191.5°. The infrared spectrum showed strong bands at 1590 and 1640 cm.$^{-1}$ (amidine). This compound was insoluble in cold water, and was converted by hydrochloric acid into a sparingly soluble salt, m.p. 248°, which we were not able to obtain analytically pure.

Anal. Calcd. for $C_{22}H_{17}N_3$: C, 81.80; H, 5.32; N, 13.01. Found: C, 81.68; H, 5.39; N, 12.88.

In another experiment, 0.470 g. of IV was added slowly to 5 ml. of phenylacetonitrile in which 0.046 g. of sodium had been dissolved. There was lively gas evolution. When the dark red reaction mixture had become quiet, it was heated at 100° for about 10 min., cooled, and diluted with petroleum ether. The oil that separated soon became a yellow solid (XIII). It was slurried with alcohol and sucked dry; wt. 0.40 g., m.p. 254–258° dec. It was insoluble even in boiling water, but dissolved in cold hydrochloric acid to give an orange solution, and slightly in hot alcohol, from which an analytical sample, yellow needlets, m.p. 258°, was obtained. The infrared spectrum was similar to that of XII.

Anal. Calcd. for $C_{22}H_{17}N_3$: C, 81.80; H, 5.32; N, 13.01. Found: C, 81.63; H, 5.33; N, 12.85.

Interconversion of Compounds XII and XIII.—When 100 mg. of XIII was heated for an hour on a steam bath with concentrated hydrochloric acid, in which it dissolved, and the solution then concentrated, 70 mg. of a yellow hydrochloride, m.p. 240° dec., was obtained. There was no depression of melting point when mixed with XII hydrochloride, and XII itself was obtained by treatment with sodium bicarbonate solution.

When 0.10 g. of XII was boiled for *ca.* 5 min. with a solution of 3 g. of potassium hydroxide in 12 ml. of 50% ethanol and then cooled, 80 mg. of yellow solid, m.p. 200–210°, was obtained. Recrystallization from ethanol gave pure XIII, m.p. and mixture m.p. 254°.

Hydrolysis of XII and XIII.—When a solution of 0.20 g. of XIII in 10 ml. of concentrated hydrochloric acid was boiled for 2 min., the orange color faded and a yellow-green solid began to separate before cooling. After cooling, the solid was filtered off, washed well with water, and recrystallized from benzene; yellow-green needles, m.p. 218° (reported[30] for diphenylmaleimide, m.p. 217°), wt. 0.11 g. (72%). A portion was boiled briefly with 25% potassium hydroxide solution for a few minutes, and then acidified. The colorless substance, m.p. 156°, that separated[31] was identified as diphenylmaleic anhydride (reported m.p. 156–157°).

Attempts to hydrolyze XII by boiling it with concentrated hydrochloric acid alone, or in ethanol or acetic acid, or by heating it with sirupy phosphoric acid, yielded only starting material or its hydrochloride.

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Electrical Effects of *ortho*-Substituents in Pyridines and Quinolines

BY MARVIN CHARTON

Correlation of the σ_0 constants proposed by various workers to represent the electrical effects of *o*-substituents with σ_I, σ_m, and σ_p constants shows that in general $\sigma_0 = m\sigma_p + c$ (1) represents the "normal" electrical effect of *o*-substituents. By contrast, *o*-substituted pyridines, quinolines, and isoquinolines show an "abnormal" electrical effect. Correlation of rate and equilibrium data for these systems with σ_I, σ_m, and σ_p constants shows that σ_m and/or σ_I generally give the best results. This behavior is in accord with the electrical effect of *o*-substituents on deuterium–protium exchange at the *o*-position in substituted benzenes. It is proposed that this behavior is due to a short range localized electrostatic effect. These results invalidate the use of the 2-substituted pyridines as a reference series for the "normal" *ortho* electrical effect.

Brown and McDaniel[1] have suggested that ionization constants of 2-substituted pyridines represent a good reference series for the electrical effects of *o*-substituents as, of course, steric effects in this series are minimal. This approach has been criticized by Roberts and Carboni,[2] who felt that the electrical effects in this series would not be equivalent to those generally found in *o*-substituted reaction series. Hall, Piccolini, and Roberts[3] found that rates of deuterium–protium exchange in substituted benzenes are dependent on a localized electrostatic effect which they believed to be a combination of inductive and field effects. They found no significant resonance effect. Shatenstein[4] noted that these data, combined with some of his own work, when plotted against σ_I constants[5] gave a linear relationship.

The analogy between exchange reactions in benzene and the ionization of pyridine and quinoline bases is obvious. Thus, for example, Huisgen and co-workers[6]

report a linear relationship between partial rate factors for benzyne formation of 2-, 3-, or 4-substituted bromobenzenes with the pK_a's of the corresponding pyridinium ions. It therefore seemed reasonable to determine whether substituent effects in *o*-substituted pyridines and quinolines resemble those observed for deuterium–protium exchanges in the 2-position in substituted benzenes, or whether they resemble those usually found in *o*-substituted benzene reaction series. In view of the proposal that the pyridines be used as a reference series for the electrical effects of *o*-substituents, this question is certainly significant.

The "Normal" Electrical Effects of *o*-Substituents.— Our study of the application of the Hammett equation[7-9] to *o*-substituted series[10] in which the reaction site is joined to the ring by some intervening group has shown that in these series the σ_p constants provide adequate representation of the electrical effects of *o*-substituents. To verify this point with regard to series in which the reaction site is directly joined to the ring, the σ_0 values proposed by a number of authors to re-

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TABLE I

σ_0 SUBSTITUENT CONSTANTS

A. Defined from [log $(k_X/k_H)_B$ − log $(k_X/k_H)_A$] where k's are rate constants for base- and acid-catalyzed hydrolyses, respectively, of 2-substituted ethyl benzoates[a]

X	MeO	EtO	Me	H	F	Cl	Br	I	NO$_2$
σ_0	−0.39	−0.35	−0.17	0.0	0.24	0.20	0.21	0.21	0.80

B. Defined from ionization constants of 2-substituted benzoic acids[b]

X	OH	MeO	EtO	Me	F	Cl	Br	NO$_2$
σ_0	−0.38	−0.27	−0.25	−0.14	0.06	0.21	0.20	0.76

C. Defined from equilibrium constants for association of 2-substituted benzoic acids with 1,3-diphenylguanidine in benzene[c]

X	NH$_2$	OH	Me	Cl	NO$_2$
σ_0	−0.37	−0.15	−0.15	0.38	1.00

D. Defined from infrared spectra of 2-substituted benzonitrile[d]

X	NH$_2$	OH	Me	Cl	NO$_2$
σ_0	−0.35	−0.2	−0.1	0.4	0.95

E. Defined from rates of vapor phase unimolecular homogeneous thermal decomposition of 2-substituted alkyl benzoates[e]

X	MeO	Me	H	F	Cl	NO$_2$
σ_0	−0.53	−0.16	0.0	0.16	0.31	0.94

F. Defined from rates of base-catalyzed hydrolysis of 2-substituted ethyl benzoates in 80% v./v. methanol–water at 100.8°[f]

X	Me	Et	F	Cl	Br	I
σ_0	0.003	0.036	0.291	0.219	0.296	0.341

G. Defined from ν_{OH} for 2-hydroxy-2′-substituted benzanils[g]

X	Cl	F	H	Me	MeO
σ_0	0.22	0.17	0.0	−0.14	−0.34

[a] Ref. 8, Taft. [b] A. C. Farthing and B. Nam, "Steric Effects in Conjugated Systems," Academic Press, Inc., New York, N. Y., 1958, p. 131. [c] M. M. Davis and H. B. Hetzer, *J. Research Natl. Bur. Standards*, **60**, 569 (1958). [d] H. W. Thompson and G. Stell, *Trans. Faraday Soc.*, **52**, 1451 (1956). [e] G. G. Smith and D. A. K. Jones, Abstracts, 144th National Meeting of the American Chemical Society, 1963, p. 58M. [f] N. B. Chapman, J. Shorter, and J. H. P. Utley, *J. Chem. Soc.*, 1291 (1963). [g] A. W. Baker and A. T. Shulgin, *J. Am. Chem. Soc.*, **81**, 1523 (1959).

TABLE II

RESULTS[a] OF CORRELATION OF σ_0 WITH σ_I, σ_m, σ_p, σ_p^+

Series		m	r	t	s	c	n
A	I	1.10	0.699	2.585	0.279	−0.276	9
	m	1.32	.875	4.779	.189	− .255	
	p	1.09	.974	11.30	.0890	− .0242	
B	I	1.29	.741	2.702	.269	− .425	8
	m	1.39	.913	5.482	.163	− .338	
	p	0.978	.999	56.54	.0173	− .694	
C	I	1.80	.894	3.456	.286	− .363	5
	m	1.54	.979	8.267	.131	− .157	
	p	0.973	.983	9.322	.116	.180	
D	I	1.70	.873	3.099	.300	− .335	5
	m	1.45	.965	6.333	.162	− .144	
	p	0.943	.989	11.52	.0915	.177	
E	I	1.19	.682	1.865	.405	− .242	6
	m	1.65	.879	3.691	.165	− .322	
	p	1.30	.981	10.04	.108	− .0165	
	p$^+$	0.953	.986	11.64	.093	− .158	
F	I	.501	.925	4.874	.0610	.0531	6
	m	.608	.949	6.041	.0505	.0643	
	p	.658	.908	4.345	.0672	.146	
G	I	.495	.563	1.181	.219	− .136	5
	m	.780	.680	1.607	.194	− .137	
	p	1.14	.966	6.452	.0687	.159	

[a] m = slope, r = correlation coefficient, t = "student" t test, s = standard deviation, c = intercept, n = number of points in series.

present electrical effects of o-substituents were examined. We have attempted correlations of these σ_0 values with σ_I, σ_m, and σ_p values. The σ_0 values studied are given in Table I; results of the correlations in Table II. The σ_m and σ_p values used throughout this work were taken from the compilation of McDaniel and Brown[11] when possible; otherwise they are from Jaffé's comprehensive review unless otherwise noted. σ_I

values used are from our compilation[12] when possible, otherwise from Taft.[5]

The results given in Table II show that a clear-cut superiority in correlation of σ_0 by σ_p is obtained in series A, B, D, E, and G. In series C, although best correlation is still obtained with σ_p, the difference in results between σ_p and σ_m is barely significant. Only in series F do the results indicate decidedly inferior correlation with σ_p. It must be noted that this series has the smallest variation in substituent type, including only alkyl and halogen substituents.

The results obtained show clearly that, in general, the electrical effects of o-substituents are linearly related to those of p-substituents

$$\sigma_0 = m\sigma_p + c \qquad (1)$$

These results are in accord with the suggestion made by Jaffé and co-workers[13] that o- and p-substituents should have comparable electrical effects, and with the use by other workers of σ_p values to represent the electrical effect of o-substituents.[14]

The Electrical Effect of o-Substituents in Pyridines, Quinolines, and Isoquinolines.—To determine the nature of the electrical effect of o-substituents in 2-substituted pyridines and quinolines we have correlated data (extant in the literature) for ionization constants of 2-substituted pyridines in water at 25° (series 1) and 20° (series 2), and in 50% aqueous ethanol at 25° (series 3), 2-substituted quinolines in water at 25° (series 4), and 1-substituted-isoquinolines in water

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at 20° (series 5) with the Hammett equation using the σ_I, σ_m, and σ_p constants. The rates of reaction of 2-substituted pyridines with methyl iodide at 25° in nitrobenzene (series 6) and with perbenzoic acid in nitrobenzene (series 7) have also been studied. For purposes of comparison, ionization constants of 3- or 4-substituted pyridines in water at 20° (series 8), or 3- or 4-substituted quinolines in water at 25° (series 9) and in 10% aqueous ethanol at 25° (series 10), 4-substituted quinolines in 50% aqueous ethanol at 20° (series 11), and 2-substituted pyridine N-oxides in water at 25° (series 12) were correlated with the Hammett equation using σ_m or σ_p as appropriate. Rates of reaction of 3- or 4-substituted pyridines with methyl iodide at 25° in nitrobenzene (series 13) and with perbenzoic acid in nitrobenzene at 25° (series 14) were also considered. The data used are given in Table III. The results of the correlations are given in Table IV. Amino substituents have been included in the series studied as it has been reported on the basis of infrared and ultraviolet spectra, and ionization constants, that these compounds exist predominantly as the amino rather than the imino tautomer.[15]

Pyridines.—The ionization constants of series 1, 2, and 3 and the rate constants of series 6 and 7 all show good correlation with σ_m and all series but series 2 also show good correlation with σ_I. However, only series 2 includes the amino substituent. As σ_I and σ_m for NH₂ are 0.10 and −0.16, respectively, this substituent should emphasize any difference between correlation with σ_I and correlation with σ_m. It must also be noted that series 3, 6, and 7 are very limited in regard to diversity of substituent type as they contain only H, alkyl, and halo substituents. The σ_p constant in all cases show poor correlation. By contrast, Jaffé and Doak[16] have studied the correlation of the ionization constants of 3- or 4-substituted pyridines in water at about 25° with the Hammett equation using the appropriate σ_m and σ_p values and they report $\rho = 5.714$, $r = 0.989$, $s = 0.196$, $n = 12$. We have examined the correlation of the ionization constants of 3- or 4-substituted pyridines in water at 20° (series 8), again using σ_m and σ_p as appropriate, and find excellent correlation. The rate constants for the reaction of 3- or 4-substituted pyridines with methyl iodide at 25° and with perbenzoic acid in nitrobenzene at 25° also give good correlation with the appropriate σ_m and σ_p values. These results show that substituents in the 3- or 4-position on a pyridine ring have the expected electrical effects, whereas substituents in the 2-position behave abnormally and do not show the type of electrical effect customarily exerted by an *o*-substituent.

We have also examined the ionization constants of 2-substituted pyridine N-oxides in water at 20° (series 12). In this series the reaction site is the oxygen atom whereas in the other series studied the ring nitrogen atom is the reaction site. By far the best correlation in this series was with σ_p constants, indicating a "normal" electrical effect for the *o*-substituent.

Quinolines and Isoquinolines.—The ionization constants of 2-substituted quinolines in water at 25° (series 4) show best correlation with σ_m and worst with

σ_p. For comparison, we have examined the ionization constants of 3- or 4-substituted quinolines under varying conditions (series 9,10,11) using σ_m and σ_p constants as appropriate. Good correlations are obtained showing that substituents in the 3- or 4-position of the quinoline ring exert their normal effect. Substituents in the 2-position on the quinoline ring show an abnormal electrical effect in accord with the results obtained for pyridines.

The ionization constants of isoquinolines (series 5) also show best correlation with σ_m, in accord with the results obtained for pyridines and quinolines.

Discussion

The preceding results seem to have clearly established the following points: (1) The "normal" electrical effect of a substituent in an *o*-position is proportional to its effect in the *p*-position. (2) The electrical effect on an *o*-substituent on reactions involving the lone pair electrons of the nitrogen atom in pyridine, quinoline, and isoquinoline is "abnormal"; it is best represented by the σ_I, or more probably the σ_m substituent constant. (3) Pyridines and quinolines which are *m*- or *p*-substituted show the expected electrical effects. (4) *o*-Substituted pyridines in which the ring nitrogen atom (or any other ring atom) is not the reaction site show a "normal" electrical effect. (5) The electrical effect exerted by *o*-substituents on reactions involving the lone pair electrons of the nitrogen atom in pyridines, quinolines, and isoquinolines is comparable to the electrical effect of *o*-substituents on protium–deuterium exchange in substituted benzenes or on the partial rate factors for benzyne formation in substituted bromobenzenes. This exchange presumably involves a phenide ion in which the reaction site is the carbon atom bearing the lone pair electrons.

One possible explanation of these observations is that they are due to lack of resonance interaction between the π-orbitals of the ring and the lone pair electrons involved in the reactions. This proposal does not account for the normal behavior of 4-substituted pyridines and quinolines, nor does it account for the normal behavior of 2- or 4-substituted benzene series in which ring and reaction site are separated by some group Z which does not permit resonance interaction between ring and reaction site (*e.g.*, Z = CH₂CH₂, OCH₂, SCH₂, SeCH₂).

A more probable explanation of the observed substituent effects is that a short range localized electrostatic effect is operating in these systems. Such an effect would be significant over only one bond length. We can envisage its operation by considering the composition of electrical substituent effects. The total electrical effect of a substituent, σ_T, may be represented, according to Taft, by the equation

$$\sigma_T = \lambda\sigma_I + \delta\sigma_R \qquad (2)$$

where σ_I represents an "inductive" effect and σ_R the resonance effect; λ and δ are empirical parameters. The composition of σ_I may be represented by

$$\lambda\sigma_I = \phi\sigma_f + i\sigma_i \qquad (3)$$

where σ_f represents the field or direct effect and σ_i the true inductive effect; ϕ and i are empirical parameters. We believe that the σ_I values of Taft actually repre-

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TABLE III
DATA USED IN CORRELATIONS

1. Ionization constants of 2-substituted pyridines in H₂O at 25°

X	MeO	PhCH₂	C₂H₃	H	F	Cl	Br	I	Me	Et
pK_a	3.06	5.13	4.98	5.17	−0.44	0.72	0.90	1.82	5.97	5.97
Ref.	a	b	b	c	c	c	c	c	d	d

X	Pr	i-Pr	t-Bu
pK_a	5.97	5.83	5.76
Ref.	d	d	d

2. Ionization constants of 2-substituted pyridines in H₂O at 20°

X	MeS	CN	NHAc	NHBz	H	MeO	NH₂	CONH₂	CO₂Me	Ph
pK_a	3.62	−0.26	4.09	3.33	5.23	3.28	6.86	2.10	2.21	4.48
Ref.	e	f	g	g	h	h	i	j	k	l

3. Ionization constants of 2-substituted pyridines in 50% aqueous ethanol at 25°

X	H	Me	Et	i-Pr	t-Bu	I
pK_a	4.38	5.05	4.93	4.82	4.68	1.11
Ref.	m	m	m	m	m	n

4. Ionization constants of 2-substituted quinolines in H₂O at 25°

X	MeS	MeO	EtO	H	Me	CO₂Me	NH₂
pK_a	3.71	3.17	3.04	4.957	5.832	1.755	7.25
Ref.	e	h	o	p	p	q	i

5. Ionization constants of 1-substituted isoquinolines in H₂O at 20°

X	H	MeS	MeO	NH₂
pK_a	5.40	3.93	3.05	7.62
Ref.	r	e	h	i

6. Rate constants for the reaction of 2-substituted pyridines with methyl iodide in nitrobenzene at 25°

X	Cl	Br	H	Me
$10^6 k$	2.04	1.1	340	160
Ref.	s	s	s	i

7. Rate constants for the reaction of 2-substituted pyridines with perbenzoic acid in nitrobenzene at 25°

X	Cl	Br	H	Me
$10^3 k$, l. mole⁻¹ sec.⁻¹	0.027	0.03	4.80	8.40
Ref.	t	t	t	t

8. Ionization constants of 3- or 4-substituted pyridines in H₂O at 20°

X	H	3-MeS	3-CN	4-CN	3-MeO	4-MeO	3-NHAc	4-NHAc	3-NHBz
pK_a	5.23	4.45	1.36	1.90	4.88	6.62	4.46	5.87	3.80
Ref.	i	e	f	f	h	h	g	g	g

X	3-Ph	4-NHBz	4-Ph	4-PhC₂	4-trans-PhCH=CH	3-CONH₂
pK_a	4.80	5.32	5.55	4.62	5.92	3.40
Ref.	l	g	l	l	l	u

X	4-CONH₂	3-CO₂Me	3-NH₂	4-CO₂Me	4-NH₂
pK_a	3.61	3.26	5.98	3.13	9.17
Ref.	i	k	i	k	i

9. Ionization constants of 3- or 4-substituted quinolines in H₂O at 25°

X	H	3-MeS	4-MeO	3-Me	4-Me	3-Br	3-NO₂	3-NH₂	4-NH₂
pK_a	4.882	3.88	6.65	5.092	5.597	2.69	1.03	4.86	9.08
Ref.	p	e	v	p	p	w	w	i	i

10. Ionization constants of 3- or 4-substituted quinolines in 10% ethanol–water at 25°

X	H	3-F	3-Br	3-Cl	4-Cl	3-Me	4-Me
$10^{12} K_b$	493	2.3	3.2	2.3	26	190	2200
Ref.	x	x	y	z	z	z	z

11. Ionization constants of 4-substituted quinolines in 50% ethanol–water at 21–22°

X	Cl	H	OMe	NH₂
pK_a	2.59	5.0	5.35	8.47
Ref.	aa	aa	aa	aa

12. Ionization constants of 2-substituted pyridine N-oxides in water at 20°

X	AcNH	BzNH	H	NH₂	MeO	EtO
pK_a	−0.42	−0.44	0.56	2.67	1.23	1.18
Ref.	bb	bb	cc	dd	dd	dd

13. Rate constants for the reaction of 3- and 4-substituted pyridines with methyl iodide in nitrobenzene at 25°

X	3-Cl	4-Cl	3-Br	4-Br	H	3-Me	4-Me
$10^6 k$, l. mole⁻¹ sec.⁻¹	3.0	7.3	3.5	16.9	34	71	76
Ref.	s	s	s	s	s	s	s

TABLE III (*Continued*)

14. Rate constants for the reaction of 3- or 4-substituted pyridines with perbenzoic acid in nitrobenzene at 25°

X	3-Cl	4-Cl	H	3-Me	4-Me
$10^3 k$, 1. mole^{-1} sec.$^{-1}$	0.61	1.02	4.80	7.20	7.25
Ref.	*t*	*t*	*t*	*t*	*t*

a R. K. Murmann and F. Basolo, *J. Am. Chem. Soc.*, **77**, 3486 (1955). *b* R. H. Linnell, *J. Org. Chem.*, **25**, 2290 (1960). *c* H. C. Brown and D. H. McDaniel, *J. Am. Chem. Soc.*, **77**, 3752 (1955). *d* H. C. Brown and X. R. Mihm, *ibid.*, **77**, 1723 (1955). *e* A. Albert and G. B. Barlin, *J. Chem. Soc.*, 2384 (1959). *f* S. F. Mason, *ibid.*, 1251, 1247 (1959). *g* R. A. Jones and A. R. Katritzky, *ibid.*, 1317 (1959). *h* A. Albert and J. N. Phillips, *ibid.*, 1294 (1956). *i* A. Albert, R. J. Goldacre, and J. N. Phillips, *ibid.*, 2240 (1948). *j* J. H. G. Jellinek and J. R. Urwin, *J. Phys. Chem.*, **58**, 548 (1954). *k* R. W. Green and H. K. Tong, *J. Am. Chem. Soc.*, **78**, 4896 (1956). *l* A. R. Katritzky and P. Simmons, *J. Chem. Soc.*, 1511, 1516 (1960). *m* H. C. Brown and B. Kanner, *J. Am. Chem. Soc.*, **75**, 3865 (1953). *n* J. Holubek and J. Volke, *Coll. Czech. Chem. Commun.*, **27**, 680 (1962). *o* I. Kabachnik, S. T. Ioffe, and Y. Sheinker, *Chem. Abstr.*, **51**, 5077*f* (1957). *p* R. Riccardi and M. Bresesti, *Ann. Chim.*, **49**, 1891 (1959). *q* P. O. Lumme, *Suomen Kemi.*, **32B**, 151 (1959). *r* A. R. Osborn, K. Schofield, and L. N. Short, *J. Chem. Soc.*, 4191 (1956). *s* G. Coppens, F. Declerck, C. Gillet, and J. Nasielski, *Bull. soc. chim. Belges*, **72**, 25 (1963). *t* A. Dondoni, G. Modena, and P. E. Todesco, *Gazz. chim. ital.*, **91**, 605 (1961). *u* H. H. G. Jellinek and M. G. Wayne, *J. Phys. Chem.*, **55**, 173 (1951). *v* G. F. Tucker and J. L. Irvin, *J. Am. Chem. Soc.*, **73**, 1923 (1951). *w* A. Bryson, *ibid.*, **82**, 4871 (1960). *x* W. K. Miller, S. B. Knight, and A. Roe, *ibid.*, **72**, 4763 (1950). *y* S. B. Knight, R. H. Wallick, and J. Bowen, *ibid.*, **76**, 3780 (1954). *z* S. B. Knight, R. H. Wallick, and C. Balch, *ibid.*, **77**, 2577 (1955). *aa* A. Albert, *J. Chem. Soc.*, 1356 (1949). *bb* R. A. Jones and A. R. Katritzky, *ibid.*, 2937 (1960). *cc* H. Hirayama and T. Kubota, *J. Pharm. Soc. Japan*, **75**, 1546 (1955). *dd* J. N. Gardner and A. R. Katritzky, *J. Chem. Soc.*, 4375 (1957).

TABLE IV

RESULTS OF CORRELATION[a]

Series		ρ	r	s	t	Q_H	n
1	I	−10.3	0.993	0.360	27.13	5.48	13
	m	−11.8	0.967	0.628	12.64	5.03	
	p	−9.82	.739	1.67	3.641	3.61	
2	I	−10.9	.893	0.920	5.165	6.15	10
	m	−9.04	.972	.478	11.76	5.12	
	p	−4.64	.891	.926	5.568	3.77	
3	I	−8.47	.992	.214	15.67	4.43	6
	m	−8.69	.989	.254	13.14	4.22	
	p	−8.09	.956	.495	6.536	3.62	
4	I	−10.1	.804	1.22	3.028	5.92	7
	m	−10.40	.950	0.639	6.838	5.00	
	p	−4.14	.734	1.39	2.423	3.71	
5	I	−11.0	.672	1.81	1.282	6.64	4
	m	−13.7	.960	0.684	4.855	5.36	
	p	−4.13	.645	1.87	1.194	4.04	
6	I	−4.45	.978	0.329	6.580	1.24	4
	m	−5.14	.974	.354	6.088	1.16	
	p	−5.84	.889	.716	2.746	0.69	
7	I	−4.84	.9999	.0255	92.18	0.68	4
	m	−5.60	.9981	.103	22.79	0.60	
	p	−6.70	.957	.481	4.687	0.11	
8		−5.70	.985	.315	23.58	5.39	20
9		−5.72	.984	.420	15.17	4.81	9
10		−5.15	.974	.304	9.592	2.37	7
11		−6.15	.972	.691	5.878	4.27	4
12	I	−4.02	.400	1.20	0.8733	1.58	6
	m	−7.26	.879	0.627	3.688	1.38	
	p	−4.13	.960	.369	6.835	0.046	
13		−2.57	.969	.158	8.793	1.56	7
14		−2.23	.981	.114	8.708	0.60	5

[a] r = correlation coefficient, s = standard deviation, t = "student" t test, Q_H = intercept, and n = number of points in the series.

sent largely the field effect; that is, these σ_I values were obtained from systems in which i/ϕ approaches zero. The short range electrostatic effect which accounts for the observed abnormal electrical effect we believe to be the inductive effect. The manner in which this

effect operates may be pictured as

$$\sigma_i = k\sigma_f \tag{4}$$

$$\lambda\sigma_I = (\phi + ik)\sigma_f \tag{5}$$

In series in which the substituent and reaction site are separated by only one bond (other than the bond joining the substituent and the group G to which it and the reaction site are attached) ik will have a significant value; in other series the value of ik will approach zero. Now let us define the quantity

$$\epsilon = \delta/\lambda \tag{6}$$

Values of ϵ for various types of substituent constant are given in Table V.

TABLE V

VALUES OF ϵ

Substituent constant	ϵ	Ref.
σ_I	0	*a*
σ_m	0.3–0.5	*b,c*
σ_p	1	*d*
σ_0	1	*e*

a From eq. 2. *b* R. W. Taft, Jr., and I. C. Lewis, *J. Am. Chem. Soc.*, **81**, 5343 (1959); J. L. Roberts and H. H. Jaffé, *ibid.*, **81**, 1635 (1959); H. Van Bekham, P. E. Verkane, and B. M. Wepster, *Rec. trav. chim.*, **78**, 815 (1959). *c* From the results of Bryson (ref. *w* in Table III), for the ionization of 3-substituted pyridines in water at 25°, ϵ 0.39; for the ionization of 3-substituted quinolines in water at 25°, ϵ 0.25; for the ionization of 4-substituted isoquinolines in water at 25°, ϵ 0.40. *d* By definition. *e* From eq. 1.

When the "inductive" effect represented by σ_I becomes significant, λ will include the term ik and ϵ for σ_0 will decrease from the normal value of 1 to the abnormal value of 0.3 to 0.5 found for the reactions of *o*-substituted pyridines, quinolines, and isoquinolines.

An important result of this investigation is that the ionization constants of 2-substituted pyridines cannot be used as a reference series for the normal electrical effect of *o*-substituents.