

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

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

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.

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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 σ_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.

We have previously shown that the total integrated intensity area of the infrared ring stretching bands near 1600 cm^{-1} for monosubstituted³ and for *para*-,⁴ *meta*-,¹ and *ortho*-disubstituted¹ benzenes are related to the σ_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 durenene an equation similar to (1) applies in the absence of steric hindrance.³

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

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

(1) Part V: A. R. Katritzky, M. V. Sinnott, T. T. Tidwell, and R. D. Topsom, *J. Am. Chem. Soc.*, **91**, 628 (1969).

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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).

(4) P. J. Q. English, A. R. Katritzky, T. T. Tidwell, and R. D. Topsom, *ibid.*, **90**, 1767 (1968).

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

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

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 semi-quantitative work on the infrared intensities of 2-,⁵ 3-,⁶ and 4-monosubstituted⁷ pyridines and 2-,⁸ 3-,⁹ and 4-monosubstituted¹⁰ pyridine 1-oxides had indicated that correlations did indeed exist with the nature of the substituent, and especially for compounds of C_{2v} sym-

(5) A. R. Katritzky and A. R. Hands, *J. Chem. Soc.*, 2202 (1958).

(6) A. R. Katritzky, A. R. Hands, and R. A. Jones, *ibid.*, 3165 (1958).

(7) A. R. Katritzky and J. N. Gardner, *ibid.*, 2198 (1958).

(8) A. R. Katritzky and A. R. Hands, *ibid.*, 2195 (1958).

(9) A. R. Katritzky, J. A. T. Beard, and N. A. Coats, *ibid.*, 3680 (1959).

(10) A. R. Katritzky and J. N. Gardner, *ibid.*, 2192 (1958).

Table I. 1-Substituted Pyridinium Derivatives

Compound	Solvent	1600-cm ⁻¹ band		1585-cm ⁻¹ band		Substituent, σ_R°	A_{obsd}
		Postn	ϵ_a	Postn	ϵ_a		
Pyridine 1-oxide	CHCl ₃ ^a	1618	17	1608	87	-0.212	894
1-Methoxypyridinium iodide	CH ₃ CN	1617	43	-0.171	615
1- <i>t</i> -Butoxypyridinium perchlorate	CH ₃ CN	1639	3	1613	46	...	437
Pyridine	CCl ₄ ^a	1598	30	1582	100	0.268	1360
Pyridine borane	CHCl ₃	1623	10	1578	1	0.209	870
1-Methylpyridinium iodide	CH ₃ CN	1635	15	1588	2	0.281	1490
Pyridine 1-oxide borofluoride	CH ₃ CN	1682 ^b	4	1621	23	...	369

^a Values for other solvents are shown in Table VI. ^b Shoulder.

Table II. 4-Substituted Pyridines^a

Substituent	1600-cm ⁻¹ band		1585-cm ⁻¹ band		Substituent, σ_R°	A_{para}^b	A_{para}^c	A_{obsd}
	Postn	ϵ_a	Postn	ϵ_a				
N(CH ₃) ₂	1598	843	-0.533	7740	13,600	13,600
OCH ₃	1593	623	1573	67	-0.428	5860	9,890	9,100
SCH ₃	1577	382	1538 ^d	27	-0.250	3340	5,040	4,670
Cl	1590	135	1580 ^d	43	-0.217	2950	4,320	4,870
<i>i</i> -C ₃ H ₇	1602	247	1585	22	-0.115	1900	2,450	2,800
C ₂ H ₅	1602	201	1560	36	-0.103	1790	2,270	2,730
CH ₃	1606	270	1565	22	-0.099	1760	2,210	2,600
CH=CH ₂	1597	327	-0.050	1360	1,550	2,400
CH ₂ OH ^e	1606	97	1563	35	0	1018	1,020	2,280
CN	1593	159	1552	75	0.085	565	...	1,550
NO ₂	1606	26	1573	109	0.174	274	...	1,080
COOC ₂ H ₅	1598	52	1564	83	0.180	447	...	1,290
CH ₃ CO	1594	19	1555	41	0.219	225	...	700
4'-C ₃ H ₄ N	1604	98	1590	335	2,730

^a Solutions in carbon tetrachloride. ^b Calculated using eq 2 or 5. ^c Calculated using eq 6 for donor substituents. ^d Shoulder. ^e Solution in chloroform.

Table III. 4-Substituted Pyridine 1-Oxides*

Substituent	1600-cm ⁻¹ band		1585-cm ⁻¹ band		Substituent, σ_R°	A_{para}^b	A_{para}^c	A_{obsd}
	Postn	ϵ_a	Postn	ϵ_a				
N(CH ₃) ₂	1632	194	-0.533	1390	5070	5370
OCH ₃	1634	69	-0.428	743	2160	1830
Cl	-0.217	170	199	0
<i>i</i> -C ₃ H ₇	1620	6	-0.115	281	...	115
C ₂ H ₅	1623	3	1609	2	-0.103	310	203	100
CH ₃	1624	6	-0.099	321	213	48
H	1618	17	1608	87	0	894	894	894
CN	1614	278	+0.085	1210	1960	2180
NO ₂	1603	385	1582	149	+0.174	1930	4650	5290
CO ₂ C ₂ H ₅	1615	223	+0.180	1890	3570	3390
CH ₃ CO	1618 ^d	33	1609	379	+0.219	2290	4660	4580

^a Solutions in chloroform. ^b Calculated from eq 2 or 5. ^c Calculated from eq 7. ^d Shoulder.

metry the general pattern of the variations was qualitatively well understood.¹¹ The Freiburg school have demonstrated that their quantitative relation between the intensity of CH stretching bands and the inductive constant, σ_I , holds for substituted pyridines,¹² and they have also investigated solvent variation.¹³ The limited published work on the normal coordinate analysis of pyridines¹⁴ indicates that the forms of the 1600-cm⁻¹ vibrations are not very different from those in substituted benzenes. Some quantitative intensity work has been reported on pyridine substituent vibrations; thus the $\nu(\text{C}\equiv\text{N})$ intensity in coordinated 3-cyano-

pyridines is proportional to the coordination constant.¹⁵

Experimental Section

Compounds were obtained commercially or prepared by published methods and purified by preparative vapor phase chromatography or recrystallization. Purities were checked by vpc or melting point. Spectra were obtained on a Perkin-Elmer 125 spectrophotometer under the conditions previously specified.³ Solvents were purified as before.³ Intensity area, A , values are quoted as averages of eight readings. The effect of concentration on the measured A values was checked for pyridine in carbon tetrachloride and no significant variation was found.¹⁶

Results and Discussion

Compounds were measured where possible in carbon tetrachloride; the integrated intensities and frequencies

(11) A. R. Katritzky, *J. Chem. Soc.*, 4162 (1958).
 (12) E. D. Schmid and R. Joeckle, *Spectrochim. Acta*, **22**, 1645 (1966).
 (13) R. Joeckle and R. Mecke, *Ber. Bunsenges. Phys. Chem.*, **71**, 165 (1967).
 (14) E. Wachsmann and E. W. Schmid, *Z. Phys. Chem. (Frankfurt)*, **27**, 145 (1961).

(15) D. G. Brewer and P. T. T. Wong, *Can. J. Chem.*, **44**, 1407 (1966).
 (16) For full details see C. R. Palmer, Ph.D. Thesis, University of East Anglia, 1967.

Table IV. 3-Substituted Pyridines^a

Substituent	1600-cm ⁻¹ band		1585-cm ⁻¹ band		Substituent, σ_R^o	A_{meta}	$A_{meta}(as/s)$	A_{obsd}
	Postn	ϵ_a	Postn	ϵ_a				
N(CH ₃) ₂	1586	295	1562	35	-0.533	4370	...	4210
ND ₂	1600	103	1579	235	-0.467	3450	...	2940
OCH ₃	1589	78	1578	126	-0.428	2990	{3480 2550}	230
SCH ₃	1570	20	1560	55	-0.250	1610	...	630
Br	1572	51	1559	22	-0.231	1530	...	790
Cl	1572	53	1567	39	-0.217	1480	...	570
C ₂ H ₅	1588	12	1575	57	-0.103	1370	...	702
CH ₃	1596	14	1580	48	-0.099	1380	...	830
CH ₂ OH ^b	1596	31	1580	60	0	1690	...	1110
CN	1594	14	1588	81	0.085	2260	...	650
CO ₂ C ₂ H ₅	1592	183	1576	48	0.180	3210	{3850 2410}	1760
CH ₃ CO	1587	226	1570 ^c	52	0.219	3700	{4330 2960}	2490

^a Solutions in carbon tetrachloride. ^b Solution in chloroform. ^c Shoulder.

Table V. 2-Substituted Pyridines^a

Substituent	1600-cm ⁻¹ band		1580-cm ⁻¹ band		Substituent, σ_R^o	A_{ortho}^b	A_{ortho}^c	A_{obsd}
	Postn	ϵ_a	Postn	ϵ_a				
N(CH ₃) ₂	1,600	779	1,561	133	-0.533	7,840	9,547	10,200
OCH ₃	{1,606 1,586 ^d }	{204 98}	1,573	202	-0.428	{8,530 4,940}	{12,500 6,030}	5,790
SCH ₃					-0.250	3,110	3,620	4,200
Br	1,572	209	1,564	264	-0.231	2,880	3,330	3,130
Cl	1,580	192	1,569	134	-0.217	2,730	3,140	3,110
C ₂ H ₅	1,592	138	1,571	69	-0.103	1,660	1,810	2,110
CH ₃	{1,596 ^d 1,590}	{66 70}	1,572	57	-0.099	1,630	1,780	2,130
CH ₂ OH	1,597	103	1,574	66	0	1,120	1,060	1,860
CN	{1,595 ^d 1,583}	{17 138}	1,571	65	0.085	809	...	1,540
CO ₂ C ₂ H ₅	{1,596 ^d 1,586 ^d }	{26 53}	{1,574 1,559}	{65 26}	0.180	{1,480 204}	...	1,640
CH ₃ CO	1,584	86	1,569	81	0.219	{1,680 212}	...	950

^a Solutions in carbon tetrachloride. ^b Calculated using eq 4 and 9; for asymmetric substituents the two alternative values are shown. ^c Calculated using eq 10. ^d Shoulder.

Table VI. Intensity Variations with Solvents

Compound	Intensity ^a				
	CCl ₄	CHCl ₃	CH ₃ CN	<i>i</i> -C ₃ H ₇ OH	C ₆ H ₁₂
4-Acetylpyridine	1,170	1,090	1,070	1,040	<i>b</i>
3-Acetylpyridine	2,490	2,510	2,260	2,470	<i>b</i>
2-Acetylpyridine	949	1,040	960	1,100	992
4-Dimethylaminopyridine	13,600	13,800	13,000	14,600	<i>c</i>
3-Chloropyridine	571	661	562	686	578
2-Methoxypyridine	5,790	5,360	5,430	5,670	5,660
Pyridine	1,360	1,230	1,080	1,250	1,230
Pyridine 1-oxide	<i>c</i>	841	650	418	<i>c</i>
4-Nitropyridine 1-oxide	<i>c</i>	5,290	4,200	<i>c</i>	<i>c</i>

^a In *A* units. ^b Immiscible. ^c Insufficient solubility.

are recorded in Tables I-V. Some compounds were insufficiently soluble in carbon tetrachloride; the solvent in these cases is noted in the tables. Solvent variation studies are recorded in Table VI.

Pyridine and N-Substituted Derivatives. Pyridine and N-substituted pyridinium derivatives (I) are considered as monosubstituted benzenes, and the values of A_{obsd} (Table I) have been used with eq 1 to derive σ_R^o values for the "substituents" :N[·] and :N⁺(Z)[·] (Z = CH₃, BH₃⁻, O⁻ etc.) where the substituent replaces a ring CH group. In Table VII, the values of σ_R^o are

compared with the corresponding benzenoid substituents to give the net effect of replacing CH by N, or replacing C by N⁺. Values for acetonitrile are quoted where possible to facilitate comparison.

Whereas the aza substituent is a moderately strong electron acceptor, the N-oxide group is a donor of considerable magnitude particularly in nonpolar solvents where little solute-solvent interaction occurs (the directions of these effects are confirmed by results for substituted derivatives). It is of interest that quaternization of the nitrogen atom does not increase its acceptor

Table VII. Resonance Effects of N and N⁺ in Pyridine and Pyridinium Derivatives

"Hetero substituent"	Solvent	σ_R° of heterocyclic "substituent"	σ_R° of benzenoid substituent	Net effect of N or N ⁺ replacement by CH
$\overset{+}{N}-\bar{O}$	CHCl ₃	-0.212	-0.593	+0.381
$\overset{+}{N}-CH_3$	CH ₃ CN	+0.281	-0.099	+0.380
N	CH ₃ CN	+0.236
$\overset{+}{N}-OCH_3$	CH ₃ CN	+0.171	-0.428	+0.599
$\overset{+}{N}-O-t-Bu$	CH ₃ CN	+0.138
$\overset{+}{N}-\bar{O}BF_3$	CH ₃ CN	+0.123
$\overset{+}{N}-\bar{B}H_3$	CHCl ₃	+0.209

power very markedly, and coordination with BH₃ apparently significantly decreases it. The small increase in electron withdrawal on quaternization is in agreement with the effect of ring substituents on the basicity of pyridine being governed by normal σ values rather than σ^+ values.¹⁷ For σ values determined by reactivity methods, there is a very large difference between the uncharged and protonated pyridine nitrogen;¹⁸ evidently this is mainly due to inductive effects. We were unable because of solubility difficulties to obtain a value for the protonated aza group NH⁺, but we should expect it to be *ca.* +0.35 (*cf.* Table VII).

Previous values of σ_R° for aza nitrogen are not available for comparison, and other σ values vary considerably:¹⁷ σ_m and σ_p are both positive with σ_p *ca.* +0.3 greater than σ_m . The value now found for σ_R° is not incompatible with these data.

Resonance interaction of OR groups with a ring is evidently impeded when they occur as part of a :N⁺-(OR) group, compared to the usual :C(OR) environment (*cf.* Table VII).

4-Substituted Pyridines. The 4-substituted pyridines may be considered as a special type of *para*-disubstituted benzene. Values for A_{para} (Table II) were calculated from eq 2, using the σ_R° of +0.268 for the pyridine nitrogen and the appropriate σ_R° for the other substituents; for asymmetric substituents, a correction according to eq 5 has been made, as previously.⁴

$$A_{para(as/s)} = 11,800\{(\sigma_R^\circ s - \sigma_R^\circ as)^2 + 2\sigma_R^\circ s(\sigma_R^\circ as - \sigma_R^\circ x)\} + 170 \quad (5)$$

Figure 1 shows a plot of A_{obsd} against A_{para} calculated according to eq 2 or 5. The deviations for the electron-donor substituents presumably correspond to direct interaction between the substituents and the cyclic nitrogen atom. Such interactions were found to require, in the *para*-disubstituted benzenes, a correction term in eq 2 of type ($k_X \sigma_R^\circ D$) for interaction of a donor with a d-orbital acceptor and of type $k_A(\sigma_D^+ - \sigma_D)$ for interaction with a π -bond acceptor. The first type of correction successfully correlates the donor pyridines with $k_X = 0.50$ (see eq 6 and Figure 1).

$$A_{4-Py/D} = 11,800\{0.268 - \sigma_R^\circ D + 0.50\sigma_R^\circ D\}^2 + 170 \quad (6)$$

(17) H. H. Jaffé and H. L. Jones, *Advan. Heterocyclic Chem.*, **3**, 209 (1964).

(18) J. H. Blanch, *J. Chem. Soc., B*, 937 (1966).

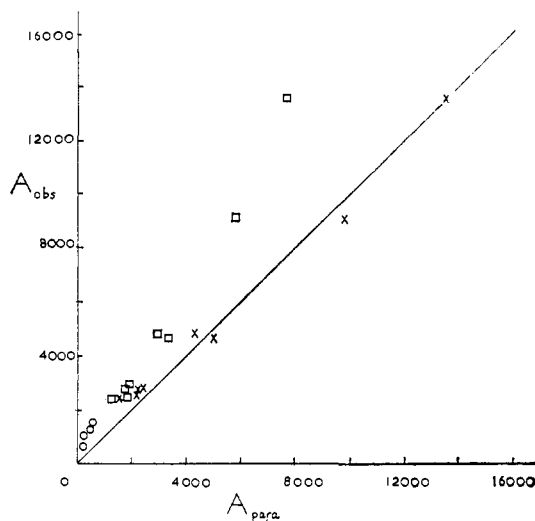


Figure 1. Observed intensities for 4-substituted pyridines with donor (\square) and acceptor (\circ) substituents plotted against A_{para} (eq 1) or $A_{para(as/s)}$ (eq 5). Corrected values for the donor substituents by eq 6 are shown (\times). The line shown has unit slope.

Moderate deviations shown by the electron-acceptor substituents are less easy to account for. Apparently electron-acceptor substituents are able to conjugate far less effectively with the 4 position of a pyridine ring than with benzene, as indicated by the tabulation in Table VIII.

Table VIII

	Substituent			
	CN	NO ₂	CO ₂ Et	CH ₃ CO
σ_R° (monobenzene)	+0.08	+0.18	+0.18	+0.22
Effective σ_R° (4-pyridine)	-0.07	-0.01	-0.04	+0.06
Effective σ_R° (<i>p</i> -nitrobenzene)	-0.18	-0.18

Other evidence is available for this reduced interaction. Thus Schofield and coworkers¹⁹ found that 3 substituents of varying size did not apparently alter the conjugation of a 4-position nitro group with the pyridine ring, and concluded that the resonance interaction was small even in 4-nitropyridine itself, and a similar conclusion was reached by other workers.²⁰ The work of Exner²¹ (*cf.* discussion in ref 3) indicates that the conjugation of an electron-withdrawing group with the benzene ring is reduced significantly by another withdrawing group in the *para* position. The σ values derived for the 4-pyridyl group from carboxylic acids is lower than for acetic acid ionization,¹⁸ again suggesting reduced interaction of the substituent with the ring.

4-Substituted Pyridine 1-Oxides. These compounds were also treated as a class of *para*-disubstituted benzenes (Table III). Values of A_{obsd} are plotted against A_{para} in Figure 2. The line shown has unit slope. Here marked discrepancies are noticed for both strong

(19) J. M. Essery and K. Schofield, *J. Chem. Soc.*, 2225 (1963).

(20) A. Fischer, W. J. Galloway, and J. Vaughan, *ibid.*, 3591 (1964).

(21) O. Exner, *Collection Czech. Chem. Commun.*, **31**, 65 (1966).

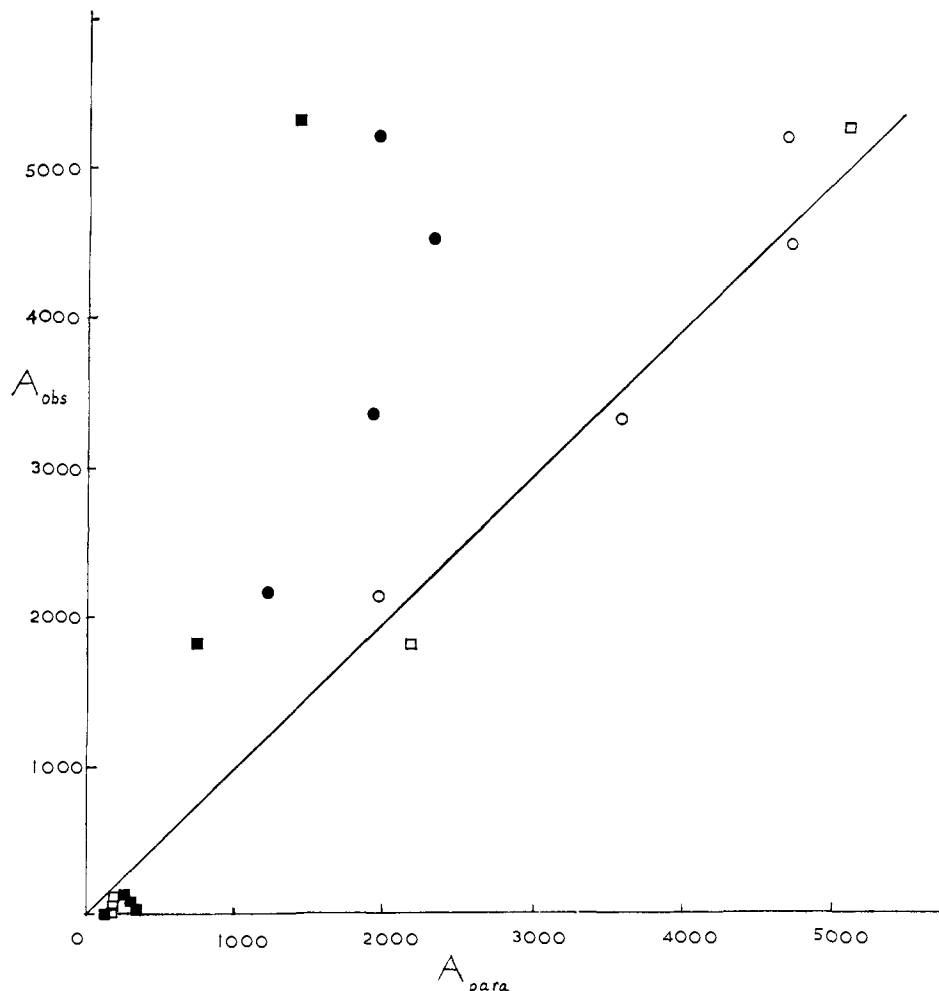


Figure 2. Observed intensities for 4-substituted pyridine 1-oxides with donor (■) and acceptor (●) substituents plotted against A_{para} or $A_{para(as/s)}$ (eq 1, 5). Corresponding corrected values using eq 7 are shown (□ and ○). The line shown has unit slope.

acceptor and strong donor substituents. Qualitatively, this result is in agreement with previous work which has demonstrated that the N-oxide group in 4-substituted pyridine 1-oxides can conjugate strongly with both donor and acceptor substituents by evidence derived from dipole moments,²² ultraviolet spectra,²³ and the infrared frequencies of substituent groups.²⁴ The infrared intensity discrepancies shown in Figure 2 can be correlated quantitatively by eq 7,⁴ using a value of -0.42 for $(\sigma^+ - \sigma)$ for the pyridine 1-oxide "substituent" interacting with the acceptor substituted derivatives and using a value of $k_A = 0.372$ for the $:N^+(O^-)$ group with donor substituted compounds. Figure 2 also shows the correlation after the corrections have been made.

$$A_{para(A/D)} = 11,800\{(\sigma_R^{\circ 1} - \sigma_R^{\circ 2}) - k_A(\sigma_{D^+} - \sigma_D)\}^2 + 170 \quad (7)$$

3-Substituted Pyridines. 3-Substituted pyridines may be treated as a type of *meta*-disubstituted benzene,¹ and

(22) A. R. Katritzky, E. W. Randall, and L. E. Sutton, *J. Chem. Soc.*, 1769 (1957).

(23) A. R. Katritzky, A. M. Monro, and J. A. T. Beard, *ibid.*, 3721 (1958).

(24) For a review see A. R. Katritzky and A. P. Ambler in "Physical Methods in Heterocyclic Chemistry," A. R. Katritzky, Ed., Vol. II, Academic Press, London, 1963, p 161.

correlated using eq 3 for the derivative with a substituent of at least C_{2v} symmetry and eq 8 for those compounds with less symmetrical substituents. The two values obtained by using eq 7 refer to the two alternative rotamers, *e.g.*, II and III. Results are given in Table IV and are shown in Figure 3 in which A_{obsd} is

$$A_{meta(as/s)} = 19,000\{(\sigma_R^{\circ 1})^2 + (\sigma_R^{\circ 2})^2 + \sigma_R^{\circ 1}(\nu \pm \sqrt{3}z)\} + 340 \quad (8)$$

plotted against A_{meta} : the horizontal lines in the figure indicate the range between the extreme values calculated for $A_{meta(as/s)}$. The points are poorly correlated by the solid line of unit slope and zero intercept; there is large improvement by using the alternative dashed line. The altered intercept would imply a different overtone correction, and the slightly altered slope a somewhat different a constant. Such differences could possibly be caused by the different type of pseudo symmetry in a 3-substituted pyridine from that in a normal *meta*-disubstituted benzene: in the former an axis of "near" symmetry passes through the single substituent and the opposite carbon atom of the ring, whereas in the latter the analogous axis bisects the angle between the two substituents.

The calculated ranges for the acetyl and ethoxycarbonyl compounds imply that conformations of type II are

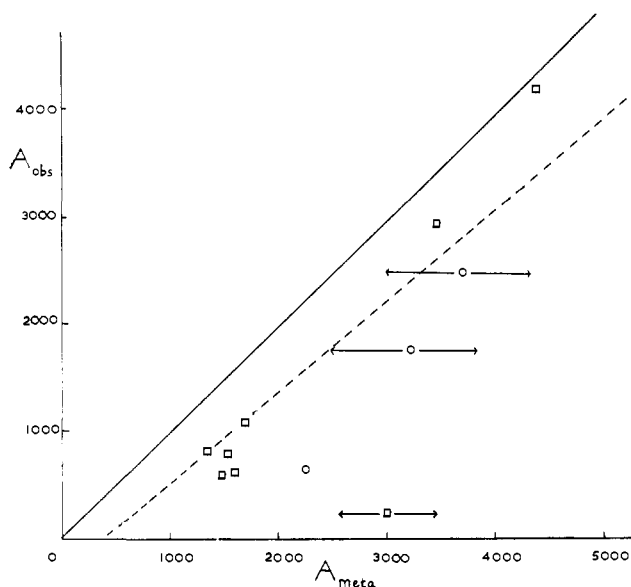
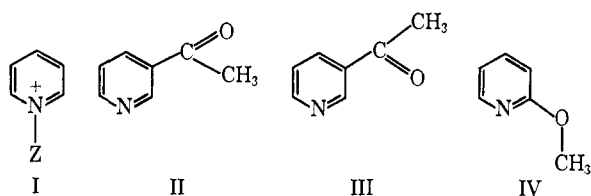


Figure 3. Observed intensities for 3-substituted pyridines with donor (\square) and acceptor (\circ) substituents plotted against A_{meta} (eq 3). For unsymmetrical substituents, the range of possible values of $A_{meta(as/s)}$ is given. The solid line has unit slope.

avored over those of type III; a similar preference for the *O-trans* conformation was found in analogous *meta*-disubstituted benzenes.¹ 3-Methoxypyridine is very anomalous; a similar anomaly was found¹⁹ for the pK_a value which at 4.78 is somewhat higher than the expected value of *ca.* 4.3.



2-Substituted Pyridines. These compounds have been treated as *ortho*-disubstituted benzenes and correlated using eq 4 for symmetrical substituents and eq 9¹ for unsymmetrical substituents. The treatment is

$$A_{ortho(as/s)} = 15,900\{(\sigma_R^{\circ 1})^2 + (\sigma_R^{\circ 2})^2 - \sigma_R^{\circ 1}(\gamma \pm \sqrt{3z})\} - 80 \quad (9)$$

less complex than that required¹ for the more usual *ortho*-disubstituted benzene derivatives, for steric ef-

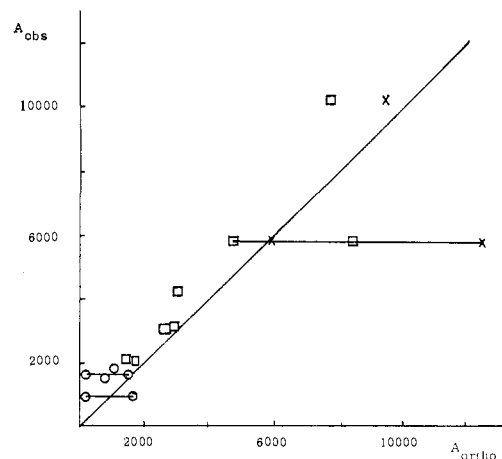


Figure 4. Observed intensities for 2-substituted pyridines with donor (\square) and acceptor (\circ) substituents plotted against A_{ortho} (eq 4). For unsymmetrical substituents, the range of possible values of $A_{meta(as/s)}$ is given. For donor substituents, corrected values (\times) are shown, calculated according to eq 10.

fects between the substituents and the cyclic nitrogen atom are relatively unimportant (see however ref 25). Indeed the coefficients for eq 4 and 9 were originally determined¹ using a combination of *ortho*-disubstituted benzenes with symmetrical substituents and 2-substituted pyridines, except for the OMe and NMe₂ derivatives, for which considerable direct resonance interaction with the pyridine nitrogen could be expected. Figure 4 shows the plot with the ranges of values for the unsymmetrical substituents, and also corrected points for donor substituents using eq 10 to correct for direct

$$A_{2-Py/D} = 15,900\{[0.268^2 + (\sigma_R^{\circ D})^2 - 0.268\sigma_R^{\circ D}]^{1/2} + 0.136\sigma_R^{\circ D}\} - 80 \quad (10)$$

conjugation between substituent and ring nitrogen. Dipole moments indicate²⁶ that 2-methoxypyridine exists principally in the conformation IV, and this is in agreement with the infrared intensity.

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