The Correlation of the Electronic Spectra, Ground-State pK_A Values, and Excited-State pK_A* Values of 5-Substituted 3-Nitroanilines with Substituent Constants[1a]

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The electronic spectra and pK_A values of a series of 5-substituted 3-nitroanilines have been measured. Good quantitative correlations have been found between pK_A and σ_m, $\sigma_m{}^+$, or σ_I. The correlation between pK_A and σ_R is poor. The ρ values indicate that the substituent effect is primarily inductive. No significant relationship was found between any set of possibly pertinent substituent constants and ν_A, ν_B, ν_B', $\Delta\nu$, or $\Delta\nu'$, where $\nu_A = (1/\lambda_{max}^{HCl}) \times 10^7$ for the ^1L_a band, $\nu_B = (1/\lambda_{max}^{NaOH}) \times 10^7$ for the ^1L_b band, $\nu_B' = (1/\lambda_{max}^{NaOH}) \times 10^7$ for the ^1L_a band, $\Delta\nu = \nu_B - \nu_A$, and $\Delta\nu' = \nu_B' - \nu_A$. As suggested previously, lack of correlation between substituent constants and wavenumbers is probably due to the operation of a maximal "area" effect. A good correlation does exist bebetween ν_B and ν_A and between ν_B' and ν_A. The calculated excited-state pK_A* values for five of the 5-substituted 3-nitroanilines are fairly well correlated with σ_I values. Resonance effects appear to be minimal since exalted σ values and other substituent parameters which reflect resonance contribution fail to yield even fair correlations.

Recently, Jaffé and Jones[3] have investigated the possibility of applying the Hammett equation to the acid–base equilibrium constants of excited states of aromatic acids and bases. The most important conclusion drawn was that excited-state pK*'s conform roughly to linear free-energy relations with ground-state parameters. Also, it appears that resonance effects are of substantial importance since exalted σ values[4a,5] were required for the correlations. These observations lead to two suggestions:[3] (1) that in excited states *meta* substituents may enter into direct resonance interaction with a side chain, and (2) that *meta-* and *para*-substituted compounds may fall on different correlation lines, *i.e.*, may require different reaction constants. A series ideally suited to investigate the first of these suggestions is the 5-substituted 3-nitroanilines. In this series, the only *direct* effect of any one group on another will be an inductive one since they are sufficiently removed from one another to avoid any steric interaction and their positions relative to one another prohibit any direct resonance interaction. The second of the above suggestions will not be treated in the present discussion.

Earlier reports from this laboratory have indicated that the acidities and certain aspects of the electronic spectra of 4-substituted 2-nitrophenols,[6] 5-substituted 2-nitrophenols,[7] 4-substituted 2-chlorophenols,[8] and 4-substituted 2-nitroanilines[9] correlate with substituent constants. In view of these successful studies, it seemed desirable to extend them to a series of 1,3,5-trisubstituted benzenes, such as the 5-substituted 3-nitroanilines.

Results and Discussion

The pK_A's and absorption spectra of a series of 5-substituted 3-nitroanilines have been measured and the pK_A*'s have been calculated. The resulting data are shown in Table I.

Correlation of pK_A's and Electronic Spectra of 5-Substituted 3-Nitroanilines with Substituent Constants.—Good correlations exist between the pK_A's and Hammett's σ_m,[4a] Brown's $\sigma_m{}^+$,[5] or Taft's σ_I[10–11] as shown by eq 1–3.[12a,13] The relationship between pK_A and σ_m is shown in Figure 1. In contrast, however, the correlation of the pK_A's with Taft's σ_R,[10a] as shown in eq 4, is poor. In eq 1–4, the negative values for the various ρ's[14a] indicate that an electron-withdrawing substituent increases the acidity of a 5-substituted 3-nitroanilinium ion relative to the 3-nitroanilinium ion and this is observed in every case. Also since σ_I gives a significant correlation with pK_A, whereas σ_R does not, this would seem to indicate that the substituent effect is primarily an inductive one. Linear regression analyses of $(\sigma_p - \sigma_m)$, $(\sigma_m - \sigma_I)$, or $(\sigma_m{}^+ - \sigma_I)$ on pK_A give no significant correlations. The magnitudes of the ρ values also seem to indicate that the electronic characteristics of the 5 substituent, insofar as the pK_A is affected, are transmitted most effectively by an inductive mechanism; that is, ρ_I in eq 3 is more negative than ρ_m in eq 1. From the additivity principle,[4b] one would predict that the ρ_m value for the 5-substituted 3-nitroanilines would be about the same as that for a series of *meta*-substituted anilines. The correlation of the pK_A's of eight *meta*-substituted anilines[15] (the substituents are the same as those in Table I) with σ_m

$$\begin{array}{lccrr} & r & s & & \\ pK_A = 2.27 - 2.87\sigma_m & -0.982 & 0.17 & 100.0\% & (1) \\ pK_A = 2.26 - 2.98\sigma_m{}^+ & -0.986 & 0.15 & 100.0\% & (2) \\ pK_A = 2.35 - 3.21\sigma_I & -0.928 & 0.34 & 99.9\% & (3) \end{array}$$

$$\begin{array}{lccrr} & r & s & & \\ pK_A = 1.28 - 2.54\sigma_R & -0.678 & 0.67 & 93.5\% & (4) \end{array}$$

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(13) In the equations throughout this paper, r is the linear correlation coefficient and s is the standard deviation from regression. The percentage value given at the end of each equation is the percentage confidence level as determined by Student's t test.[12b]

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TABLE I

ACIDITY AND SPECTRAL DATA FOR 5-SUBSTITUTED 3-NITROANILINES

No.	5 substituent	pK_A[a]	pK_A^*[b]	λ_B,[c] mμ	ν_B[d] × 10^{-4} cm^{-1}	ϵ_B[e] × 10^{-3}	λ_B',[f] mμ	ν_B'[g] × 10^{-4} cm^{-1}	ϵ_B'[h] × 10^{-3}	λ_A,[i] mμ	ν_A[j] × 10^{-4}	ϵ_A[k] × 10^{-3}	$\Delta\nu'$[l] × 10^{-4} cm^{-1}	$\Delta\nu$[m] × 10^{-4} cm^{-1}
1	H	2.29[n]	−2.81	357	2.80	1.37	277	3.61	4.37	259.5 (256)[o]	3.85	7.23	−0.244	−1.052
2	NO_2	0.23[p]	−8.71	377	2.65	1.92	257.5	3.88	12.33	232 (241.5)[o]	4.31	17.80	−0.427	−1.658
3	I	1.44	−8.15	351.5[q]	2.84	1.20	299	3.34	1.75	263[r] (262)[o]	3.80	4.47	−0.458	−0.957
4	CF_3	0.82	...	357	2.80	1.43	...[s]	...	...	249[t]	4.02	7.36	...	−1.215
5	OCH_3	2.13[u]	−7.19	327	3.06	2.54	303[v]	3.30	3.56	267[w] (273.5)[o]	3.75	4.74	−0.445	−0.687
6	CN	0.45[x]	...	360	2.78	1.64	...[y]	...	...	...[z]	...	...	...	...
7	$CO_2C_2H_5$	0.98	...	362	2.76	1.56	...[aa]	...	...	...[bb]	...	...	...	...
8	CH_3	2.38	−4.88	351[cc]	2.85	1.41	290[dd]	3.45	4.45	263.5 (253.5)[o]	3.80	8.16	−0.347	−0.946

[a] The pK_A's are apparent except for **2** and **6** which are thermodynamic. [b] Excited-state pK_A^*. [c] $\lambda_B = \lambda_{max}^{NaOH}$ for the ^1L_b bands. [d] $\nu_B = 1/\lambda_B \times 10^7$. [e] ϵ_B = extinction coefficient in alkaline solution for λ_B. [f] $\lambda_B' = \lambda_{max}^{NaOH}$ for the ^1L_a bands. [g] $\nu_B' = 1/\lambda_B' \times 10^7$. [h] ϵ_B' = extinction coefficient in alkaline solution for λ_B'. [i] $\lambda_A = \lambda_{max}^{HCl}$ for the ^1L_a bands. [j] $\nu_A = 1/\lambda_A \times 10^7$. [k] ϵ_A = extinction coefficient in acid solution. [l] $\Delta\nu' = (\nu_B' - \nu_A)$. [m] $\Delta\nu = (\nu_B - \nu_A)$. [n] Lit.[15] pK_A (thermodynamic) = 2.50. [o] The λ_A values in parentheses are ^1L_a bands (B bands) for *meta*-substituted nitrobenzenes as reported in ref 24. [p] In $HClO_4$, pK_A = 0.17. [q] The spectrum in basic solution, where the longest wavelength maximum absorption occurred, consisted of a plateau fused to an absorption peak at slightly shorter wavelength. The midpoint of this plateau was 351.5 mμ and the pK_A was calculated at this wavelength. The peak at shorter wavelength was at 327 mμ and occurred in the acid, base, and buffered solutions. The plateau disappeared in acid solution. There is also a short wavelength absorption peak in the basic solution at 230 mμ (ϵ_{max} 13,300). [r] This is an inflection. There is a peak at 237.5 mμ (ϵ_{max} 11,737). [s] There is a peak at 230 mμ (ϵ_{max} 14,534). [t] H. H. Szmant and J. F. Anzenberger, *J. Am. Chem. Soc.*, **76,** 3785 (1954), report λ_{max} 247 mμ (ϵ_{max} 6900) for *m*-nitrobenzotrifluoride in 95% ethanol. [u] Lit.[15] pK_A (thermodynamic) = 2.11. [v] There is also a peak at 227.5 mμ (ϵ_{max} 19,150). [w] There are also peaks at 324 mμ (ϵ_{max} 1980) and 226.5 mμ (ϵ_{max} 13,600). [x] In $HClO_4$, pK_A = 0.47. [y] There is a peak at 249 mμ (ϵ_{max} 13,366). [z] The only clearly distinguishable peak in acid solution occurs at 217.5 mμ (ϵ_{max} 30,050). There is an inflection at 249 mμ (ϵ_{max} 9257). [aa] There is a peak at 251 mμ (ϵ_{max} 9068). [bb] There is a peak at 217.5 mμ (ϵ_{max} 24,265) and at 251 mμ (ϵ_{max} 6716). [cc] The spectrum in basic solution, where the longest wavelength maximum absorption occurs, consists of a plateau fused to an absorption peak at slightly shorter wavelength. The midpoint of the plateau is 351 mμ and the pK_A was calculated at this wavelength. The plateau disappears in acid solution. [dd] There is also a peak at 224.5 mμ (ϵ_{max} 13,995).

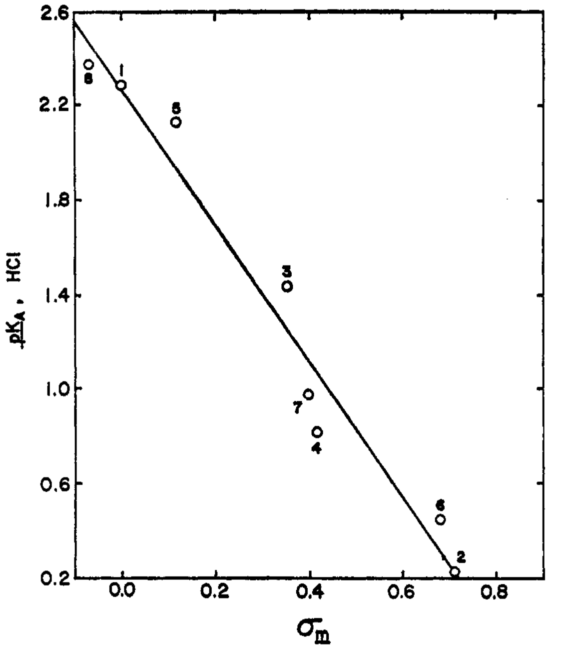

Figure 1.—The relationship between pK_A and σ_m for eight 5-substituted 3-nitroanilines. Numbers refer to compounds listed in Table I.

gives a ρ_m value of −2.76 which is in good agreement with the value of −2.87 given in eq 1 for the 5-substituted 3-nitroanilines. The corresponding ρ_I values (−3.11 and −3.21) are also in good agreement. Thus, the constant 3-nitro substituent does not significantly affect the reaction constant.

For the 5-substituted 3-nitroanilines, there is no significant correlation between pK_A and either $\Delta\nu$ or $\Delta\nu'$, where $\Delta\nu$ is the difference between ν_B (the wavenumber for the ^1L_b band in basic solution) and ν_A (the wavenumber for the ^1L_a band in acidic solution), and $\Delta\nu'$ is the difference between ν_B' (the wavenumber for the ^1L_a band in basic solution) and ν_A. As shown by eq 5 and 6, statistically significant correlations exist

	r	s		
$\nu_B' = -1783 + 0.947\nu_A$	0.927	1025	97.7%	(5)
$\nu_B = 48{,}485 - 0.515\nu_A$	−0.825	700	98.8%	(6)

between ν_B' and ν_A and between ν_B and ν_A. In spite of the lower correlation coefficient, eq 6 with 6 degrees of freedom (df) is slightly more significant than eq 5 with only 3 df. As discussed previously,[6-9] a good correlation such as those provided by eq 5 and 6 indicates that the substituents perform similar roles in both the basic and acidic series and that each series may then be treated independently with respect to substituent effects. However, linear regression analyses of ν_B, ν_B', ν_A, $\Delta\nu$, or $\Delta\nu'$ independently on σ_m, σ_m^+, or σ_I fail to yield a significant correlation in any case. Thus, correlation of absorption frequencies of 5-substituted 3-nitroanilines with structure *via* substituent constants is not satisfactory. The failure of such correlations for the 5-substituted 3-nitroanilines may be due in part to the operation of a maximal "area" effect.[6] That is, the substituent affects not only the reaction site, but the entire molecule since the spectral "reaction" encompasses the entire molecule. In an attempt to learn more about the "area" effect for the 5-substituted 3-nitroanilines, a study of the polarographic reduction and oxidation half-wave potentials of this series has been initiated.[16]

Correlation of Excited-State pK_A^*'s with Substituent Constants.—The behavior of electronically excited molecules has been studied by different investigators for various reasons. One area which has recently become of interest is the study of excited-state, acid–base reactions. The interest in this area arose mainly due to Förster's discovery that excited-state pK^*'s could be

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obtained *via* fluorescence measurements.[17] Since then, several workers have contributed significantly to this field.[18–20] In most cases, it has been found that pK* is quite different from pK, often by several units. Jaffé, *et al.*,[3,21] have outlined a method of calculating pK* which only requires measurement of the absorption frequency of the basic and acidic forms of the compounds under study. The method depends on the Förster cycle[18] and is applicable either to absorption or fluorescence spectra. Out of the Förster cycle one obtains[21] eq 7 which is used to calculate pK*. In eq 7,

$$pK_A^* = \frac{(\nu_B - \nu_{BH^+})Nhc}{2.303RT} + pK_A \qquad (7)$$

ν_B and ν_{BH^+} represent the frequencies of corresponding transitions in wavenumbers of a base and its conjugate acid, N is Avogadro's constant, h is Planck's constant, c is the velocity of light, and R is the gas constant.

Jaffé and Jones[3] have outlined the assumptions that are necessary in order to use eq 7. They all involve the requirement that the excited states be similar in nature; *i.e.*, the transitions in both the basic and acidic forms must be corresponding. Thus, the Förster cycle may be applied to absorption spectra measurements in order to calculate pK_A*'s provided pairs of corresponding states can be found. In Table I, we have assigned the long-wavelength lower intensity λ_B values as ^1L_b bands (secondary bands)[22,23] and the shorter wavelength higher intensity λ_B' values as ^1L_a bands (primary bands).[22,23] The ratio λ_B/λ_B' remains fairly close to 1.22 for compounds **1**–**3**,**5**, and **8** of Table I (the ratio average is 1.24 ± 0.22) as has been predicted for the ratio of wavelengths of the secondary (^1L_b) to primary (^1L_a) bands of substituted benzenes.[22] For several of the compounds, still shorter wavelength, very high intensity bands were observed. We have not tried to classify these latter bands. The spectra of the 5-substituted 3-nitroanilinium ions would be expected to resemble the spectra of the corresponding compounds which do not contain the NH_3^+ group, *i.e.*, the 3-substituted nitrobenzenes. The 5 substituent of the 5-substituted 3-nitroanilinium ions affects λ_A in the same way that substituents affect the primary absorption band of *meta*-substituted nitrobenzenes; *i.e.*, λ_A increases with increasing electron-donating power of R and decreases with increasing electron-withdrawing power of R.[24] Previous reports[25] for the ^1L_a bands of 3-substituted nitrobenzenes correspond very closely to the λ_A values in Table I and the latter λ_A values are therefore assigned as ^1L_A bands. Several of the compounds also gave shorter wavelength, higher intensity bands in acidic solution. No attempt was made to classify these latter bands. The classification into ^1L_a and ^1L_b bands may be complicated by contributions from localized excited and intramolecular charge-transfer states.[3] However, pK_A*'s for several other series of nitro-substituted aromatics have been calculated from bands assigned as ^1L_a and ^1L_b, and correlations of these pK_A*'s with substituent constants have been moderately successful.[3,21]

The corresponding frequencies ν_B and ν_{BH^+} are given in Table I as ν_B' and ν_A. Using these values, pK_A*'s were calculated by eq 7 for five of the 5-substituted 3-nitroanilines and are given in Table I (for three of the compounds, either ν_B' or ν_A was not found). The pK_A*'s were correlated with each of the previously mentioned substituent constants and, in addition, with σ_p^+,[5] $\sigma_p^\pm$,[4a,5] σ_R^+,[10a] σ_R^-,[10a] or σ_R'.[26] The only statistically significant correlation obtained was that given in eq 8. Even though the correlation given by eq 8

$$pK_A^* = -4.44 - 7.82\sigma_I \quad \overset{r}{-0.894} \quad \overset{s}{1.3} \quad 95.9\% \qquad (8)$$

is only fairly good, the magnitude of ρ^* [27] (−7.82) in comparison to the ρ of eq 3 (−3.21) indicates that the pK_A* is more sensitive to substituent effects than is pK_A. The substituent effect of importance here seems to be primarily inductive with resonance effects being minimal. Unfortunately, comparisons with simple *meta*-substituted anilines is not possible since as reported previously[3] there is a very poor correlation between the pK_A*'s (calculated from ^1L_a bands) and substituent constants.

Thus, the excited-state pK_A*'s for 5-substituted 3-nitroanilines are fairly well correlated *via* a Hammett-type treatment. Even though the breakdown of substituent effects into different sets of substituent constants is, of course, only an approximation, it appears that resonance effects are not of substantial importance for this series since exalted σ values or other substituent parameters which reflect resonance contribution fail to yield even fair correlations. For this series, then, one would not expect any direct resonance interaction of a *meta* substituent with the reaction center such as has been predicted for other series of *meta*-substituted compounds.[3]

If eq 3 is subtracted from eq 8 and the value of (pK_A* − pK_A) from eq 7 is substituted into the difference, eq 9 results, where $\Delta\nu' = \nu_B - \nu_{BH^+}$. Consequently, since σ_I is linear with either pK_A* or with pK_A, it appears that it should also be linear with $\Delta\nu'$. However, as shown by eq 10, there is no significant correlation between σ_I and $\Delta\nu'$. For four of the five compounds used to obtain eq 8, the algebraic signs of the deviations of experimental pK_A*'s from eq 8 are opposite to the signs of the deviations of experimental pK_A's from eq 3. In view of this difference, a multiple regression analysis[12c] was performed to obtain eq 11.

$$-6.79 - 4.61\sigma_I = \Delta\nu' Nhc/2.303RT \qquad (9)$$

$$\Delta\nu' = -3278 - 2304\sigma_I \quad \overset{r}{-0.723} \quad \overset{s}{715} \quad 83.2\% \qquad (10)$$

$$\Delta\nu' = -2906 - \underset{(89.2\%)}{2826\sigma_I} + \underset{(78.3\%)}{2104\sigma_R} \quad \overset{r}{0.903} \quad \overset{s}{544} \qquad (11)$$

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[25] W. F. Forbes, *Can. J. Chem.*, **36**, 1350 (1958). Forbes' B bands are equivalent to the ^1L_a bands and his C bands are ^1L_b bands.

[26] L. A. Cohen and W. M. Jones, *J. Am. Chem. Soc.*, **85**, 3402 (1963).

[27] ρ^* is the excited-state reaction constant.

Neither eq 11 with 2 df nor eq 10 with 3 df is statistically significant, *i.e.*, at the 95% confidence level or above. However, eq 11 more closely approaches significance than does eq 10. This may indicate that there is a small secondary resonance effect of the 5-substituent. In spite of the lack of significance of eq 11, it seems of interest that the ρ_I value of -2826 and the ρ_R value of 2104 have opposite signs. If this difference in signs is real, it means that the inductive and resonance effects of the 5 substituent are operating in opposite directions on both $pK_A{}^*$ and pK_A. This may explain the linearity of σ_I with $pK_A{}^*$ or with pK_A but not with $\Delta\nu'$. The uncertainty of the above discussion is probably due to the resonance effect being small and secondary and to the limited amount of available data.

Experimental Section

Materials.—The 5-substituted 3-nitroanilines which were commercially unavailable were prepared as indicated by footnotes to Table II.

Ultraviolet Spectra and Measurement of pK_A's.—The absorption spectra were measured with a Beckman DK-1 spectrophotometer as described previously.[6,8] Stock solutions (0.0006 *M*) were prepared by dissolving the compounds in 25 ml of absolute ethanol and diluting to 250 ml with deionized water. The 5-iodo and 5-carboethoxy compounds were less soluble and 0.0003 *M* solutions were prepared. In all cases, the alcohol content of the final solutions used to determine the spectra was 3% or less. The pK_A of *m*-nitroaniline, determined in water, was identical with that determined in the alcohol solution, and therefore it was assumed that the small amount of ethanol present does not appreciably affect the ionization equilibrium.

The pK_A's were calculated from either eq 12 or 13, whichever was appropriate.[14b]

$$pK_A = H_0 - \log \frac{A - A_A}{A_B - A} \qquad (12)$$

$$pK_A = \mathrm{pH} - \log \frac{A - A_A}{A_B - A} \qquad (13)$$

In eq 12 and 13, A is the absorbance of the solution containing either various concentrations of aqueous HCl or various Clark and Lubs HCl buffers,[28] A_A is the absorbance of the solution in concentrated HCl, A_B is the absorbance of the solution in 0.2 *N* NaOH, and H_0 is the acidity function for HCl.[29] The pH of the buffered solutions was measured on a Beckman Model-G pH meter.

TABLE II

MELTING POINTS OF 5-SUBSTITUTED 3-NITROANILINES

5 substituent	Mp, °C[a]	Lit. mp, °C
H	112.5	114[b]
NO_2	160.5–162	163,[c] 158–161[d]
I	139–140	139.5–141 dec[e]
CF_3	80–82	80–81.5[f]
OCH_3	118–120	119[g]
CN	167.5–169[h]	. . .
$CO_2C_2H_5$	158–160	155[i]
CH_3	97–99	98[j,k]

[a] Corrected. [b] I. Heilbron and H. M. Bunbury, "Dictionary of Organic Compounds," Vol. III, Oxford University Press, New York, N. Y., 1953, p 629. [c] Footnote *b*, Vol. II, p 363. [d] F. K. Beilstein, "Handbuch der Organischen Chemie," Vol. XII, 4th ed, Springer-Verlag, Berlin, 1929, p 759. [e] Aldrich Chemical Company Inc., Catalog 12, 1966, No. I-910, p 224. [f] G. C. Finger and F. H. Reed, *J. Am. Chem. Soc.*, **66,** 1972 (1944). [g] H. Vermeulen, *Rec. Trav. Chim.*, **25,** 12 (1906). [h] Prepared from 3,5-dinitrobenzonitrile by reduction with alcoholic ammonium sulfide. *Anal.* Calcd for $C_7H_5N_3O_2$: C, 51.54; H, 3.09; N, 25.76. Found: C, 51.62; H, 3.21; N, 25.46. This and the following analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn. The N-acetyl compound, prepared by reaction with acetic anhydride, had a corrected melting point of 187–189°. *Anal.* Calcd for $C_9H_7N_3O_2$: N, 20.48. Found: N, 19.97. [i] Footnote *b*, p 614. [j] O. L. Brady, J. N. E. Day, and W. J. W. Rolt, *J. Chem. Soc.*, **121,** 526 (1922). [k] R. A. Martin and A. McGookin, *ibid.*, 901 (1934).

The medium shift was minimal in all cases and the absorbance of all solutions was measured at the wavelength at which A_B was measured.

Registry No.—**1,** 99-09-2; **2,** 618-87-1; **3,** 10394-64-6; **4,** 401-94-5; **5,** 586-10-7; **6,** 10406-92-5; **7,** 10394-67-9; **8,** 618-61-1.

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