uv max 206 mμ (ε 37,500), 232 (22,600), 285 (12,200), 334 (6900), 344 (7200); uv max (0.1 N NaOH) 240 mμ (ε 34,600), 349 (8900).

Registry No.—6-chloro-2-quinoxaline carboxamide, 27925-23-1; 7-chloro-2-quinoxaline carboxamide, 27925-24-2; 2-amino-6-chloroquinoxaline, 6726-76-7; 2-amino-7-chloroquinoxaline, 2427-70-5; 6-chloro-2-quinoxalinone, 27925-27-5; 7-chloro-2-quinoxalinone, 27925-28-6.

On the Transmission of Polar Effects by the Amide Moiety

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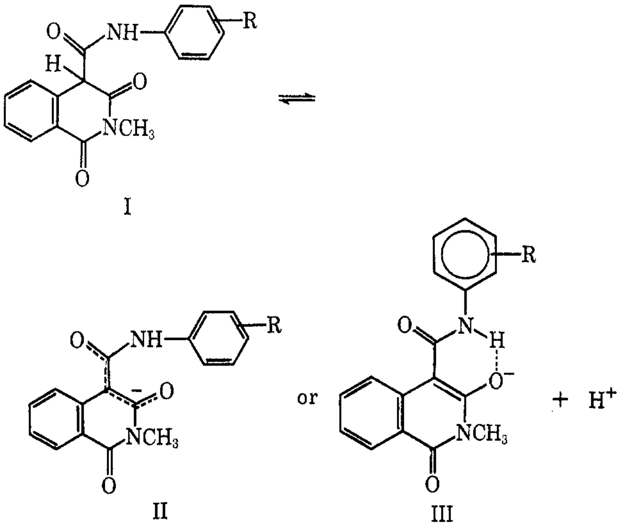
Recent, conflicting reports[1,2] concerning the proficiency of the amide group in transmitting electronic effects based on amide resonance contributions[3] prompt us to describe our results in this area.

Treatment of 2-methylisoquinoline-1,3(2*H*,4*H*)-dione with aryl isocyanates leads to 2-methyl-1,3(2*H*,4*H*)-dioxoisoquinoline-4-carboxanilides (I).[4,5] These compounds, which also may be prepared by the aminolysis of ethyl 2-methyl-1,3(2*H*,4*H*)-dioxoisoquinoline-4-carboxylate with appropriate anilines,[5] display acidic properties involving a keto–enolate anion equilibrium (Scheme I) to which the enol tautomer makes little or no contribution.[5]

SCHEME I

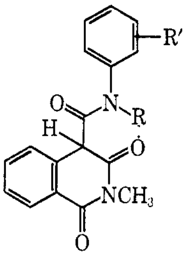


When the pK_a' values of anilides **1–13** (Table I) are plotted against the pK_a values of the correspondingly substituted anilines,[6] the equation for the resulting linear correlation is

$$\mathrm{p}K_{a}'{}_{\text{anilide}} = 3.54 + 0.46\,\mathrm{p}K_{a_{\text{aniline}}} \pm 0.155 \text{ (95\% confidence)}$$
$$(r = 0.968,\ n = 13) \quad (1)$$

TABLE I

PHYSICAL PROPERTIES AND METHODS OF PREPARATION OF 2-METHYL-1,3(2*H*,4*H*)-DIOXOISOQUINOLINE-4-CARBOXANILIDES[a]



Compd	R	R′	pK_a'	Mp, °C	Method of prepn	Solvent of recrystn
1	H	H	5.68	243–244 dec	[b]	CH_3CN
2	H	3-CH_3	5.72	224–225 dec	A[c]	CH_3CN
3	H	4-CH_3	5.85	232–234 dec	A	CH_3CN
4	H	3-OCH_3	5.60	206–207 dec	B[c]	CH_3CN
5	H	4-OCH_3	5.90	222–224	A	CH_3CN
6	H	4-OEt	5.96	210–211 dec	A	CH_3CN
7	H	3-F	5.21	217 dec	B	CH_3CN
8	H	4-F	5.60	222–224 dec	B	EtOAc
9	H	3-Cl	5.22	206–208	A	CH_3CN
10	H	4-Cl	5.20	213–214 dec	A	CH_3CN
11	H	4-Br	5.32	228–229 dec	B	CH_3CN
12	H	3-CF_3	5.05	188–190 dec	B	C_6H_6
13	H	3-$COCH_3$	5.23	177–178 dec	B	CH_3CN
14	H	4-COOEt	4.98	229–230 dec	B	CH_3CN
15	H	4-CF_3	4.94	210–211 dec	B	CH_3CN
16	H	4-SO_2NH_2	4.91	231–232 dec	B	CH_3CN
17	CH_3	H	7.57	160–162	[b]	C_6H_6–C_6H_{14}

[a] All analyses are within ±0.3% of calculated values. [b] See ref 5. [c] See Experimental Section.

The data for the *p*-carbethoxy-, *p*-trifluoromethyl-, and *p*-sulfamoylanilide–aniline pairs (Table I, no. **14–16**) do not fit this relationship and have not been included in calculating eq 1.

A Hammett plot of the same data (Figure 1)[7] yields a ρ value of 1.25. Significantly, the *p*-carbethoxy, *p*-trifluoromethyl, and *p*-sulfamoyl groups are included in this correlation; however, this is true only when their σ values, and not when their σ^- values, are utilized. This, together with the failure of these pairs to fit eq 1, indicates that polar effects are transmitted to the amide linkage but effects which depend upon direct resonance interaction of the anilide nitrogen with the substituent group are only slightly, if at all, so transmitted.

These Hammett results are in general agreement with those of Johnson and coworkers[1] who found a ρ value of 1.77 in their study of the kinetics of ethanol addition to substituted acrylanilides. The failure of Donohue and coworkers[2] to obtain a significant ρ value in correlating the pK_a values of various 4-substituted 4′-aminobenzanilides with σ may reflect the fact that the substituents in their system were not on the ring bearing the anilide nitrogen. In the present system, as well as in that of the acrylanilide study,[1] the substituents are located on the anilide moiety.

The question of whether the primary effect of the substituents (Scheme I) is directed at the capacity of the anilide carbonyl functionality to stabilize the enolate anion (II) or at the ability of the hydrogen on the anilide nitrogen to bond to the enolate anion

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(1) H. W. Johnson, Jr., E. Ngo, and V. A. Pena, *J. Org. Chem.*, **34**, 3271 (1969).

(2) J. A. Donohue, R. M. Scott, and F. M. Menger, *ibid.*, **35**, 2035 (1970).

(3) L. Pauling, "The Nature of the Chemical Bond," 3rd ed, Cornell University Press, Ithaca, N. Y., 1960, p 281.

(4) S. B. Kadin and E. H. Wiseman, *Nature*, **222**, 275 (1969).

(5) S. B. Kadin, *J. Org. Chem.*, **34**, 3178 (1969).

(6) D. D. Perrin, "Dissociation Constants of Organic Bases in Aqueous Solution," Butterworths, London, 1965.

(7) σ values are from the compilation of D. H. McDaniel and H. C. Brown, *J. Org. Chem.* **23**, 420 (1958), except for the value of the *p*-fluoro substituent which is from A. I. Biggs and R. A. Robinson, *J. Chem. Soc.*, 388 (1961).

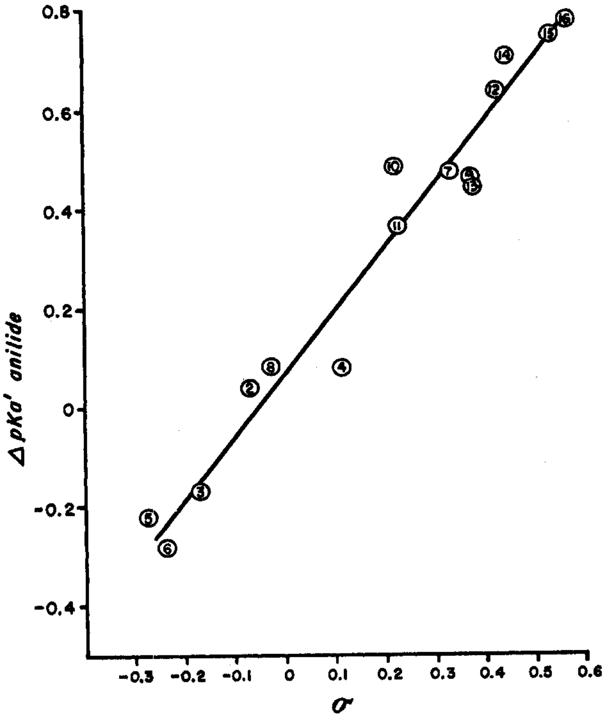

Figure 1.—Correlation of relative anilide pK_a' values with σ (ref 7). The equation for this linear relationship is $\Delta pK_a' = 1.25\sigma + 0.06 \pm 0.136$ (95% confidence), $r = 0.982$, $n = 15$. Numbers refer to compounds in Table I.

(III) remains unanswered. Topping and Tutt,[8] in reporting an almost 100-fold increase in acidity obtained when comparing the pK_a' value of salicylamide with that of *N*-salicoylmesitamide, favored an explanation based upon hydrogen bonding of the phenolate anion to the imide proton. The importance of the hydrogen on the anilide nitrogen and, therefore, of the likely meaningful contribution of the hydrogen bonded species III is also attested to by the failure of the *N*-methylanilide–aniline pair (Table I, no. **17**) to fit the relationship described by eq 1.

The amide moiety, therefore, does appear to be capable of transmitting electronic effects, apparently on a "one-way" basis, depending upon the location of the substituents *vis-à-vis* the anilide nitrogen.

Experimental Section

Melting points are uncorrected. pK_a' determinations were performed at 25° in 1:2 (v/v) water–dioxane using a Metrohm automatic potentiograph (Model E436) which had been standardized against both phthalate and phosphate buffers. Isocyanates used were commercial materials.

Method A.—A solution of appropriate aryl isocyanate in THF was added dropwise to a refluxing solution of equimolar amounts of triethylamine and 2-methylisoquinoline-1,3-(2*H*,4*H*)-dione[9] in THF. Reaction completion, usually in *ca.* 2 hr, was determined by tlc. Work-up included pouring the clear reaction solution into aqueous acid, filtering and drying the resulting precipitate, and recrystallization.

Method B.—A solution of equimolar quantities of ethyl 2-methyl-1,3(2*H*,4*H*)-dioxoisoquinoline-4-carboxylate and appropriate aniline in xylene was heated at reflux for 2–4 hr, during which time solvent was slowly removed by means of a still head. The product precipitated during the reflux period and, after cooling, was filtered, dried, and recrystallized.

Registry No.—**1,** 21389-75-3; **2,** 22367-26-6; **3,** 22416-10-0; **4,** 27799-74-2; **5,** 22367-28-8; **6,** 22367-30-2; **7,** 27669-98-3; **8,** 21925-91-7; **9,** 22367-24-4; **10,** 21925-90-6; **11,** 22351-31-1; **12,** 27670-01-5; **13,** 22351-45-7; **14,** 22351-36-6; **15,** 22351-19-5; **16,** 27670-04-8; **17,** 21389-81-1.

Acknowledgment.—The author thanks Professor D. S. Kemp for many helpful discussions.

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[8] R. M. Topping and D. E. Tutt, *J. Chem. Soc. B*, 1346 (1967).

[9] S. Gabriel, *Ber.*, **19**, 2363 (1886).

Borylation of 2,5-Heterosubstituted 1,4-Benzoquinoid Systems

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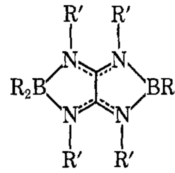
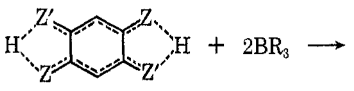
Received July 6, 1970

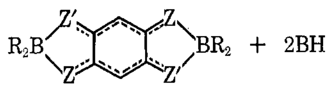
The facile reaction of *sym*-tetraalkyl- or *sym*-tetraaryloxamidine with trialkyl- or triarylboranes to yield the highly stable, symmetrical heterocycles I, doubly bridged with BR_2 groups,[2] prompted an investigation of the benzologous system II. Its borylation should give rise to analogous doubly bridged heterocycles, III.



I



IIa, Z = Z' = O
b, Z = O; Z' = NR'
c, Z = Z' = NR'



IIIa, Z = Z' = O
b, Z = O; Z' = NR'
c, Z = Z' = NR'

The types of II most thoroughly studied in this reaction were 2,5-bis(alkylamino)-1,4-benzoquinones (IIb).

The reaction of triethylborane with 2,5-bis(ethylamino)-1,4-benzoquinone proceeded in refluxing xylene with evolution of ethane. However, gas evolution did not stop at the theoretical point and proceeded further necessitating quenching of the reaction by cooling. The product was isolated by chromatography in 7% yield. It was an air-stable, yellow solid; the analytical and spectral data were in accord with structure IIIb

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[1] Plastics Department, E. I. du Pont de Nemours and Co., Wilmington, Del.

[2] S. Trofimenko, *J. Amer. Chem. Soc.*, **89**, 7014 (1967).