

The Physical Properties of the Aminoazobenzene Dyes. III. Tautomerism of 4-Aminoazobenzene Salt Cations in Acid Solution¹

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The cationic tautomerism of 16 aminoazobenzene dyes was investigated in 50% alcoholic hydrochloric acid solution. The importance of intramolecular hydrogen bonding, steric hindrance and electronic effects on the basicity and tautomerism of the dyes has been discussed and correlated. All 4-aminoazobenzene dyes gave a mixture of 2 tautomers in acid solution, involving proton addition to the β -nitrogen, and proton addition to the amino nitrogen. The possibility of a third tautomer was also discussed. In the range of acid concentrations where only the monoacid salt was present, increasing acid concentration caused the tautomeric equilibrium, $C \rightleftharpoons A$, to shift to the left. 3-Amino- and probably 2-aminoazobenzene gave exclusive proton addition to the amino nitrogen while 4-methylthioazobenzene gave exclusive proton addition to the β -nitrogen.

The research in this paper is based on the important correlations of the structures of dyes with their spectra as reported by such organic spectroscopists as Brode,² Brooker,³ Burawoy,⁴ Kiprianov,⁵ Lewis,⁶ and many others.

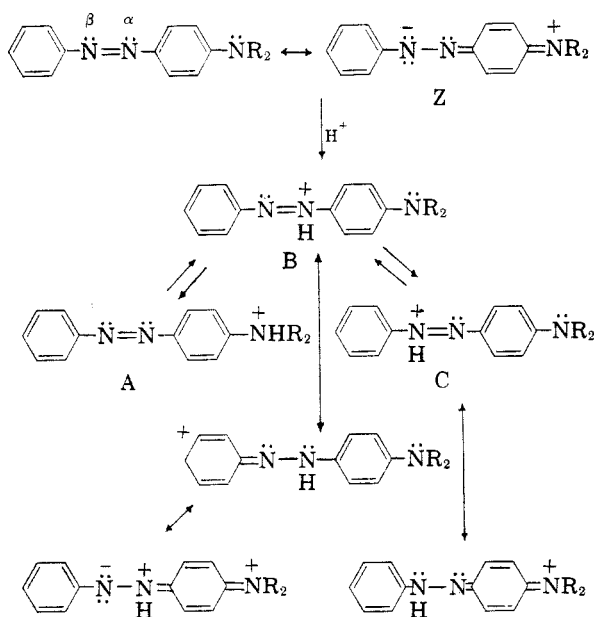
The 4-aminoazobenzene derivatives are excellent examples of a family of compounds in which a zwitterionic resonance system, Z, contributes to some extent to the ground state and strongly to the

excited state. Addition of a proton to 4-aminoazobenzene can give the three tautomers—A, which is iso- π -electronic with azobenzene, B, for which the more important cationic and zwitterionic resonance forms are shown, and C, for which the limiting cationic resonance forms are shown.

Hantzsch and Burawoy⁷ have studied the spectra of some 4-aminoazobenzene dyes in acid solution. They presented evidence that the salt cations exist in solution as an equilibrium mixture of tautomeric forms in which the ammonium, A, form of the salt is associated with the band at 320 m μ and the cationic resonating form, C, is associated with the long wave length band. Excellent concise reviews have been given by Badger, Buttery, and Lewis⁸ and Rogers, Campbell, and Maatman⁹ directing attention to the relation between the position of proton addition and the resulting spectra. Many examples of dyes whose long wave length band is associated with somewhat similar cationic resonance forms, have been furnished by Brooker.³

Badger, Buttery, and Lewis⁸ have further investigated the tautomerism of the salt cations of 9 N-substituted 4-aminoazobenzene dyes. Their results support the view that the salt cations exist in solution as an equilibrium mixture of two tautomeric forms in which the proton is attached to the β -nitrogen and to the amino nitrogen respectively.

On the other hand recent workers have investigated proton addition to the 4-aminoazobenzenes and assuming only two alternatives—exclusive proton addition either to an azo nitrogen or to the amino nitrogen—have reached opposite conclusions. Rogers, Campbell, and Maatman⁹ have concluded on the basis of a study of the basicities and the Hammett substituent constants, σ , that the first proton adds to the β -nitrogen. Klotz, Fiess, Ho, and Mellody¹⁰ concluded in a study of the basicity



(1) This investigation was supported by research grants C-1308 and C-1066 from the National Cancer Institute of the National Institutes of Health, U.S. Public Health Service.

(2) Brode, Seldin, Spoerri, and Wyman, *J. Am. Chem. Soc.*, **77**, 2762 (1955), and previous papers.

(3) Brooker and Keyes, *J. Am. Chem. Soc.*, **73**, 5356 (1951), and previous papers in this series.

(4) Burawoy, Liversedge, and Vellins, *J. Chem. Soc.*, 4481 (1954), and previous papers.

(5) Kiprianov, Ivanov, and Fridman, *Ukrain. Khim. Zhur.*, **20**, 641 (1954), and previous papers.

(6) Lewis, *J. Am. Chem. Soc.*, **67**, 770 (1945), and previous papers.

(7) Hantzsch and Burawoy, *Ber.*, **63**, 1760 (1930).

(8) Badger, Buttery, and Lewis, *J. Chem. Soc.*, 1888 (1954).

(9) Rogers, Campbell, and Maatman, *J. Am. Chem. Soc.*, **73**, 5122 (1951).

(10) Klotz, Fiess, Ho, and Mellody, *J. Am. Chem. Soc.*, **76**, 5136 (1954).

TABLE I
 SPECTRAL DATA IN 50% ALCOHOLIC ACID^a

Compound	M.P., °C.	<i>p</i> Ka ^b	$\lambda_{\max.}$ ($\epsilon \times 10^{-3}$)		$\lambda_{\max.}$ ($\epsilon \times 10^{-3}$)		Normal-ity HCl	$\frac{C_e}{A_e}$
			A Band		C Band			
I 4-Methylthioazobenzene ^c	81-82		320	(3.0) ^d	532	(57.3)		(19) ^e
II 2'-Carbomethoxy-2-methyl DAB	119-120		335	(4.1)	513	(51.8)	1.2	12.6
III 2-Methyl DAB ^f	68-69	3.08	327	(4.82)	515	(48.2)	1.2	10.0
IV 3'-Chloro-2-methyl DAB	89-90.5	2.67	328	(5.1)	507	(48.2)	1.2	9.5
V 4'-Nitro DAB	231-232.5 ¹⁵	1.8	332	(7.1)	512	(61.6)	1.0	8.7
VI DAB	117-118 ¹⁴	2.28	320	(9.8)	517	(35.5)	1.2	3.6
VII N-Ethyl-4-AB ^g	87-88 ¹⁴	2.58	318	(12.0)	508	(29.6)	1.0	2.5
VIII 3'-Nitro-N-methyl-N-ethyl-4-AB	122-123 ¹⁵	2.00	313	(15.2)	500	(23.6)	1.2	1.6
IX 4'-Methoxy DAB	160-161 ¹⁵	2.40	352	(18.2)	550	(18.5)	1.2	1.0
X 2'-Methyl DAB	73-74 ¹⁴	2.04	326	(17.6)	514	(5.0)	1.0	0.28
XI 2',3-Dimethyl-4-AB	101-102 ¹⁶	2.29	326	(19.0)	490	(2.50)	1.0	0.13
XII 4'-Nitro-3-methyl DAB	122-123 ¹⁷		328	(25.5)	492	(1.02)	3.0	0.040
XIII 4'-Acetyl-3-methyl DAB	127.5-128 ¹⁵	3.27	325	(28.3)	485	(0.98)	1.2	0.035
XIV 3-Methyl DAB oil ¹⁴		3.48	319	(19.8)	500 ^h	(0.50)	1.0	0.025
XV 3'-Nitro-3-methyl DAB	72-73 ¹⁵	3.2	310	(22.4)	500 ^d	(0.34)	1.2	0.015
XVI 2-AB	59-60 ¹⁵	1.8	328	(20.3)	500 ^d	(0.38)	1.0	0.019
XVII 3-AB	64-65 ¹⁵	2.8	322	(20.0)	500 ^d	(0.15)	6.0	(0.01) ^e
XVIII Azobenzene ⁱ	67-68		320	(21.3)	500 ^d	(0.15)		(0.01) ^e

^a Absorption spectral region covered from 300-600 $m\mu$. ^b Determined in 50% ethanol.^{13,14,17} ^c Solvent is 75 ml. of sulfuric acid (*d.* 1.84) diluted to 100 ml. with 95% ethanol. ^d Determined for comparison. Not a wave length maximum. I has a shoulder at 370 $m\mu$ ϵ 6400 in the acid solution which could be due to the base, for I in alcohol has $\lambda_{\max.}$ 361 $m\mu$, ϵ 24,000. XV has an R band in 1 *N* HCl with $\lambda_{\max.}$ 452 $m\mu$, ϵ 550. XVI has an R band in 1 *N* HCl with an inflection at 415 $m\mu$, ϵ 820. XVII has an R band in 1 *N* HCl with $\lambda_{\max.}$ 430 $m\mu$, ϵ 750. XVIII has an R band in 95% ethanol with $\lambda_{\max.}$ 443 $m\mu$, ϵ 510. ^e Not a C_e/A_e ratio, but useful in showing the approximate upper and lower limits of this ratio. ^f DAB is 4-dimethylaminoazobenzene. ^g AB is aminoazobenzene. ^h Shoulder. XIV has an R band with $\lambda_{\max.}$ 349 $m\mu$, ϵ 634 in 1 *N* HCl. ⁱ In 95% ethanol.¹⁸

of 4-dimethylaminoazobenzene, DAB, and 4'-hydroxy DAB and seven other diverse types of azobenzene dyes that in the former two dyes the first proton added exclusively and unequivocally to the amino nitrogen and not to the β -nitrogen. Jaffe¹¹ in a study of the comparative values of the Hammett substituent constants of the same dyes studied by the Rogers group⁹ also concluded that the first proton added exclusively to the amino nitrogen and not to the β -nitrogen. How a proton could add exclusively to the amino nitrogen of DAB and cause a shift toward the visible of approximately 100 $m\mu$ is a questionable spectral anomaly that these latter authors have not explained.

To simplify the discussion the ratio, C_e/A_e , is introduced here. C_e is the molar extinction coefficient at the wave length maximum of the C band; A_e is the molar extinction coefficient at the wave length maximum of the A band. This ratio gives a crude idea of the tautomeric equilibrium. Some of the more important factors which would interfere with an accurate determination of this equilibrium are (a) the presence of the hidden R¹² or $n \rightarrow \pi^*$ ¹³ band

at approximately 430 $m\mu$, (b) in some of the compounds the probable presence of a weak band near 320 $m\mu$ enveloped by the A band, (c) in addition to the tautomeric effect diverse substituents could have hyper- or hypo-chromic effects on the intensities of either the A or C bands, (d) a third tautomer involving proton addition to the α -nitrogen might be present in the solutions of some appropriately substituted 4-aminoazobenzene salts and (e) steric effects could influence the intensities of either the A or C bands. In spite of these factors it is believed that the tautomeric equilibrium, $C \rightleftharpoons A$, is gradually displaced to the right as we proceed down the series of compounds in Table I. The C_e/A_e values for these compounds are given at approximately 1 *N* hydrochloric acid, the acidity necessary for the complete formation of the first cation.

In 4-methylthioazobenzene there is only an intense C band in alcoholic 75% sulfuric acid. A weak wide shoulder is present at approximately 370 $m\mu$, ϵ 6400. This might be due to the presence of a small amount of the base, $\lambda_{\max.}$ 361, ϵ 24,000 in alcohol.

(11) Jaffe, *J. Chem. Phys.*, **21**, 415 (1953).

(12) Burawoy, *Ber.*, **63**, 3155 (1930), and subsequent papers.

(13) Kasha, *Faraday Soc. Disc.*, No. 9, 14, 72, 74, 75 (1950) contains controversy on origin and naming of this band with Burawoy, *Faraday Soc. Dis.*, No. 9, 70, 73, 78 (1950).

(14) Sawicki and Ray, *J. Org. Chem.*, **19**, 1686 (1954).

(15) Sawicki and Gerber, *J. Org. Chem.*, **21**, 410 (1956).

(16) Crabtree, *Brit. J. Cancer*, **3**, 389 (1949).

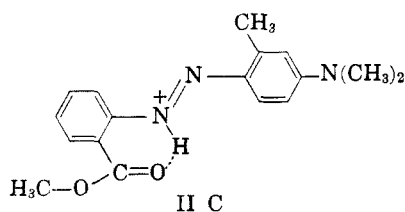
(17) Bamberger, *Ber.*, **28**, 843 (1895).

(18) Birnbaum, Linford, and Style, *Trans. Faraday Soc.*, **49**, 735 (1953).

There is no sign of a band near 320 $m\mu$. This would involve proton addition to the sulfur which would appear unlikely. In line with this it has been shown that azoanisole and 4-phenylaminoazobenzene in acid solution have C bands but no A bands.⁸

In previous work the pK_a 's of about 60 aminoazobenzene dyes in 50% ethanol were reported.^{14,15,19} The basicity in 50% ethanol of some 17 4-aminoazobenzene dyes has also been reported by two other groups of workers.^{8,9} The 2-methyl group has been postulated as increasing the electron density of the β -nitrogen in III¹⁴ because of the 0.8 unit increase in the pK_a of III as compared to VI. Consequently it is not surprising that the tautomeric equilibrium, $C \rightleftharpoons A$, in III is shifted to the left as compared to VI, because of the greater proton-attracting power of the β -nitrogen. In IV the 3'-chloro group decreases the electron density on the β -nitrogen through an inductive effect. Consequently there is a decrease in the C_e/A_e ratio.

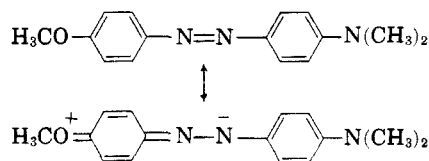
Addition of a 2'-carbomethoxy group to III causes a further increase in the C_e/A_e ratio. This must mean that in the salt, IIC, the attachment of the proton to the β -nitrogen must be stabilized by an intramolecular hydrogen bond.



A more spectacular example of this phenomenon has been given by Kiprianov and Zhmurova.²⁰ The sterically hindered 2'-carboxy-3-methyl DAB has λ_{max} 505, ϵ 45,000 in "alcoholic hydrochloric acid." This spectral data is particularly striking when compared to similar data on XII, XIII, XIV, and XV in Table I. It must mean that Kiprianov's compound has a surprisingly high C_e/A_e ratio of approximately 5 to 7 in the particular solvent system employed. Here a particularly strong intramolecular hydrogen bond must stabilize the C form of the salt in spite of the fairly strong steric effect due to the 3-methyl group.

In VII there is an increase in basicity as compared to VI, but it is the basicity of the amino nitrogen that is directly effected by the base-strengthening ethyl group. Consequently the amino nitrogen has a greater attraction for the proton and the C_e/A_e ratio is decreased. In VIII the N-ethyl group increases the basicity of the amino nitrogen while the 3'-nitro group decreases the electron density of the β -nitrogen. These effects lower the C_e/A_e ratio even further.

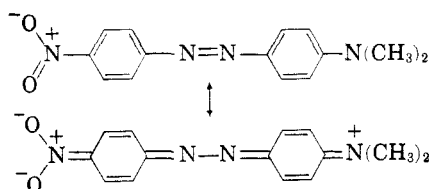
For IX a new effect comes into play—the electron density at the α -nitrogen is increased somewhat by the following type of competing resonance.



As a consequence the electron density at the β -nitrogen and the resulting C_e/A_e ratio are decreased relative to that of VI. It is possible that the tautomeric salt with the proton on the α -nitrogen could be present, but it would be difficult to detect for it would probably have a wave length maximum in the same region as is found for the C tautomer. Presence of the A cation is shown by the band at 350 $m\mu$, ϵ 17,200. This fits in nicely with the presence in the iso- π -electronic 4-methoxyazobenzene of a band at 350 $m\mu$, ϵ 16,000 in 95% ethanol.

The presence of a 2'-methyl group in the 4-aminoazobenzenes has been shown to have a base-weakening effect especially on the adjacent β -nitrogen.¹⁴ The effect of this phenomenon is strikingly demonstrated by the low C_e/A_e ratios for X and XI.

There appears to be interaction between an electronegative group in the 4'-position with the 4-amino group, thus:



One could expect some contribution from this type of zwitterionic structure to the ground state. This would have a definite base-weakening effect on the amino nitrogen and would increase the proportion of the C tautomer in acid solution. In this respect V has a C_e/A_e ratio of 8.7 as compared to the 3.6 of VI. A large part of this increase in the C_e/A_e ratio might be due to the hyperchromic effect of the 4'-nitro group on the C band. There is also a hyperchromic effect on the A band. For example, azobenzene has a band at 320 $m\mu$, ϵ 21,300 while 4-nitroazobenzene has its analogous band at 333 $m\mu$, ϵ 31,000 in 95% ethanol.²¹ Similarly 30 esters of 4'-nitro-4-carboxyazobenzene are reported to have wave length maxima at 331–332 $m\mu$, ϵ 29,700–33,000 in alcohol.²² This compares fairly well with the A band of XII in acid solution with λ_{max} 328 $m\mu$, ϵ 25,500.

(19) Sawicki and Ray, *Federation Proc.*, **12**, 263 (1953).

(20) Kiprianov and Zhmurova, *Zhur. Obshchei Khim.*, **23**, 626 (1953) [*Chem. Abstr.*, **48**, 6981 (1954)].

(21) Pongratz, Markgraf, and Mayer-Pitsch, *Ber.*, **71**, 1287 (1938).

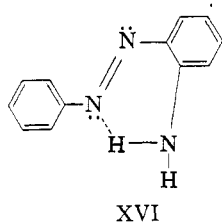
(22) Hecker, *Chem. Ber.*, **88**, 1666 (1955).

The base-strengthening effect of a 3-methyl group in DAB derivatives is apparently due to the 4-dimethylamino group being crowded out of the plane of the molecule. The strong electron attraction of the azobenzene portion of the molecule on the dimethylamino group is decreased and the basicity of the 4-dimethylamino group is consequently increased. This explains the low C_e/A_e ratio for XII, XIII, XIV, and XV. The base-weakening interaction between the electronegative group in the 4'-position with the 4-amino group explains the higher C_e/A_e ratio of XII and XIII as compared to XIV and XV. In XV the inductive effect of the 3'-nitro group on the β -nitrogen decreases its electron density and thus there is a weaker attraction for the proton with the result that the C_e/A_e ratio is the lowest in this series.

The R band at 452 $m\mu$ of XV in acid solution is unsymmetrical, the slope being more gradual at the long wave length side. This indicates the presence of a small amount of the C tautomer.

There is no possibility of zwitterionic resonance between the amino group and the β -nitrogen in XVII. Consequently the electron density of the β -nitrogen would be of the same order of strength as in XVIII and the amino nitrogen would be the exclusive proton-attractor. Pertinent to this is the strong spectral resemblance of XVII in acid solution to XVIII in alcohol.

Evidence from the infrared spectra indicates the presence of intramolecular hydrogen bonding in XVI.¹⁵



This would bind the free electrons on the β -nitrogen and would seriously interfere with proton addition to the β -nitrogen. The spectrum of XVI in 1 *N* hydrochloric acid solution exhibits 2 broad shoulders at 410 $m\mu$ and 570 $m\mu$. The shoulder at 410 $m\mu$ receives some contribution from the R band while the less intense shoulder at 570 $m\mu$ is most likely due to an impurity (phenazine derivative?). The local heating engendered by the addition of concentrated hydrochloric acid to form a 50% alcoholic 6 *N* hydrochloric acid solution apparently forms a somewhat larger quantity of impurity for two more intense maxima at 420 $m\mu$ and 570 $m\mu$ are formed. The overlapping of two fairly close (20–30 $m\mu$) absorption bands of low intensity in either the 1 *N* or 6 *N* hydrochloric acid solution is suggested by the curves in the 410–440 $m\mu$ range. With the high intensity of the A band of XVI in 1 *N* hydrochloric

acid it would seem that the proton adds exclusively to the amino group.

In a tautomeric equilibrium one would expect that as the intensity of the spectral band of one tautomer would increase, the intensity of the band of the other tautomer would decrease. This is apparent in Tables I and II. All the examined 4-aminoazobenzene dyes had increasing C_e/A_e values with increasing acid concentration to the point where the second proton began to add. This means that the tautomeric equilibrium, $C \rightleftharpoons A$, is gradually displaced to the left in increasing acid concentration, Table II. At the acidities employed the

TABLE II
EFFECT OF DECREASING ACID CONCENTRATION ON THE
TAUTOMERIC EQUILIBRIUM

Compound	Normality HCl	$m\mu$ ($\epsilon \times 10^{-3}$)		$m\mu$ ($\epsilon \times 10^{-3}$)		C_e/A_e
		λ_{max} A Band		λ_{max} C Band		
II	6.1	336	(3.58)	516	(53.2)	14.9
	3.0	336	(4.0)	516	(51.9)	13.0
	1.2	335	(4.1)	513	(51.8)	12.6
	0.6	336	(4.16)	512	(51.5)	12.4
III	6.1	331	(3.14)	515	(53.0)	16.9
	3.0	328	(4.20)	515	(49.9)	11.9
	1.2	327	(4.82)	515	(48.2)	10.0
VI	6.1	324	(5.26)	519	(47.3)	9.0
	3.0	320	(8.1)	518	(40.3)	5.0
	1.2	320	(9.8)	517	(35.5)	3.6
	0.6	320	(10.1)	516	(34.0)	3.4
XII	6.1	328	(25.4)	508	(1.27)	0.050
	3.0	328	(25.8)	492	(1.02)	0.040
XIII	6.1	325	(27.7)	510	(1.29)	0.047
	3.0	325	(27.9)	496	(1.07)	0.038
	0.6	325	(28.3)	485	(0.98)	0.035
XV	6.1	310	(22.3)	455	(0.56)	(0.020) ^a
	1.2	310	(22.4)	452	(0.55)	(0.015) ^a
XVIII		320	(21.3)	443	(0.51)	(0.01) ^{a,b}

^a A crude C_e/A_e ratio was determined as in Table I from the molar absorption at 500 $m\mu$. The bands at approximately 450 $m\mu$ are R bands. ^b In 95% ethanol. Not a C_e/A_e ratio, but useful in showing the lower limit of this ratio.

band due to the base was absent in the spectra of all the aminoazobenzene dyes. The table also shows that with decreasing acid concentration the long wave length bands of the sterically hindered dyes, XII, XIII and XV, show a blue shift and intensity decrease. This is due to the greater contribution of the shorter wave length, low intensity R band of the A tautomer, and the weaker contribution of the longer wave length, high intensity C band of the C tautomer at lower acid concentrations to the long wave length band system. This effect on the wave length and molecular extinction coefficient is also shown by gradually increasing the size of the 3-alkyl group in 3-alkyl DAB derivatives. From the results of Kiprianov and Zhmurova²⁰ the spectral data in 'alcoholic hydrochloric acid' for the long wave length band of 3-substituted-4'-nitro DAB derivatives are given in the order—substituent in 3-

position, λ_{\max} . in $m\mu$ (molecular extinction coefficient), *e.g.*, —H, 508 (56800); —CH₃, 508 (2600); —CH₂CH₃, 490 (1000); —CH(CH₃)₂, 460 (600). Thus, with increasing steric hindrance a greater percentage of the A salt is formed. Kiprianov's spectral data in 'alcoholic hydrochloric acid' for 4'-nitro-3-methyl-4-diethylaminoazobenzene, λ_{\max} . 460–480, ϵ 700, indicates that this compound, like the much more sterically hindered 4'-nitro-3-isopropyl DAB, has a very low C_e/A_e ratio. In the diethyl derivative steric hindrance and the base-strengthening effect of the ethyl groups on the amino nitrogen would appear to be the cause of the very low C_e/A_e ratio.

At lower acid concentrations there was a smaller increase in the C_e/A_e ratio of II, III and VI as compared to increases at higher acidities, Table II. Although the 2-methyl group and the 2'-carbomethoxy group tend to increase C_e/A_e ratios in 4-aminoazobenzene dyes, they apparently do not have a purely additive character. In fact at higher acid concentrations there appears to be an antagonistic action between these two substituents. In II intramolecular hydrogen bonding in the C tautomer may play a buffer role in the weaker effect of hydrogen ion concentration on the tautomeric equilibrium of this compound as compared to III and VI.

EXPERIMENTAL²³

4-Methylthioazobenzene. A solution of 0.24 g. of 4-thiocyanoazobenzene,²⁴ m.p. 71–72°, and 0.11 g. of potassium hydroxide in 10 ml. of methanol was refluxed for 20 minutes, cooled, and then 0.1 ml. of methyl iodide was added. An hour later 10 ml. of water was added. Recrystallization from hexane gave 0.18 g. (80%) of yellow crystals, m.p. 81–82°. Lit.²⁵ m.p. 83–84°.

2'-Carbomethoxy-2-methyl-4-dimethylaminoazobenzene, II. This compound was prepared by the standard procedure of reacting 2-carbomethoxybenzene diazonium chloride with N,N-dimethyl-*m*-toluidine in dilute acid solution. An 80–85% yield of large red crystals were obtained after crystallization from heptane, m.p. 119–120°.

Anal. Calc'd for C₁₇H₁₉N₃O₂: N, 14.1. Found: N, 14.0.

Absorption spectral data. The spectra of all compounds were measured with a Beckman Model DU spectrophotometer in 50% alcohol at 26 ± 1° unless otherwise stated. As in the previous papers^{14,15,19} a 50% alcoholic acid solution consisted essentially of 50 ml. of aqueous hydrochloric acid diluted to 100 ml. with commercial 95% ethanol. It was found that the percentage of alcohol in this solution was close enough to that made by mixing equal volumes of aqueous acid and absolute alcohol so as not to cause any differences of consequence in the spectra.

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(23) Melting points are uncorrected. Analyses are by Peninsular ChemResearch, Inc., Gainesville, Florida.

(24) Badger and Lewis, *J. Chem. Soc.*, 2147 (1953).

(25) Fox and Pope, *J. Chem. Soc.*, 101, 1498 (1912).