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

Tautomeric Equilibria. V. The Basicities of Disubstituted Azobenzenes[1,2]

BY SI-JUNG YEH AND H. H. JAFFÉ

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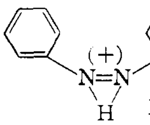
The basicities of 19 disubstituted derivatives of azobenzene are discussed. New evidence is produced indicating that the conjugate acid of azobenzene derivatives is not a tautomeric mixture of two compounds involving localized NH bonds, but involves a proton bonded to both N-atoms.

Azobenzene contains two equivalent basic centers, the azo-nitrogen atoms, which become distinguishable upon introduction of substituents into one or both benzene nuclei. Since there is no reason to expect that the substituents would exert the same effect on the basicity of the two azo-nitrogen atoms, it is of interest to investigate substituent effects on the basicity of each azo-nitrogen separately. This has been done for monosubstituted azobenzenes in the preceding paper of this series[2] where it has been proposed that the conjugate acid of azobenzene can be represented by a structure (I) in which the proton is not bonded exclusively to either nitrogen atom but shared by both of them.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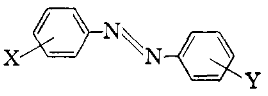
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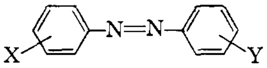
TABLE I

pK's OF 

X	σ	Y = *m*-NO_2 −*pK*	Y = H −*pK*	Y = *p*-OCH_3 −*pK*	Y = *p*-OH −*pK*
4-OEt	−0.250	2.48 ± 0.03	1.28 ± 0.02	....	....
4-OMe	− .268	2.54 ± .03	1.36 ± .03	0.75 ± 0.03	0.56 ± 0.03
4-Me	− .170	3.83 ± .02	2.35 ± .02	1.03 ± .02	0.84 ± .03
3-Me	− .069	4.32 ± .02	2.70 ± .03	....	....
H	0	4.63 ± .02	2.90 ± .02	1.36 ± .03	1.02 ± .01
4-Br	0.232	5.04 ± .01	3.47 ± .02	1.74 ± .03	1.42 ± .01
3-Br	.391	5.52 ± .02	3.83 ± .03	2.06 ± .02	1.67 ± .01
3-$COCH_3$	.306	5.69 ± .02	....	....	....
4-$COCH_3$	.516	5.96 ± .02	3.98 ± .04	2.23 ± .02	....
4-CN	.628	6.50 ± .04	4.52 ± .02	....	....
3-NO_2	.710	6.57 ± .07	4.63 ± .02	2.54 ± .03	....
4-NO_2	.778	....	4.70 ± .02	....	....

It is the purpose of this study to extend the analysis of *pK* data to disubstituted azobenzenes and to investigate the effect of substituents in both benzene rings on the basicity of the azo group. Some 19 disubstituted derivatives (II) of azo benzene have been investigated; their preparation, physical properties, analyses and the determination of their basicities have been described previously.[3] For the purpose of the present discussion, these compounds are grouped into several series, in each one of which Y remains constant while X is being varied. Aside from the monosubstituted compounds (Y = H), there are three main series, the *m*-(phenylazo)-nitrobenzenes (Y = *m*-NO_2), *p*-(phenylazo)-phenols (Y = *p*-OH) and *p*-(phenylazo)-anisoles (Y = *p*-OCH_3). Use of the same X in these four series further permits the construction of three additional series, Y = *p*-Me, *p*-Br and *m*-Br; these latter series, consisting of only four compounds each, will not be discussed extensively. The *pK*'s in 20% ethanol–80% water–sulfuric acid of all the compounds under discussion are summarized in Table I. The *pK*'s of the monosubstituted azobenzenes previously reported by Jaffé and Gardner[2] have been recalculated on the basis of the revised H_0 function.[3]

The *pK*'s for the four main series of compounds are plotted against σ_X in Fig. 1. Two distinctly different patterns of Hammett plots appear; one is represented by the plots for the series Y = H and Y = *m*-NO_2, the other by those of the series Y = *p*-OH and Y = *p*-OCH_3. For the first two series, for electron-releasing groups in the *p*-position, $\sigma_X{}^+$-values[4] must be used to obtain good straight lines. On the contrary, for the series Y = *p*-OH and Y = *p*-OCH_3, normal σ_X-values for the electron-releasing groups are required to obtain satisfactory Hammett plots. The peculiar pattern observed here, *i.e.*, the choice of substituent constants, can be understood if we consider resonance structures in the free bases and their conjugate acids. For the two series, Y = H and Y = *m*-NO_2, resonance between structures III and IV is important in the free bases, but this resonance is

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

[2] For paper IV of this series, see H. H. Jaffé and R. W. Gardner, THIS JOURNAL, **80**, 319 (1958).

[3] Si Jung Yeh and H. H. Jaffé, *ibid.*, **81**, 3274 (1959).

[4] H. C. Brown and Y. Okamoto, *ibid.*, **79**, 1913 (1957); **80**, 4979 (1958).

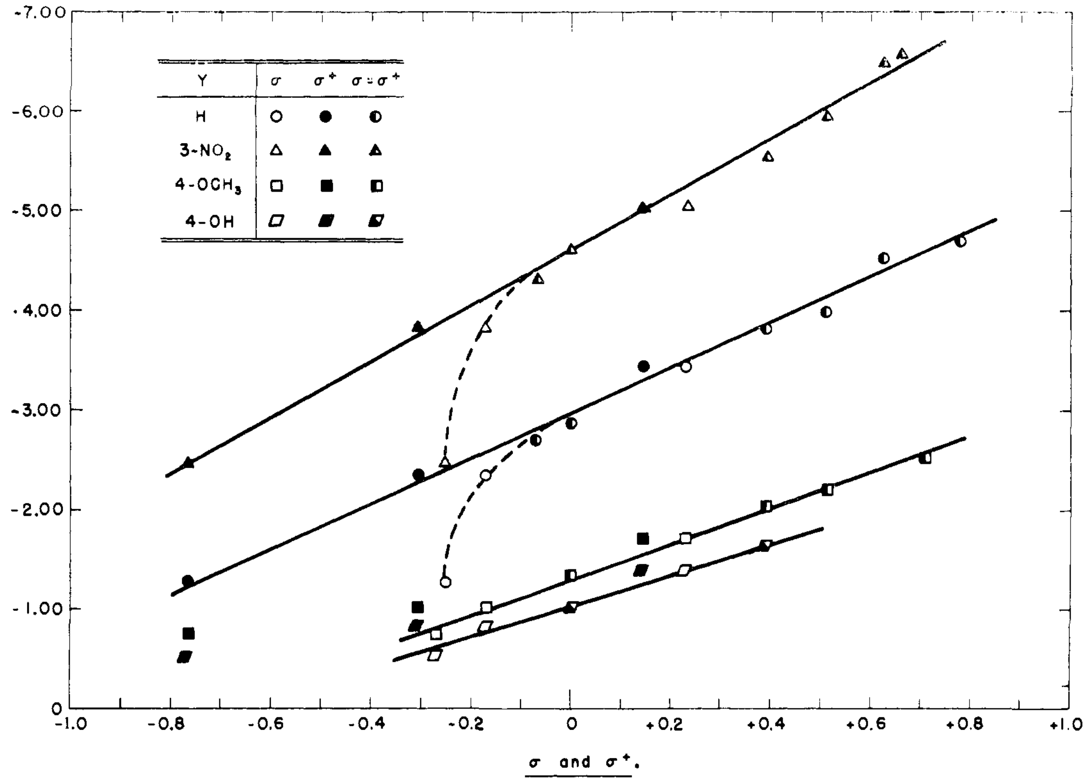
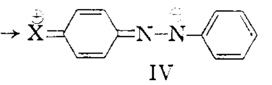
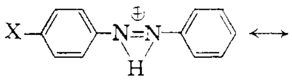


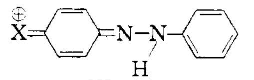
Fig. 1.—A plot of pK *vs.* σ_X for the four main series.

greatly enhanced in the conjugate acids (*cf.* structures V ⟷ VI); hence mesomerically electron-repelling substituents require the use of σ_X^+.

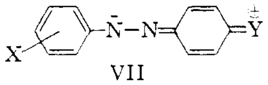

III

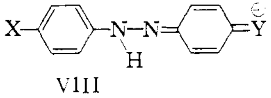

IV


V

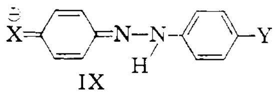

VI

For the Y = *p*-OCH_3 series and Y = *p*-OH series, however, the situation is quite different. The *p*-OCH_3 and *p*-OH groups themselves are capable of exerting a strong + E effect according to structure VII which is again enhanced in the conjugate acid (*cf.* VIII). Due to the important contribution of resonance structure VIII throughout the whole of the Y = *p*-OCH_3 and Y = *p*-OH series,


VII


VIII

and the consequent lesser contribution of the resonance structure IX, the use of (normal) σ_X-value, is


IX

required. This is also true for symmetrically disubstituted compounds, *i.e.*, 4,4'-dimethoxyazobenzene, for which normal σ_{OCH_3} must be used to obtain a good fit of the Hammett plot. It must be remembered that, in these series, the conjugative effect of one electron-repelling group through structure VII and VIII is already included in K^0, and that σ_X only needs to express the additional effect of the X group. To the extent that contributions from structure VIII are important, contributions from structure IX are reduced. The reaction constants for each of the series were calculated by the method of least squares[5] and are summarized in Table II.

Figure 2 shows the plot of pK's of all the compounds against the sum of the substituent constants

TABLE II

REACTION CONSTANTS FOR THE DISSOCIATION OF THE CONJUGATE ACIDS OF SUBSTITUTED AZOBENZENES

	Y = *m*-NO_2	Y = *m*-Br	Y = *p*-Br	Y = H	Y = *p*-CH_3	Y = *p*-OCH_3	Y = *p*-OH	Over-all
ρ	2.75	2.34	2.22	2.20	1.83	1.80	1.61	2.30
r	0.996	1.00	1.00	0.995	0.998	0.997	0.993	0.988
s	.13	0.03	0.04	.12	.10	.05	.06	.28
s_ρ	.09	0.03	0.003	.08	.08	.06	.02	.07
log K^0	4.61	3.85	3.47	3.00	2.47	1.31	1.04	3.07
n	10	4	4	9	4	7	5	31

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(5) H. H. Jaffé, *Chem. Revs.*, **53**, 253 (1953).

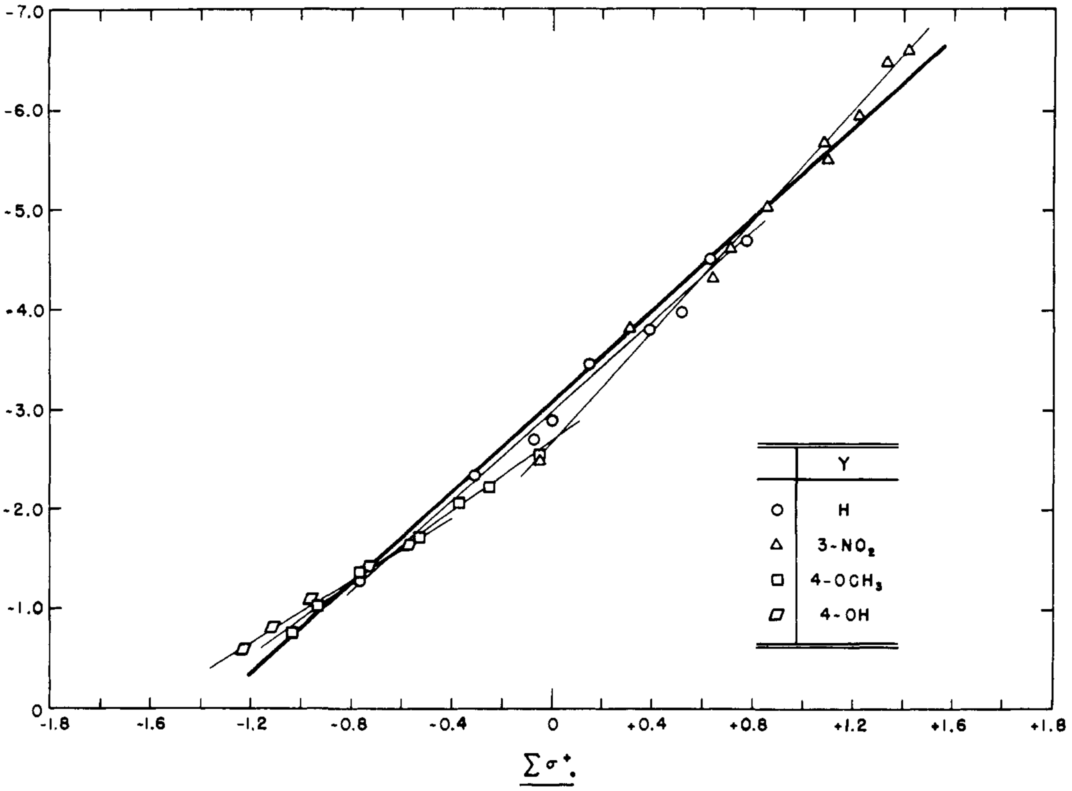


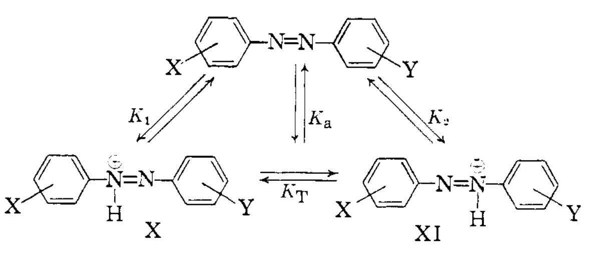
Fig. 2.—A plot of pK vs. the sum of the substituent constants.

to test the applicability of the extended Hammett equation[6]

$$\log(K/K^0) = \rho\Sigma\sigma \qquad (1)$$

Here K^0 refers to the dissociation constant of the conjugate acid of azobenzene, and the term, $\Sigma\sigma$ is the sum of substituent constants for the substituents present in both benzene nuclei. For those substituents which have dual substituent constants, *i.e.*, $\sigma \neq \sigma^+$, the choice between σ and σ^+ was made according to the principle discussed above; for compounds with two mesomerically electron-releasing substituents, σ^+ was used for the more electron-releasing one, regular σ for the other. The reaction constant for eq. 1 is included in Table II. The correlation coefficient, r = 0.988 indicates that eq. 1 represents quite adequately the pK's of the mono and disubstituted azobenzenes. This finding suggests that the azo group of both mono- and disubstituted azobenzenes can be treated as a single reaction center, *i.e.*, a single basic center, in agreement with our earlier proposal.[2]

In a previous paper[2] we have discussed the various alternative formulations possible for the structure of the conjugate acid of azo-compounds. We considered at that time the possibility of a tautomeric equilibrium between structures X and XI, and rejected this possibility. Our argument has been questioned by Wepster,[7] and hence we reexamined this possibility in the light of the new data. Assuming that the tautomers X and XI exist in equilibrium after a proton is added to the azo-linkage of substituted azobenzenes, we must consider the various equilibria



Here K_1 and K_2 refer to the dissociation constants of species X and XI, respectively; K_a is the dissociation constant of the conjugate acid (equilibrium mixture) of the substituted azobenzenes measured experimentally. Let ρ_1 be the reaction constant for the dissociation of the species X, ρ_2 that of species XI. It can readily be shown that

$$K_a = K_1K_2/(K_1 + K_2)$$

and for azobenzene (X = Y = H), $K_1^0 = K_2^0 = 2K_a^0$, $K_T^0 = 1$. Dividing eq. 2 by K_a^0, we obtain

$$\frac{K_a}{K_a^0} = \frac{2}{K_1^0}\frac{K_1K_2}{K_1 + K_2} = \frac{2}{K_2^0}\frac{K_1K_2}{K_1 + K_2} \qquad (3)$$

It is reasonable to assume that the effects of substituents X and Y on the basicity of each azonitrogen atom are separately represented by the Hammett equation, and that these substituent effects are additive. Then we have

$$K_1/K_1^0 = 10^{(\sigma_X\rho_1 + \sigma_Y{}^+\rho_2)} \qquad (4)$$

$$K_2/K_2^0 = 10^{(\sigma_X{}^+\rho_2 + \sigma_Y\rho_1)} \qquad (5)$$

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[6] H. H. Jaffé, *Science*, **118**, 246 (1953).

[7] B. M. Wepster, private communication. We are indebted to Prof. Wepster for an extensive discussion of this problem.

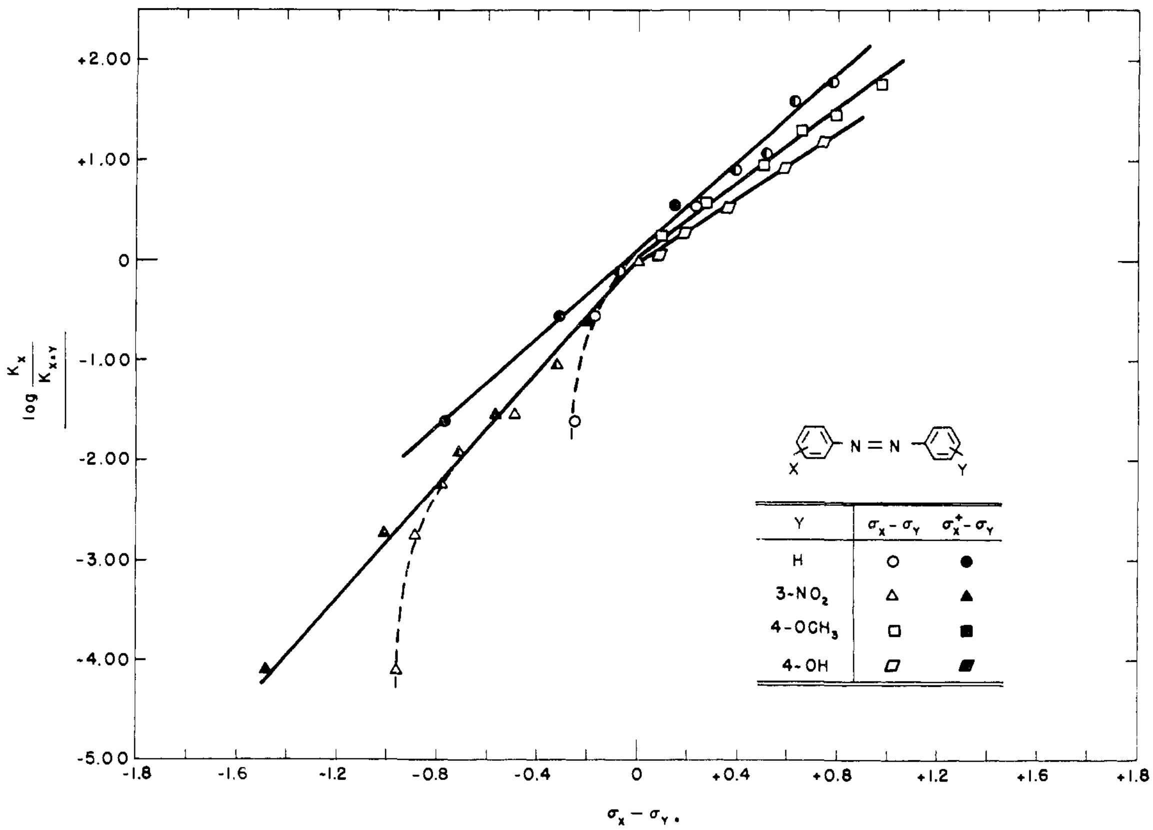


Fig. 3.—A plot of log $K_X/K_{X=Y}$ against $\sigma_X - \sigma_Y$.

Substituting eqs. 4 and 5 into eq. 3, we obtain

$$\frac{K_a}{K_a^0} = 2\,\frac{10^{(\sigma_X\rho_1 + \sigma_Y{}^+\rho_2)} \times 10^{(\sigma_X{}^+\rho_2 + \sigma_Y\rho_1)}}{10^{(\sigma_X\rho_1 + \sigma_Y{}^+\rho_2)} + 10^{(\sigma_X{}^+\rho_2 + \sigma_Y\rho_1)}} \qquad (6)$$

Thus, we can calculate ρ_1 and ρ_2 by eq. 6 from available *pK* data, and expect ρ_1 and ρ_2, to be constant throughout the whole series. Values of ρ_1 and ρ_2 calculated from each series are summarized in Table III, and are seen to vary widely.

TABLE III

COMPARISON OF ρ_1 AND ρ_2 CALCULATED FROM DIFFERENT SERIES[a]

Series, Y =	ρ_1	ρ_2
m-NO$_2$	3.08 or	1.85
	1.85	3.08
p-OCH$_3$	1.19 or	2.61
	7.50	0.40
p-OH	0.95 or	3.06
	8.72	0.33

[a] Two values are given for each since they arise as solutions of quadratic equations.

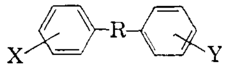
It will now be profitable to consider the three series of disubstituted azobenzenes, the Y = *m*-NO$_2$, Y = *p*-OCH$_3$ and Y = *p*-OH series as derivatives of symmetrically disubstituted parent compounds, *i.e.*, of 3,3′-dinitroazobenzene, 4,4′-dimethoxyazobenzene and 4,4′-dihydroxyazobenzenes, respectively. Then each series can be represented by eq. 7 in analogy with the monosubstituted

$$\frac{K_X}{K_{X=Y}} = 2\,\frac{10^{(\sigma_X-\sigma_Y)\rho_1} \times 10^{(\sigma_X-\sigma_Y)\rho_2}}{10^{(\sigma_X-\sigma_Y)\rho_1} + 10^{(\sigma_X-\sigma_Y)\rho_2}} \qquad (7)$$

azobenzenes.[2] Thus, a plot of log K_X vs. ($\sigma_X - \sigma_Y$) for each disubstituted azobenzene should be curved, and the appropriate plots for the four series should fall on a *single* curve. This postulate can be tested by plotting log ($K_X/K_{X=Y}$) *vs.* ($\sigma_X - \sigma_Y$) for the four series as shown in Fig. 3. It is seen in this plot that each series is represented by a separate straight line with a slightly different slope rather than by a smooth curve. This analysis serves as confirmatory evidence that we are not dealing with the tautomeric equilibrium between the two possible isomers X and XI.

In the foregoing discussions we have seen that the azo-linkage of mono- and disubstituted azobenzenes can be treated as a single reaction center, and that the existence of tautomeric isomers of the conjugate acid of substituted azobenzenes is highly improbable. Based on these results of the analysis of the *pK* data throughout the four series, we believe that the conjugated acids of substituted azobenzenes are best represented by a structure in which the proton is shared by both azo-nitrogen atoms (structure I). This conclusion is further supported by the following consideration. In the plot of *pK*'s *vs.* $\Sigma\sigma$ (Fig. 2), although the over-all correlation is quite satisfactory, close examination of the plot reveals that the compounds of each of the four series define a separate straight line with appreciably different slopes (*cf.* Table II). The difference in ρ-values is probably related to the relative importance of structures such as VIII; the more important such structures, the greater the extent to which the charge in the conjugate 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 σ_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.

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.

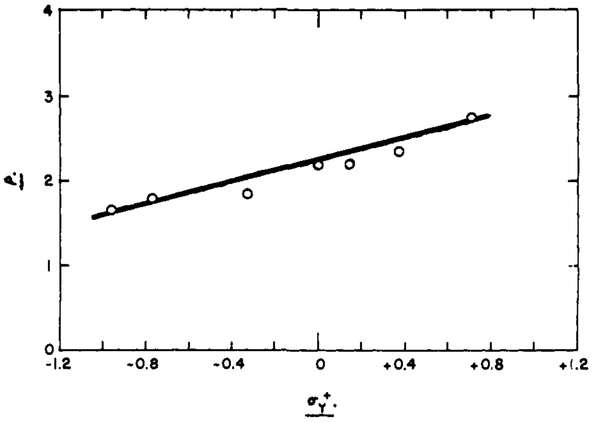


Fig. 4.—A plot of ρ-values against σ_Y^+ for seven series.

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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).