line was dissolved in 150 ml. of benzene. The solution was refluxed for 5 hr. during which time an insoluble precipitate of morpholine hydrobromide separated. The reaction mixture was cooled and the mixture filtered. There was obtained 4.8 g. (73%) of morpholine hydrobromide. The filtrate was extracted four times with 50 ml. portions of 6*N* hydrochloric acid and upon basification of the acidic extract with 6*N* sodium hydroxide a red-brown emulsion was obtained. The mixture was extracted with ether, the ethereal layer washed with water and then dried. The solvent was removed under reduced pressure and 4.60 g. (50%) of crude product was obtained in the form of a brown oil. A 2.30 g. portion of the oil was distilled through a short path molecular still, block temperature 127–129°, pressure 1.0 mm., yield 1.2 g.

Anal. Calcd. for $C_{14}H_{17}NO_2$: C, 72.71; H, 7.41; N, 6.06. Found: C, 71.74; H, 7.20; N, 6.18.

Willgerodt reaction with 2-morpholino-1-tetralone. A mixture of 0.60 g. (2.6 mmoles) of redistilled 2-morpholino-1-tetralone, 0.25 ml. (2.8 mmoles) of morpholine and 0.06 g. (2.8 mmoles) of sulfur was refluxed for 8 hr. After 30 min., the odor of hydrogen sulfide was detectable and at the end of the reaction, the mixture was dark brown. The cooled mixture was washed four times with dilute hydrochloric acid to leave a tan solid residue. The acidic solution was made alkaline with ammonium hydroxide and 0.06 g. of a yellow oil was obtained. The infrared spectrum of the material was different from that of morpholine or 2-morpholinonaphthalene. The product was not further identified.

The tan solid residue, remaining after the acid washing, was dissolved in 6*N* sodium hydroxide and the alkaline solution filtered and the filtrate acidified. The white solid formed was filtered and recrystallized from aqueous ethanol. The material so obtained was 1-naphthol, m.p. 93–95° (no depression on admixture with authentic sample), yield 0.30 g. (77%).

When this reaction was repeated using 1.65 g. (7.2 mmoles) of 2-morpholino-1-tetralone, 0.87 g. (7.2 mmoles) of acetophenone, 0.62 g. (7.2 mmoles) of morpholine and 0.23 g. (7.2 mmoles) of sulfur, the acidic wash, after basification, yielded 0.173 g. of material. Steam distillation of the oil, followed by recrystallization of the solid distillate yielded 6 mg. of 2-morpholinonaphthalene, m.p. 85–86°, mixed m.p. with authentic sample, m.p. 85.0–86.5°.

Willgerodt reaction with 1,2-dihydronaphthalene. A mixture of 4.97 g. (0.038 mole) of 1,2-dihydronaphthalene, 3.39 g. (0.039 mole) of morpholine, and 1.23 g. (0.038 mole) of sulfur was allowed to react under the usual conditions. The cooled reaction mixture which had partially solidified was washed, by decantation, with dilute hydrochloric acid. The acidic solution was made alkaline with concentrated ammonia and the dark suspension was extracted with ether. After removal of the solvent, the small amount of yellow oil was directly steam distilled. The white solid distillate, which had a strong blue fluorescence, was filtered and recrystallized from dilute ethanol to yield 0.05 g. (0.6%) of 2-morpholinonaphthalene, m.p. 84.5–85.0°. The material gave no depression upon admixture with an authentic sample and possessed an infrared spectrum identical with that of 2-morpholinonaphthalene.

The acid insoluble residue from the reaction was steam-distilled and the white solid distillate was recrystallized from dilute ethanol to yield 3.95 g. (83%) of naphthalene, m.p. 76.0–77.0°.

Willgerodt reaction with 1,4-dihydronaphthalene. A mixture of 0.71 g. (5.4 mmoles) of 1,4-dihydronaphthalene,[6] 0.50 g. (5.6 mmoles) of morpholine and 0.17 g. (5.4 mmoles) of sulfur was treated and processed as described above for the 1,2-dihydro isomer. From the acid extract, after steam distillation and recrystallization, there was obtained 2 mg. of 2-morpholinonaphthalene and from the insoluble residue there was obtained 0.6 g. (88%) of naphthalene.

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[CONTRIBUTION FROM THE CANCER RESEARCH LABORATORY, UNIVERSITY OF FLORIDA]

Physical Properties of the Aminoazobenzene Dyes. IV. The Position of Proton Addition[1]

EUGENE SAWICKI[2]

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The basicity and absorption spectra of some azo dyes have been correlated with the position of proton addition to these dyes. Further spectral evidence has been given for the tautomer concept of proton addition to the 4-aminoazobenzene dyes.

Recently Klotz *et. al.*[3] in a study of the basicities of some 4-aminoazobenzene dyes concluded that the first proton added exclusively and unequivocally to the amino nitrogen. The spectral conclusions cited by these authors in support of their doctrine have been more carefully re-examined by Cilento, Miller, and Miller,[4] who have also given further spectral evidence for the presence of cationic tautomers in acid solutions of the 4-aminoazobenzene dyes.

But as Klotz's conclusions are based mainly on his basicity studies, the tautomer concept must fit in with the basicity data to be valid. For this reason the basicity and the spectral data of some azo dyes are compared in Fig. 1.

The following conclusions are drawn by an examination of these data. The addition of a proton to 4-dimethylaminoazobenzene, DAB, gives 2 tautomers. The ammonium, or A, tautomer λ_{max} 320, where the proton has added to the amino group, is apparently iso-*pi*-electronic with azobenzene, λ_{max} 320 mμ. The cationic resonating, or C, tautomer, where the proton has added to the β-nitrogen, is associated with the band at 516 mμ. The addition of

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

[4] Cilento, Miller, and Miller, *J. Am. Chem. Soc.*, 78, 1718 (1956).

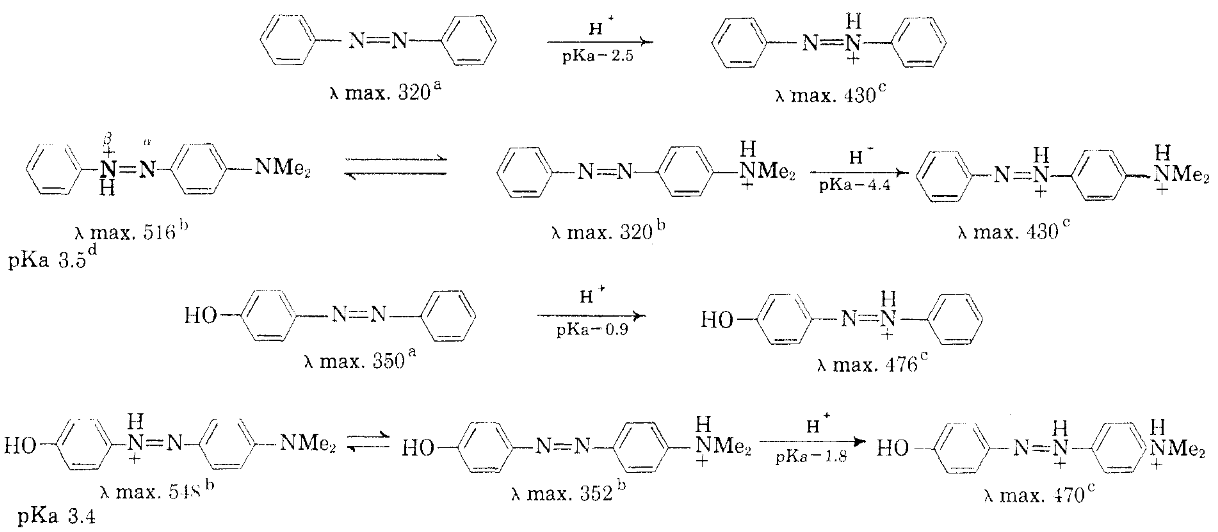
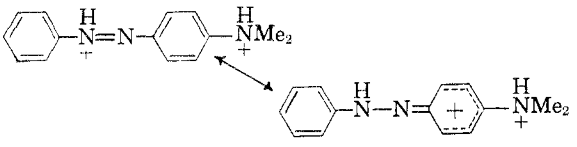


FIG. 1. SPECTRAL DATA AND BASICITY OF SOME AZO DYES. [a] In 95% ethanol. Azobenzene and 4-hydroxyazobenzene also have low intensity R bands at 443 and 440 mμ, respectively. [b] In 50% alcoholic 1*N* hydrochloric acid. [c] In 95% sulfuric acid. [d] All basicity data from ref. 3.

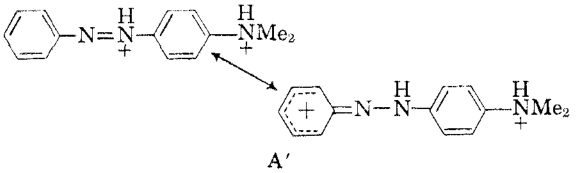
a proton to 4′-hydroxy-DAB gives a mixture of tautomers. The presence of the A tautomer, which must be iso-*pi*-electronic with 4-hydroxyazobenzene, λ_{max} 350 mμ, is shown by the band at 352 mμ. The presence of the C tautomer is shown by the band at 548 mμ. This red shift as compared to the long wave length band of the C tautomer of DAB, λ_{max} 516 mμ, is due to the extra conjugation of the 4′-hydroxy group.

The first pK_a's of DAB and 4′-hydroxy-DAB in water have been reported to be 3.5 and 3.4, respectively.[3] These basicities would be expected to be fairly close whether the first proton went to the amino nitrogen and/or to the β-nitrogen.

In acidic solutions of 4-aminoazobenzene dyes the tautomeric equilibrium, C ⇌ A, is slowly displaced to the left as the acidity is increased.[5] With a further increase in acidity a second proton could add to the C and A tautomers to give the dicationic tautomers, C′ and A′, respectively.



C′



A′

In the excited state the C′ tautomer involves a high energy resonance structure containing a quinone ring and two adjacent charges. This means that this type of tautomer should show a definite blue shift in its absorption spectrum as compared to the monocationic salt of azobenzene. On the other hand, the excited state of the A′ tautomer has as its main contributor a comparatively lower energy resonance structure involving a quinone ring and two well separated positive charges. Consequently the absorption spectrum of this tautomer should be closely similar to that of the monocationic salt of azobenzene. As the dicationic salt of DAB, λ_{max} 430, is closely similar spectrally to the monocationic salt of azobenzene, λ_{max} 430, and the dicationic salt of 4′-hydroxy-DAB, λ_{max} 470, is closely similar spectrally to the monocationic salt of 4-hydroxyazobenzene, λ_{max} 476, it is reasonable to believe that the dicationic salt of these compounds present in strong aqueous sulfuric acid is the A′ tautomer.

These conclusions are further strengthened by the basicity data of Klotz *et. al.*[3] Azobenzene has a pK_a of −2.5. With the electronegative dimethylammonium group para *to the basic α-nitrogen* of the A tautomer of DAB the drop in basicity to −4.4 is reasonable. On the other hand, 4-hydroxyazobenzene, pK_a −0.9, should be more basic than azobenzene, pK_a −2.5, for the lower energy of its zwitterionic resonance structure confers a greater electron density at the β-nitrogen. The second pK_a of 4′-hydroxy-DAB, −1.8, would be expected to be lower than the pK_a of 4-hydroxyazobenzene, −0.9, because of the presence of the electronegative dimethylammonium group *para* to the basic α-nitrogen of the A tautomer. These data and the resultant conclusions are in close agreement with the results of Hantzsch and Burawoy[6] who first pointed out the relation between proton addition and absorption spectra in the azo dyes.

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(5) Sawicki, *J. Org. Chem.*, 21, 605 (1956).

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

TABLE I

$C_6H_5NNC_6H_4X$

		λ_{max} (log ϵ)[a]		
X	A Band	C Band	R Band	Solvent
4—NH$_2$	319 (4.23)	500 (4.09)		50% ETOH; 1N HCl
3—NH$_2$	322 (4.30)		430 (2.88)	50% ETOH; 1.2N HCl
H[b]	320 (4.33)		443 (2.71)	95% ETOH
4—N(CH$_3$)$_2$	320 (3.99)	517 (4.55)		50% ETOH; 1N HCl
3—CH$_3$—4—N(CH$_3$)$_2$	319 (4.30)	$\underline{500}$[c] (2.70)	440–450 (2.80)	50% ETOH; 1N HCl
4—N(CH$_3$)$_3$$^+I^-$ [d]	319 (4.32)		443 (2.73)	ETOH

[a] Spectral data for the 310–550 mμ region. [b] Birnbaum, Linford, and Style, *Trans. Faraday Soc.*, **49**, 735 (1953). [c] Underlined values are shoulders. [d] Pongratz, Markgraf, and Mayer-Pitsch, *Ber.*, **71**, 1287 (1938).

Further evidence for the tautomer concept is given in Table I where the ultraviolet-visible absorption spectra of several simple azobenzene derivatives are compared. In the 300–550 mμ region investigated three band systems were found. 4-Amino- and 4-dimethylaminoazobenzene formed C and A tautomers in acid solution. The R[7] or $n \rightarrow \pi$[8] band of the latter tautomer must be hidden by the much more intense C band of the C tautomer. In 3-aminoazobenzene there is no conjugation of the phenylazo group with the amino group. Consequently in acid solution the proton adds to the much more basic amino group in preference to the weakly basic azo nitrogen. This is shown by the presence of A and R bands and the absence of the C band. The 3-aminoazobenzene cationic salt is very closely similar spectrally to the iso-*pi*-electronic azobenzene and 4-trimethylammoniumazobenzene iodide. On the other hand, the spectrum of 3-methyl-DAB in acid solution shows the presence of three bands. This solution contains the A tautomer almost entirely as shown by the presence of the A and R bands in almost full intensity, and about 1% of the C tautomer. The small amount of C tautomer present appears to be a direct result of the steric inhibition of the resonance, wherein the dimethylamino group would have trouble assuming a coplanar configuration and would consequently be much more basic and thus a more potent proton-attractor.

In a recent paper McGuire, Izzo, and Zuffanti[9] have reiterated that the proton adds wholly to the amino groups of DAB and methyl orange in acid alcohol. This conclusion is based upon (1) the greater basicity of the dimethylamino as compared to an azo group and (2) the resemblance of the spectra of azobenzene, DAB, and methyl orange in alcoholic acid solution. The conclusion that the proton adds to an amino nitrogen on the basis of (1) cannot be maintained, for in the ethyleneamines where the amino group is much more basic than the ethylene carbon, the proton has been shown to add to the β-carbon.[10] In the same manner the conclusion (2) cannot be upheld by the spectral curves presented by the authors where the spectrum of azobenzene is obviously different from the spectra of DAB and methyl orange in acid solution. This is mainly due to the presence of the bands of the C tautomers at about 280 mμ and 500 mμ in the latter two dyes and their absence in azobenzene. This difference between azobenzene and DAB is clearly shown in the data of Table I.

EXPERIMENTAL

Preparation of compounds. The 4-dimethylaminophenylazo dyes were prepared by coupling the appropriate diazotized aromatic amine with dimethylaniline. Physical constants and references have been given for many of the dyes in previous papers of the series.

Ultraviolet-visible absorption spectra. The absorption spectra were determined with a Beckman Model DU Quartz spectrophotometer.

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(7) Burawoy, *Ber.*, **63**, 3155 (1930).

(8) Kasha, *Faraday Soc. Disc.*, *No. 9*, 14, 72, 74, 75 (1950).

(9) McGuire, Izzo, and Zuffanti, *J. Org. Chem.*, **21**, 632 (1956).

(10) Leonard, Hay, Fulmer, and Gash, *J. Am. Chem. Soc.*, **77**, 439 (1955).