

tion (mass polymer per unit volume), and  $T_0$  a standard absolute temperature. These are plotted against a reduced frequency,  $\omega\eta T_0/TC$ , where  $\omega$  is the circular frequency. For a given polymer-solvent system, all data at different temperatures and concentrations superpose to give two universal dispersion functions for the reduced dynamic rigidity and viscosity. A single function is also obtained, approximately,

if  $\bar{G}$ , the wave rigidity, is substituted for  $G'$ .

2. These relations can be derived by postulating a set of elasticity mechanisms, each of which contributes to the rigidity in proportion to the total mass of polymer per unit volume and to the absolute temperature, and is relaxed by a viscous mechanism such that all relaxation times depend identically on temperature and concentration.

MADISON, WISCONSIN

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF KENTUCKY]

## 1,2-Diamines. II.<sup>1</sup> Thermodynamic Acidity Constants of 1,2,3,4-Tetrahydroquinoxaline and its 6-Methyl and 6-Methoxy Derivatives<sup>2</sup>

BY J. C. CAVAGNOL AND GORDON WILSON, JR.

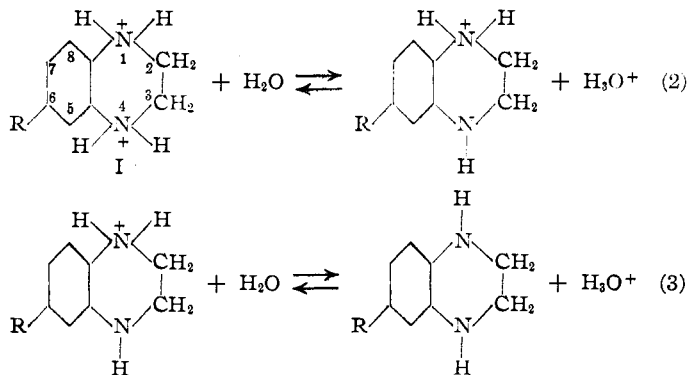
**Introduction.**—Compelling experimental evidence has been presented by Hammett<sup>3,4</sup> for the existence of a quantitative relationship between the type and position of a nuclear substituent and the effect of the concomitant internal electronic displacement on side-chain reactions. His substituent constant  $\sigma$  is defined as

$$\sigma = \log K_1 - \log K_1^0 = pK_1^0 - pK_1 \quad (1)$$

where  $K_1^0$  and  $K_1$  are the thermodynamic acidity constants of unsubstituted, and the corresponding meta- or para-substituted, acids. This constant is characteristic of the substituent only and is practically independent of the type of equilibrium involved. Since a series of these constants were derived from studies involving side-chain reactions of simple benzene derivatives, the possibility existed that a new variation in the structure of the reactive moiety might produce molecules that were capable of yielding similar correlations. One interesting aspect of this theory is a consideration of the effect of structural modifications upon the reactivity of bifunctional heterocyclic systems. The present paper is concerned with the feasibility of extending Hammett's equation to equilibria involving diprotic 1,2,3,4-tetrahydro-6-substituted quinoxalines (I), where the 6-position is "meta" to  $N^4$  and "para" to  $N^1$ , as shown.

A number of methods have been developed for calculating acidity constants of dibasic acids from  $pH$  measurements of solutions containing the acid and various amounts of inorganic base. Britton<sup>5</sup>

and Gane and Ingold<sup>6</sup> determined the first and second acidity constants of several aliphatic dicarboxylic acids in the concentration range of 0.00125–0.05  $M$ , but made no corrections for activity coefficients. Speakman,<sup>7</sup> in a similar study, limited the concentration of acid to below  $10^{-3} M$  and was able to closely approximate the ionic strength from simple solution constants. Activity coefficients were calculated by using the Debye-Hückel limiting law.<sup>8</sup> German, *et al.*,<sup>9</sup> used Britton's method for computing the classical acidity constants of several series of dicarbox-



ylic acids, then converted these values to thermodynamic acidity constants by utilizing the Debye-Hückel limiting law. These workers determined ionic strengths accurately with an equation derived by considering the degree of dissociation of the weak acid and acid anion.

The thermodynamic acidity constants of 1,2,3,4-tetrahydroquinoxaline dihydrochloride were determined previously<sup>1</sup> after evaluating activity coefficients by means of Bjerrum's<sup>10</sup> equation.

(6) Gane and Ingold, *ibid.*, 2153 (1931).

(7) Speakman, *ibid.*, 855 (1940).

(8) Glasstone, "Introduction to Electrochemistry," D. Van Nostrand Co., Inc., New York, N. Y., 1942, Chapter V.

(9) German, Jeffery and Vogel, *J. Chem. Soc.*, 1624 (1935); German and Vogel, *THIS JOURNAL*, 58, 1546 (1936).

(10) Bjerrum, *Z. Elektrochem.*, 24, 321 (1918).

(1) This paper is an extension of the work described in the article entitled, "1-Alkyl-1,2,3,4-tetrahydroquinoxalines," by Cavagnol and Wiselogle, *THIS JOURNAL*, 69, 795 (1947).

(2) Abstracted from a thesis submitted to the Graduate School by Gordon Wilson, Jr., in partial fulfillment of the requirements for the degree of Master of Science.

(3) Hammett, *THIS JOURNAL*, 59, 96 (1937).

(4) See also "Physical Organic Chemistry," McGraw-Hill Book Co., New York, N. Y., 1940, Chapter VII.

(5) Britton, *J. Chem. Soc.*, 127, 1896 (1925).

The dearth of data presented and the uncertainties introduced by using Bjerrum's equation in place of the more rigorously derived Debye-Hückel-Brønsted expression<sup>8</sup> for moderately concentrated solutions cast some doubt on the cogency of these results.

We have redetermined these constants with good precision from potentiometric titration data after calculating ionic strengths and making suitable corrections for activity coefficients by using the Debye-Hückel-Brønsted equation. Application of the same treatment to the data from the 6-methyl and 6-methoxy compounds yielded concordant results except for one apparently discontinuous value. We postulate that the first proton comes from N,<sup>4</sup> equation (2), for reasons which will become apparent later. Accordingly, sigma values were assigned to the *m*-CH<sub>3</sub>, *p*-CH<sub>3</sub>, *m*-CH<sub>3</sub>O and *p*-CH<sub>3</sub>O groups by substituting the proper constants into Equation (1).

**Derivations.**—The two stages of dissociation of a diprotic tetrahydroquinoxaline are represented by Equations (2) and (3). Using the symbol *Q* for the free base, the thermodynamic acidity constants are defined by

$$K_1 = a_{\text{H}_3\text{O}^+}[\text{QH}^+]/[\text{QH}_2^{++}]f_2 \quad (4)$$

$$K_2 = a_{\text{H}_3\text{O}^+}[\text{Q}]/[\text{QH}^+]f_1 \quad (5)$$

*f* = activity coefficient, with charge of cation indicated by subscript.

By writing Equations (4) and (5) in logarithmic form and assuming that the activity coefficient *f*<sub>0</sub> is unity, the following expressions are obtained

$$pK_1 = pH + \log ([\text{QH}_2^{++}]/[\text{QH}^+]) + \log f_2/f_1 \quad (6)$$

$$pK_2 = pH + \log ([\text{QH}^+]/[\text{Q}]) + \log f_1 \quad (7)$$

After evaluating the activity coefficients by means of the Debye-Hückel-Brønsted equation<sup>8</sup> and rearranging terms, the *apparent acidity constants* *pK*'<sub>1</sub> and *pK*'<sub>2</sub> are defined by

$$pK'_1 = pK_1 - C\mu = pH + \log [\text{QH}_2^{++}]/[\text{QH}^+] - 3A\sqrt{\mu} \quad (8)$$

$$pK'_2 = pK_2 - C_1\mu = pH + \log [\text{QH}^+]/[\text{Q}] - A\sqrt{\mu} \quad (9)$$

At the mid-point of the first neutralization  $[\text{QH}_2^{++}] = [\text{QH}^+]$ ; therefore Equation (8) reduces to

$$pK'_1 = pK_1 - C\mu = pH - 3A\sqrt{\mu} \quad (10)$$

The right side of Equation (10) can be evaluated from titration data; the *pH* at half-neutralization can be determined from the flex point and *A* = 0.509 for aqueous<sup>8</sup> solutions at 25°. The ionic strength is calculated by making the total acid concentration equal to the sum of  $[\text{QH}_2^{++}] + [\text{QH}^+]$  since the concentrations of these ions are about 1000 times as great as that of the free base.

The value of the empirical constant *C* is not known but may be eliminated by evaluating the right side of Equation (10) from a series of titrations at different concentrations and plotting these values against ionic strength. By extrapolating to  $\mu = 0$ , the term involving *C* becomes

zero and the extrapolated value of *pH* - 3*A*√*μ* is then equal to *pK*'<sub>1</sub>. The *pK*'<sub>2</sub> is determined similarly by substituting the corresponding titration data from the mid-points of the second neutralizations in the equation

$$pK'_2 = pK_2 - C_1\mu = pH - A\sqrt{\mu} \quad (11)$$

and again extrapolating to infinite dilution.

With suitable modifications in the method<sup>6</sup> and derivations<sup>8,9</sup> of previous workers, values for *pK*'<sub>1</sub> - *C*μ and *pK*'<sub>2</sub> - *C*<sub>1</sub>μ have been determined at points *other* than half-neutralization points. This entails a knowledge of  $[\text{QH}^{++}]$ ,  $[\text{QH}^+]$  and  $[\text{Q}]$  at any point on the titration curve. By setting up the expressions for the classical acidity constants  $k_1 = [\text{H}_3\text{O}^+][\text{QH}^+]/[\text{QH}_2^{++}]$  and  $k_2 = [\text{H}_3\text{O}^+][\text{Q}]/[\text{QH}^+]$ , and defining the total amount of acid as

$$a = [\text{QH}_2^{++}] + [\text{QH}^+] + [\text{Q}]$$

the following relationships are readily derived

$$[\text{QH}_2^{++}] = \frac{a}{\frac{k_1 k_2}{[\text{H}_3\text{O}^+]^2} + 1 + \frac{k_1}{[\text{H}_3\text{O}^+]}} \quad (12)$$

$$[\text{QH}^+] = \frac{a}{\frac{k_2}{[\text{H}_3\text{O}^+]} + 1 + \frac{[\text{H}_3\text{O}^+]}{k_1}} \quad (13)$$

$$[\text{Q}] = \frac{a}{\frac{[\text{H}_3\text{O}^+]}{k_1 k_2} + 1 + \frac{[\text{H}_3\text{O}^+]}{k_2}} \quad (14)$$

These equations were used to approximate the concentrations of the ions and free base by placing *k*<sub>1</sub> and *k*<sub>2</sub> equal to *pH*'s at the first and second mid-points, respectively, of two stages of neutralization. The total acid *a* is the molar concentration of the dihydrochloride, and the hydronium-ion concentration is calculated from the *pH* by making use of the Debye-Hückel limiting law. Substitution of terms calculated from Equations (12), (13) and (14) into Equations (8) and (9) yield *pK*'<sub>1</sub> and *pK*'<sub>2</sub> values for "other points" on the titration curves.

### Experimental<sup>11</sup>

**Materials.**—The 0.2000 *M* potassium acid phthalate, 1.426 *N* sodium hydroxide and 2.208 *N* hydrochloric acid solutions and distilled water were prepared and stored under oxygen- and carbon dioxide-free conditions by connecting a source of purified nitrogen to the apparatus through a manostatic valve.<sup>12</sup>

The preparation of 1,2,3,4-tetrahydro-6-substituted quinoxalines has been described in the previous<sup>1</sup> paper. In some runs a persistent yellow impurity was present which could be removed by precipitating the hydrochloride of the parent quinoxaline. Liberation of the free base with alkali followed by distillation under reduced pressure produced a water-white liquid.<sup>13</sup> After reducing the quinoxaline to the tetrahydro form, the product was sublimed at 1 mm. pressure to yield snow-white crystals that were stored under nitrogen.

(11) All temperatures were checked by reference to a calibrated National Bureau of Standards Thermometer.

(12) Cavagnol, *Anal. Chem.*, **21**, 695 (1949).

(13) Bruhl, *Z. physik. Chem.*, **22**, 384, 390 (1897), describes 6-methylquinoxaline (compound no. 191) as a wine-yellow liquid having *n*<sub>D</sub><sup>20</sup> 1.62112, *d*<sub>4</sub><sup>20</sup> 1.1180 and *d*<sub>4</sub><sup>25</sup> 1.1164. In this work the constants found were: *n*<sub>D</sub><sup>20</sup> 1.6180 and *d*<sub>4</sub><sup>25</sup> 1.1125.

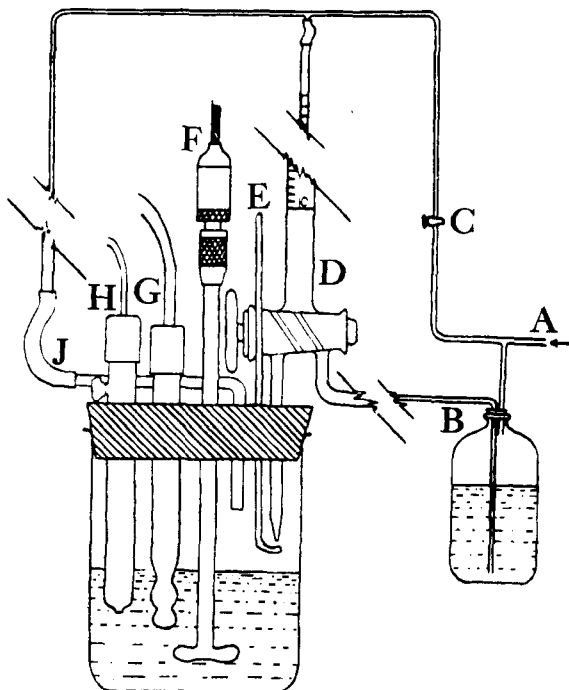


Fig. 1.—Titration assembly: A is the inlet for purified nitrogen. Closing stopcock C forces stock solution of sodium hydroxide B into micro buret D. E is for removing small drops from the tip of D. F is connected to a motor by a flexible shaft. G, Beckman No. 1190 Glass Electrode; H, Beckman no. 1170 calomel electrode. Cell is swept with nitrogen entering at J, and escapes through bearing sleeve of stirrer.

**Apparatus.**—Figure 1 shows a sketch of the titration assembly. The 30" leads from electrodes H and G were connected to a model G Beckman pH meter. A rubber stopper drilled to accommodate the various inserts was fitted to a 200-ml. Berzelius beaker and the whole apparatus was mounted in a constant-temperature bath kept at  $25.0 \pm 0.1^\circ$ . The stirring motor and cell were shielded with grounded copper screens to eliminate electrical interference. All volumetric glassware and analytical weights were calibrated before use.

**Method.**—The pH meter was checked before and after each titration at pH 4.005 with the stock solution of potassium acid phthalate diluted to 0.0500 M as recommended by Dole.<sup>14</sup> Less frequent checks were made at pH's 6, 8 and 10 with commercial buffer solutions. Weighed samples of purified potassium acid phthalate were used to standardize the sodium hydroxide solution potentiometrically under the conditions existing during the main experimental work. The hydrochloric acid solution was standardized against the base by the same procedure.

The sample of tetrahydroquinoxaline was weighed into a 250–1000 ml. volumetric flask, twice the equivalent quantity of hydrochloric acid was added, and the whole made up to volume with distilled water. One hundred ml. of the solution was pipetted into the cell and allowed to equilibrate at  $25^\circ$  in a nitrogen<sup>16</sup> atmosphere before

(14) Dole, "The Glass Electrode," John Wiley and Sons, Inc., New York, N. Y., 1941, p. 298.

(15) Unless precautions were taken to rigidly exclude oxygen from the cell, the solutions invariably assumed a yellow to pale-brown color during the course of a titration. This was due, presumably, to rapid oxidation of the amines in alkaline media. While no quantitative study was made of the effect on color on the pH only, those titrations that yielded colorless solutions are reported here.

starting the titration. Volume changes were minimized by making the sodium hydroxide solution considerably stronger than the amine hydrochloride solution. Duplicate determinations that agreed, on an average, within 0.01 pH unit over the pH range of 1.5–11.5 were considered acceptable.

## Discussion of Results

**A. Acidity Constants.**—The exploratory work indicated that extensive hydrolysis occurred at concentrations less than  $10^{-2}$  M of the amine salts, making it necessary to work in the range of 0.015–0.05 molar concentration. Figure 2 illustrates a typical family of curves obtained by titrating various concentrations of 1,2,3,4-tetrahydroquinoxaline dihydrochloride solutions. For

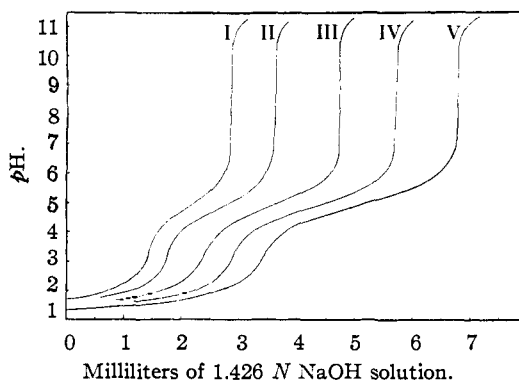


Fig. 2.—Titration curves for 1,2,3,4-tetrahydroquinoxaline dihydrochloride. Molar concentrations of salt: I, 0.02030; II, 0.02569; III, 0.03363; IV, 0.04076; V, 0.04792.

the sake of clarity and brevity only five of the nine curves are reproduced. Similarly, Fig. 3 depicts the best straight lines obtained (by the method of least squares) for the same compound by plotting ionic strengths *versus* apparent acidity constants and extrapolating to infinite dilution.

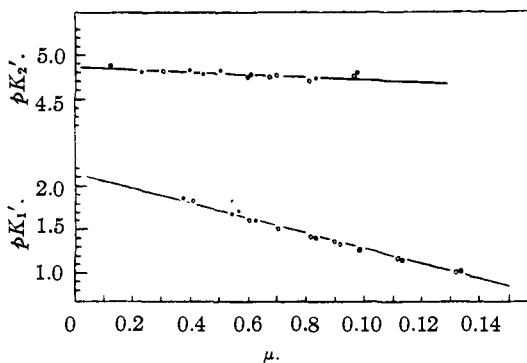


Fig. 3.—Extrapolation of titration data for 1,2,3,4-tetrahydroquinoxaline dihydrochloride to infinite dilution:  $\circ$ , mid-points;  $\bullet$ , other points.

In Table I are summarized the calculations made from titration data using Equations (8)–(14). The accuracy of weighing a sample of the amine,

TABLE I  
 SUMMARY OF CALCULATIONS

1 Substituent	2 Molarity	3		4		5		6		7		8		9		10		11		12	
		Dev. <sup>a</sup>	1st Mid-point μ	Mid-point μ	pK <sub>1</sub> '	Other points μ	pK <sub>1</sub> '	Dev. <sup>a</sup>	2nd Mid-point μ	Mid-point μ	pK <sub>2</sub> '	Other points μ	pK <sub>2</sub> '	Dev. <sup>a</sup>	2nd Mid-point μ	Mid-point μ	pK <sub>2</sub> '	Other points μ	pK <sub>2</sub> '	Other points μ	pK <sub>2</sub> '
Unsubstituted	0.04792	3.3	0.1325	1.05	0.1329	1.10	2.7	0.09635	4.75	0.09700	4.81										
	.04076	9.7	.1128	1.16	.1136	1.13	4.0	.08170	4.71	.08321	4.73										
	.03481	12.6	.09544	1.31	.09813	1.33	3.0	.06980	4.75	.06988	4.75										
	.03363	8.7	.09228	1.33	.09228	1.33	3.0	.06739	4.74	.06740	4.74										
	.02987	3.0	.08204	1.39	.08261	1.39	0.3	.05976	4.74	.06006	4.75										
	.02569	4.4	.07080	1.49	.07125	1.49	4.8	.05173	4.77	.05086	4.82										
	.02223	4.5	.06096	1.59	.06229	1.59	2.5	.04452	4.75	.04455	4.75										
	.02030	1.0	.05561	1.65	.05709	1.70	1.0	.04072	4.78	.04066	4.83										
	.01501	5.3	.04135	1.83	.03809	1.85	1.3	.03026	4.80	.02368	4.81										
											.01227	4.88									
6-Methyl	.04212	7.0	.1154	1.19	.1189	1.17	1.2	.08458	5.01	.08464	5.01										
					.1075	1.27															
	.03723	8.4	.1016	1.28	.1026	1.22	1.1	.07454	5.01	.07474	5.01										
					.08881	1.22															
	.03037	5.6	.08373	1.37	.08692	1.36	7.7	.06092	5.00	.06077	5.05										
					.08361	1.35					.05841	4.96									
	.02916	2.5	.08103	1.36	.07704	1.40	0.6	.05724	4.98	.05791	4.96										
					.06704	1.38					.05584	5.01									
	.02306	7.8	.06334	1.58	.06654	1.57	0.9	.04526	5.03	.04619	5.03										
					.06263	1.60															
6-Methoxy	.01779	15.2	.04924	1.67	.05134	1.74	3.4	.03492	4.99	.03551	4.98										
					.04489	1.69				.03542	4.96										
	.04324	4.0	.1186	1.17	.1255	1.13	0.5	.08662	5.21	.08680	5.21										
					.1159	1.16				.08667	5.21										
	.03962	1.2	.1075	1.25	.1080	1.24	1.2	.07847	5.22	.07868	5.23										
					.1029	1.25				.07828	5.21										
	.03689	5.4	.1014	1.25	.09520	1.28	3.0	.07409	5.21	.07406	5.21										
					.08592	1.35															
	.03392	6.8	.09389	1.28	.07901	1.37	4.1	.06830	5.21	.06820	5.20										
					.07143	1.38															
.02912	4.7	.08069	1.37	.06669	1.41	2.7	.05822	5.18	.05850	5.18											
				.06473	1.56				.05830	5.17											
.02302	3.0	.06334	1.57	.06380	1.57	8.4	.04635	5.25	.04637	5.27											
				.05817	1.57				.04628	5.27											

<sup>a</sup> Deviation in parts per thousand.

adding two equivalents of hydrochloric acid solution, and titrating an aliquot with standard base may be judged from the deviations listed in columns 3 and 8 of the table. The differences between the calculated and observed equivalents of acid are much larger at the first end-point (av. = 5.9 parts per 1000) than at the second end-point (av. = 2.9 parts per 1000) since the change in pH with alkali added is much sharper in the latter case. An over-all average deviation of 4.3 parts per 1000 was obtained (median = 3.3 parts per 1000), hence the accuracy realized was within the reading error of the pH meter. Indeed, a deviation of 4 parts per 1000 in the estimation of the flex point changes the  $pK'$  by less than 0.005 unit. The calculations listed in columns 6, 7, 11 and 12 are the result of selecting one or two points at random from each titration curve between 25% and 75% neutralization.

In Table II the extrapolated  $pK$  values and corresponding thermodynamic acidity constants are given for the three amine dihydrochlorides.

 TABLE II  
 ACIDITY CONSTANTS OF TETRAHYDROQUINOXALINE DIHYDROCHLORIDES

Substituent	$pK_1$	$pK_2$	$K_1$	$K_2$
None	2.11	4.84	$7.8 \times 10^{-3}$	$1.45 \times 10^{-5}$
6-Methyl	2.03	4.97	$9.3 \times 10^{-3}$	$1.07 \times 10^{-5}$
6-Methoxy	1.93	5.26	$1.17 \times 10^{-2}$	$5.5 \times 10^{-6}$

**B. Sigma Values.**—It is readily deduced from Hammett's table of meta and para substituents and the corresponding sigma values that  $m$ -CH<sub>3</sub>- and  $m$ -CH<sub>3</sub>O-substituted aromatic acids exhibit a greater dissociation in water than the  $p$ -CH<sub>3</sub> and  $p$ -CH<sub>3</sub>O derivatives. As a result, the substituent constants of the latter groups are more negative than those of the former, where electronegativity denotes electron-release, *i. e.*, an acid-weakening effect. As a logical extension of the quantitative relationships demonstrated by Hammett it is reasonable to suppose that the primary step in the dissociation of the 6-methyl or 6-methoxy derivative of 1,2,3,4-tetrahydroquinoxaline

line dihydrochloride is the loss of a proton from the "meta" nitrogen N<sup>4</sup>, according to Equation (2). It follows that the secondary dissociation results from the removal of a proton from N<sup>1</sup>, the "para" nitrogen as shown in Equation (3).

TABLE III  
COMPARATIVE SUBSTITUENT CONSTANTS

Group	$\sigma_Q$	$\sigma_H$	$r$	$\sigma_A$	$\sigma_Q - \sigma_H$	$\sigma_A - \sigma_H$
<i>p</i> -CH <sub>3</sub> O	-0.42	-0.268	0.063	-0.67	-0.15	-0.40
<i>p</i> -CH <sub>3</sub>	-.13	-.170	.080	-.45	+.04	-.28
<i>m</i> -CH <sub>3</sub>	+.08	-.069	.045	-.07	+.15	.00
<i>m</i> -CH <sub>3</sub> O	+.18	+.115	.102	+.42	-.06	+.30

In Table III the substituent constants calculated for the methyl and methoxy groups from data obtained in this investigation are tabulated under  $\sigma_Q$ .  $\sigma_H$  is the average value of the substituent constant according to Hammett,  $r$  denotes the median deviation of the value of  $\sigma_H$ , and  $\sigma_A$  is the substituent constant of substituted anilines<sup>16</sup> only. From the relative magnitudes of the deviations in the last two columns it can be seen that the sigma values determined in this study approach, in general, Hammett's average values more closely than do those of the structurally simpler aniline system. An exception is evident in the small positive value of  $\sigma_Q$  found for the *m*-CH<sub>3</sub> group when compared with the small negative value of  $\sigma_H$  determined from thirty-two equilibrium and rate constants. Here the weak electron-releasing effect is reversed and the *m*-CH<sub>3</sub> groups seems to exhibit a weak attraction for electrons. Oddly enough the sigma value for *m*-toluidine shows excellent agreement with  $\sigma_H$  in both magnitude and sign, in contrast to the deviations observed when *p*-toluidine, *m*-anisidine, and *p*-anisidine are compared.

In view of the numerous experimental findings

(16) Hall and Sprinkle, *THIS JOURNAL*, **54**, 3469 (1932).

that support the weak electronegativity of the *m*-CH<sub>3</sub> group in monofunctional systems, any rational interpretation of the apparent electropositivity discovered in this work is subject to several considerations. In the first place, the stereochemical departure from simple side chains to bifunctional heterocyclic structures adumbrates an alteration of electron density within the molecules. Secondly, the supposition that "meta" and "para" positions exist between the substituent and each amino group, independent of a possible *proximity effect* arising from vicinal nitrogen atoms, implies an absence of ortho interaction. However, by comparing  $\sigma_Q$  with  $\sigma_H$  in Table III it is readily seen that the order of electronegativity (*p*-CH<sub>3</sub>O > *p*-CH<sub>3</sub> > *m*-CH<sub>3</sub> > *m*-CH<sub>3</sub>O) found by other workers is substantiated qualitatively by this research notwithstanding the presence of one or more superimposed or second-order effects.

**Acknowledgment.**—One of us (G. W.) wishes to express his appreciation to Mr. Albert Resnick for preparing most of the 1,2,3,4-tetrahydro-6-methylquinoxaline used in this work.

#### Summary

Solutions of the dihydrochlorides of 1,2,3,4-tetrahydroquinoxaline, 1,2,3,4-tetrahydro-6-methylquinoxaline and 1,2,3,4-tetrahydro-6-methoxyquinoxaline in the concentration range of 0.015–0.048 molar were titrated potentiometrically with standard base. Thermodynamic acidity constants were calculated for these compounds after ionic strengths and suitable corrections for activity coefficients had been determined.

The *sigma values* or *substituent constants* for the *m*-CH<sub>3</sub>, *p*-CH<sub>3</sub>, *m*-CH<sub>3</sub>O and *p*-CH<sub>3</sub>O groups calculated from *pK*'s show substantial agreement with those given by Hammett.

LEXINGTON, KENTUCKY RECEIVED JANUARY 16, 1950

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, UNIVERSITY OF MARYLAND]

## The Electric Moments of Some Keto and Hydroxy Derivatives of Cyclohexane

BY W. J. SVIRBELY AND JOHN J. LANDER<sup>1</sup>

The electric moments<sup>2</sup> of the various dihydroxy derivatives of benzene were determined recently. It was deemed worthwhile to measure the electric moments of some analogous saturated cyclic compounds and also of some keto derivatives of cyclohexane, particularly those which on enolization would lead to structures which at least partially resembled those of the corresponding dihydroxy benzenes. Consequently, the electric

moments of *cis*-cyclohexanediol-1,2, *trans*-cyclohexanediol-1,2, *cis*-cyclohexanediol-1,4, *trans*-cyclohexanediol-1,4, cyclohexanedione-1,2 and  $\alpha$ -hydroxycyclohexanone have been measured in benzene. An attempt is made to correlate the results with the possible structures of those compounds.

#### Materials and Experimental Procedure

**Benzene.**—The benzene was purified and the measurements of dielectric constant were made by means of the heterodyne beat apparatus and by methods previously described.<sup>3</sup>

*cis* and *trans*-Cyclohexanediol-1,2.—The crude mixture of isomers was prepared by hydrogenating catechol in ethanol over Raney nickel at about 195°. The crude

(1) (a) Part of a thesis submitted by John J. Lander to the Graduate School of the University of Maryland in partial fulfillment of the requirements for the degree of Doctor of Philosophy, June, 1948. (b) Presented in part at the Atlantic City meeting of the American Chemical Society, September, 1949.

(2) Lander and Svirbely, *THIS JOURNAL*, **67**, 322 (1945).