1930(vs) cm.$^{-1}$; other bands at 1441(s), 1382(w), 1336(m), 1320(vw), 1288(m), 1258(s), 1229(m), 1215(m), 1173(s), 1145(s), 1120(s), 1035(m), 987(m), 951(vw), 905(w), 767(w), and 736(w) cm.$^{-1}$.

Anal. Calcd. for $C_{18}H_{14}F_6O_4Mo$: C, 42.9; H, 2.8. Found: C, 42.9; H, 2.9.

Acknowledgment.—The author wishes to acknowledge the suggestions of Dr. C. G. Krespan of the Central Research Department of du Pont in connection with the preparation of the bis-(trifluoromethyl)-tetramethylbicyclo[2,2,2]octatriene.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CINCINNATI, CINCINNATI 21, OHIO]

The Structures of the Conjugate Acids of *cis*- and *trans*-Azobenzenes[1]

BY J. H. COLLINS[2] AND H. H. JAFFE

RECEIVED DECEMBER 28, 1961

The basicities of seven *cis–trans* pairs of monosubstituted azobenzenes have been measured in an acetic acid medium. σ-Values were required to obtain a good fit of the data for the *cis* isomers, while σ^+-values were needed to correlate the *trans* constants. These results are given the interpretation that the *cis* compounds are electronically and structurally related to anilines, and that the benzene rings in these molecules are not far from being perpendicular to the —N=N— plane. A careful mathematical and statistical analysis of the data which lead to the previously proposed delocalized bonding structure of the *trans* conjugate acid is also reported.

In earlier papers,[3] we have proposed that the structure of the conjugate acid of *trans*-azobenzene involves delocalized bonding of the proton to the azo group rather than a localized N–H bond. We arrived at this conclusion from an analysis of pK data, which seem to indicate that the behavior of unsymmetrically substituted derivatives of *trans*-azobenzene was not that expected of a tautomeric mixture of α- and β-protonated species. As a corrollary to our conclusion, we proposed that the conjugate acid of *trans*-azobenzene might have a *cis* configuration. Uncontrovertible evidence has since been produced that the conjugate acid of *cis*-azobenzene, formed by treatment of this compound with strong acid, has properties different from those of the *trans* conjugate acid.[4] The same conclusion was suggested by experiments performed in this Laboratory, in which we failed to obtain *cis*-azobenzene by neutralization of the conjugate acid of its *trans* isomer at Dry Ice temperature. Consequently the corollary to our conclusion must be abandoned; the arguments which led to our original conclusion will be critically re-examined in this paper by the use of careful mathematical and statistical analysis of the data.

Also in order to obtain a better understanding of the electronic and structural nature of the *cis* and *trans* configurations of azobenzene, the basicities of seven *cis–trans* pairs of substituted azobenzenes have been measured by spectrophotometric methods. Because of the instability of the *cis* isomers in strongly acidic aqueous solution, measurements were made in a non-aqueous medium consisting of perchloric acid in acetic acid.[5] The *cis* isomers were quite stable in this medium; no *cis–trans* conversion was observed during the measurements. The constants reported in this paper, determined by standard spectrophotometric methods,[6] represent the equilibrium

$$B + HClO_4 \underset{}{\overset{K}{\rightleftharpoons}} BH^+ClO_4^- \rightleftharpoons BH^+ + ClO_4^-$$

$$K = \frac{\Sigma[BH^+]}{[B][HClO_4]}$$

and will be reported as association constants.

Since the basicities of the *trans* isomers in aqueous acid solution have already been determined in this Laboratory,[3] measurement of $K_{assoc.}$ in acetic acid permits estimation of the pK_a's of the *cis* compounds, on the assumption that the relation between the two solvent systems is the same for the two configurations.

Experimental

***trans*-Monosubstituted azobenzenes** were prepared by the condensation of nitrosobenzene with the appropriately substituted anilines.[3] Purification was achieved by chromatography on alumina followed by recrystallization, usually from aqueous alcohol.

***cis*-Monosubstituted Azobenzenes.**—A solution of a *trans* isomer was irradiated with ultraviolet light for a period of about 1 hour, after which the equilibrium mixture of *cis* and *trans* isomers formed was chromatographed on a column of alumina to afford separation. The *trans* isomer was washed from the column while the *cis* isomer remained absorbed. The *cis* compound was then eluted from the column with anhydrous ether, isolated from the solution by evaporation to dryness at room temperature, and then recrystallized from petroleum ether (60–90° fraction). Care was taken to allow the *cis* compounds to be in solution only for a minimum length of time.

The solvents used for the chromatographic separations varied from petroleum ether to benzene through a series of mixtures of the two. In preparing *p*-acetyl, *p*-cyano- and *m*-nitro-*cis*-azobenzene a third product was separated in small yields from the irradiated mixtures; this compound was undoubtably some decomposition product, and could only be separated from the *cis* isomer by the use of a proper chromatographic solvent. A 1:1 mixture of petroleum ether and benzene was found to be successful for the *p*-acetyl and *p*-cyano compounds and petroleum ether alone was used for the *m*-nitro compound. No attempt was made to identify the decomposition products.

These isomers were identified by their ultraviolet spectra and by analysis. Data on the *cis* and *trans* compound which were prepared are listed in Table I.

Standard Acid Solution.[5]—Standard solutions of perchloric acid were prepared by adding a calculated amount of 70% perchloric acid to 300 ml. of spectroscopic grade glacial

(1) Presented in part before the Organic Division of the American Chemical Society in Chicago, Ill., September, 1961.

(2) Procter and Gamble Fellow, University of Cincinnati, 1961–1962.

(3) (a) H. H. Jaffé and R. W. Gardner, *J. Am. Chem. Soc.*, **80**, 319 (1958); (b) Si-Jung Yeh and H. H. Jaffé, *ibid.*, **81**, 3279 (1959).

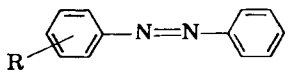
(4) F. Gerson, F. Heilbronner, A. van Veen and B. M. Wepster, *Helv. Chim. Acta*, **43**, 1889 (1960).

(5) I. M. Koltholf and S. Bruckenstein, *J. Am. Chem. Soc.*, **78**, 1 (1956).

(6) L. A. Flexser, L. P. Hammett and A. Dingwall, *ibid.*, **57**, 2103 (1935).

TABLE I

MELTING POINTS OF *cis*- AND *trans*-MONOSUBSTITUTED AZOBENZENES



R	*trans* m.p., °C. Found	*trans* m.p., °C. Lit.[6a]	*cis* m.p., °C. Found	*cis* m.p., °C. Lit.	N,[a] % *cis*-isomers Calcd.	N,[a] % *cis*-isomers Found
p-CH_3O	54–55	54–55	Oil	..	13.20	13.17
p-CH_3	70	69	37	Oil[7]	14.28	14.'6
H	68	68–69.5	71	71[7]	15.38	15.39
p-Br	89–89.5	89–89.5	53–54	47[7]	10.73	10.55
p-Ac	115	115	88–89	..	12.49	12.78
p-CN	121	120.5–121.5	45–46	..	20.28	20.54
m-NO_2	95.5–96	95–96.5	69–70	69–71[8]	18.50	18.43

[a] Microanalyses were performed by Alfred Bernhardt, Microanalytisches Laboratorium, Muhlheim (Ruhr), Germany.

acetic acid, the solution frozen, then twice the amount of acetic anhydride needed to take up the water present was added carefully. (It was found that an excess of acetic anhydride had no effect on the acid–base equilibrium whereas water has a pronounced effect.) The solution was then diluted to one liter with acetic acid and standardized by titration against potassium acid phthalate with crystal violet as indicator. The solutions prepared in this way were all below 2 *M* in $HClO_4$, because of the large volume of acetic anhydride needed per mole of 70% perchloric acid.

Spectrophotometric Measurements.—All measurements were made with a Beckman model DU spectrophotometer with 1-cm. quartz absorption cells. The samples were thermostated to 25.0 ± 0.5° using a thermospacer assembly, and the room temperature was kept at 25 ± 1°.

The absorbances of the free base and the conjugate acid along with at least four equilibrium mixtures of varying acid concentrations were determined at at least two wave lengths for each compound. The concentrations of the azo bases ranged from 2.5–6 × 10^{-5} *M*, depending on the extinction coefficients of individual compound. The reference solutions were prepared by exactly the same method as the sample solutions except for the presence of the azo compound.

The association constants were calculated by standard procedures, using the equation

$$K_{assoc.} = (\epsilon - \epsilon_B)/C_a(\epsilon_{BH^+} - \epsilon)$$

where ϵ_B and ϵ_{BH^+} are the absorbances of the free base and its conjugate acid at wave length λ, ϵ is the absorbance of an equilibrium mixture at wave length λ, and C_a the molar concentration of perchloric acid.

The above equation may be rewritten linearly as

$$(\epsilon - \epsilon_B)/C_a = -K\epsilon + K\epsilon_{BH^+}$$

which is a straight line with slope $-K_{assoc.}$ and intercept $K\epsilon_{BH^+}$. One can perform a least squares fit on the data and obtain the best K and ϵ_{BH^+} for each wave length measured. Because of the limitations previously stated on the maximum concentration of perchloric acid in this solvent system, ϵ_{BH^+} could not be obtained directly for a few of the weaker bases, and therefore a least squares fit of the equilibrium data on these compounds was performed, giving the best $K_{assoc.}$ and ϵ_{BH^+} for the data. The standard deviations were then obtained by using this ϵ_{BH^+} to calculate $K_{assoc.}$ for each equilibrium concentration.

Results and Discussion

Figure 1a is a plot of log $K_{assoc.}$ for the *cis* compounds *vs.* those for the corresponding *trans* compounds. The observed non-linearity indicates some considerable difference in the nature of the acid–base process. The reason for this non-linearity seems to be found in the difference in geometries of the isomers. It has previously been

(7) P. P. Birnbaum, H. J. Linford and D. W. G. Styles, *Trans. Faraday Soc.*, **49**, 735 (1953).

(8) Neil Campbell, Andrew W. Henderson and Duncan Taylor, *J. Chem. Soc.*, 1281 (1953).

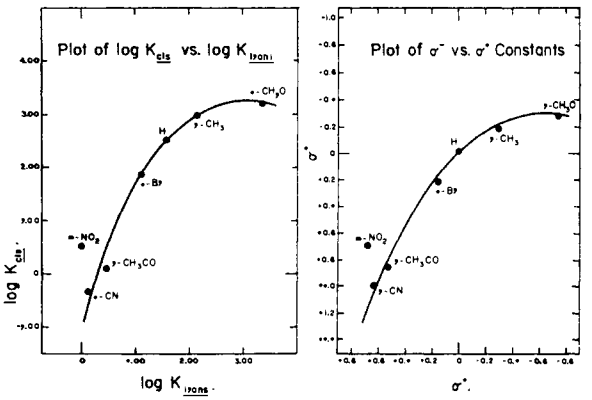


Fig. 1a.—Plot of log $K_{assoc.}$ for the *cis* compounds *vs.* log $K_{assoc.}$ of their *trans* isomers. Fig. 1b.—Plot of σ^+ *vs.* σ^-.

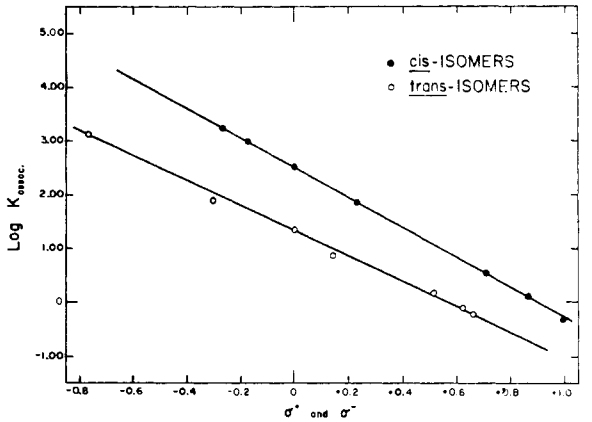
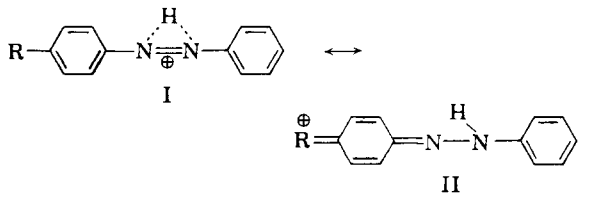


Fig. 2.—Plot of $K_{assoc.}$ for the *trans* compounds *vs.* σ^+ constants and $K_{assoc.}$ for their *cis* isomers *vs.* σ^- constants.

shown[3] that a Hammett equation treatment of the pK's of the *trans* compounds requires the use of σ^+-values, presumably because of the importance of resonance structures such as I and II in the conjugate acid



I

II

An attempt to treat the association constants reported here by the Hammett equation[9] shows that the data for the *trans* compound are well correlated by σ^+-values, but that the *cis* compounds can be correlated only by σ^--constants. A plot of σ^+ *vs.* σ^--constants, as shown in Fig. 1b, confirms this finding since it has the same shape as the plot of the $K_{assoc.}$ of the *cis* and *trans* pairs. Table II gives the measured $K_{assoc.}$'s for the *cis* and *trans* pairs along with the σ^-- and σ^+-constants, respectively, for each substituent. The plot of these data is given in Fig. 2. Both sets of data are seen to give good straight lines with their respective constants (see Table III).

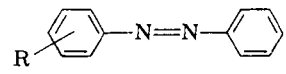
An analysis of variance[10] was performed on the

(9) H. H. Jaffé, *Chem. Revs.*, **53**, 191 (1953).

(10) H. H. Jaffé, *J. Org. Chem.*, **23**, 874 (1958).

TABLE II

LOG $K_{assoc.}$'S FOR



R	σ^+	*trans*	σ^-	*cis*
p-CH_3O–	−0.764	3.14 ± 0.03	−0.286	3.22 ± 0.06
p-CH_3–	−0.306	1.90 ± .02	−0.170	2.98 ± .04
H	0	1.35 ± .03	0	2.50 ± .05
p-Br–	0.148	0.86 ± .02	0.232	1.85 ± .03
p-CH_3CO–	.516	.22 ± .01	0.870	0.08 ± .01
p-CN–	.628	− .11 ± .03	1.000	− .34 ± .01
m-NO_2–	.662	− .24 ± .02	0.710	.52 ± .02

TABLE III

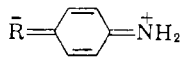
REACTION CONSTANTS FOR THE ACID–BASE EQUILIBRIA OF *cis*- AND *trans*-AZOBENZENES AND PERCHLORIC ACID IN ACETIC ACID AT 25°

	trans isomers	*cis* isomers
ρ	2.308	2.780
r	1.000	1.000
S	0.067	0.036
$S\rho$	0.052	0.028
log $K°$, calcd.	1.31	2.48
n	7	7

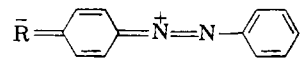
crude experimental data of four determinations of log $K_{assoc.}$ at each of two wave lengths for fourteen compounds. The total variance was broken up into the various contributions indicated in Table IV.

From the table it can be seen that compound differences explain the vast majority of the total variance, as anticipated. The wave length differences are non-significant, as they should be. The *cis–trans* character significance indicates there is something different in the two sets of data, but, of course, this could be due to differences in ρ-values. However, the tremendous significance of the substituent–*cis-trans* interactions is indicative that there is something vastly different in nature between the two sets.

The fact that σ^--values must be used in the *cis* compounds demonstrates the vast difference in the electronic and structural nature of the two sets of geometrical isomers. Obviously structures of the type II cannot be important in the *cis* configuration, but resonance structures similar to those making a large contribution in anilines (III), which also require σ^--values,[9] must also be important here (IV). Thus, the resonance effects



III



IV

in *cis*-azobenzenes must be very similar to those in anilines.

These results also have some structural significance. The *trans* configuration is known to be essentially planar and, therefore, the lone pairs of electrons on the nitrogens lie in the nodal plane of the ring π-electrons and there is conjugation between the π-electrons of the benzene rings and those of the double bond (V). In aniline the lone pair is in a plane perpendicular to the plane of the benzene ring and is in the π-system of the ring. Therefore, in the *cis* configuration of

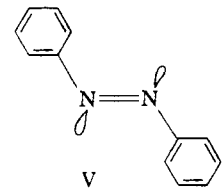
TABLE IV

ANALYSIS OF VARIANCE

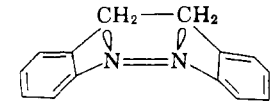
Source of variation	Degrees of freedom	F^a
Total	112	...
Mean	1	...
Different compounds	13	>10,000**
Different substituents	6	>20,000**
cis-trans character	1	>8,000**
Substituent *cis-trans* interaction	6	>1,000**
Due to regression	2	>90,000**
Deviations from regression	11	>700**
Wave length differences	1	2.01
Compd.–w.l. interaction	13	1.68
Wave length *cis–trans* interaction	1	<1
Wave length subst. interaction	6	1.39
Threefold interaction	6	2.17
Error	84	...

[a] Significance at the 95% level is indicated by one asterisk, at the 99% level by two; unmarked values are non-significant.

azobenzene the benzene rings must also be not far from perpendicular to the lone pairs on the nitrogens and therefore to the —N=N— plane. Only in such a structure could resonance structures such as IV be of importance.



V



VI

The spectrum of *cis*- azobenzene when compared with that of 2,2′-azobibenzyl (VI)[4] in which the benzene rings must be essentially at right angles to the —N=N— plane, also indicates that *cis*-azobenzene must have a very similar structure, which is consistent with our findings (see Fig. 3).

The only previous information on the structure of the *cis* configuration was that obtained from X-ray data on crystalline *cis*-azobenzene.[11] From these data it was calculated that the rings were turned 56° out of the —N=N— plane because of steric repulsion between the hydrogen atoms in the 2,2′-positions. This, of course, is the configuration in the crystalline lattice and would not necessarily be the configuration in solution.

Conjugate Acid of *trans*-Azobenzene.—It had previously been suggested that the azo group in *trans*-azobenzene and its derivatives acts as a single basic center. Although the suggestion of a *cis* structure for its conjugate acid has been disproved, no clearcut evidence has been provided that the nitrogen atoms act as separate basic centers. Examination of the present data on the *cis* compounds leads to the same conclusion, since, in these again, no indication of a curvature of the Hammett plot is apparent. In view of the larger ρ-value, and the different resonance types discussed above, one might have anticipated a much larger difference of ρ-values for two separated basic centers, and hence a more apparent curvature.

(11) C. C. Hampson and J. Monteath Robertson, *J. Chem. Soc.*, **409** (1941).

The findings with the *cis* compounds have prompted us to make a very careful analysis of the data on the pK_a's of the *trans* compounds, using an analysis of variance.

We have considered 3 equations as potentially representing the experimental data. Tautomeric equilibrium between α- and β- protonated forms, assuming that the Hammett equation is applicable to each separate acid–base equilibrium, leads to[3b]

$$\log K = \log K^0 + \log 2 + \log [10^{Q_1}10^{Q_2}/(10^{Q_1} + 10^{Q_2})] \quad (1)$$

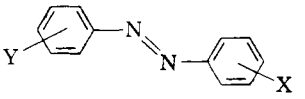
where

$$Q_1 = \sigma_x\rho_1 + \sigma_y{}^+\rho_2, \text{ and}$$
$$Q_2 = \sigma_x{}^+\rho_2 + \sigma_y\rho_1$$

The simplest expression for an azo-group acting as a single basic center would be[3b]

$$\log K = \log K^0 + (\sigma_x{}^+ + \sigma_y)\rho \quad (2)$$

However, we had noted earlier that this equation did not give a completely satisfactory representation of the data, but that a much better representation was attained by treating separately groups of compounds on which the substituent (Y) on one



benzene ring was held constant, and only that (X) on the other ring was varied, and by applying to each such group the simple Hammett equation

$$\log K = \log K_y{}^0 + \sigma_x\rho_y \quad (3')$$

We had further noted that the Hammett equation was applicable to monosubstituted *trans*-azobenzene derivatives,[3a] and that the log $K_y{}^0$ and ρ_y-values in eq. 3′ were proportional to $\sigma_y{}^+$-values

$$\log K_y{}^0 = \log K_0{}^0 + \sigma_y{}^+\rho_0 \quad (3'')$$
$$\rho_y = \rho^0 + \sigma_y{}^+\rho' \quad (3''')$$

Hence, substituting (3″) and (3‴) into (3′) gives[12]

$$\log K = \log K_0{}^0 + (\sigma_x + \sigma_y{}^+)\rho_0 + \sigma_x\sigma_y{}^+\rho' \quad (3)$$

We have now evaluated the fit of the 31 available experimental data for substituent *trans*-azobenzenes[3b] to equations 1 to 3 by the use of analysis of variance; the results are given in Table V.

TABLE V

ANALYSIS OF VARIANCE OF EQ. 1 TO 3

Source	Tested against	DF	F^a
Reqr. eq. 2	Devn. eq. 2	1/29	2479**
	Devn. eq. 1	1/28	3617**
	Devn. eq. 3	1/28	9095**
Reqr. eq. 1	Devn. eq. 1	2/28	1815**
	Devn. eq. 3	2/28	4565**
Reqr. eq. 3	Devn. eq. 3	2/28	4658**
Devn. eq. 2	Devn. eq. 1	29/28	1.46
	Devn. eq. 3	29/28	3.67**
Devn. eq. 1	Devn. eq. 3	28/28	2.57**

[a] See footnote Table IV.

First, it should be noted that all three equations provide an excellent fit to the data. This fact could have been anticipated, since none of them could readily be discarded by inspection alone.

(12) The use of σ or σ^+ for the variable substituent X depended on the nature of Y.[3b]

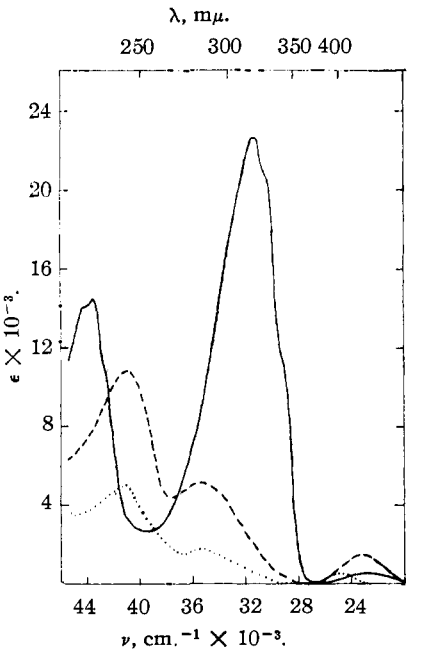


Fig. 3.—Spectra of *cis*- and *trans*-azobenzene in 95% EtOH compared with the spectrum of 2,2′-azobibenzyl which was reported in Fig. 1a of ref. 4: ———, *trans*-azobenzene; – – – –, *cis*-azobenzene; . . . . . , 2,2′-azobibenzyl.

As anticipated, eq. 2 provides the least satisfactory fit, but, of course, it involves only a single adjustable parameter (aside of log K^0). It is also worth noting that eq. 1, although employing two adjustable parameters,[13] leads to a considerably smaller variance ratio (F). It should also be noted that the deviations from eq. 2, though larger than those from eq. 1, when tested against the latter give an F of only 1.46, which is *not* significant, even with 29 and 28 degrees of freedom. Equation 3, also employing 2 parameters, leads to a better fit than either of the other two equations and an F-values almost 2.5 times larger than that for eq. 1.

The deviations from eq. 1 when compared to those from eq. 3, with an F-values of 2.5 are *highly* significant (*i.e.*, at the 99% level), only slightly less so than the deviations from eq. 2 similarly compared ($F = 3.7$).

The remaining statistical data for eq. 3, which thus seem to be the best representation of the data, are: $\rho_0 = 2.227 \pm 0.026$, $\rho' = 0.709 \pm 0.253$, $R = 0.998$, $s = 0.105$ and $n = 31$.

Finally, we have examined the actual representation of the data by eq. 1 and 3; a similar examination for eq. 2 has been given before (Fig. 2 of ref. 3b). Figure 4 shows a plot of $\Delta\ pK = pK_{\text{exptl.}} - pK_{\text{calcd.}}$ *vs.* $pK_{\text{exptl.}}$ It is readily seen that use of eq. 1, just as was observed for eq. 2, provides *systematic* deviations from the experimental data; at the extremes these amount to about −0.3 on the pK scale, and in the middle to about + 0.2; these deviations considerably exceed the estimated experimental uncertainties in the data. The deviations of eq. 3 exceed the average experimental

(13) Or maybe because of this fact, since the sum of the squares due to regression is slightly larger than for eq. 2, but is divided by 2 degrees of freedom.

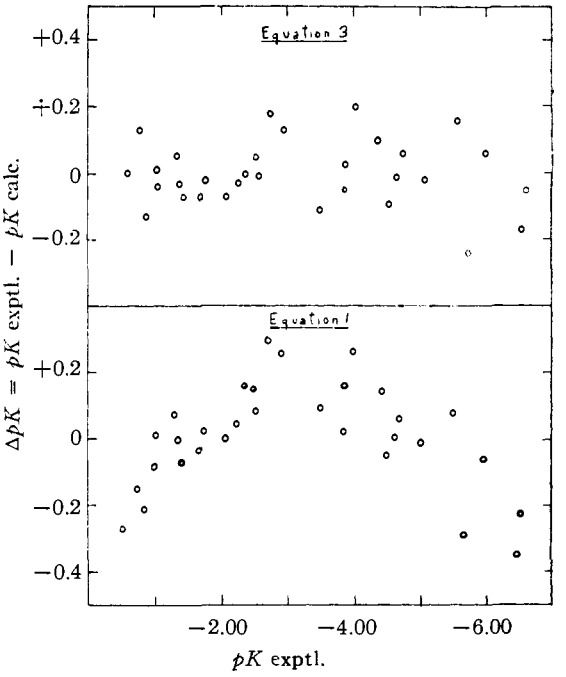


Fig. 4.—Plot of $\Delta pK = pK_{\text{exptl.}} - pK_{\text{calcd.}}$ *vs.* $pK_{\text{exptl.}}$ for eq. 1 and 3.

uncertainty in much fewer cases, and do not appear to be in any way systematically distributed.

In view of the above finding, we are justified in concluding that eq. 3 is a much better representation of the experimental data than the other two equations. Since this equation was derived on the basis of the hypothesis that the azo group acts as a single basic center, and that no tautomeric equilibrium between α- and β-protonated forms exists, these findings provide support for this hypothesis. This hypothesis may now be further extended to include the *cis* compounds, which also appear to involve a single basic center. Unfortunately, however, eq. 1 still provides a sufficiently good fit to the data that it appears premature to state that the hypothesis has been proved, particularly in view of the fact that the conjugate acid of *trans*-azobenzene does not have a *cis* configuration, and no alternate geometry has been suggested.

Finally, since the constancy of σ-values has recently been questioned,[14] it has been suggested[5] that the lack of fit of eq. 1 is due to an inconstancy of σ-values. Such a suggestion is difficult if not impossible to dismiss, since the entire treatment of data by the Hammett equation is dependent on such constancy. However, the excellence of the fit of eq. 3, using the accepted best σ^-- and σ^+-values, with $R = 0.998$ can hardly be a coincidence, and on the basis of the existence of this excellent fit of eq. 3 we believe there is no compelling reason to accept the notion of a tautomeric equilibrium with inconstant σ-values.

Computation in Statistical Analysis

The fits of eq. 2 and 3 were performed by standard least square methods.[15] For fitting of the non-linear eq. 1, a special method was developed which consisted of expanding log K as a function of the parameters log K_0^0, ρ_1 and ρ_2 about its correct value by a Taylor series, thus obtaining a linear equation in corrections, $\Delta \log K_0^0$, $\Delta\rho_1$ and $\Delta\rho_2$. These were fitted by a standard least squares method, used to correct the initial approximates, and the process repeated until no further changes occurred. As few as four iterations sufficed to obtain convergence, even with very poor initial estimates (even all set equal to 0). The computations were performed using an IBM 650 MDDPM. The σ^+-values used were the same standard values always used in this Laboratory.[16]

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