That their composition (as measured by ϵ) is the same as that of the σ_p constants is purely fortuitous. Their success in correlating many sets of ortho-substituted data is due to the variability of the ortho-electrical effect which ranges from $\epsilon = 0$ to $\epsilon = 2$. We will expand on this point in another paper.

Solvent Effects on the Composition of the ortho-Electrical Effect. We have shown elsewhere that when the pK_a values of 2-substituted benzoic acids in various solvents are correlated with eq 4, α is constant whereas β is a function of solvent.[5] The results obtained in aqueous acetone at 25° suggest the possibility of a solvent dependence of β for the correlations obtained with the rates of alkaline hydrolysis of 2-substituted ethyl benzoates. More telling evidence on this point is obtained from a consideration of the β values obtained for 65, 85, and 95% aqueous dimethyl sulfoxide. The β values are 0.838, 1.55, and 2.59, respectively. While the results are certainly not conclusive, they do indicate the strong possibility that β is a function of solvent for the alkaline hydrolysis of benzoate esters.

As was the case for the benzoic acid ionization, α seems to be largely or entirely free of solvent dependence.

Infrared Intensities as a Quantitative Measure of Intramolecular Interactions. V.[1] ortho- and meta-Disubstituted Benzenes. The ν_{16} Band near 1600 cm⁻¹

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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 June 26, 1968

Abstract: The integrated intensity is reported for the 1600-cm⁻¹ band for many meta- and ortho-disubstituted benzenes. Equations relating the expected intensities with $\sigma_R°$ parameters for the substituents are deduced and shown to hold. Conformational isomerism for meta-substituted benzaldehydes and other compounds with asymmetrical substituents is discussed and tentative values for the corresponding equilibrium constants are calculated. Steric and mesomeric interactions in ortho-disubstituted compounds are discussed.

Previous papers in this series have shown that the total integrated area of the bands near 1600 and 1580 cm⁻¹ for mono-[5] and para-disubstituted benzenes[1] and for monosubstituted durenes[5] are related by eq 1, 2, and 3 to the $\sigma_R°$ value(s) of the substituent(s); in eq 2 the algebraic signs of the $\sigma_R°$ values result in over-all addition for "unlike" substituents and over-all subtraction for "like" substituents. The different values of the coefficients in eq 1, 2, and 3 (also 11; see later) are believed to arise from variations in the precise form of the normal mode as between various substitution types of benzenes. Equation 2 applies to para-disubstituted

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

$$A_{para} = 11{,}800(\sigma_R°1 - \sigma_R°2)^2 + 170 \qquad (2)$$

$$A_{durene} = 11{,}300(\sigma_R°)^2 - 30 \qquad (3)$$

compounds in which direct resonance interaction between the two substituents does not occur; discrepancies from eq 2 are useful for the investigation of substituent interactions.[1] Equation 3 applies in the absence of steric effects.

The extension of such infrared intensity measurements to other polysubstituted systems was expected to be a useful means for the examination of the combined effects of resonance and steric interaction. For example, meta substituents should be incapable of direct interaction either sterically or by ordinary conjugation, whereas ortho substituents can interact by both such means. Earlier semiquantitative work by one of us[6] had indicated that whereas the intensity of the para-disubstituted derivatives varied as the algebraic difference between the electronic effects of the substituents[7] the intensity of the meta-disubstituted compounds varied as approximately their sum,[8] and the ortho-disubstituted derivatives showed intermediate behavior.[9] Little other work has appeared on the

(1) Part IV: P. J. Q. English, A. R. Katritzky, T. T. Tidwell, and R. D. Topsom, *J. Am. Chem. Soc.*, **90**, 1767 (1968).

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(5) R. T. C. Brownlee, A. R. Katritzky, T. T. Tidwell, and R. D. Topsom, *J. Am. Chem. Soc.*, **90**, 1757 (1968).

(6) A. R. Katritzky and P. Ambler in "Physical Methods in Heterocyclic Chemistry," Vol. II, A. R. Katritzky, Ed., Academic Press, New York, N. Y., p 161.

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

(8) A. R. Katritzky and P. Simmons, *ibid.*, 2058 (1959).

(9) A. R. Katritzky and R. A. Jones, *ibid.*, 3670 (1959).

infrared intensities of these compounds. Extinction coefficients for *ortho*-disubstituted benzenes have been reported by Brigodiot and Lebas.[10] Bobovitch and Belyaevskaya[11] found no simple dependence between log A for the 1600-cm^{-1} band in the Raman spectrum and Hammett parameters for *meta*-disubstituted compounds similar to the relation that they reported for *para*-disubstituted derivatives; however, Schmid[12] has successfully correlated the infrared intensities of CH stretching bands in *ortho*-disubstituted benzenes with σ_I values for the substituents.

meta- and *ortho*-disubstituted benzenes have now been investigated using the more accurate techniques developed for the correlation of ν_{16} ring vibrations. The normal-coordinate analysis of *meta*-dichlorobenzene[13] indicates that the form of the 1600-cm^{-1} vibration is similar to that in monosubstituted benzenes. Various authors have shown that *ortho*-[14] and *meta*-disubstituted[15] benzenes can be treated as of pseudo C_{2v} symmetry. It is thus possible to predict the intensities of the bands for these compounds in terms of the corresponding monosubstituted derivatives. The argument is first developed for compounds in which both substituents are of at least C_{2v} symmetry; correlations for less symmetrical compounds are considered later.
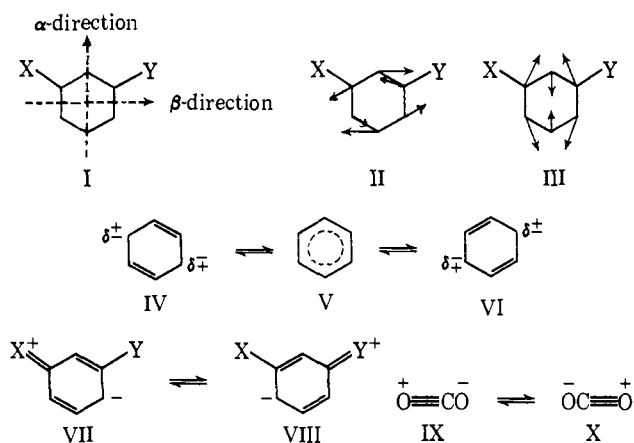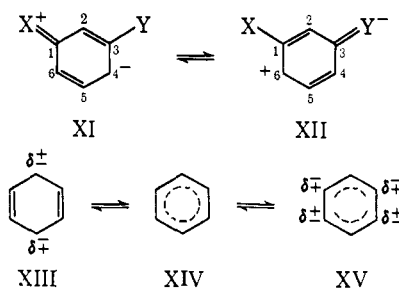

meta-Disubstituted Compounds. For a *meta*-disubstituted benzene (I), the forms of the vibrations are as given in II and III.[13] A molecular orbital representation of the vibration II takes account of the varying p-orbital overlap between adjacent atoms in the ring; using double bonds to represent greater, and single bonds lesser overlap, the vibration may thus be described as IV $\rightleftharpoons$ VI, where the signs are alternative. The equivalent valence bond representation is that canonical forms of type IV and VI contribute more significantly to the resonance hybrids in the corresponding extreme stretched forms than in the nonvibrating molecule. If the two *meta* groups are both either elec-

(10) M. Brigodiot and J.-M. Lebas, *J. Chim. Phys.*, **62**, 347 (1965).
(11) Y. S. Bobovitch and N. M. Belyaevskaya, *Opt. Spectry.*, **19**, 111 (1965).
(12) E. D. Schmid, *Ber. Bunsenges. Phys. Chem.*, **67**, 39 (1963); *Spectrochim. Acta*, **22**, 1659 (1966).
(13) J. R. Scherer, "Planar Vibrations in Monosubstituted Benzenes," Dow Chemical Co., Midland, Mich., 1963.
(14) G. Varsányi, S. Holly, and T. Faragó, *Spectrochim. Acta*, **19**, 683 (1963).
(15) G. Varsányi, S. Holly, and T. Faragó, *ibid.*, **19**, 675 (1963).

tron donors or electron acceptors, we have an alternating dipole moment in the β direction (*cf.* I) during the vibration (*cf.* VII $\rightleftharpoons$ VIII), which may be compared to the analogous situation in the CO$_2$ active stretching mode (IX $\rightleftharpoons$ X). Let $\sigma_R°1$ and $\sigma_R°2$ represent the $\sigma_R°$ values of the substituents X and Y, respectively. Then the infrared intensity arising from the alternating dipole in the β direction of the molecule in mode II is given by eq 4 where b is a proportionality constant. The algebraic signs of $\sigma_R°1$ and $\sigma_R°2$ result in over-all addition for substituents of similar type and over-all subtraction for dissimilar substituents (for which compare XI $\rightleftharpoons$ XII).

$$A(\text{mode II, } \beta \text{ direction}) = b(\sigma_R°1 \cos 30° + \sigma_R°2 \cos 30°)^2 = \text{}^3/_4 b(\sigma_R°1 + \sigma_R°2)^2 \quad (4)$$

During vibrational mode II, in general there is also an alternating dipole moment in the α direction of the molecule; this is exemplified by the motion XI $\rightleftharpoons$ XII by which atoms 1 and 3 simultaneously become alternately more negatively (XII) and positively (XI) charged with respect to atoms 6 and 4, respectively. The infrared intensity arising from the alternating dipole in the α direction is given by eq 5. Here the algebraic signs result in over-all subtraction for substituents of similar type and over-all addition for dissimilar substituents.

$$A(\text{mode II, } \alpha \text{ direction}) = b(\sigma_R°1 \cos 60° - \sigma_R°2 \cos 60°)^2 = \text{}^1/_4 b(\sigma_R°1 - \sigma_R°2)^2 \quad (5)$$
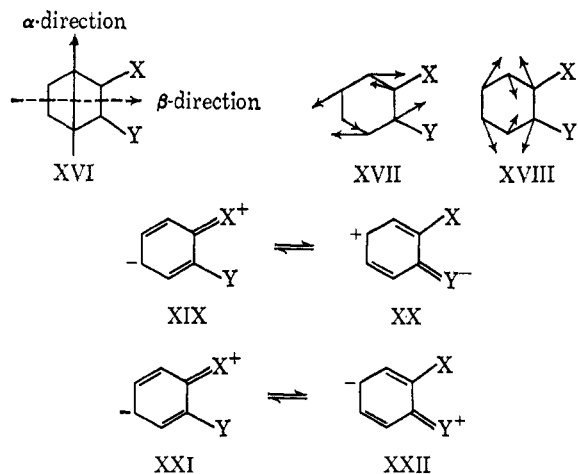

Vibration III may be represented by XIII $\rightleftharpoons$ XV and it is evident that for this vibration to be active in the infrared region, canonical forms of type XIII or XV must be preferentially stabilized by a substituent. To the approximation of using the simple VB method, this does not occur for the *meta*-disubstituted derivatives, for which the total intensity hence arises almost entirely from mode II, and is given by addition of the A values deduced for directions α and β (eq 6). The constant c is then introduced to take account of overtone and combination contributions to the total intensity; we find that A_{meta} is given by eq 7.

$$A_{meta} = b\{ \text{}^3/_4(\sigma_R°1 + \sigma_R°2)^2 + \text{}^1/_4(\sigma_R°1 - \sigma_R°2)^2 \} \quad (6)$$

$$A_{meta} = b\{(\sigma_R°1)^2 + (\sigma_R°2)^2 + \sigma_R°1\sigma_R°2\} + c \quad (7)$$

It may be noted that eq 7 corresponds to vector addition of $\sigma_R°1$ and $\sigma_R°2$ at 60°, and that the third term is positive for two substituents of the same type, and otherwise negative.

ortho-**Disubstituted Compounds.** As for the *meta*-disubstituted derivatives, the *ortho*-disubstituted compounds (XVI) have vibrations of types XVII and XVIII. Vibration XVII can be represented by IV $\rightleftharpoons$ VI; dissimilar-type *ortho* substituents cause considerable charge alternation in the β direction as indicated (XIX $\rightleftharpoons$ XX), whereas the effects of substituents of similar type will partially cancel. The intensity thus arising is given by eq 8.

$$A(\text{mode XVII}, \beta \text{ direction}) =$$
$$b'\{(\sigma_R{}^\circ 1 - \sigma_R{}^\circ 2) \cos 30^\circ\}^2 =$$
$$^3/_4 b'(\sigma_R{}^\circ 1 - \sigma_R{}^\circ 2)^2 \quad (8)$$

For charge displacement during mode XVII in the α direction, groups X and Y reinforce each other if of similar type, as shown for two donor groups in XXI $\rightleftharpoons$ XXII, whereas dissimilar groups partially cancel. Hence

$$A(\text{mode XVII}, \alpha \text{ direction}) =$$
$$b'\{(\sigma_R{}^\circ 1 + \sigma_R{}^\circ 2) \cos 60^\circ\} =$$
$$^1/_4 b'(\sigma_R{}^\circ 1 + \sigma_R{}^\circ 2)^2 \quad (9)$$

By reasoning similar to that already given for the *meta*-disubstituted compounds, mode XVIII will not contribute to the *ortho* intensity to a first approximation and thus, by addition of eq 8 and 9, the total intensity is given by eq 10.

$$A_{ortho} = b'\{(\sigma_R{}^\circ 1)^2 + (\sigma_R{}^\circ 2)^2 - \sigma_R{}^\circ 1 \sigma_R{}^\circ 2\} + c' \quad (10)$$

This corresponds to vector addition of $\sigma_R{}^\circ 1$ and $\sigma_R{}^\circ 2$ at 120° with the addition of the overtone–combination band constant c'. The third term is now positive for dissimilar type substituents and negative for those of similar type.

Experimental Section

The techniques of sample preparation, infrared measurement, and band integration were the same as used previously.[1] For all compounds the entire absorption contained within the principal band or bands was integrated, as the nearby combination bands may share intensity with the principal ring vibrations. In some cases, particularly toluenes and fluoro derivatives, the absorptions were quite complex, giving sometimes three equivalent bands. Values for nitro derivatives have low reliability because of extensive overlap of the ring vibrations by the N–O stretch of the nitro group around 1520 cm^{-1}.

The samples used were from commercial sources or were prepared by simple alkylations of phenols, amines, or acids. Solids were purified by recrystallization to constant melting point in
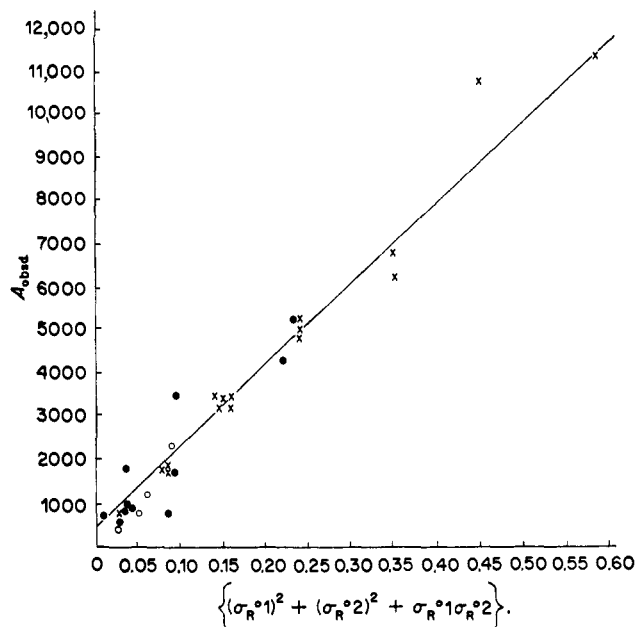
Figure 1. Plot of A_{obsd} for *meta*-disubstituted benzenes with substituents of at least C_{2v} symmetry against $\{(\sigma_R{}^\circ 1)^2 + (\sigma_R{}^\circ 2)^2 + \sigma_R{}^\circ 1 \sigma_R{}^\circ 2\}$: X, two donor substituents; ●, one donor and one acceptor; O, two acceptor substituents.

agreement with literature values. The purity of liquids was investigated by vapor phase chromatography, and in most cases direct comparisons were made to determine the efficiency of separation of *ortho*, *meta*, and *para* isomers. In most, but not all, of the compounds the isomers could be separated, and in the remaining cases the isomeric compounds were not detectable by the nmr spectrum (*i.e.*, <3% concentration). In all cases the liquids were purified by distillation or vpc separation until the detectable impurities amounted to less than 1% as determined by weighing vpc peaks.

Solvents for the ir measurements were carbon tetrachloride, chloroform, or cyclohexane, depending upon the solubility of the compound in question. The absence of any significant variation in the A values with solvent was confirmed for methyl *m*-dimethylaminobenzoate, *m*-methoxyacetophenone, *m*-chlorobenzotrifluoride, *m*-fluorotoluene, and *m*-methoxy-N,N-dimethylaniline.

Measured intensities for the *meta*- and *ortho*- disubstituted compounds studied are recorded in Tables I and II, respectively, and the frequencies of these bands are given in Tables III and IV. The frequencies are in reasonable agreement with literature data where available. Precise intensity data for comparison are scarce; a series of *o*-chlorophenyl compounds has been reported;[16] the data are for liquid films with A_{obsd} values in poor agreement with the present measurements.

Discussion

meta-**Disubstituted Compounds with Both Substituents of C_{2v} Symmetry.** Observed values of A_{meta} are plotted against $\{(\sigma_R{}^\circ 1)^2 + (\sigma_R{}^\circ 2)^2 + \sigma_R{}^\circ 1 \sigma_R{}^\circ 2\}$ in Figure 1; a fair straight line plot is found, with compounds of donor–donor and donor–acceptor type showing good regularity, but with more scatter for acceptor–acceptor type substituted compounds. From this line (correlation coefficient 0.990) eq 7 can be modified to 11.

$$A_{meta} = 19,000\{(\sigma_R{}^\circ 1)^2 + (\sigma_R{}^\circ 2)^2 +$$
$$\sigma_R{}^\circ 1 \sigma_R{}^\circ 2\} + 340 \quad (11)$$

(16) M. G. K. Pillai, K. Ramaswamy, and S. G. Gnanadesikan, *Indian J. Chem.*, **4**, 415 (1966).

Table I. Measured Integrated Intensities (A_{obsd}) for *meta*-Disubstituted Benzenes

	CHO	COMe	CO₂Me	NO₂	CF₃	Me	Cl	I	Br	F	OMe	NMe₂
NMe₂			6690	4330	a	a	a			a	13,700[c]	16,100[c]
OMe		4480	4410	1550		a	6400	6990		a	11,000	
F	2670	2680	2990	740	a	a	a	a	a	6230	9,030	11,500[c]
Br	1770		1580		a	1880	a		3400	5070	7,530	
I			1510		a	1750		3180		5240	a	
Cl	1820		1606		a	1820	3510		3430	4890	a	10,800
Me		1260	930	500		830	a	a	a	3270	4,730	6,870[c]
CN				740[b]	340	720	1900			3480		
CF₃			660[b]	1200			806[b]	950	860	1710		5,270[c]
NO₂	2320[b]	1510[b]	1230[b]	2350[b]	a	a				a	a	a
CO₂Me			800	a	a	a	a	a	a	a	a	a
CHO	2710[b]											

a Result appears elsewhere in table.   All results refer to carbon tetrachloride solutions except where denoted.   b CHCl₃.   c C₆H₁₂.

Table II. Measured Integrated Intensities (A_{obsd}) for *ortho*-Disubstituted Benzenes

	CHO	COMe	CO₂Me	NO₂	Me	Cl	I	Br	F	OMe
NMe₂					1090[c]				1550[c]	1780
OMe					a	a	1680	2200[c]	a	
F	3620	2660	2770		a	a	a	a	1550	1680
Br	1840		1300		a	450		380	1090	a
I			1160		a		410		1140	a
Cl	2130		1310		a	320		a	1080	1940
Me		700	780[c]		250	440	830	580	1010	1660
CN				910[b]	390	890			1800[c]	
CF₃						1850	1440	1850		
NO₂	660	630			810					

a Result appears elsewhere in table.   All results refer to carbon tetrachloride solutions except where noted.   b CHCl₃.   c C₆H₁₂.

Table III. Measured Frequencies of Peak Maxima (cm⁻¹) for *meta*-Disubstituted Benzenes

	CHO	COMe	CO₂Me	NO₂	CF₃	Me	Cl	I	Br	F	OMe	NMe₂
NMe₂			1604 1581	1622 1573							1615 1580	1609 1581
OMe		1599 1587	1602 1589	1622 1587			1598 1582	1587 1570			1613 1594	
F	1612 1594	1591	1618 1594	1622 1665 1595 1571						1613 1604	1618 1596	1622 1586
Br	1593 1575		1595 1573			1603 1591 1571			1575 1567	1593	1592 1574	
I			1592 1568			1596 1567		1594		1586		
Cl	1593 1573		1600 1577			1605 1598 1578	1580	1572		1600 1595	1596 1564	
Me		1605 1588	1611 1593	1587 1560		1615 1591				1620 1596 1584	1604 1586	1605 1586
CN				1620	1615	1603 1586	1594 1572 1566			1611 1589		
CF₃			1620 1599	1627 1599			1608 1502	1601 1576	1605 1581	1620 1604	1616 1589	
NO₂	1616 1585	1617 1581	1620 1585	1616 1505								
CO₂Me			1612 1588									
CHO	1607											

Table V shows the discrepancies between the values of A_{meta} from eq 11 and observed values for compounds with both substituents of C₂ᵥ symmetry, expressed in terms of $\sigma_R{}^\circ$ values. The average discrepancy is 0.036 unit. Of the 32 values, 18 are within 0.03 unit, and only 6 above 0.06 unit. Poorest agreement is found for cyano compounds.

meta-Disubstituted Compounds with One Substituent of Less Than C₂ᵥ Symmetry. Compounds containing CO₂Et, COMe, CHO, and OMe groups show marked deviations from the simple relation 11. These groups are asymmetric, and complications therefore arise. Methyl *m*-fluorobenzoate, for example, is expected to have two stable conformations, XXIII and XXIV, which
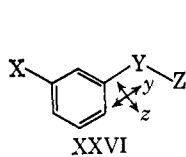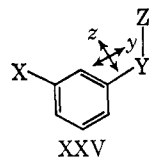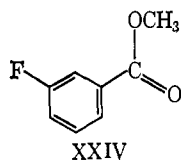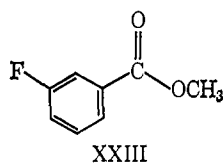
Katritzky, et al. / ortho- and meta-Disubstituted Benzenes

Table IV. Measured Frequencies of Peak Maxima (cm⁻¹) for *ortho*-Disubstituted Benzenes

	CHO	COMe	CO₂Me	NO₂	Me	Cl	I	Br	F	OMe
NMe₂					1600 1580				1619 1579	1594 1584
OMe	1602 1584	1601 1581	1603 1587				1582 1572	1591 1573		
F	1614 1587	1612 1584	1613 1585						1618 1669 1595 1581	1619 1592
Br	1589 1569		1593 1568			1577 1571		1598 1568	1595 1579	
I			1587 1565				1599 1576 1554		1584	
Cl	1595 1569		1595 1577			1605 1576			1597 1589	1592 1580
Me		1603 1572	1604 1585		1607 1483	1595 1575	1590 1564	1597 1570	1612 1591	1604 1592
CN				1615 1577	1625 1603	1595			1615 1588 1576	
CF₃						1598 1583	1580 1561	1598 1575		
NO₂	1609 1578	1612 1576			1615 1581				1611 1586	

Table V. Discrepancies[a] in Units of $\sigma_R{}^\circ$ for *meta*-Disubstituted Benzenes with Both Substituents of at Least C_{2v} Symmetry

	NO₂	CF₃	Me	Cl	I	Br	F	NMe₂
NMe₂	−0.012	+0.023						−0.045
F	−0.149	−0.031	−0.007				−0.033	+0.004
Br		−0.031	−0.008	+0.017		+0.003	+0.002	
I		−0.011	−0.017		+0.004		+0.018	
Cl		−0.001	−0.002	+0.034			+0.003	+0.075
Me	−0.060		−0.012					−0.002
CN	−0.083	−0.167	+0.047	+0.099			+0.101	
CF₃	−0.034							
NO₂	+0.026							

[a] Discrepancy $= [(A_{obsd} - 340)^{1/2}/(19{,}000)^{1/2}] - \{(\sigma_R{}^\circ 1)^2 + (\sigma_R{}^\circ 2)^2 + \sigma_R{}^\circ 1\sigma_R{}^\circ 2\}^{1/2}$.

XXIII   XXIV

XXV   XXVI

may coexist in unknown proportions. The calculation leading to eq 7 can be modified to cover such cases. Let XXV and XXVI represent the two conformations of a compound with a symmetrical substituent X of $\sigma_R{}^\circ 1$, and an unsymmetrical substituent YZ with components y and z of $\sigma_R{}^\circ 2$, respectively, along, and perpendicular to, the ring–Y bond. The magnitude and sign of component y and the magnitude of component z are the same for XXV and XXVI, but the sign of z is different. Hence eq 4 and 5 must be modified to the following, where the upper and lower signs refer to the alternative conformations XXV and XXVI.

$$A(\text{mode II, }\beta\text{-direction}) = b(\sigma_R{}^\circ 1 \cos 30° + y \cos 30° \pm z \cos 60°)^2$$

$$A(\text{mode II, }\alpha\text{-direction}) = b(\sigma_R{}^\circ 1 \cos 60° - y \cos 60° \pm z \cos 30°)^2$$

Hence relation 12 follows, setting $y^2 + z^2 = (\sigma_R{}^\circ 2)^2$, where the alternative signs apply to the possible configurations XXV and XXVI.

$$A_{meta(\text{as/s})} = 19{,}000\{(\sigma_R{}^\circ 1)^2 + (\sigma_R{}^\circ 2)^2 + \sigma_R{}^\circ 1(y \pm \sqrt{3}z)\} + 340 \quad (12)$$

The deviations shown by *meta*-disubstituted compounds containing an unsymmetrical substituent from eq 11, and also independent evidence from nmr coupling constants[17] and torsional frequencies,[18] indicate that the population of conformer pairs of type XXIII and XXIV are far from equal. If a reliable method of calculating y and z were available, then it would be possible to estimate the relative populations. Unfortunately this is not so; however, we have earlier[1] made the arbitrary assumption that the populations of the *cis* and *trans* forms in symmetrically *para*-disubstituted compounds (*e.g.*, terephthalaldehyde) are equal, which enables the calculation (*cf.* ref 1) of the following values of y and z shown in Table VI. Using these values, we

(17) G. J. Karabatsos and F. M. Vane, *J. Am. Chem. Soc.*, **85**, 3886 (1963).
(18) F. A. Miller, W. G. Fateley, and R. E. Witkowski, *Spectrochim. Acta*, **23A**, 891 (1967).

Table VI

	CO₂Me	CHO	COMe	OMe
y	0.128	0.224	0.204	0.425
z	0.087	0.097	0.077	0.053
$\sigma_R°$	0.155	0.244	0.219	0.428

Table VII. Integrated Intensities (A_{obsd}) Compared with A_{cis} and A_{trans} Values Calculated by Eq 12 for *meta*-Disubstituted Benzenes with One Substituent of at Least C_{2v} Symmetry and One of Lower Symmetry

——Substituents——					
Asymmetric	Symmetric	A_{obsd}	A_{trans}	A_{cis}	% trans
CHO	F	2,670	3,310	1,160	70
	Cl	1,820	2,130	750	78
	Br	1,770	2,000	650	83
	NO₂	2,320	2,220	3,330	91
COMe	F	2,660	3,060	1,200	79
	Me	1,260	1,300	790	93
	NO₂	1,510	2,050	2,930	(>100)
CO₂Me	NMe₂	6,690	5,310	3,550	(>100)
	F	2,990	3,160	1,200	92
	Cl	1,610	1,770	540	87
	Br	1,580	1,880	600	76
	I	1,510	1,810	550	76
	Me	920	1,020	460	83
	CF₃	660	990	1,600	(>100)
	NO₂	1,260	1,300	2,290	96
OMe	NMe₂	13,700	12,590	14,400	52
	F	9,020	8,160	9,360	28
	Cl	6,400	6,060	6,820	56
	Br	6,620	6,170	7,090	50
	I	6,990	6,130	6,900	0
	Me	4,730	4,610	4,970	65
	NO₂	1,550	3,290	2,670	(<0)

can calculate (Table VII) from eq 12 values of A_{meta} for the alternative configurations, and hence the equilibrium constant, K, between the forms. Figure 2 shows the results graphically. The line shown has unit slope; although it usually passes through the range of the A values calculated, there are strong indications that the compounds do not exist in the two conformations to an equal extent. If the mole fraction existing in the *cis* conformation is n, then eq 13 follows, and the

$$n = \frac{A_{obsd} - A_{trans}}{A_{cis} - A_{trans}} \qquad (13)$$

percentage of *cis* and *trans* forms can then be deduced (Table VII). Because of the assumptions made,[19] values of n must be very approximate. However, it is of interest that *m*-chlorobenzaldehyde is deduced to exist *ca.* 80% in the O-*trans* form XXVII, and 20% in the O-*cis* form XXVIII. From long-range coupling constants of *m*-chlorobenzaldehyde in carbon tetrachloride, acetone, and cyclohexane solutions, Kara-

(19) The further assumption is made that the $\sigma_R°$ vector in benzaldehyde is displaced toward the carbonyl bond as in A and that the $\sigma_R°$ vector in anisole is aligned as in B.
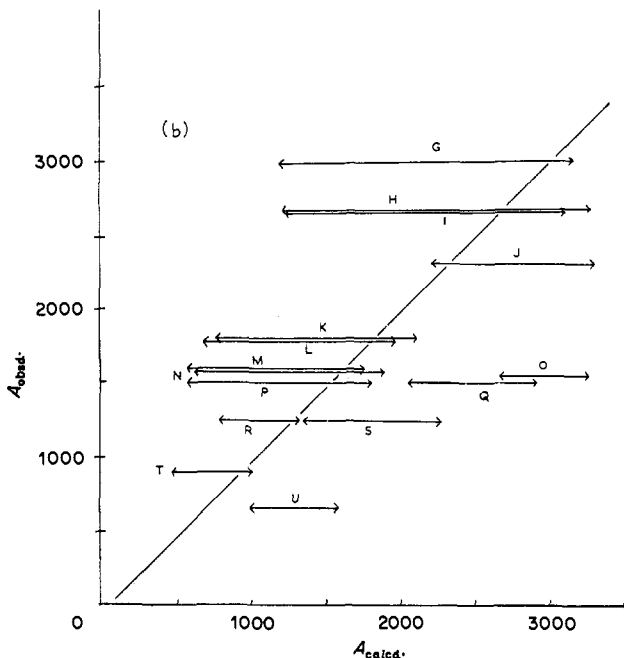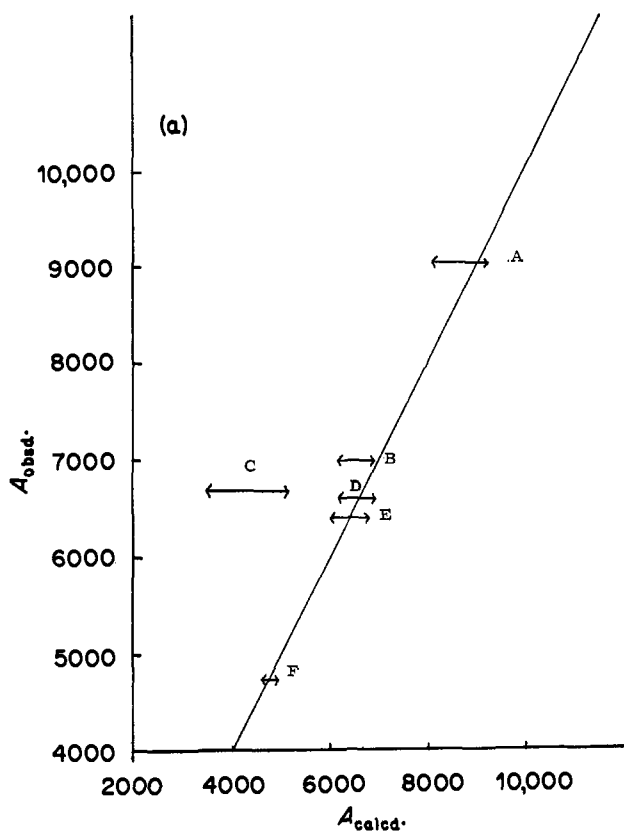
A

B

Figure 2. Plots of A_{obsd} against the calculated $\sigma_R°$ values for the alternative conformations of *meta*-disubstituted benzenes containing one or two unsymmetrical substituents (the line is that of Figure 1): (a) A, OMe and F; B, OMe and I; C, CO₂Me and NMe₂; D, OMe and Br; E, OMe and Cl; F, OMe and Me; (b) G, F and CO₂Me; H, F and CHO; I, F and COMe; J, CHO and NO₂; K, Cl and CHO; L, Br and CHO; M, CO₂Me and Cl; N, CO₂Me and Br; O, OMe and NO₂; P, CO₂Me and I; Q, COMe and NO₂; R, Me and COMe; S, CO₂Me and NO₂; T, CO₂Me and Me; U, CF₃ and CO₂Me.

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batsos and Vane[17] deduced that *m*-chlorobenzaldehyde existed 60–70% in the O-*trans* form, whereas Miller, *et al.*,[18] using torsional frequencies in the far-infrared, came to the opposite conclusion; however, these last measurements related to the vapor phase.

XXVII   XXVIII   XXIX
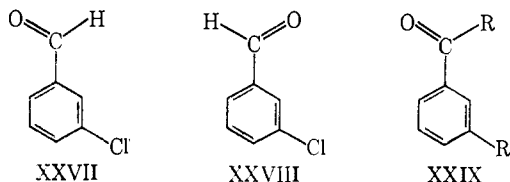
All the *meta*-substituted benzaldehydes, acetophenones, and methyl benzoates appear (Table VII) to prefer the O-*trans* configuration (XXIX, R = H, Me, OMe) by ΔG values of up to at least 1 kcal. The origin of these energy differences may be due largely to dipole–dipole interactions. Rough calculations[20] for *meta*-chloro- and *meta*-fluorobenzaldehyde indicate that the O-*trans* conformers should be stabilized by ΔG values of the order of 400 cal/mol. The *meta*-substituted anisoles either show little difference of stability between the two forms, or favor a predominance of the *cis* isomer.

meta-Disubstituted Compounds with Both Substituents of Less Than C_{2v} Symmetry. With two asymmetric substituents the treatment is more complicated but (using the symbolism of XXX) it leads to the individual intensities of the four possible conformers (*cf.* XXXI–XXXIV) given by eq 14 and 15. Calculated values for the four individual conformers are compared with observed A values in Table VIII.

Table VIII. Integrated Intensities (A_{obsd}) for *meta*-Disubstituted Benzenes with Both Substituents of Lower Than C_{2v} Symmetry Compared with A Values Calculated by Eq 14 and 15

| Substituents	A_{obsd}	$A_{I}{}^a$	A_{II}	A_{III}	A_{IV}
CHO, CHO	2,710	4790	1,940	3,720	3,720
CO₂Me, CO₂Me	800	2810	690	1,710	1,710
COMe, OMe	4,480	2270	3,710	1,710	4,590
CO₂Me, OMe	4,410	2160	4,120	1,880	4,750
OMe, OMe	10,960	9150	12,130	10,750	10,750

^{a} Forms denoted by A_I–A_{IV} refer to structures of type XXXI–XXXIV, respectively.

$$A_{meta(as/as)} = 19,000\{(\sigma_R{}°1)^2 + (\sigma_R{}°2)^2 +$$
$$xy - az \pm \sqrt{3}(xz + ay)\} + 340 \quad (14)$$

$$A_{meta(as/as)} = 19,000\{(\sigma_R{}°1)^2 + (\sigma_R{}°2)^2 +$$
$$xy + az \pm \sqrt{3}(xz - ay)\} + 340 \quad (15)$$

For four of the compounds, the results indicate the conformations shown (XXXV, XXXVI, XXXVII, and XXXVIII). Hence, as in the compounds with one asymmetric group, there appears to be a general tendency for the CHO, CO₂Me, and COMe groups to adopt a *trans* configuration, whereas the OMe group prefers the *cis* configuration. We intend to investigate this phenomenon further.

(20) J. M. Lehn and G. Ourisson, *Bull. Soc. Chim. France*, 1113 (1963).

XXX   XXXI   XXXII

XXXIII   XXXIV   XXXV

XXXVI   XXXVII

XXXVIII   XXXIX
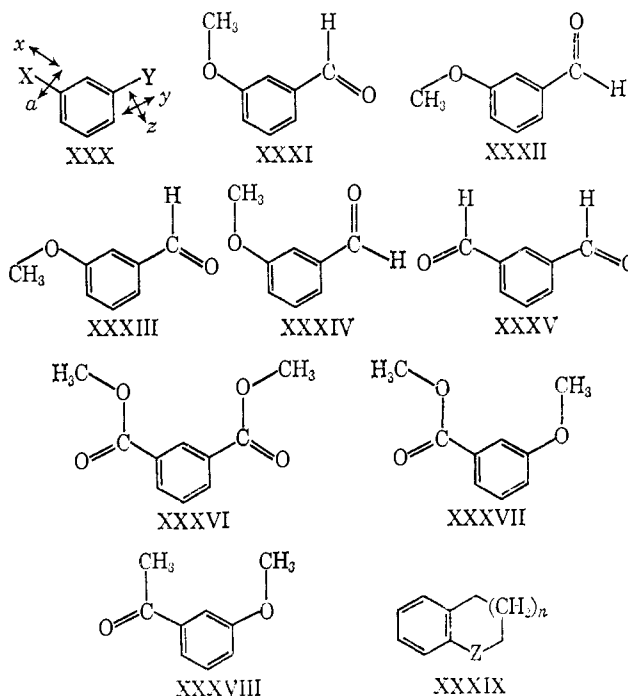
ortho-**Disubstituted Compounds. Symmetry Type of Substituent.** In considering the *ortho*-disubstituted derivatives, three classes of substituent must be distinguished: (i) cyclindrically symmetrical (*i.e.*, F, Cl, Br, Me, and CN) for which the conjugation with the ring will be little impaired by another substituent; (ii) substituents of C_{2v} and pseudo C_{2v} symmetry (NO₂, ND₂, and NMe₂) for which an *ortho* substituent can cause loss of conjugation by twisting; (iii) asymmetric substituent (OMe, CHO, CO₂Me, and COMe) where the situation is complex due to the simultaneous possibilities of two planar rotamers, and of partial conjugation loss by twisting. In addition direct resonance interaction between the substituents is possible in all the above types of *ortho*-disubstituted benzenes, and some steric distortions are possible even with cylindrically symmetrical substituents as in, *e.g.*, *ortho*-dibromobenzene.

ortho-**Disubstituted Compounds with Two Cylindrically Symmetrical Substituents.** Observed values of A_{ortho} are plotted against $\{(\sigma_R{}°1)^2 + (\sigma_R{}°2)^2 - \sigma_R{}°1 \cdot \sigma_R{}°2\}$ in Figure 3. A considerable degree of scatter is evident, probably as a result of steric interaction between the two *ortho* positions which will cause ring distortion and other effects. The range of available A values is rather small, and we therefore also plotted in Figure 3 observed intensity values for 2-substituted pyridines,[21] in which such steric effects will be effectively absent. Constants b and c of eq 16 were obtained by a least-squares plot on all the data of Figure 3, which yields the line shown (correlation coefficient 0.78). Fair agreement is shown between the data for the *ortho*-disubstituted benzenes and the 2-substituted pyridines. The small negative value for c is not significant.

$$A_{ortho} = 15,900\{(\sigma_R{}°1)^2 + (\sigma_R{}°2)^2 -$$
$$\sigma_R{}°1\sigma_R{}°2\} - 80 \quad (16)$$

(21) *Cf.* A. R. Katritzky, C. R. Palmer, F. J. Swinbourne, T. T. Tidwell, and R. D. Topsom, *J. Am. Chem. Soc.*, 91, 636 (1969).
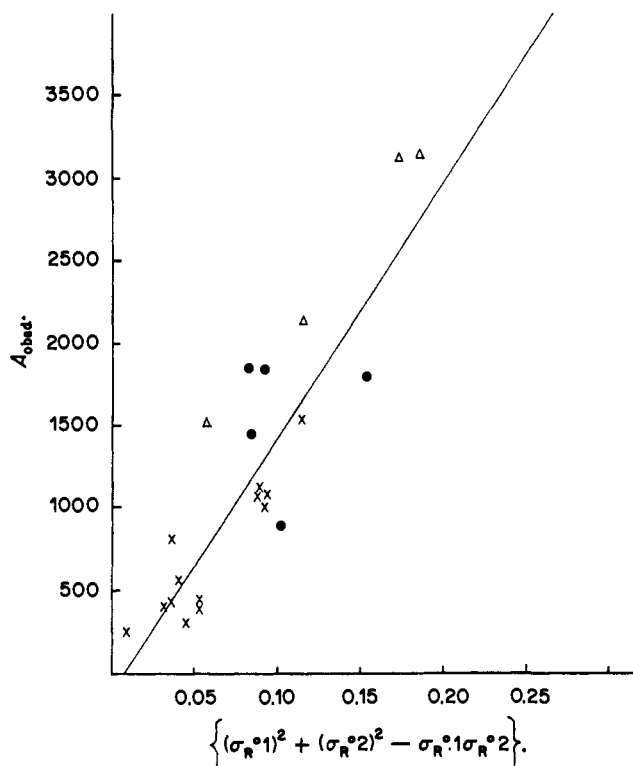
Figure 3. Plot of A_{obsd} for *ortho*-disubstituted benzenes with both substituents of cylindrical symmetry against $\{(\sigma_R°1)^2 + (\sigma_R°2)^2 - \sigma_R°1\sigma_R°2\}$: $\times$, two donor substituents; ●, one donor and one acceptor; and $\triangle$, values for 2-substituted pyridines.

Table IX shows discrepancies in $\sigma_R°$ units between A_{ortho} values from eq 16 and observed values for compounds with both substituents of cylindrical symmetry; as expected for the lower correlation coefficient, the average discrepancies are greater than those for the *meta*-disubstituted benzenes; however, only two discrepancies (both for cyano compounds) are greater than 0.06 unit. The poorer correlations for the *ortho* compounds than for the *meta* and *para* analogs are not unexpected in view of possible steric and direct resonance interactions. Inductive and field effects may also be important here.

Table IX. Discrepancies[a] in Units of $\sigma_R°$ for *ortho*-Disubstituted Benzenes with Two Cylindrically Symmetrical Substituents

	Me	Cl	I	Br	F
F					−0.020
Br		+0.005		−0.060	−0.031
I			−0.003		−0.022
Cl		−0.052			−0.028
Me	+0.045	−0.060	+0.048	+0.003	−0.042
CN	−0.073	−0.106			+0.017
CF₃		+0.046	+0.017	+0.047	

[a] Discrepancy $= [(A_{obsd} + 80)^{1/2}/(15,900)^{1/2}] - \{(\sigma_R°1)^2 + (\sigma_R°2)^2 - \sigma_R°1\sigma_R°2\}^{1/2}$.

***ortho*-Disubstituted Compounds with One Cylindrically Symmetrical and One C_{2v} Substituent.** Table X indicates the deviations from eq 16 for compounds containing NMe_2 and NO_2 substituents. Compounds containing dimethylamino groups show intensities much less than would be expected, which is obviously a consequence of steric hindrance to reso-
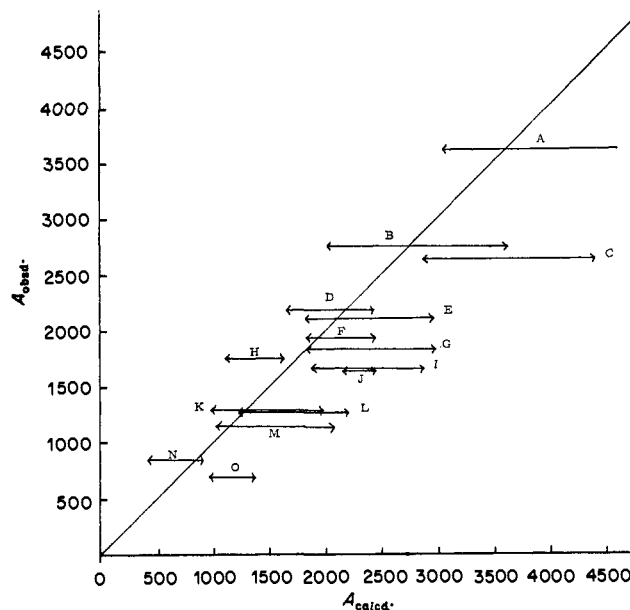
nance between this group and the ring. Compounds with NHMe and ND_2 groups are at present under investigation to test this hypothesis. Compounds with nitro groups may be anomalous (*cf.* the corresponding *para*-disubstituted derivatives), but insufficient examples are presently available.

Figure 4. Plots of A_{obsd} against A_{calcd} for *ortho*-disubstituted benzenes with one asymmetric substituent; A, CHO and F; B, CO_2Me and F; C, COMe and F; D, OMe and Br; E, CHO and Cl; F, OMe and Cl; G, CHO and Br; H, CHO and Me; I, OMe and F; J, OMe and Me; K, CO_2Me and Cl; L, CO_2Me and Br; M, CO_2-Me and I; N, CO_2Me and Me; O, COMe and Me.

Table X. Discrepancies for *ortho*-Disubstituted Benzenes with One Cylindrically Symmetrical Substituent and One Substituent of at Least C_{2v} Symmetry

Substituents	A_{obsd}	Discrepancy[a]
NMe_2, Me	1090	−0.160
NMe_2, F	1550	−0.147
NO_2, Me	810	−0.002
NO_2, CN	910	+0.096

[a] Discrepancy $= [(A_{obsd} + 80)^{1/2}/(15,900)^{1/2}] - \{(\sigma_R°1)^2 + (\sigma_R°2)^2 - \sigma_R°1\sigma_R°2\}^{1/2}$.

Table XI. Integrated Intensities (A_{obsd}) Compared with A_{cis} and A_{trans} Values Calculated by Eq 12 for *ortho*-Disubstituted Benzenes with One Substituent of at Least C_{2v} Symmetry and One of Lower Symmetry

Substituents		A_{obsd}	A_{trans}	A_{cis}	% *trans*
CHO	F	3620	4850	3040	32
	Cl	2130	2960	1800	28
	Br	1840	2980	1830	1
	Me	1752	1630	1110	(>100)
COMe	F	2660	4410	2850	(<0)
	Me	700	1370	940	(<0)
CO_2Me	F	2770	3660	2030	45
	Cl	1310	2000	970	33
	Br	1300	2160	1090	20
	I	1160	2070	1000	17
	Me	840	890	430	90
OMe	F	1680	1880	2880	(>100)
	Cl	1940	1790	2440	77
	Br	2200	1680	2440	32
	I	1680	1780	2470	(>100)
	Me	1660	2160	2470	(>100)

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ortho-Disubstituted Compounds with One Cylindrically Symmetrical and One Asymmetrical Substituent. A treatment similar to that outlined above for the *meta*-disubstituted compounds leads to eq 17 for this type

$$A_{ortho(as/s)} = 15,900\{(\sigma_R °1)^2 +$$
$$(\sigma_R °2)^2 - \sigma_R °1(y \pm \sqrt{3}z)\} - 80 \quad (17)$$

of compound, where the alternative values apply to the two possible planar configurations. Using the previous values of x and y, alternative values of $A_{ortho(as/s)}$ are calculated, and compared in Table XI with the A_{obsd} values. The results are shown graphically in Figure 4. It is clear that some of the A_{obsd} values lie quite outside

the possible A_{cis}/A_{trans} ranges; we believe that this indicates the effects of steric hindrance and rotation of substituents out of the ring plane. Compounds of fixed orientations (XXXIX; Z = CO, O, and COO; n = 1, 2, and 3) will be the subject of future investigations. When these are complete it will be easier to assess the significance of the *cis/trans* proportions shown in Table XI; the pattern appears to be quite different from that appertaining to the *meta* compounds.

Infrared Intensities as a Quantitative Measure of Intramolecular Interactions. VI.[1] Pyridine, Pyridine 1-Oxide, and Monosubstituted Derivatives. The ν_{16} Band near 1600 cm⁻¹

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Abstract: Integrated intensities for pyridine, pyridine 1-oxide, and 1-substituted pyridinium compounds are used to derive $\sigma_R °$ values for $:N\cdot$ and $:N^+(X)\cdot$ "substituents." Intensities for series of 4-substituted pyridines and pyridine 1-oxides provide evidence for direct interaction between the substituent and the hetero group for donor pyridines and for both acceptor and donor pyridine oxides. Intensities for 3-substituted pyridines show fair agreement with those calculated using the treatment discussed for *meta*-disubstituted benzenes. 2-Substituted pyridines are compared and discussed with reference to *ortho*-disubstituted benzenes.

W e have previously shown that the total integrated intensity area of the infrared ring stretching bands near 1600 cm⁻¹ for monosubstituted[3] and for *para*-,[4] *meta*-,[1] and *ortho*-disubstituted[1] benzenes are related to the $\sigma_R °$ values of the substituent(s) by relations 1–4. These equations refer to substituents of at least C_{2v} symmetry—for less symmetrical substituents, appropriate correction factors have been derived.[1,4] For *para*-disubstituted benzenes a further correction must be applied where direct interaction occurs.[4] For durenes an equation similar to (1) applies in the absence of steric hindrance.[3]

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

$$A_{para} = 11,800(\sigma_R °1 - \sigma_R °2)^2 + 170 \quad (2)$$

$$A_{meta} = 19,000\{(\sigma_R 1)^2 + (\sigma_R °2)^2 + \sigma_R °1\sigma_R °2\} + 340 \quad (3)$$

$$A_{ortho} = 15,900\{(\sigma_R °1)^2 + (\sigma_R °2)^2 - \sigma_R °1\sigma_R °2\} - 80 \quad (4)$$

We have now studied pyridine, pyridine 1-oxide, and several series of their monosubstituted derivatives to examine the generality of these equations and as part of a general investigation of substituent–ring interactions in heteroaromatic compounds. Earlier semiquantitative work on the infrared intensities of 2-,[5] 3-,[6] and 4-monosubstituted[7] pyridines and 2-,[8] 3-,[9] and 4-monosubstituted[10] pyridine 1-oxides had indicated that correlations did indeed exist with the nature of the substituent, and especially for compounds of C_{2v} sym-

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(3) R. T. C. Brownlee, A. R. Katritzky, and R. D. Topsom, *J. Am. Chem. Soc.*, **88**, 1413 (1966); R. T. C. Brownlee, A. R. Katritzky, T. T. Tidwell, and R. D. Topsom, *ibid.*, **90**, 1757 (1968).
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