lized. Recrystallization from hexane produced 42 g. of a white solid, m.p. 76–77.5°. In addition, 24 g. of hexane-insoluble matter was recovered. This proved to be unreacted ketone. Rehydrogenation and workup resulted in the recovery of 19.7 g. of additional product bringing the yield to 90%. An analytical sample produced by recrystallization from hexane melted at 77.5–78.5°. The phenolic nature of this material was indicated from its solubility in hot 10% sodium hydroxide.

Anal. Calcd. for $C_{20}H_{20}O$: C, 86.95; H, 7.25; mol. wt., 276. Found: C, 86.96; H, 7.03; mol. wt. (ebullioscopic in benzene), 275, 283.

II. **Synthesis of 1-(4-Hydroxy-3,5-dimethylbenzyl)-pyrene.**—The ketone was synthesized as previously described by BF_3-catalyzed condensation of 1-pyrenecarboxylic acid and 2,6-xylenol. A 20-g. batch of acid produced 23.7 g. (83%) of crude ketone, m.p. 245–246°. An analytical sample was prepared by recrystallization from toluene, producing yellow-orange prisms, m.p. 246–247°.

Anal. Calcd. for $C_{25}H_{18}O_2$: C, 85.59; H, 5.18. Found: C, 85.79; H, 5.55.

The ketone reduction procedure was modified due to the very low solubility of the pyrene ketones in methanol. A mixture of 25 g. of ketone, 7 g. of copper chromite and 100 g. of phenol, as a solvent, was hydrogenated (cold pressure 2000 p.s.i.) at 140° for 4 hours. The contents of the bomb were dissolved in a minimum of hot benzene and the benzene solution was filtered to remove catalyst. The filtrate was distilled at atmospheric pressure to remove benzene. The residue was distilled at 50 mm. to remove the bulk of the phenol. The last traces of phenol were removed by repeated leaching of the solid ketone with methanol followed by aqueous methanol. The yield of crude product was 17.0 g. (70% yield), m.p. 124–126°. An analytical sample was prepared by recrystallizing twice from absolute methanol producing white needles, m.p. 130–131°.

Anal. Calcd. for $C_{25}H_{20}O$: C, 89.26; H, 5.99. Found: C, 89.06; H, 6.88.

An analytical sample of the acetate ester prepared by reaction with acetic anhydride and pyridine melted at 117.7–118.7°.

Anal. Calcd. for $C_{27}H_{22}O_2$: C, 85.68; H, 5.86. Found: C, 85.58; H, 6.55.

III. **Synthesis of 1-[β-(4-Hydroxy-3,5-dimethylphenyl)-ethyl]-pyrene.**—The ketone was synthesized by BF_3-catalyzed condensation of 1-pyreneacetic acid and 2,6-xylenol. A 39-g. batch of acid produced 49 g. of crude ketone (90% yield), m.p. 234–236.5°. An analytical sample was obtained by recrystallization from xylene yielding white crystals, m.p. 235–238°.

Anal. Calcd. for $C_{26}H_{20}O_2$: C, 85.70; H, 5.53. Found: C, 85.66; H, 5.77.

The ketone (20 g.) was reduced using the procedure described in section II. The yield of crude substituted ethane was 16.4 g. (90%), m.p. 130–140°. An analytical sample was prepared by recrystallizing twice from absolute methanol yielding colorless plates (weak blue-green fluorescence) m.p. 153.5–154.4°. This compound was hygroscopic.

Anal. Calcd. for $C_{26}H_{22}O$: C, 89.15; H, 6.33. Found: C, 88.89; H, 6.49.

An acetate ester was synthesized using acetic anhydride and pyridine. An analytical sample produced by recrystallization from ethanol was recovered as cream-colored plates, m.p. 152.3–153.3°; mixed melting point with the ethane model was depressed to 139.5–144.5°.

Anal. Calcd. for $C_{28}H_{24}O_2$: C, 85.68; H, 6.16. Found: C, 85.44; H, 6.35.

IV. **Synthesis of 1-[γ-(4-Hydroxy-3,5-dimethylphenyl)-butyl]-pyrene.**—The ketone was synthesized by BF_3-catalyzed condensation of γ-1-pyrenebutyric acid and 2,6-xylenol. A 76.9-g. batch of acid produced 100 g. of crude ketone (100% yield), m.p. 152–160°. An analytical sample was prepared by recrystallization from toluene, yielding fine yellow needles, m.p. 168–169°.

Anal. Calcd. for $C_{28}H_{24}O_2$: C, 85.68; H, 6.16. Found: C, 85.77; H, 6.24.

The crude ketone was reduced using the procedure described under II. A 25-g. batch of ketone produced 24.1 g. of crude substituted butane, m.p. 94–97° (100% yield). An analytical sample resulted from recrystallizing twice from methanol, yielding colorless prisms, m.p. 101.6–103.6°.

Anal. Calcd. for $C_{28}H_{26}O$: C, 88.84; H, 6.93. Found: C, 88.82; H, 7.11.

Spectra of the Pyrene Derivatives.—All the pyrene derivatives showed a characteristic OH absorption band at 2.9–3.0 μ in the infrared and the absence of any appreciable carbonyl absorption. The ultraviolet spectra of the compounds were determined in $CHCl_3$ on a Beckman model DU spectrophotometer. Each compound showed a typical pyrene spectrum. This would indicate that there has been little hydrogenation of the pyrene nucleus during hydrogenolysis of the carbonyl group.

Acknowledgment.—We wish to thank Emmy Lee McWilliams and R. J. Laufer for development of the synthesis conditions for production of 1-pyreneacetic acid and actual preparation of the material used in this investigation.

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[CONTRIBUTION FROM THE MCARDLE MEMORIAL LABORATORY, MEDICAL SCHOOL, UNIVERSITY OF WISCONSIN, AND THE DEPARTMENTO DE QUIMICA DA FACULDADE DE FILOSOFIA, CIENCIAS E LETRAS, UNIVERSIDADE DE SÃO PAULO, SÃO PAULO, BRASIL]

On the Addition of Protons to Derivatives of 4-Aminoazobenzene[1]

BY G. CILENTO, E. C. MILLER AND J. A. MILLER

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The absorption spectra of 4-aminoazobenzene and a variety of its derivatives in acid–alcohol solution have been investigated. Study of the spectra indicates that two absorbing species are present: one in which the proton is added to the amino group and the other in which the proton is on the azo nitrogen farthest from the amino group. The influence of methyl and fluoro substituents upon the proportions of the tautomeric forms is considered.

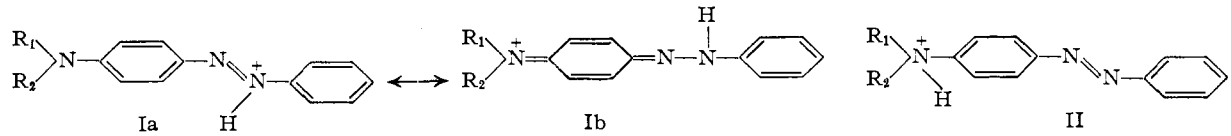
Introduction

As a part of our studies on the relationship between structure and hepatocarcinogenic activity in the series of aminoazo dyes related to 4-dimethylaminoazobenzene, we have studied the absorption spectra of ethanolic and acid–ethanolic solutions of about thirty derivatives of 4-aminoazobenzene. This is a continuation of earlier work in which the spectra of the C-monomethyl derivatives of 4-dimethylaminoazobenzene were examined.[2]

These compounds are yellow in non-acidic media, but exhibit an intense red color on the addition

(1) This investigation was supported by research grant C355 from the National Cancer Institute, U. S. Public Health Service, Institutional Grant 71 of the American Cancer Society and the Alexander and Margaret Stewart Trust Fund.

(2) J. A. Miller, R. W. Sapp and E. C. Miller, THIS JOURNAL, 70, 3458 (1948).



Ia Ib II

of acid. One objective of the present investigation was to locate the positions in which protons are added to these molecules. It has been rather generally believed that the first proton adds to the β-azo nitrogen (*i.e.*, the one farthest from the amino group)[3], although Hantzsch and Burawoy[4] and Badger, Buttery and Lewis[5] concluded that the addition of hydrogen ions to aminoazo dyes in solution resulted in a mixture of the two conjugate acids I and II. On the other hand, Klotz, *et al.*,[6] have recently maintained that protonation occurs only at the amino group. Our data are in agreement with the results of Hantzsch and Burawoy[4] and Badger and associates[5] in indicating that the first proton can be added to either the β-azo nitrogen or to the amino nitrogen to give a mixture of tautomeric forms. For the purposes of this discussion the two forms are considered to be I and II. However, the structure of I may need to be modified in view of the *p*K data.[6,7] The effects of methyl and fluoro substituents upon the proportions of the two conjugate acids also have been investigated.

Experimental

All the dyes were available from other investigations in these laboratories and had been purified by chromatography on aluminum oxide. The acid–alcohol solutions were prepared as described previously[2] just prior to use; 28.56 ml. of 7 *N* HCl was added to an alcoholic (redistilled 95% ethanol) solution of the dye in a 50-ml. volumetric flask, and the flask was filled to the mark with alcohol. The acidity of the final solution was essentially 4 *N*, and the dye concentration was usually between 1.5 and 2.5 × 10^{-5} *M*. The spectra were measured from 225 to 600 mμ with a Beckman DU spectrophotometer. Readings were taken at 4-mμ intervals above 320 mμ, except that near the maxima measurements were taken every 2 mμ. Below 320 mμ readings were made at 2-mμ intervals. Several transmission values were routinely checked after each spectrum was completed. With a few of the dyes small discrepancies (less than 2%) were noted. The 2-, 3- and 3′-methyl derivatives of 4-aminoazobenzene, 2,3′-dimethyl-4-aminoazobenzene and 3-fluoro-4-dimethylaminoazobenzene were slowly destroyed by irradiation with the ultraviolet light; the spectra in the visible range were obtained on fresh solutions.

Results

Typically the spectra of derivatives of 4-aminoazobenzene in acid–alcohol solution (4 *N* HCl) show four main bands. These are illustrated by the absorption curves of 4-aminoazobenzene and its C-monomethyl derivatives in Fig. 1, in which the bands have been designated as A, B, C and D. Bands B and D are similar to those found in the ultraviolet spectrum of azobenzene in either alcohol or acid–alcohol solution.[2,8] As seen in Fig. 1 for the primary aminoazobenzene derivatives and in our previous paper for derivatives of 4-dimethylaminoazobenzene,[2] the intensities of bands A and B bear an inverse relationship to one another. This

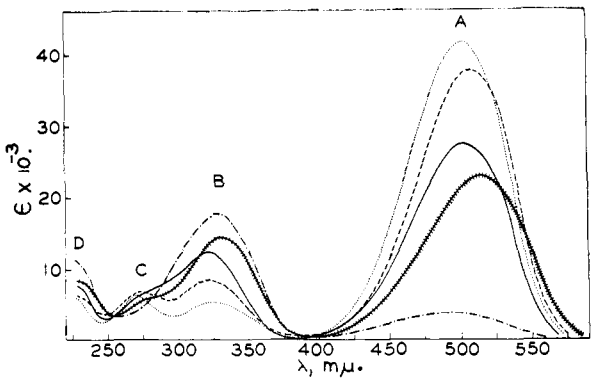


Fig. 1.—The absorption spectra of 4-aminoazobenzene and its C-monomethyl derivatives in acid–alcohol: ——, 4-aminoazobenzene; -----, 2-methyl-4-aminoazobenzene; – – –, 3-methyl-4-aminoazobenzene; +++++, 4′-methyl-4-aminoazobenzene; – – – –, 2′-methyl-4-aminoazobenzene. The spectrum of 3′-methyl-4-aminoazobenzene is not included since it is very similar to that of 4-aminoazobenzene.

relationship is shown more clearly by Fig. 2, in which the intensity of the A band has been plotted against that of the B band for 4-aminoazobenzene, 4-monomethylaminoazobenzene and their C-monomethyl derivatives, for 4′-fluoro-4-dimethylaminoazobenzene and for several C-dimethyl derivatives of 4-aminoazobenzene. With the exception of the 2- and 2′-methyl derivatives[9] the points in Fig. 2 fall very close to the line drawn through the values for 4-aminoazobenzene and its 3-methyl derivative. The deviations from this line probably represent effects of substitution on the true absorption intensities. The line intersects the ordinate at 60,800 and the abscissa at 22,300.

The spectra of several fluoro derivatives of 4-dimethylaminoazobenzene also were studied. These compounds were not included in Fig. 2 because their absorption curves in the visible region had overlapping bands. However, the intensities of the A and B bands again showed an inverse relationship, and the ϵ_{max} values for these bands and the wave lengths at which maximum absorption occurred are given in Table I.

Discussion

Evidence for a Tautomeric Mixture of Conjugate Acids.—From the inverse relationship between the intensities of bands A and B of the aminoazo dyes (Figs. 1 and 2), the dyes apparently occur in acid solution as a mixture of tautomeric forms. These

(3) See M. T. Rogers, T. W. Campbell and R. W. Maatman, THIS JOURNAL, **73**, 5122 (1951).

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

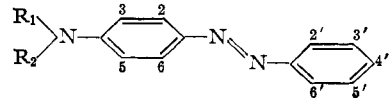
(5) G. M. Badger, R. B. Buttery and G. E. Lewis, *J. Chem. Soc.*, 1888 (1954).

(6) I. M. Klotz, H. A. Fiess, J. Y. Chen Ho and M. Mellody, THIS JOURNAL, **76**, 5136 (1954).

(7) H. H. Jaffé, *J. Chem. Phys.*, **21**, 415 (1953).

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

(9) The position nomenclature used is



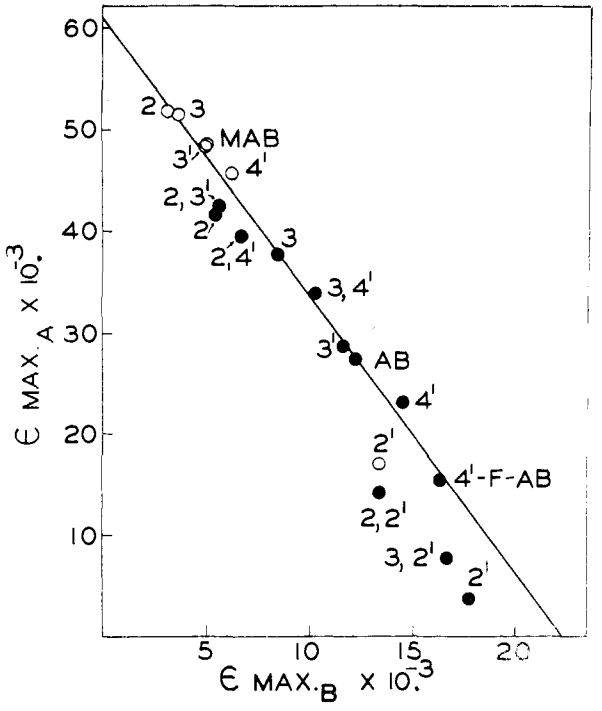


Fig. 2.—The reciprocal relationship between the intensities of the visible band (A band) and of the major ultraviolet band (B band) for derivatives of 4-aminoazobenzene (AB) (●) and 4-monomethylaminoazobenzene (MAB) (○). The wave lengths at which the maxima of the A and B bands, respectively, occur are as follows: MAB (510, 320), 2-methyl-MAB (508, 327), 3-methyl-MAB (514, 325), 2′-methyl-MAB (506, 328), 3′-methyl-MAB (515, 327), 4′-methyl-MAB (523, 331), AB (503, 319), 2-methyl-AB (502, 326), 3-methyl-AB (508, 322), 2′-methyl-AB (495, 328), 3′-methyl-AB (506, 326), 4′-methyl-AB (513, 332), 2,3′-dimethyl-AB (507, 330), 2,4′-dimethyl-AB (512, 333), 3,4′-dimethyl-AB (520, 334), 2,2′-dimethyl-AB (496, 331), 3,2′-dimethyl-AB (498, 329), 4′-fluoro-AB (505, 322).

TABLE I

ϵ_{max} VALUES FOR THE A AND B BANDS IN THE ABSORPTION SPECTRA OF FLUORO DERIVATIVES OF 4-DIMETHYLAMINOAZOBENZENE[a]

Position(s) substd. by fluorine	A band ϵ_{max} × 10⁻³	A band Wave length, mμ	B band ϵ_{max} × 10⁻³	B band Wave length, mμ
2,6	53.2	496	2.0	328
2,6,3′,5′	48.2	480	1.8	324
2	47.6	512	3.0	330
3′,5′	43.4	504	6.6	318
None	42.8	518	7.0	320
3′	40.8	512	8.0	319
3,′4′	27.4	513	11.0	320
4′	24.0	520	11.0	324
2′	15.0	510	14.8	321
2′,5′	13.8	503	13.0	321
2′,4′	6.8	509	18.7	324
2,5,2′,5′	5.2	502	15.2	336
2′,4′,6′	4.2	470	19.1	314
3	3.2	534	20.0	322

[a] Spectra determined in acid–alcohol solution.

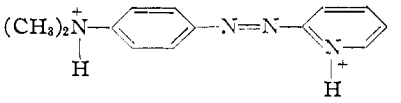
appear to be primarily structures in which the hydrogen ion is attached either to the amino nitrogen or to the azo nitrogen which is farthest from the amino group. The quaternary ammonium form, being similar to azobenzene in its absorption,[3,5] would be responsible for the absorption at bands B and D, while the absorption at bands A and C would be due to the form involving the β-azo nitrogen (hereafter called the azonium form). Except for the 2′-derivatives in which there is a reduced molar absorption of the azonium form, probably as a result of steric effects, the relative absorptions at A and C *versus* those at B and D would indicate the proportions of the two acids for any dye. The data of Rogers, *et al.*,[3] indicate that the tautomer with the proton added to the α-azo nitrogen is not present in appreciable quantities.

Our conclusion is in agreement with that of Hantzsch and Burawoy[4] and Badger, *et al.*,[5] on the basis of similar data. On the other hand, Klotz, *et al.*,[6] have stated on the basis of their pK data that "it can be concluded unequivocally that the benzenoid structure is the correct one," *i.e.*, that the first proton adds only to the amino nitrogen of 4-aminoazobenzene and its derivatives. Although they emphasize that their studies were carried out in aqueous solution, the solvent does not appear to be the decisive factor. The aminoazo dyes show the same characteristic red color in aqueous acid solutions as in acid–alcohol. This red color must be due to an azonium form, since quaternary ammonium dyes such as 4-dimethylaminoazobenzene methiodide have spectra similar to that of azobenzene and different from that of 4-dimethylaminoazobenzene,[4,10] while N-phenyl-4-aminoazobenzene, which is protonated only at the azo nitrogen, is intensely red in acid solution.[5] The inverse relationship between the intensities of the A and B bands of various substituted derivatives of 4-aminoazobenzene (Fig. 2) can best be explained on the basis of tautomeric mixtures. This is especially true, since the extrapolated ϵ_{max} value of 22,300 for a dye having only the B band is very close to those of 21,300[8] and 21,100[5] for azobenzene in ethanol solution, while the extrapolated ϵ_{max} value of 60,800 for a dye with only the A band is very close to that of 61,000 for N-phenyl-4-aminoazobenzene. The benzenoid structure offered by Klotz, *et al.*, does not explain the color of these dyes in acid or the spectral relationships observed here.

The problem appears to arise from certain of the assumptions made by Klotz and co-workers. One of these is that the similarity between the first pK_a (3.5) of 4-dimethylaminoazobenzene and the second pK_a (3.4) of pyridine-4-azo-(*p*-dimethylaniline), which is presumably protonated first at the pyridine nitrogen, indicates that these protons are added to analogous nitrogen atoms of the two dyes. They assumed that the charged pyridine nitrogen would not affect pK_a of the amino nitrogen, but would decrease the basicity of the azo nitrogen, and that the second proton could add only to the amino nitrogen of this dye. By analogy it was concluded that the first proton would add to 4-dimethylaminoazobenzene also only at the amino nitrogen. Even if the assumptions on the points of addition of the protons to the pyridine derivatives are cor-

(10) A. Hantzsch and F. Hilscher, *Ber.*, **41**, 1171 (1908).

rect, they do not furnish a sound basis for concluding that 4-dimethylaminoazobenzene and related dyes necessarily accept the first proton in the same manner. Thus, the amino and azo nitrogens of 4-dimethylaminoazobenzene and its derivatives may have similar basicities which are also approximately the same as those of the amino groups of the pyridinium dyes. Actually, one might question the conclusion that the second proton adds to the pyridinium dyes at the amino group. Thus, the absorption band near 460 mμ in the spectrum of pyridine-2-azo-(*p*-dimethylaniline)[11] at low *p*H's is not readily ascribed to



since this structure might be expected to have a spectrum similar to that of azobenzene.

To emphasize the problem associated with the use of spectral evidence in studying tautomerism, Klotz and associates cited two examples to show that "relatively small changes in the structure of a substituent, changes which should have only minor effects on the resonance structures, produce major shifts in absorption spectra. . ." One of these was the shift of the absorption maximum at 380 mμ of 4-aminoazobenzene in neutral aqueous solution to 450 mμ in 4-dimethylaminoazobenzene. However, as shown in Fig. 3, the spectra of both compounds in neutral aqueous solution show bands near 375 and 445 mμ; the band at 375 mμ is the stronger in the case of 4-aminoazobenzene and that at 445 mμ is more intense with the N-dimethyl derivative. These spectra are similar to those reported by Brode, *et al.*,[12] for these compounds in 10% ethanol; the absorption at 445 mμ apparently is due to a hydrated form. The second example was the shift in absorption maxima from 468 to 556 mμ and from 475 to 553 mμ on the addition of one proton to pyridine-2-azo-(*p*-dimethylaniline) and pyridine-4-azo-(*p*-dimethylaniline), respectively. These authors further stated that "the first proton in each case undoubtedly goes to the pyridine nitrogen . . .; although it should have little effect on resonance between structures corresponding to V and VI, the proton produces major shifts in spectra." If, in these cases the proton added only to the pyridine nitrogen and further resonance structures were not involved, one would expect the corresponding pyridine-2-azobenzene and pyridine-4-azobenzene to undergo comparable shifts in spectra on addition of acid. Hantzsch and Burawoy[13] have studied pyridine-4-azobenzene and shown that this is not the case. The solid monohydrochloride of this dye is orange, and the positions of the absorption maxima in 2 *N* acid and in alcohol are similar; practically all the absorption occurs below 500 mμ. Thus, while the formation of the pyridinium ion does not markedly affect the resonance structures in the simple pyridineazobenzenes, it apparently produces a new resonating system in the case of the pyridine-

(11) I. M. Klotz and W.-C. Ming, THIS JOURNAL, **75**, 4159 (1953).
(12) W. R. Brode, I. L. Seldin, P. E. Spoerri and G. M. Wyman, *ibid.*, **77**, 2762 (1955).
(13) A. Hantzsch and A. Burawoy, *Ber.*, **63**, 1775 (1930).

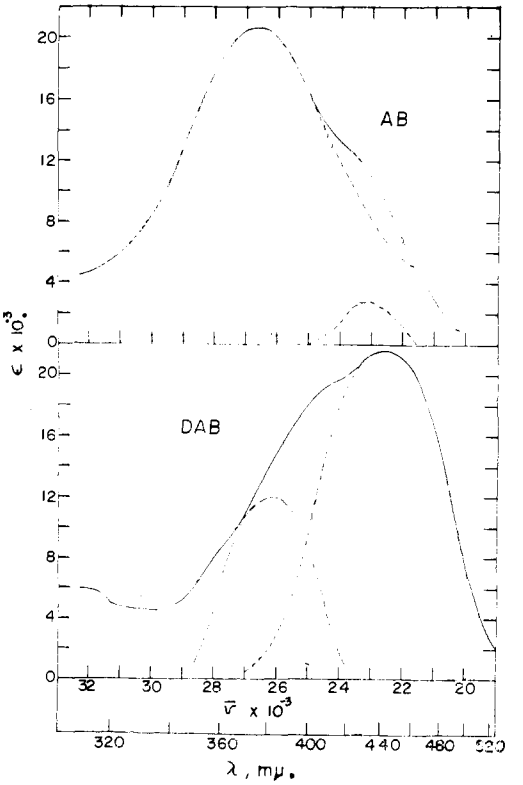
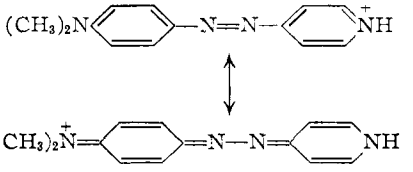


Fig. 3.—The absorption spectra of 4-aminoazobenzene (AB) and 4-dimethylaminoazobenzene (DAB) in neutral aqueous solution (0.001 *M* phosphate buffer, *p*H 7.0). The solid lines show the observed spectra. The dotted lines represent the resolved spectra, determined on the basis of symmetry, to indicate the approximate positions of the two main bands.

azodimethylanilines. In the latter case one may consider resonance between the two extreme structures



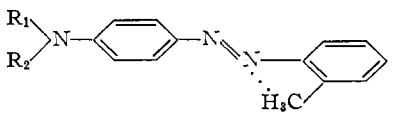
Perhaps the *pK* data and the spectral data can be rationalized if one assumes that, in the form involving the β-azo nitrogen, there is an association of molecules in such a way that the proton is shared by the β-azo nitrogen of one molecule and the amino nitrogen of another molecule. This would be similar to the mesohydric structures suggested by Hunter[14] for a wide variety of compounds containing mobile hydrogens associated with O, N or S.

Influence of Substitution on the Proportions of the Two Isomers.—Under the conditions employed in these experiments protonation of 4-aminoazobenzene and its N-monomethyl derivative occurs to approximately 45 and 75%, respectively, at the azo nitrogen, so that N-methyl substitution may be considered to hamper amino protonation. This is probably the resultant of two opposing effects[15]

(14) L. Hunter, *J. Chem. Soc.*, 806 (1945).
(15) See A. F. Trotman-Dickenson, *ibid.*, 1293 (1949).

(a) an increase in the electron density at the amino nitrogen by the +I effect of the methyl group, and (b) a decrease in solvation energy stabilization since the methyl group does not form hydrogen bonds with the solvent molecules. The latter factor is particularly important, since the analyses were carried out in the presence of ethyl alcohol. The +I effect of the methyl group would also increase the +M effect of the basic group to cause a concomitant increase in the electron density at the β-azo nitrogen.

The effect of ring-methyl substitution on the extent of azo nitrogen protonation of 4-amino- and 4-monomethylaminoazobenzene is 2′-CH_3 < 4′-CH_3 < H ~3′-CH_3 < 3-CH_3 < 2-CH_3 (Fig. 2). The lack of effect of a 3′-methyl group on azo nitrogen protonation is in line with its weak +I effect. A methyl group in the 4′-position favors proton addition at the amino group. This may probably be ascribed to the +M hyperconjugation effect of the methyl group which increases the stability of the ammonium form relative to the bases and the azonium form. A fluoro substituent, being a +M, −I group, hinders azo protonation even more than the methyl group in the 4′-position. A 2′-methyl substituent greatly reduces the concentration of the form protonated on the β-azo nitrogen. This is the resultant of several factors, of which only the +I effect of the substituent would favor addition of the proton to the azo nitrogen. Factors hindering addition of the proton to the azo nitrogen would include (a) a hyperconjugation effect, as in the case of the 4′-isomer; (b) a primary steric effect,[16] hindering solvation of the azonium form; and (c) interaction between the methyl group and the unshared electron pair of the protonable azo nitrogen in the base III[17]

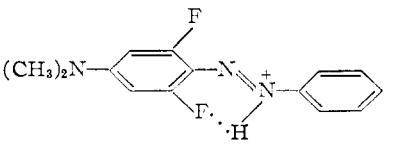


In this connection it is of interest that a 2′-methyl group appears to reduce the intensity of the —N=N— band in the electronic spectra of the 4-aminoazobenzenes, as judged by the approximate resolution of the visible absorption curves.[18]

A 3-methyl group hinders amino protonation. This group is *ortho* to the amino group and, hence, the situation is in some respects similar to that of the 2′-methyl isomer. There should be a primary steric effect hampering solvation and therefore reducing the relative thermodynamic stability of the substituted ammonium group. This may well be the major factor,[16] but interaction between the methyl group and the unshared electron pair of the amino nitrogen may also be important.[19] A 2-methyl substituent favors protonation of the azo nitrogen, probably through its inductive and, especially, its hyperconjugation effects. Further, the effects of various dimethyl substitutions on the proportions of the two acids appear to be additive.

Except for some uncertainty in the case of the 3′-fluoro derivative, the effects of monofluoro substitutions on the degree of β-azo nitrogen protonation of 4-dimethylaminoazobenzene are as follows (Table I): 3-F < 2′-F < 4′-F < 3′-F < H < 2-F. Reference was made above to the influence of a 4′-fluoro group. Like a 2′-methyl group a 2′-fluoro substituent markedly lowers the concentration of the azonium form, although to a lesser extent. One reason for this difference between methyl and fluoro groups appears to be the smaller volume of the fluorine atom, although the lack of interaction as in III may be another factor.

The presence of a 2-fluoro substituent favors the azonium form. In this case the main factor is probably the +M effect of the 2-fluoro substituent; the −I effect, although reducing the basicity of both reacting centers, would be expected to have more effect on the protonable azo nitrogen. With 2,6-difluoro-4-dimethylaminoazobenzene there is a further increase in the concentration of the azonium form, in spite of the greater steric compression in this acid and the secondary steric effect. This may probably be ascribed to hydrogen bond formation



The effects of the other polyfluoro substitutions cannot be profitably considered at this time on account of the increased spectral alterations found with these dyes.

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(16) See C. K. Ingold, "Structure and Mechanism in Organic Chemistry," G. Bell and Sons, Ltd., London, Chap. 13, p. 153.

(17) A. Burawoy and A. R. Thompson, *J. Chem. Soc.*, 1443 (1953).

(18) G. Cilento, unpublished results.

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