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The Tautomeric Equilibria of 4-(Dialkylamino)azobenzene Derivatives. II.[1]
2- and/or 2′-Methyl-4-(dimethylamino)azobenzene Derivatives

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The tautomeric equilibrium constants, K_t=[ammonium ion]/[azonium ion], of the first conjugate acids of 2- and/or 2′-methyl-4-dimethylaminoazobenzene derivatives were estimated by the spectrophotometric method. The effects of the 2- and 2′-methyl groups on the basicity of the amino and the azo nitrogens were examined in order to explain the effects on the tautomeric equilibrium. The effects of the 2- and 2′-methyl groups on the basicity of the amino nitrogen is an inductive one only, while the effects on the basicity of the azo nitrogens are both electronic and steric. The latter effect of the 2′-methyl group is very large, but that of the 2-methyl group is not significant. The order of K_t in a series of compounds is almost the same as that of the basicity of the azo nitrogens. That is to say, the magnitude of K_t is mainly governed by the basicity of the azo nitrogens.

The tautomeric equilibrium constants between the ammonium and the azonium ions of 4-dimethylaminoazobenzene derivatives have been reported by several workers.[2–6] Jaffé *et al.*[4] reported that the constants for 4′-substituted-4-dimethylaminoazobenzenes follow the Hammett equation.

In a previous paper,[7] we studied the effects of *N*-alkyl groups on the tautomeric equilibria for 4-dialkylaminoazobenzene derivatives and found that the base strength of the azo and the amino nitrogens is mainly governed by the degree of resonance interaction between the amino group and the rest of the molecule.

Recently, Haselbach[8] measured the pK_a values of a number of *p*- and *o*-substituted azobenzenes and showed that the *o*-methyl group exhibits both electronic and steric effects. For 2- and/or 2′-methyl-4-dimethylaminoazobenzene derivatives, the basicity of the azo nitrogens may be similarly influenced by the 2- and 2′-methyl groups, but the basicity of the amino nitrogen may be not so much influenced. Therefore, it can be expected that the tautomeric equilibrium is greatly affected by the 2- and 2′-methyl groups. As far as we know, there has been no systematic study of the effects of 2- and/or 2′-methyl groups 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-dimethylaminoazobenzene derivatives is influenced by the introduction of the methyl groups into the *ortho* positions.

Experimental

Compounds. The 4-dimethylaminoazobenzene derivatives were prepared and purified by procedures described in previous papers.[7,9]

2-Methyl-4-dimethylaminoazobenzene: mp 67—67.5 °C (lit, 68—68.5 °C)

2′-Methyl-4-dimethylaminoazobenzene: mp 73.5 °C (lit, 73.5—74 °C)

2,4′-Dimethyl-4-dimethylaminoazobenzene: mp 126 °C (lit, 121 °C)

2′,4′-Dimethyl-4-dimethylaminoazobenzene: mp 137 °C (Found: C, 75.48; H, 7.70; N, 16.32%. Calcd: C, 75.85; H, 7.56; N, 16.59%).

2-Methyl-4′-chloro-4-dimethylaminoazobenzene: mp 96 °C (Found: C, 65.61; H, 6.31; N, 15.67%. Calcd: C, 65.81; H, 5.89; N, 15.35%).

2′-Methyl-4′-chloro-4-dimethylaminoazobenzene: mp 117 °C (Found: C, 65.41; H, 6.13; N, 15.09%. Calcd: C, 65.81; H, 5.89; N, 15.35%).

Measurements. The absorption spectra of the azo compounds and their conjugate acids, and the pH values of the solutions, were measured in *ca.* 50% aqueous ethanol at 25±0.5 °C by the methods described in a previous paper.[7] The dissociation constants, pK_a, were calculated by a standard method.[10] The average deviations for all the compounds were within ±0.05 pH units.

Results and Discussion

Table 1 shows the absorption bands of 4-dimethylaminoazobenzene derivatives and their conjugate acids (the B band is the conjugation band of the base, and the A and C bands are the conjugation bands of the ammonium and the azonium ions respectively). The $\varepsilon_a/\varepsilon_c$ ratio gives a measure of the tautomeric equilibrium, where ε_a is the apparent molar extinction coefficient at the peak of the A band, and where ε_c is that at the peak of the C band. As is shown in Table 1, the tautomeric equilibrium is sensitive to 2- and 2′-methyl groups. Especially for 2-methyl derivatives, the equilibrium greatly shifts to the azonium form, while for 2′-methyl derivatives the equilibrium shifts to the ammonium form.

According to Eq. (2) in Ref. (7), the tautomeric equilibrium constant, K_t, may be expressed as:

$$K_t = \frac{[\text{ammonium ion}]}{[\text{azonium ion}]} = \frac{\varepsilon_c^{\text{III}}}{\varepsilon_a^{\text{II}}} \cdot \frac{\varepsilon_a}{\varepsilon_c} - \frac{\varepsilon_a^{\text{III}}}{\varepsilon_a^{\text{II}}} \qquad (1)$$

where $\varepsilon_a^{\text{II}}$ and $\varepsilon_a^{\text{III}}$ are the molar extinction coefficients of the ammonium and azonium ion at the wavelength

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TABLE 1. ABSORPTION SPECTRA OF 4-DIMETHYLAMINOAZOBENZENE DERIVATIAES AND THEIR CONJUGATE ACIDS

No.	Substituent	λ_{max} ($\varepsilon \times 10^{-3}$)			$\varepsilon_a/\varepsilon_c$
		A band	B band[a]	C band	
1	Unsubstituted	320(10.1)	400(30.4)	516(33.6)	0.30
2	2-Methyl	327(6.3)	405(30.2)	516(47.1)	0.13
3	2′-Methyl	327(19.7)	394(29.9)	515(5.8)	3.40
4	2, 2′-Dimethyl	330(14.8)	400(28.8)	514(17.0)	0.87
5	4′-Methyl	331(13.2)	400(31.8)	528(30.1)	0.44
6	2, 4′-Dimethyl	336(6.5)	405(30.5)	528(45.2)	0.14
7	2′, 4′-Dimethyl	340(20.9)	393(31.0)	522(4.1)	5.10
8	2, 2′, 4′-Trimethyl	342(17.8)	399(29.9)	525(12.7)	1.40
9	4′-Chloro	325(12.9)	410(34.1)	520(33.0)	0.39
10	2-Methyl-4′-chloro	332(7.4)	415(32.8)	517(47.4)	0.16
11	2′-Methyl-4′-chloro	334(22.7)	413(32.6)	511(3.5)	6.49
12	2,2′-Dimethyl-4′-chloro	335(20.1)	411(31.0)	513(12.4)	1.62

a) Conjugation band of the base in cyclohexane.

TABLE 2. VARIOUS EQUILIBRIUM CONSTANTS OF 4-DIMETHYLAMINOAZOBENZENE DERIVATIVES

Group	No.[a]	$\varepsilon_a/\varepsilon_c$	$\varepsilon_c^{III}/\varepsilon_a^{II}$	K_t	pK_a	pK_1	pK_2
1	1	0.30	2.64	0.78	2.00	1.64	1.75
	2	0.13	2.65	0.24	2.81	2.10	2.72
	3	3.40	2.32	7.89	2.00	1.95	1.05
	4	0.87	2.75	2.39	2.42	2.27	1.89
2	5	0.44	2.54	1.12	2.17	1.89	1.85
	6	0.14	2.40	0.24	2.84	2.13	2.75
	7	5.10	2.50	12.75	2.08	2.05	0.95
	8	1.40	2.67	3.74	2.53	2.43	1.85
3	9	0.39	2.53	0.99	1.88	1.58	1.58
	10	0.16	2.34	0.27	2.63	1.96	2.53
	11	6.49	2.50	16.23	1.90	1.87	0.69
	12	1.62	2.75	4.46	2.20	2.11	1.46

a) Key is shown in Table 1.

maximum of the A band, and where ε_c^{III} is that of the azonium ion at the wavelength maximum of the C band. As has been described in the previous paper, when ε_a is sufficiently large ($\varepsilon_a > 10000$), as in the cases of dimethylaminoazobenzene and the like, the contribution of the second term on the right-hand side of Eq. (1) can be neglected. For 2-methyl derivatives, however, the second term can not be neglected. This can be estimated in the following way. According to Jaffé and Yeh,[4] the molar extinction coefficient (ε_a^{III}) of the azonium ion at about 320 nm is about 2000. On the other hand, ε_a^{II} is more than 20000.[7] Therefore, the $\varepsilon_a^{III}/\varepsilon_a^{II}$ value is about 0.1. The $\varepsilon_c^{III}/\varepsilon_a^{II}$ values were estimated in the manner described in a previous paper;[7] they are listed in Table 2. The K_t values calculated are listed in Table 2.

The tautomeric equilibrium constant is a measure of the difference between the basicity of the amino nitrogen (pK_1) and that of the azo nitrogen (pK_2). Hence, an examination of the effects of 2- and 2′-methyl groups on both pK_1 and pK_2 is necessary in order to interpret the effects on K_t. The pK_1 and pK_2 values were calculated according to the method described in a previous paper;[7] they are given in Table 2.

For all three groups in Table 2, the pK_1 increases in this order: unsubstituted < 2′-methyl < 2-methyl < 2,2′-dimethyl derivatives. The resonance effects of the 2-methyl group might not be significant, since this group is in the *meta* position to the amino group. As for the 2′-methyl group, this effect also does not seem to be important. Further, the steric effect of these groups on the pK_1 is not significant, since these groups are apart from the amino group. Therefore, of the effects of the 2- and 2′-methyl groups the inductive effect may be predominant.

The ΔpK_1 and ΔpK_2 values, which show the differences in pK_1 and pK_2 between 2- and/or 2′-methylated and the corresponding unmethylated compounds, are shown in Table 3 (a) and (b). An inspection of the ΔpK_1 values in Table 3 (a) shows that the introduction of an extra methyl group on the 2-position always results in a definite increase in pK_1. The same thing holds for the 2′-methyl group as well (see Table 3 (b)). This can easily be understood by remembering that the effects of the 2- and 2′-methyl groups on the pK_1 are only inductive.

As is shown in Table 2, the introduction of a methyl group into the 2-position increases the pK_2, while that into the 2′-position decreases the pK_2. These findings

Table 3. The effects of 2- and 2'-methyl groups on pK_1 and pK_2

a) 2-methyl group

No.[a]	2'- and/or 4'-substituents	2-substituent	pK_1	ΔpK_1	pK_2	ΔpK_2
1	H	H	1.64		1.75	
2	H	CH$_3$	2.08	0.44	2.73	0.98
5	4'-CH$_3$	H	1.89		1.85	
6	4'-CH$_3$	CH$_3$	2.10	0.21	2.76	0.91
9	4'-Cl	H	1.58		1.58	
10	4'-Cl	CH$_3$	1.93	0.38	2.53	0.95
3	2'-CH$_3$	H	1.95		1.03	
4	2'-CH$_3$	CH$_3$	2.27	0.32	1.89	0.86
7	2',4'-diCH$_3$	H	2.05		0.95	
8	2', 4'-diCH$_3$	CH$_3$	2.43	0.38	1.82	0.87
11	2'-CH$_3$-4'-Cl	H	1.87		0.73	
12	2'-CH$_3$-4'-Cl	CH$_3$	2.11	0.24	1.46	0.73
	average			0.33±0.02		0.88±0.02

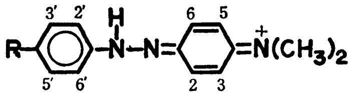
a) Key is shown in Table 1.

b) 2'-methyl group

No.[a]	2- and/or 4'-substituents	2'-substituent	pK_1	ΔpK_1	pK_2	ΔpK_2
1	H	H	1.64		1.75	
3	H	CH$_3$	1.95	0.31	1.03	−0.72
5	4'-CH$_3$	H	1.89		1.85	
7	4'-CH$_3$	CH$_3$	2.05	0.16	0.95	−0.90
9	4'-Cl	H	1.58		1.58	
11	4'-Cl	CH$_3$	1.87	0.29	0.73	−0.85
2	2-CH$_3$	H	2.08		2.72	
4	2-CH$_3$	CH$_3$	2.27	0.19	1.89	−0.83
6	2, 4'-diCH$_3$	H	2.10		2.76	
8	2, 4'-diCH$_3$	CH$_3$	2.43	0.33	1.82	−0.94
10	2-CH$_3$-4'-Cl	H	1.93		2.53	
12	2-CH$_3$-4'-Cl	CH$_3$	2.11	0.18	1.46	−1.07
	average			0.24±0.02		−0.89±0.03

a) Key is shown in Table 1.

show that the 2'-methyl group sterically hinders the addition of a proton and decreases the pK_2, while the 2-methyl group does not hinder the addition, but, rather, increases the pK_2 through its electronic effect.[9] This supports the idea that the azonium ion of 4-dimethylaminoazobenzene derivatives is of the following resonance-stabilized type:[11]



As is shown in Table 3 (a) and (b), the constancy of the ΔpK_2 values shows the additivity of the effects of 2- and 2'-methyl groups on the basicity of the azo nitrogens. The values of 0.88 and −0.89 for the ΔpK_2 values of the 2- and 2'-methyl groups roughly agree with the corresponding values obtained by Haselbach[8] for 4-methoxyazobenzene derivatives.

The effects of the 2- and 2'-methyl groups on pK_1 are only inductive; therefore, the order of pK_1 is simple (unsubstituted < 2'-methyl < 2-methyl < 2,2'-dimethyl derivatives). On the other hand, the effects on pK_2 may be both electronic and steric, and the order of pK_2 is more complicated (2'-methyl < 2,2'-dimethyl ≈ unsubstituted < 2-methyl derivatives). The order of K_t is almost the same as that of pK_2. This shows that the magnitude of K_t is mainly governed by the basicity of the azo nitrogens.

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