The Tautomeric Equilibria of 4-(Dialkylamino)azobenzene Derivatives

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The tautomeric equilibrium constants, K_t=[ammonium ion]/[azonium ion], of the first conjugate acids of 4-dialkylaminoazobenzene derivatives were estimated by the spectrophotometric method. The K_t values increase in this order: pyrrolidino- <dimethylamino- <diethylaminoazobenzenes. The effects of *N*-alkyl groups on the base strength of the amino and azo nitrogens were examined in order to explain the effects on the tautomeric equilibrium. The base strength of azo nitrogens is governed by the degree of the resonance interaction between the amino group and the rest of the molecule. For dimethylamino- and pyrrolidinoazobenzenes, the base strength of the amino nitrogen can also be explained in terms of the resonance effects, but the amino nitrogen of diethylaminoazobenzenes exhibits an anomalously high base strength, arising from the steric inhibition of the hydrogen bonding in the free base. The above order of K_t can be explained in terms of these cumulative resonance and steric effects.

The structures of the first conjugate acids of 4-aminoazobenzene derivatives have been the subject of much discussion.[1-4] Some authors[1,2] have identified the ammonium structure as the exclusive one of the conjugate acids of 4-dimethylaminoazobenzene. Others,[3,4] on the other hand, have concluded that the conjugate acid has the azonium structure.

Recently it has become clear, however, that there is a tautomeric equilibrium between the ammonium and the azonium forms.[5-8] The tautomeric equilibrium constants have been determined by several workers.[7-9] Jaffé *et al.*[7] determined the constants for a series of substituted derivatives of 4-dimethylaminoazobenzene by various methods, and found that the constants follow the Hammett equation.

A number of attempts[10-12] have been made to explain the structural effects on the basicities of alkylanilines. The base strength of *N,N*-dialkylaniline derivatives in 50% aqueous ethanol are in this order: *N*-phenylpyrrolidine< dimethylaniline< diethylaniline.[11] It has been proposed that solvation on the alkaline side of the ionization equilibrium lowers the free energy of *N*-phenylpyrrolidine and dimethylaniline, and that it is, therefore, base-weakening. The steric inhibition of solvation occurs with diethylaniline and is base-strengthening. It can be expected, therefore, that for 4-dialkylaminoazobenzenes the basicity of the amino nitrogen atom is similarly influenced by the alkyl groups, but the basicity of the azo nitrogen atoms is not so much influenced. As far as we know, there has been no study of the effect of *N*-substituents on the tautomeric equilibrium. The purpose of the present paper is to examine to what extent the tautomeric equilibrium of the first conjugate acids of 4-dialkylaminoazobenzene derivatives is influenced by a change in the alkyl groups.

Experimental

Compounds. The 4-dimethylamino- and 4-diethylaminoazobenzene derivatives were prepared by procedures described in a previous paper.[13] The 4-pyrrolidinoazobenzene derivatives were prepared by diazotizing aniline derivatives and by coupling the resulting diazonium salt with *N*-phenylpyrrolidine, which had been prepared by the methods given in the literature.[14] These azo compounds were purified by dissolving them into benzene, passing them through an alumina column, and then crystallizing them from benzene. The *N,N,N*-trimethyl-*p*-phenylazoanilinium chlorides were prepared by procedures described by Jaffé and Isaks.[7]

4-Dimethylaminoazobenzene: Mp 118—119°C (lit, 119—120°C.

4-Methyl-4'-dimethylaminoazobenzene: Mp 170—171°C (lit, 169.5—170°C).

4-Chloro-4'-dimethylaminoazobenzene: Mp 158—158.5°C (lit, 158—158.5°C).

4-Diethylaminoazobenzene: Mp 97—97.5°C (lit, 98°C).

4-Methyl-4'-diethylaminoazobenzene: Mp 112.5—113°C (lit, 113°C).

4-Chloro-4'-diethylaminoazobenzene: Mp 114°C. Found: C, 67.03; H, 6.42; N, 14.45%. Calcd: C, 66.77; H, 6.30; N, 14.60%.

4-Pyrrolidinoazobenzene: Mp 166—167°C. Found: C, 76.70; H, 6.68; N, 16.69%. Calcd: C, 76.46; H, 6.82; N, 16.72%.

4-Methyl-4'-pyrrolidinoazobenzene: Mp 187—188°C. Found: C, 77.07; H, 7.03; N, 15.79%. Calcd: C, 76.94; H, 7.22; N, 15.84%.

4-Chloro-4'-pyrrolidinoazobenzene: Mp 197—198°C. Found: C, 67.51; H, 5.72; N, 14.76%. Calcd: C, 67.24; H, 5.64; N, 14.70%).

N,N,N-*Trimethyl*-p-*phenylazoanilinium Chloride*: Mp 185.5—186°C (decomp.) (lit, 186—187°C).

N,N,N-*Trimethyl*-p-*(4-methylphenylazo)anilinium Chloride*: Mp

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178.5—179°C (decomp.) (lit, 178—179°C).

N,N,N-*Trimethyl*-p-*(4-chlorophenylazo)anilinium Chloride*: Mp 183—184°C (decomp.) (lit, 184—185°C).

Measurements. The dipole moments and the absorption spectra of the bases were measured by the methods described in a previous paper.[13] The absorption spectra of unbuffered solutions were measured in *ca.* 50% aqueous ethanol (25 ml of the solution contained 12.5 ml of commercial 99% ethanol) with various concentrations of acids. The concentrations of all the azo compounds were about 3×10^{-5}M. The pH of the solutions was measured by means of a Hitachi-Horiba pH meter, Model M-5, calibrated with standard buffer solutions at 25±0.5°C. The dissociation constants, pK_a, were calculated by a standard method. The average deviations for all the compounds were within ±0.05 pH units.

Results

The spectra of some 4-dialkylaminoazobenzene derivatives in *ca.* 1N hydrochloric acid (50% aqueous ethanol), the acidity of which is necessary for the complete formation of the first conjugate acid, are given in Fig. 1. The A band at about 320 nm has been attributed to the conjugation band of the species of the ammonium form (II), while the C band at about 510 nm has been ascribed to that of the azonium form (III).[5-8] The spectra show that the first conjugate acids of 4-dialkylaminoazobenzene derivatives are equilibrium mixtures of II and III, as has been proposed by earlier workers.[5-8] It seems that the $\varepsilon_a/\varepsilon_c$ ratio gives a crude idea of the tautomeric equilibrium. The ε_a value is the apparent molar extinction coefficient at the wavelength maximum of the A band, and the ε_c value is that at the wavelength maximum of the C band. The $\varepsilon_a/\varepsilon_c$ ratio for various substituted

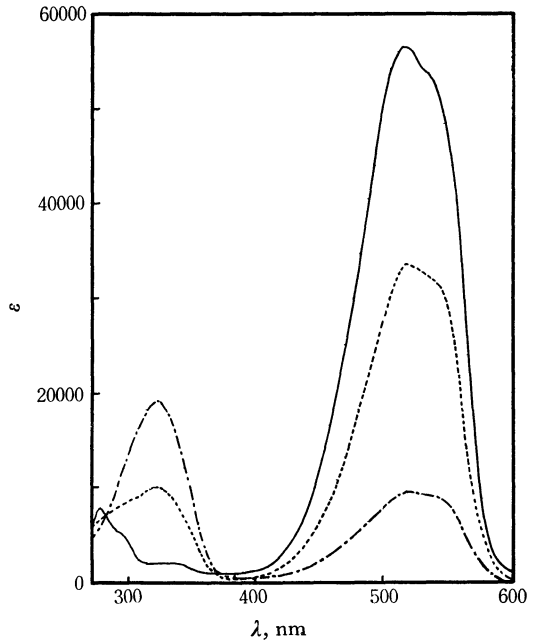


Fig. 1. Absorption spectra of 4-*N,N*-dialkylaminoazobenzene derivatives in *ca.* 1N hydrochloric acid in 50% aqueous ethanol.
------: 4-*N,N*-Dimethylaminoazobenzene
-·-·-: 4-*N,N*-Diethylaminoazobenzene
——: 4-Pyrrolidinoazobenzene

Table 1. Absorption spectra of 4-*N,N*-dialkylaminoazobenzene derivatives and their first conjugate acids

No	λ_{max} ($\varepsilon\times10^{-3}$)			$\varepsilon_a/\varepsilon_c$
	A band	B band[a]	C band	
1	320(10.1)	400(30.4)	516(33.6)	0.30
2	331(13.2)	400(31.8)	528(30.1)	0.44
3	325(12.9)	410(34.1)	520(33.0)	0.39
4	318(19.1)	407(32.3)	516(9.5)	2.03
5	332(21.8)	407(33.4)	528(6.7)	3.23
6	325(21.0)	416(34.0)	518(7.0)	2.98
7	324(3.0)	407(33.0)	516(57.7)	0.05
8	335(2.9)	407(32.8)	528(54.4)	0.05
9	329(3.0)	417(35.0)	520(58.1)	0.05

a) Conjugation band of base in cyclohexane

No.	Substituent
1	4-dimethylamino
2	4-methyl-4′-dimethylamino
3	4-chloro-4′-dimethylamino
4	4-diethylamino
5	4-methyl-4′-diethylamino
6	4-chloro-4′-diethylamino
7	4-pyrrolidino
8	4-methyl-4′-pyrrolidino
9	4-chloro-4′-pyrrolidino

4-dialkylaminoazobenzenes are shown in Table 1.

As is shown in Table 1, $\varepsilon_a/\varepsilon_c$ varies widely from compound to compound. This shows that the tautomeric equilibrium is sensitive to *N*-substituents; especially for 4-pyrrolidinoazobenzene derivatives the equilibrium greatly shifts to the azonium form.

It has been shown for 4-aminoazobenzene derivatives that ε_c increases, and that, simultaneously, ε_a decreases, with an increase in the sulfuric acid concentration.[9] In a very concentrated sulfuric acid (>12N), both bands, A and C, disappear, and at the same time a

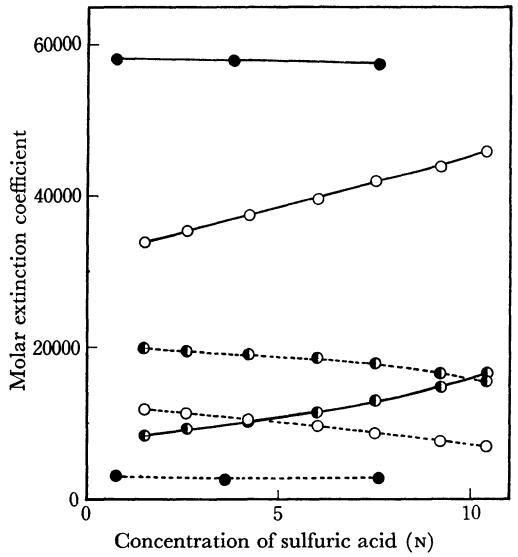


Fig. 2. Plots of molar extinction coefficients (ε_a and ε_c) against concentration of sulfuric acid.
------ ε_a —— ε_c
○: 4-chloro-4′-*N,N*-dimethylaminoazobenzene
◐: 4-chloro-4′-*N,N*-diethylaminoazobenzene
●: 4-chloro-4′-pyrrolidinoazobenzene

new band appears at about 410 nm; this latter band has been assigned to the diprotonated form.[7,8] Figure 2 shows a plot of ε_a and ε_c against the sulfuric acid concentration. As is shown in Fig. 2, for 4-dimethylamino- and 4-diethylaminoazobenzene derivatives ε_c increases and ε_a decreases with an increase in the sulfuric acid concentration. For 4-pyrrolidinoazobenzene, however, ε_a and ε_c are almost uninfluenced by the change in the acid concentration. This shows that, for dimethylamino- and diethylaminoazobenzenes, the tautomeric equilibrium shifts from the ammonium to the azonium form with an increase in the sulfuric acid concentration,[9] while for pyrrolidinoazobenzene the equilibrium does not change, since it has almost completely shifted to the azonium form even at lower concentrations of sulfuric acid. The molar extinction coefficient of the azonium form at *ca.* 510 nm (Band C) for dimethylamino- and diethylaminoazobenzenes cannot be obtained by direct photometric measurement, since they exist in both the azonium and ammonium forms. However, since pyrrolidinoazobenzenes exist exclusively in the azonium form, the ε_c values can be regarded as true molar extinction coefficients. If the molar extinction coefficients of the azonium forms (Band C) are the same for these three types of compounds with the same 4′-substituents, the tautomeric equilibrium constants can be estimated in the following way:

$$\text{Fraction of III} = \frac{\varepsilon_c}{\varepsilon_c^0}$$

$$\text{Fraction of II} = 1 - \frac{\varepsilon_c}{\varepsilon_c^0}$$

Therefore,
$$K_t = \frac{[\text{II}]}{[\text{III}]} = \frac{\varepsilon_c}{\varepsilon_c^0} - 1 \qquad (1)$$

where ε_c^0 is the ε_c value of 4-pyrrolidinoazobenzene derivatives.

According to Gerson and Heilbronner,[8] the equilibrium in question can be expressed as in the following chart:

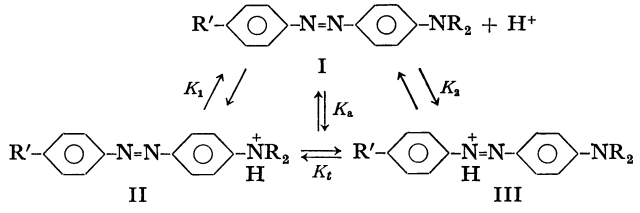


Chart 1.

In this case, the following equations may hold:

$$\begin{aligned} \varepsilon_a C &= \varepsilon_a^{\text{II}}[\text{II}] + \varepsilon_a^{\text{III}}[\text{III}] \\ \varepsilon_c C &= \varepsilon_c^{\text{II}}[\text{II}] + \varepsilon_c^{\text{III}}[\text{III}] \\ C &= [\text{II}] + [\text{III}] \end{aligned} \qquad (2)$$

where $\varepsilon_a^{\text{II}}$ and $\varepsilon_a^{\text{III}}$ are the molar extinction coefficients of II and III at the wavelength maximum of the A band, where $\varepsilon_c^{\text{II}}$ and $\varepsilon_c^{\text{III}}$ are those of II and III at the wavelength maximum of the C band, where [II] and [III] represent the concentrations of II and III respectively, and where C is the concentration of the free base added. Since $\varepsilon_a^{\text{III}}$ is small compared with $\varepsilon_a^{\text{II}}$, and since $\varepsilon_c^{\text{II}}$ is nearly zero, the tautomeric equilibrium constant, K_t, may be expressed as:

$$K_t = \frac{[\text{II}]}{[\text{III}]} = \frac{\varepsilon_c^{\text{III}}}{\varepsilon_a^{\text{II}}} \frac{\varepsilon_a}{\varepsilon_c} \qquad (3)$$

Gerson and Heilbronner[8] assumed that the value of the $\varepsilon_c^{\text{III}}/\varepsilon_a^{\text{II}}$ ratio for 4-dimethylaminoazobenzene is 3 on the basis of the data of Isaks and Jaffé, and that this value is valid for other 4-dimethylaminoazobenzene derivatives as well.

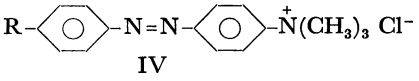
In the present case, however, $\varepsilon_c^{\text{III}}/\varepsilon_a^{\text{II}}$ was estimated in a different manner. From Eq. (2), it follows that

$$\varepsilon_c = \left(\frac{\varepsilon_c^{\text{II}} - \varepsilon_c^{\text{III}}}{\varepsilon_a^{\text{II}} - \varepsilon_a^{\text{III}}}\right)\varepsilon_a + \frac{\varepsilon_c^{\text{III}}\varepsilon_a^{\text{II}} - \varepsilon_c^{\text{II}}\varepsilon_a^{\text{III}}}{\varepsilon_a^{\text{II}} - \varepsilon_a^{\text{III}}}$$

Since $\varepsilon_a^{\text{II}} \gg \varepsilon_a^{\text{III}}$, and $\varepsilon_c^{\text{II}} \approx 0$,

$$\varepsilon_c = -\frac{\varepsilon_c^{\text{III}}}{\varepsilon_a^{\text{II}}}\varepsilon_a + \varepsilon_c^{\text{III}} \qquad (4)$$

According to Eq. (4), there should be a linear relationship between ε_c and ε_a. Various sets of ε_c and ε_a were obtained by changing the sulfuric acid concentrations; they were then plotted according to Eq. (4). A representative one is given in Fig. 3, which shows the validity of Eq. (4). The values of $\varepsilon_c^{\text{III}}/\varepsilon_a^{\text{II}}$ and $\varepsilon_c^{\text{III}}$ were obtained from the slope and the intercept of the line in Fig. 3. These values are given in Table 2. In Table 2, $\varepsilon_a^{\text{IV}}$ denotes the molar extinction coefficinet of *N,N,N*-trimethyl-*p*-phenylazoanilinium chlorides (IV) at the wavelength maximum of the band corresponding to that of the ammonium form (II).



IV

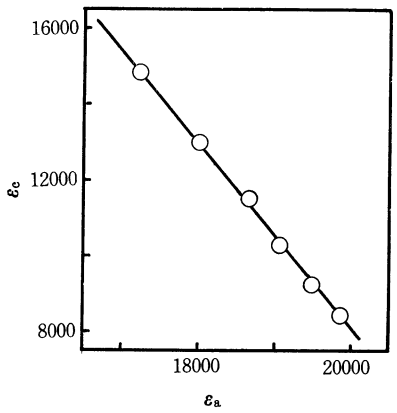


Fig. 3. Relationship between ε_a and ε_c for 4-chloro-4′-*N,N*-diethylaminoazobenzene

Table 2. Molar extinction coefficients of conjugate acids of 4-*N,N*-dialkylaminoazobenzenes

No[a)]	$\varepsilon_c^{\text{III}}/\varepsilon_a^{\text{II}}$	$\varepsilon_c^{\text{III}}$	$\varepsilon_a^{\text{II}}$	$\varepsilon_a^{\text{IV}}$
1	2.64	60400	22900	20400
2	2.54	61600	24200	22900
3	2.53	64000	25300	24100
4	2.67	59200	22200	—
5	2.43	58000	23900	—
6	2.43	56800	23400	—

a) Key is shown in Table 1.

Table 3. Tautomeric equilibrium constants of 4-*N*,*N*-dialkylaminoazobenzene derivatives

No[a)]	Tautomeric Equilibrium Constants			
	A	B	C	D
1	0.72	0.78	0.14	0.90
2	0.82	1.1	0.24	1.17
3	0.75	1.0	0.20	1.23
4	4.9	5.4	—	—
5	7.3	7.8	—	—
6	7.3	7.2	—	—
7	0.0	0.14	—	—
8	0.0	0.14	—	—
9	0.0	0.14	—	—

a) Key is shown in Table 1.
A : Obtained according to Eq (1).
B : Obtained according to Eq (3).
C : Ref. 7.
D : Ref. 8.

Since the electronic effect of the $-\overset{+}{N}(CH_3)_3$ group on the A band may be similar to that of the $-\overset{+}{N}H(CH_3)_2$ group, it should be $\varepsilon_a^{II} \approx \varepsilon_a^{IV}$. As expected, the agreement is quite satisfactory (Table 2), indicating again the validity of Eq. (4).

As is shown in Table 2, the $\varepsilon_c^{III}/\varepsilon_a^{II}$ ratio varies slightly from compound to compound. The tautomeric equilibrium constants calculated according to Eq. (3) are shown in Table 3. These values are in fair agreement with the corresponding values obtained according to Eq. (1). According to Jaffé and Yeh,[7] the molar extinction coefficient at *ca.* 320 nm of the azonium form is about 2000. In this case, therefore, ε_a is the sum of the contributions of both the ammonium and azonium forms. When ε_a is sufficiently large, as in the cases of dimethylamino- and diethylaminoazobenzenes, the contribution of the azonium form to ε_a can be neglected. However, as is shown in Table 1, ε_a is so small for pyrrolidinoazobenzenes as not to permit us to neglect the contribution of the azonium form. Therefore, the value (0.14) for pyrrolidinoazobenzenes obtained by Eq. (3) must be overestimated.

The values for 4-dimethylaminoazobenzene and the 4'-methyl and 4'-chloro derivatives are in good agreement with the values given by Gerson and Heilbronner,[8] but they differ from those obtained by Isaks and Jaffé,[7] as is shown in Table 3. This large discrepancy is due to the difference in the composition of the solvent. The present values were obtained in *ca.* 1N hydrochloric acid, whereas Isaks and Jaffé obtained theirs in much more acidic solutions. In their case, therefore, the equilibrium must have shifted to the azonium form, for the reason mentioned above.

Discussion

The tautomeric equilibrium constant, K_t, is a measure of the difference between the basicity of the amino nitrogen (pK_1) and that of the azo nitrogens (pK_2). Hence, an examination of the effects of *N*-alkyl groups on both pK_1 and pK_2 is necessary in order to interpret the effects on K_t. The values of K_1 and K_2 were calculated according to the following equations:

$$\frac{1}{K_2} = \frac{1}{K_a}\frac{1}{1+K_t}$$

$$\frac{1}{K_a} = \frac{1}{K_1} + \frac{1}{K_2} \qquad (5)$$

where K_1 and K_2 are the acid dissociation constants of the ammonium and the azonium ions respectively, and where K_a is the apparent acid dissociation constant of the first conjugate acid (Chart 1). All the pK_a values were determined by using a standard spectrophotometric method.[14] These values are listed in Table 4.

Table 4. Various equilibrium constants of 4-*N*,*N*-dialkylaminoazobenzene derivatives

Group[a)]	No[b)]	pK_a	K_t[c)]	pK_1[d)]	pK_2[d)]	K_t[e)]	pK_1[f)]	pK_2[f)]
1	1	2.00	0.72	1.62	1.76	0.78	1.64	1.75
	4	2.89	4.9	2.81	2.12	5.4	2.82	2.09
	7	2.38	0.0	—	2.38	0.14	1.46	2.38
2	2	2.17	0.82	1.83	1.91	1.1	1.89	1.85
	5	3.09	7.3	3.03	2.17	7.8	3.04	2.12
	8	2.43	0.0	—	2.43	0.14	1.57	2.43
3	3	1.88	0.75	1.52	1.63	1.0	1.58	1.58
	6	2.65	7.3	2.59	1.73	7.2	2.60	1.71
	9	2.15	0.0	—	2.15	0.14	1.23	2.15

a) Group 4'-Substituent
1 -H
2 $-CH_3$
3 -Cl
b) Key is shown in Table 1.
c) Obtained according to Eq. (1)
d) Obtained according to Eq. (5) using K_t values in the fourth column.
e) Obtained according to Eq. (3).
f) Obtained according to Eq. (5) using K_t values in the seventh column.

For all three groups in Table 4, pK_1 increases in this order: pyrrolidino-<dimethylamino-<diethylaminoazobenzenes. On the other hand, pK_2 increases in this order: dimethylamino-<diethylamino-<pyrrolidinoazobenzenes. The difference in pK_2 is rather smaller than that in pK_1.

The dipole moments of these compounds were measured in order to examine the electronic effect of the *N*-alkyl groups on both pK_1 and pK_2. As may be seen in Table 5, the dipole moments increase step-by-step in this order: dimethylamino-<diethylamino-<pyrrolidinoazobenzenes in each group. The increment is too large to ascribe to the inductive effect of these substituents.

Nash *et al.*[11] have shown, from comparisons of the ^{13}C chemical shifts, the ultraviolet spectra, and the molar refractions of *N*,*N*-dialkylaniline derivatives, that the degree of resonance interaction between the lone-pair electrons on nitrogen and the π-electrons of the

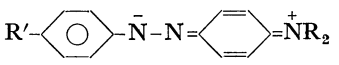
14) In order to obtain pK_a, the absorption spectra of the compounds were measured in various hydrochloric acid concentrations up to *ca.* 1N. For all of the compounds, three isosbestic points were observed in the range from 240 to 600 nm. This indicates that K_t is constant over these acid concentrations. Therefore, the standard method can be used for the determination of pK_a.

TABLE 5. DIPOLE MOMENTS OF 4-*N,N*-DIALKYLAMINOAZOBENZENE DERIVATIVES WITH RELEVANT DATA[a,b]

Group[c]	No[c]	*a*	*b*	R_M cc	*P* cc	μ D
1	1	5.27	0.19	71.9	281.6	3.17
	4	5.74	0.27	78.7	332.9	3.50
	7	6.60	0.29	76.6	369.4	3.76
2	2	3.50	0.15	76.5	225.2	2.66
	5	3.76	0.21	83.3	257.7	2.90
	8	4.80	0.22	81.2	306.5	3.20
3	3	9.20	0.22	76.7	516.3	4.61
	6	9.80	0.28	83.5	597.1	5.00
	9	10.40	0.30	81.4	623.0	5.13

a) Measured in benzene.
b) For notations used here see Ref. 13.
c) Key is shown in Tables 1 and 4.

benzene ring increases in this order: dimethylaniline< diethylaniline≈*N*-phenylpyrrolidine. In the case of dialkylaminoazobenzene derivatives, if it is assumed that the degree of resonance interaction between the amino group and the rest of the molecule increases in this order: dimethylamino-<diethylamino-<pyrrolidinoazobenzenes— if, that is to say, the degree of the contribution of the type



is the greatest for pyrrolidinoazobenzene and the smallest for dimethylaminoazobenzene— it can account for the order of the dipole moments. If the above proposal is reasonable, the transition energy of the conjugation band of these free bases should decrease and the molar extinction coefficient should increase in this order: dimethylamino-<diethylamino-<pyrrolidinoazobenzenes. An inspection of the data for B band in Table 1 supports this idea.

The order of pK_2 is the same as that of the dipole moments, as is shown in Tables 4 and 5. The basicity of azo nitrogens is hardly subject to inductive and steric effects of the alkyl groups, for the alkyl groups are apart from the azo group. Thus, the factor governing pK_2 must be the same as in the case of the dipole moments, since the greater the extent of the contribution of the above type, the greater the negative charge on one of the azo nitrogens.

An inhibition of the resonance decreases the potitive charge on the amino nitrogen and results in an increase in the base strength of the amino nitrogen, all other factors being equal. Therefore, pK_1 should increase in this order: pyrrolidino-<diethylamino-<dimethylaminoazobenzenes, but actually it increases in this order: pyrrolidino-<dimethylamino-<diethylaminoazobenzenes, as is shown in Table 4. This latter order is the same as that for *N,N*-dialkylaniline derivatives given by Nash and Maciel.[11] They have suggested that the alkyl groups in free diethylaniline produce so cluttered a situation in the vicinity of the nitrogen atom that the hydrogen bonding between hydroxylic solvent molecules and the nitrogen atom is inhibited. The resulting loss of solvation energy increases the free energy of the free base, reduces the energy gap between *N,N*-diethylaniline and its anilinium ion, and correspondingly increases the base strength of the former relative to dimethylaniline. Most of their discussion holds in our case as well, thus accounting for the anomalously high base strength of the amino nitrogen of diethylaminoazobenzenes.

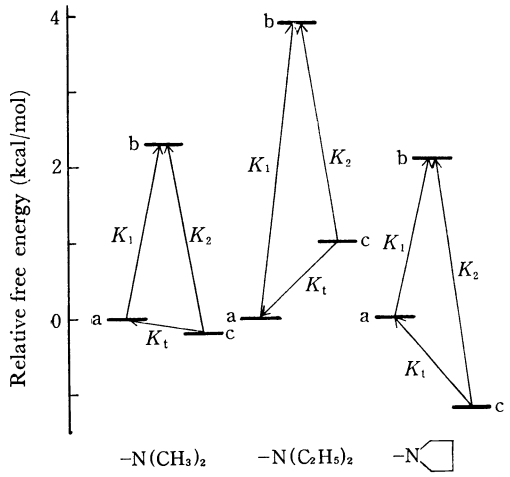


Fig. 4. The diagram of free energy.
a: ammonium ion, b: base + H^+, c: azonium ion.

On the basis of the data in Table 4, a diagram of the free energy was obtained by assuming that the ammonium ions of dimethylamino-, diethylamino-, and pyrrolidinoazobenzenes have equal free energies,[11] the energy of the ammonium ions being taken as the standard. As may be seen in Fig. 4, the free energy gaps between the ammonium ions and the azonium ions, $\Delta G = G(\text{ammonium ion}) - G(\text{azonium ion})$, increase in this order: diethylamino-<dimethylamino-< pyrrolidinoazobenzene; hence, the K_t values decrease in this same order.

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