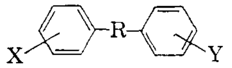
acid is placed on the Y group, far from the substituent.[8]

Separate ρ-values for the seven available series of azo-compounds II with constant Y are given in Table II and plotted against $\sigma_Y{}^+$ in Fig. 4, where a good correlation is observed. This is in accord with the above interpretation of ρ's, since the relative importance of structures like VIII is expected to be related to the electronic character of the substituents Y. It is interesting to note that the present reaction series is the first example of a series in which a constant substituent Y in a compound



undergoing a reaction at R has an appreciable effect on the reaction constant ρ for the effect of X on the reactivity of R. We had previously found[6] in a number of other reaction series that ρ-values were generally not significantly affected by Y.

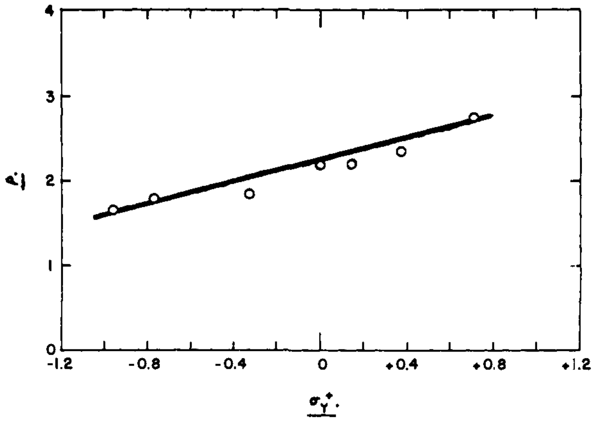


Fig. 4.—A plot of ρ-values against $\sigma_Y{}^+$ for seven series.

An additional piece of confirmatory evidence for the proposed structure of the conjugate acid of azobenzene results from spectroscopic work recently published.[9] In this work we had compared the spectra of the isoelectronic series $C_6H_5R_1{=}R_2\text{-}C_6H_5$, with R_1 and R_2 = CH, N or NH^+, and had made assignments of the various observed bands to separate electronic transitions. We had, in particular, found that in the compounds with $R_1 = R_2$, the $\pi_1 \rightarrow \pi_1{}^*$ transition was the most intense one, and contained the $\phi \rightarrow \pi_1{}^*$ transition partially submerged at the short wave length end. The spectrum of the unsymmetrical compound benzalaniline (R_1 = CH, R_2 = N), however, was interpreted to indicate that the most intense band was the $\phi \rightarrow \pi_1{}^*$ transition, and contained the $\pi_1 \rightarrow \pi_1{}^*$ transition partially submerged at the long wave length side. This reversal of the intensity relations was explained in terms of the dissymmetry of the molecule since the intensity of the $\pi_1 \rightarrow \pi_1{}^*$ band in the unsymmetrical compounds can be shown to be necessarily lower than that in a comparable symmetrical compound. By analogy one would expect the spectrum of an unsymmetrical tautomer such as X or XI to resemble that of benzalaniline in the relation of the intensities of the $\pi_1 \rightarrow \pi_1{}^*$ and $\phi \rightarrow \pi_1{}^*$ transitions, and the spectrum of a conjugate acid like I to resemble that of azobenzene itself. Since the latter is the actual case, this spectroscopic argument provides confirmation of the proposed structure.

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[8] See also the following paper, THIS JOURNAL, **81**, 3283 (1959).

[9] H. H. Jaffé, S. J. Yeh and R. W. Gardner, *Molecular Spectroscopy*, **2**, 120 (1958).

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

Tautomeric Equilibria. VI. The Structure of the Conjugate Acid of *p*-Dimethylaminoazobenzene[1,2]

BY SI-JUNG YEH AND H. H. JAFFÉ

RECEIVED DECEMBER 20, 1958

The structure of the first conjugate acid of *p*-dimethylaminoazobenzene is discussed in detail and conclusive evidence is presented that it consists of a tautomeric mixture of the ammonium (II) and azonium-quinoid (III) forms. A series of separate and independent estimates of the tautomeric equilibrium constant K_T = [II]/[III] are reported. All but one of these estimates lie in the region of 2–3.

The behavior of *p*-dimethylaminoazobenzene (I) in acidic solutions, and particularly the structure of its conjugate acid have been discussed by many authors, and several divergent views have been expressed.[3] Probably the most profitable way to discuss these views is to set up the equilibrium diagram given in Chart I, in which the two possible conjugate acids are tentatively indicated as being in equilibrium. One might, in addition, have written a third conjugate acid, with the proton on the nitrogen atom alpha to the dimethylamino group, but this structure has apparently never been considered as a probable one. Since we have shown that no α-β-tautomerism occurs in the conjugate acids of simple azobenzene derivatives not containing an amino group[2a], no α-protonated

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[1] This work was supported by a Bonita Geho Memorial Grant for Cancer Research from the American Cancer Society. This support is gratefully acknowledged.

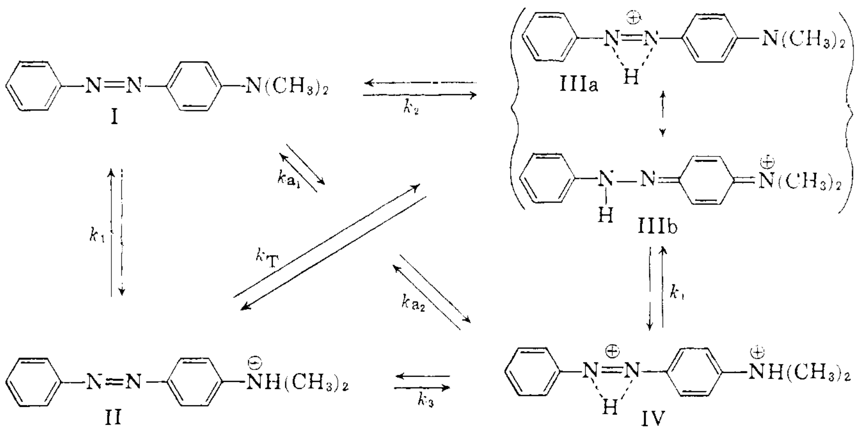
[2] (a) Paper V of this series, see S.-J. Yeh and H. H. Jaffé, THIS JOURNAL, **81**, 3279 (1959). (b) For a preliminary report on some of this work see H. H. Jaffé and Si-Jung Yeh, *J. Org. Chem.*, **22**, 1281 (1957).

[3] (a) I. M. Klotz, H. A Fiess, I. Y. Chen-Ho and M. Mellody, THIS JOURNAL, **76**, 5316 (1954); (b) H. H. Jaffé, *J. Chem. Phys.*, **23**, 415 (1953); (c) F. Kehrmann, *Ber.*, **48**, 1933 (1915); C. R. Bury, THIS JOURNAL, **57**, 2115 (1935); M. T. Rogers, T. W. Campbell and R. W. Maatman, *ibid.*, **73**, 5122 (1951); (d) A. Hantzsch and A. Burawoy, *Ber.*, **63**, 1760 (1930), G. M. Badger, R. G. Buttery and G. E. Lewis, *J. Chem. Soc.*, 1888 (1954); (e) E. Sawicki, *J. Org. Chem.*, **21**, 605 (1956); **22**, 365, 621, 743 (1957).

structure is included in the present consideration. Some previous authors have assigned the ammonium structure II as the exclusive structure of the conjugate acid of I, mostly because the *pK* of I is of the same order of magnitude as that of dimethylanilines,[3a] and since the ρ-value for the effect of substituents on the unsubstituted ring of I is of the order of magnitude one might have anticipated for a reacting amino group so far separated from the substituent.[3b] Other authors, on the other hand, have concluded that the conjugate acid of I has the azonium-quinoid structure III, predominantly on the basis of qualitative spectroscopic evidence.[3c] Finally, a third group of investigators believe that the conjugate acid is an equilibrium mixture of II and III, containing substantial amounts of both tautomers.[3d,e] Either of the first two proposals could only apply if either the equilibrium was established very slowly, or if the tautomeric equilibrium constant was very large ($K_T > 10^2$) or very small ($K_T < 10^{-2}$). Since the reaction II $\rightleftarrows$ III is a shift of a proton between two nitrogen atoms, which generally occur very rapidly, it is unthinkable that equilibrium between II and III is not established essentially instantaneously. Hence it appears possible to unequivocally determine the structure of the conjugate acid of *p*-dimethylaminoazobenzene by a determination of K_T.

The present paper presents a series of determinations of the tautomeric equilibrium constant K_T. The first of these is based on a refinement of spectroscopic methods previously employed in the study of this problem. The other determinations consist in obtaining estimates of some of the intrinsic equilibrium constants K_1, K_2, K_3 and K_4 (*cf.* Chart I for their definition). One method of estimating these constants is based on a comparison of the *pK* of the second conjugate acid of *p*-dimethylaminoazobenzene (IV) with the *pK* of the conjugate acid of *p*-phenylazo-N,N,N-trimethylanilinium ion (V). Further estimates are obtained by use of the Hammett equation, made possible by the measurements of the basicities of simple azobenzenes.[2a]

CHART I



The Spectroscopic Method.—In acidic solutions (6–24 wt. % H_2SO_4), the absorption spectrum (above 300 mμ) of *p*-dimethylaminoazobenzene has two bands, at 316 and 516 mμ, whereas *p*-dimethyl-N,N,N-trimethylanilinium ion has only a single band at 316 mμ. The ϵ_{max} of both compounds at various acidities are summarized in Table I. The absorption of I in dilute sulfuric acid can be understood if it is assumed that the first conjugate acid is a mixture of II and III. The band at 316 mμ is believed to be due to II; its intensity is considerably lower than that of the same band in V. Then the 516 mμ band must be ascribed to III. The equilibrium between II and III appears to shift slightly with the acidity of the solution in the range investigated, since, with increasing acidity, ϵ_{max} at 516 mμ increases and ϵ_{max} at 316 mμ simultaneously decreases. This fact is considered as evidence that the two bands are due to two isomers in equilibrium.

TABLE I

ϵ_{max} OF I AND V IN VARIOUS AQUEOUS ACID SOLUTIONS AT 316 AND 516 mμ

Wt. % H_2SO_4	$\epsilon_{max} \times 10^{-4}$ at 316 mμ I	$\epsilon_{max} \times 10^{-4}$ at 316 mμ V	$\epsilon_{max} \times 10^{-4}$ at 516 mμ I	K_T	K_T[a] (cor.)
6.6	0.926	2.03	3.36	1.1	1.4
12.4	.844	1.99	3.51	1.4	1.8
24.2	.663	1.99	3.91	2.0	2.8

[a] Corrected according to Wepster's estimate of ϵ_2 at 320 mμ; *cf.* text.

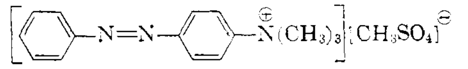
It is reasonable to assume that ϵ_{max} of the 319 mμ band of III and V have the same intensity since the compounds differ only by replacement of a H-atom by a methyl group on the quaternary nitrogen atom. Hence K_T may be estimated from the ϵ_{max} data shown in Table I. Let C_1 and C_2 be the molar concentrations of II and III, ϵ_1 and ϵ_2 the respective molar absorptivities at 316 mμ, and ϵ_{mixt} the experimentally observed molar absorptivity of the equilibrium mixture at the same wave length. Then, K_T is given by

$$K_T = \frac{C_2}{C_1} = \frac{\epsilon_{mixt} - \epsilon_1}{\epsilon_2 - \epsilon_{mixt}}$$

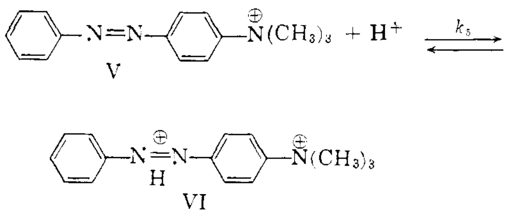
As a first approximation set $\epsilon_2 = 0$, $\epsilon_1 = \epsilon_3$ where ϵ_3 is ϵ of V at 316 mμ. Then, K_T can be calculated from the data in Table I, where the results are shown for several acid concentrations at all of which protonation to the second conjugate acid has not proceeded to any appreciable extent. Thus, K_T for the tautomeric equilibrium between II and III in aqueous sulfuric acid varies from 1 to 2 depending on the acid concentration.

A minor correction to the above calculations must be made since Wepster[4] has observed that ϵ_2 is about 2×10^3 at 320 mμ in the first conjugate acid of 4-amino-3,5-di-*t*-butylazobenzene, and that the tautomeric equilibrium is completely shifted to the azonium-quinoid form in this compound. If it is assumed that this value of ϵ_2 applies to the conjugate acid of *p*-dimethylaminoazobenzene the slightly corrected values of K_T listed in the last column of Table I are obtained.

Comparison of pK_{a_2} with the pK of *p*-Phenylazo-N,N,N-trimethylanilinium Ion.—*p*-Phenylazo-N,-N,N-trimethylanilinium methylsulfate



can add a proton in only one possible way, *i.e.*



V

VI

Assuming that the effects of the groups, $p\text{-}\overset{\oplus}{\mathrm{N}}(\mathrm{CH_3})_3$ and $p\text{-}\overset{\oplus}{\mathrm{N}}\mathrm{H}(\mathrm{CH_3})_2$ on the basicity of the azo-group are nearly the same, leads to the equality $K_3 = K_5$. This assumption is justifiable since the σ constant does not change appreciably by replacing a methyl group in the p-N(CH$_3$)$_2$– group with hydrogen ($\sigma_{p\text{-N(CH}_3)_2} = -0.84$, $\sigma_{p\text{-NHCH}_3} = 0.83$).[5] It can readily be shown that

$$K_T = (K_{a_2} - K_3)/K_3$$

and hence the above assumption leads to

$$K_T = (K_{a_2} - K_5)/K_5$$

K_{a_2} and K_5 have been determined both in aqueous sulfuric acid, and in the 20 vol. % ethanol–aqueous sulfuric acid medium. Since no H_+ function has ever been determined the H_0 function was used for the calculation of pK_{a_2} and pK_5. Since K_T is determined by the ratio of K_{a_2} and K_5, and since these constants are of the same order of magnitude, we may safely assume that the deviations in pK_{a_2} and pK_5 due to the use of the H_0 function very nearly cancel, and hence no major error is introduced by the use of the H_0 instead of the H_+ function. pK_{a_2} and pK_5 were found to be -3.65 and -3.04, respectively, in water and -5.34 and -4.91 in 20% ethanol. Hence we obtain $K_T = 3.0$ and 1.7. The value of 3.0 for the aqueous solution is in excellent agreement with the above spectroscopic values since it applies to approximately 50% sulfuric acid.

Estimation of K_T by the Hammett Equation.—The availability of data concerning the basicities of a large series of azobenzenes in 20 vol. % ethanol has permitted the estimation of several of the intrinsic K's in Chart I by the Hammett equation.

pK_{a_1} and pK_{a_2} were determined in 20 vol. % ethanolic sulfuric acid and found to be 2.96 and -5.34, respectively. For the calculation of pK_{a_2} the revised H_0 function for this particular solvent system was used.[6] Again, we have assumed that the use of the H_0 function instead of H_+ function is justifiable. The most convenient and reliable way to estimate K_T by the Hammett equation is based on pK_3 and pK_{a_2}; pK_3 is readily obtained by the Hammett equation using $\rho = 2.20$, $\log K^\circ = 3.00$[2a] and $\sigma = 0.82$.[5] Then, $\log K_3 = (2.20 \times 0.82 + 3.00) = 4.80$, $K_T = (K_{a_2} - K_3)/K_3 = 2.50$. This value is in good agreement with the value of K_T estimated by the different approaches discussed above.

Since *p*-dimethylaminoazobenzene can also be considered as a derivative of N,N-dimethylaniline, K_1 may be obtained by the Hammett equation using $\sigma = 0.64$[7] for the *p*-phenylazo group, provided that ρ and $\log K^0$ are known for the dissociation of dimethylanilium ion in 20% ethanol at 25°. Unfortunately, these data are not directly available. They can be interpolated from data for different ethanol concentrations and at slightly different temperatures.[7] Thus, we obtain $\rho = 3.18$ and $\log K^0 = -3.75$ for 20% ethanol; K_1 is then given by $\log K_1 = -3.75 + 3.18 \times 0.64 = -1.71$. However, since the free energy change in going from IV to I plus two (solvated) protons must be independent of the path, $K_3K_1 = K_{a_2}K_{a_1} = K_4K_2$. The K_1 obtained here is not consistent with the experimental values of K_{a_1} and K_{a_2} and with K_3 which is estimated based on a more reliable source: $pK_{a_1} + pK_{a_2} = -2.38 \neq pK_3 + pK_1 = -3.09$.

Examination of the available data for the dissociations of substituted anilinium and dimethylanilinium ions indicates that ρ and $\log K^0$ values in aqueous solutions at 25° are the same for these two series.[7,8] Assuming this also to be true in 20% ethanol, we obtain $\rho = 3.20$ (in close agreement with the value obtained above) but $\log K^0 = 4.42$. These data give $pK_1 = 2.38$ consistent with K_{a_1}, K_{a_2} and K_3, *i.e.*, $pK_1 + pK_3 = -2.42 \approx pK_{a_1} + pK_{a_2} = -2.38$. Using this value of K_1 we obtain $\log (1 + K_T) = pK_{a_1} - pK_1 = 2.96 - 2.38$; $K_T = 2.81$.

Application of the Hammett equation to the process $\mathrm{I} + \mathrm{H}^+ \rightleftarrows \mathrm{III}$ was not successful. With $\sigma^+ = -1.7$,[9] $\rho = 2.20$ and $\log K^0 = 3.00$,[2a] we obtain $pK_2 = 0.76$. Unfortunately we cannot test the consistency of the estimate of pK_2, since reliable

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[4] B. M. Wepster, private communications.

[5] D. H. McDaniel and H. C. Brown, *J. Org. Chem.*, **23**, 420 (1958).

[6] S.-J. Yeh and H. H. Jaffé THIS JOURNAL, **81**, 3274 (1959).

[7] H. H. Jaffé, *Chem. Revs.*, **53**, 191 (1953).

[8] J. D. Roberts, R. L. Webb and E. A. McElhill, THIS JOURNAL, **72**, 408, 2939 (1950).

[9] H. C. Brown and Y. Okamoto, *ibid.*, **79**, 1913 (1957).

estimates of K_4 are not available due to the lack of a σ-value for the *p*-phenylazonio group, $C_6H_5\,N{=}\overset{\oplus}{\underset{H}{N}}-$.

Accordingly, K_T estimated from pK_2 leads to a completely different value ($K_T = 6.4 \times 10^{-3}$) from all the other estimates. Possible reasons for this discrepancy are the uncertainty of the σ^+-values for the *p*-N(CH$_3$)$_2$ group and the uncertainty is the H_0 function for 20% ethanolic solutions, particularly in the range needed here, *i.e.*, in the region where the connection to the *p*H scale had to be made by use of *o*-nitroaniline as indicator.[6]

Table II summarizes the K_T values estimated by the various methods discussed. Despite the difficulties encountered it seems unequivocally established that the first conjugate acid of *p*-dimethylaminoazobenzene is a tautomeric mixture of the ammonium II and azonium-quinoid forms III in equilibrium, and that the equilibrium constant is of the order of 1–3 both in aqueous and 20% ethanolic solutions.

After it is established that *p*-dimethylaminoazobenzene exists as a tautomeric mixture in weakly acidic solutions, and that K_T is of the order of 1–3, we are in a position to investigate the effect of substituents on the tautomeric equilibrium constants in the first conjugate acids of *p*-arylazo-N,N-dimethylanilines. Sawicki has investigated the spectral changes associated with the change of acidity of solutions for a great number of such compounds in 50% ethanol.[3e] He has proposed that the ratio of the molar absorptivities of the absorption bands of the azonium form at *ca.* 520 mμ (C_ϵ) and of the ammonium form at *ca.* 320 mμ (A_ϵ) give a crude relative estimate of the tautomeric equilibrium constants for these compounds. A list of the data for various *p*-arylazo-N,N-dimethyl-, -N-methyl-N-ethyl- and -N,N-diethylanilines is given in Table III and the data for the first of these series are plotted against σ in Fig. 1.

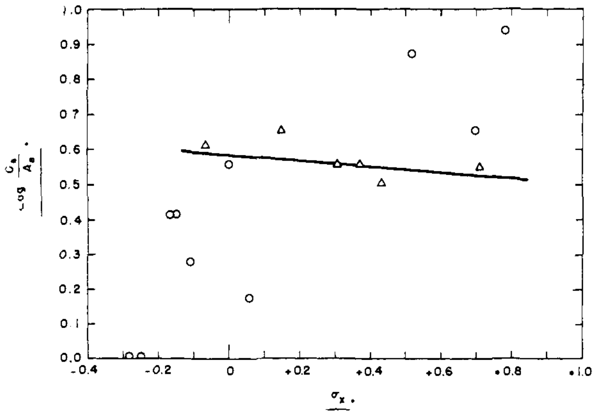


Fig. 1.—A plot of C_ϵ/A_ϵ of *p*-dimethylaminoazobenzene in 1.2 *N* HCl *vs.* σ.

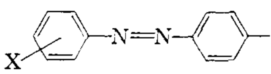
Figure 1 appears to show a complete scatter diagram; close examination of Table III and of Fig. 1 however shows that the C_ϵ/A_ϵ ratios for the *m*-substituted compounds appear to be quite insensitive to the ring substituents, although they appear sensitive to the amino substituents. The *p*-substituted compounds in each series with a constant amino group, however, show an almost random scatter. To attempt to understand this finding we must examine the assumption underlying the use of C_ϵ/A_ϵ as measures of K_T. It is quite obvious that the comparison of C_ϵ/A_ϵ ratios for different compounds can be equivalent to a comparison of K_T values only if the ratio of the molar absorptivities of II at 320 mμ and of III at 520 mμ is quite insensitive to substituent effects. Such insensitivity is likely to apply to the *m*-substituted compounds since no direct resonance interaction between substituent and azo or amino group is possible. In *p*-compounds, however, there is no reason to expect an insensitivity of C_ϵ/A_ϵ ratios to substituent effects, and it is proposed to interpret the data of Table III and Fig. 1 to indicate that K_T is insensi-

TABLE II

SUMMARY OF K_T ESTIMATED BY VARIOUS METHODS

Method	K_T H$_2$O	K_T 20% EtOH
1. *p*K of *p*-phenylazo-N,N,N-trimethylanilinium ion in ~50 wt. % H$_2$SO$_4$	3.0	1.7
2. Spectral data in 6–24 wt. % H$_2$SO$_4$	1.1–2.0	...
3. Use of the Hammett equation from pK_{a_2} and K_3 (~50 wt. % H$_2$SO$_4$)	...	2.5
4. Use of the Hammett equation from pK_{a_1} and K_1 in dil. H$_2$SO$_4$	...	2.8
5. Use of the Hammett equation from pK_{a_1} and K_2 in dil. H$_2$SO$_4$	...	6×10^{-3}

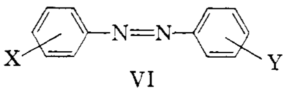
TABLE III

C_ϵ/A_ϵ FOR  NR$_1$R$_2$·HCl IN 50% EtOH[3e]

X	σ[7]	R$_1$ = R$_2$ = CH$_3$	R$_1$ = CH$_3$, R$_2$ = C$_2$H$_5$	R$_1$ = R$_2$ = C$_2$H$_5$
a. *m*-Substituted compounds (including parent compound)				
m-NO$_2$	0.71	3.6	1.6	0.56
m-CF$_3$	.43		1.3	
m-Cl	.37		1.5	
m-COCH$_3$	.31		1.5	
H	.00	3.6	1.4	0.49
m-CH$_3$	− .07		1.7	0.59
m-NHCOCH$_3$	....		1.6	
m-NH$_2$	−0.16	4.1		
b. *p*-Substituted compounds				
p-NO$_2$	0.78	8.7	6.8	2.5
p-SCN	.70	4.5		
p-COCH$_3$	.52	7.5	4.0	1.7
p-F	.06	1.5	0.61	
p-SCH$_3$	− .05	1.6		
p-NHCOCH$_3$	− .02	1.9		
p-C$_2$H$_5$	− .15	2.6	0.95	
p-*i*-C$_3$H$_7$	− .15	2.6		
p-CH$_3$	− .17	2.6		
p-OC$_2$H$_5$	− .25	1.0		
p-OCH$_3$	− .27	1.0		
p-NH$_2$	− .66	4.4		
p-NHCH$_3$	− .59	2.3		
p-N(CH$_3$)$_2$	− .60	2.7		

tive to substituent effects (*i.e.*, that the reaction constant $\rho_T \approx 0$), and that the scatter of *p*-compounds is due to a failure of Sawicki's approximation. The *p*-arylazo-N,N-dimethylanilines are being investigated further.

The value $\rho_T \approx 0$ derived in the preceding paragraph is of considerable interest. We had at one time argued that the structure of the conjugate acid of *p*-dimethylaminoazobenzene must be the ammonium form III because of the small ρ-value for the second basicity.[3b] It now appears on the basis of two lines of evidence that our argument was fallacious. We believe that we have now shown conclusively that a tautomeric equilibrium between the two possible forms exists, and if, as proposed, $\rho_T \approx 0$, it follows that no appreciable difference can exist in susceptibility of the equilibria $I + H^+ \rightleftarrows II$ and $I + H^+ \rightleftarrows III$ to substituent effects. Alternately, we can estimate the ρ-value for the second of these processes from the correlation between the ρ-values of the basicities of series of compounds with constant Y and the σ-values of the apropriate Y.[2a] Such an estimate leads to $\rho_{III} \approx 1.0$, not quite twice the magnitude expected for the ρ-value of the corresponding ammonium ion dissociation.[3b,10] Hence again $\rho_T = \rho_{III} - \rho_I$ is quite small.



VI

It then only remains to ask ourselves why the ρ-value for protonation of the azo group is so low in these cases. If one remembers, however, that the Hammett equation is really concerned with electronic effects, it becomes apparent that the factor affecting ρ most strongly is not the site of attachment of the proton, but the energy required to localize the positive charge. Since it seems very likely that the quinoid structure IIIb makes a very important, if not the predominant contribution to III, ρ_{III} then measures not so much the effect of substituents on the ease of addition of a proton at the nitrogen atom alpha to the substituent, but on the ease of placing a positive charge on the amino group. That this quantity is of a similar magnitude as ρ_{II} for the protonation of the amino group is not surprising since in both processes the charge is placed on the same atom. These arguments seem to provide an alternate explanation of the variability of ρ values with Y in the series of compounds VI. In a preceding paper we have proposed that this magnitude of ρ is dependent on the asymmetry of the proton position in the parent compound of each series. It now seems very likely that the value is ρ is more importantly dependent on the extent to which the positive charge is displaced from the azo group to the end of the ring or to Y by the intervention of quinoid structures.

Experimental

***p*-Dimethylaminoazobenzene.**—A product of the Hilton-Davis Chemical Co.[11] was recrystallized twice from 95% ethanol; m.p. 119–120° (uncor.), lit.[3a] m.p. 119–120°.

***p*-Phenylazo-N,N,N-trimethylanilinium Methylsulfate.**—Ten grams of *p*-dimethylaminoazobenzene, recrystallized from ethanol, was placed in a 500-ml. round-bottomed flask fitted with a reflux condenser. After 100 ml. of dimethyl sulfate was added to the flask, the mixture was refluxed in a water-bath for 5 hours. On standing, the red *p*-phenylazo-N,N,N-trimethylanilinium methylsulfate crystallized out. The crystals were washed with anhydrous ether until the filtrate was clear, and dried under vacuum.

Anal.[12] Calcd.: C, 54.66; H, 6.03; N, 11.97; S, 9.13. Found: C, 54.41; H, 6.26; N, 11.74; S, 9.03.

***pK* Determinations.**—All *pK*'s were determined by a standard spectrophotometric method using a Beckman DU quartz spectrophotometer.[13] The general procedure for the determination of concentration ratios, c_B/c_{BH^+} and $c_{BH^+}/c_{BH_2^{++}}$ and the calculation of *pK*'s were described elsewhere.[6] The *p*H of the solutions was measured by a Beckman model G *p*H meter calibrated with standard buffer solutions.

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[10] S.-J. Yeh and H. H. Jaffé, THIS JOURNAL, **81**, 3287 (1959).

[11] We are grateful to the Hilton-Davis Chemical Co. for a generous gift of this compound.

[12] Microanalyses were performed by A. Bernhardt, Mühlheim (Ruhr), Germany.

[13] L. A. Flexser, L. P. Hammett and A. Dingwall, THIS JOURNAL, **57**, 2103 (1935).

CINCINNATI, OHIO

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

Transmission of Electronic Effects through the —N=NC$_6$H$_4$— Group[1]

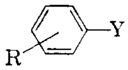
BY SI-JUNG YEH AND H. H. JAFFÉ

RECEIVED DECEMBER 20, 1958

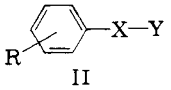
The acid dissociation constants in 20% ethanol of a series of *p*-arylazophenols are reported, and shown to obey the Hammett equation with $\rho = 0.516$. Comparison of this value with an interpolated value for phenols gives a ρ-ratio of 0.16, in fair agreement with a theoretical estimate of 0.14, and an experimental value of 0.13 from the *p*-arylazo-N,N-dimethylanilines.[2]

Some years ago we have proposed that the reaction constants (ρ)[3] for identical reactions occurring at a reaction center Y under identical conditions in two series of compounds I and II can be related by the equation

$$\rho_{II}/\rho_I = \pi' \qquad (1)$$



I



II

in which the constant π' is independent of the group

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[1] This work has been jointly supported by the Office of Ordnance Research, U. S. Army, and by the American Cancer Society through a Bonita Geho Memorial Grant for Cancer Research. This support is gratefully acknowledged.

[2] H. H. Jaffé, *J. Chem. Phys.*, **23**, 415 (1953).

[3] (a) L. P. Hammett, "Physical Organic Chemistry," Hill Book Co., Inc., New York, N. Y., 1940, Chapter VII; (b) H. H. Jaffé, *Chem. Revs.*, **53**, 191 (1953).