of anhydrous ether and added to a slurry of 27.5 g. (0.725 mol.) of lithium aluminum hydride in 200 ml. of ether. After the mixture was refluxed for 1 hr., the excess hydride was hydrolyzed by adding an ethanol ether mixture followed by 100 ml. of water. The voluminous precipitate was filtered under nitrogen and washed with 300 ml. of ether. The combined filtrate and washings were distilled under nitrogen to obtain a 43.5 g. main cut (53% yield), boiling at 143–146° at 1.3 mm. The refractive index was 1.4626 at 26.2°, and the infrared spectrum was in complete agreement with the product previously obtained by disproportionation of IA.

Anal. Found: C, 74.64%; H, 13.88%; P, 11.85%.

Explosives Department
Experimental Station
E. I. du Pont de Nemours Co.
Wilmington, Del.

The Basicity of 4,4′-Bis(dimethylamino)-Azobenzene

Giuseppe Cilento

Received February 10, 1959

Although the *p*Ka of a host of 4-aminoazobenzene derivatives has been measured,[1–3] there are no data on the basicity of 4,4′-bis(dimethylamino)-azobenzene [4′-*N*(CH$_3$)$_2$-DAB]. This dye shows an unusual behavior in dilute acids inasmuch as it gives a green color[4] and only on increasing the acidity presents the red color shown by 4-dimethylaminoazobenzene (DAB) derivatives in acid media.

The *p*Ka of this dye in 50% aqueous ethanol corresponding to the first proton addition has now been determined spectrophotometrically and found to be 3.2. This value merely represents the over-all basicity because a mixture of conjugate acids is formed on protonation.[2,3,5–7]

The observed *p*Ka value makes 4′-*N*(CH$_3$)$_2$-DAB one of the most basic 4-aminoazobenzene derivatives.

This relatively high basicity is in part due to the presence in this dye, but not in monodimethylaminoazobenzenes, of a centre of symmetry; the positions of proton capture are doubled and this statistical factor, log 2, rises the *p*Ka of 0.30 *p*H units. Yet it is possible that these positions of proton capture are more than four—*i.e.*, a third monoprotonated dye coexists besides the dimethylammonium (I) and azonium (II) cations.

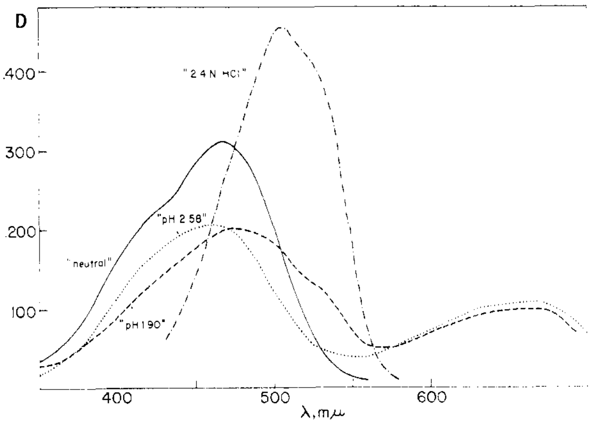
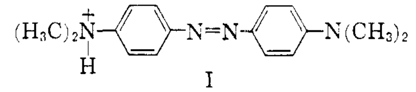
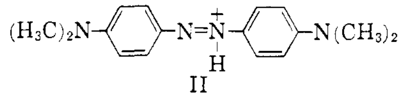


Fig. 1. Visible spectrum of 4′-N(CH$_3$)$_2$-DAB at different acidities. (Only a few curves are shown: ——— neutral; ······ *p*H = 2.58; – – – – *p*H = 1.90; - · - · - 2.4*N* HCl.)

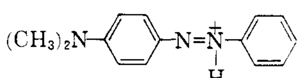


I



II

The evidence is mainly spectral. In the acid spectrum, λ_{max} of the longer transition is at 670 mμ (Fig. 1). This band cannot of course be due to the cation I. Sawicki[8] ascribed it to the cation II and interpreted the enormous shift with respect to the β-azonium cation of DAB (III) (λ_{max} 516 mμ) to extrachromophoric resonance.



III

This explanation is by no means convincing.[9] We propose that the 670 mμ transition is due to the cation IV, a π-complex resulting from incorporation of the π-electrons of the azo group in the vacant 1s orbital of the proton. In such a cation the positive charge can be efficiently distributed over the

IV

---

(1) M. Rogers, T. Campbell, and R. Maatman, *J. Am. Chem. Soc.*, **73**, 5122 (1951).

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

(3) E. Sawicki, *J. Org. Chem.*, **22**, 621 (1957).

(4) F. Kehrmann and St. Hempel, *Ber.*, **50**, 856 (1917).

(5) G. Cilento, E. C. Miller, and J. A. Miller, *J. Am. Chem. Soc.*, **78**, 1718 (1956).

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

(7) E. Sawicki, (a) *J. Org. Chem.*, **21**, 605 (1956); (b) *J. Org. Chem.*, **22**, 365 (1957).

(8) E. Sawicki, *J. Org. Chem.*, **22**, 1084 (1957).

(9) This point has also been stressed by a referee who reports that "structure IIIa-IIIb in reference (8) for the monocation should absorb at about 500 mμ, because of its aza-amidinium system; and its *p*-dimethylaminophenyl substituent would lengthen its absorption some but not up to 660 mμ, as Sawicki proposes."

whole molecule. The question then arises as to the presence of the cation II. In this connection it is very important to note that the 670 mμ band overlaps another one with a hidden maximum somewhat above 600 mμ (Fig. 1). This hidden maximum is presumably due to the cation II. To secure more evidence on this point we decided to substitute the proton by other Lewis acids, in the expectation that the relative intensities and positions of the two bands could be somewhat changed and hence a better resolution be observed. This prediction was satisfactorily realized when diphenyl tellurium dichloride was the Lewis acid[10] (Fig. 2).

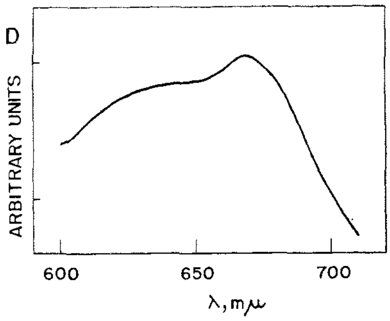


Fig. 2. Orange and red spectrum of 4'-N$(CH_3)_2$-DAB in the presence of diphenyl tellurium dichloride (solvent, ethyl alcohol).

The relatively high basicity of 4'-*N*$(CH_3)_2$-DAB makes it a useful detector of Lewis acid character, although high concentrations of the acceptor may be required. Thus, the green color is also developed with 1-benzyl-3-acetylpyridinium chloride (in ethanol), β-naphthyl sulfone (in benzene), diphenylselenium dichloride (in ethanol or benzene), and several derivatives of tellurium tetrachloride (in ethanol or benzene).

EXPERIMENTAL

4,4'-Bis(dimethylamino)azobenzene was a chromatographically pure product which melted sharply at 277°.

1-Benzyl-3-acetyl pyridinium chloride has recently been reported in the literature.[11] We have prepared it by a slightly different procedure. Benzyl chloride and 3-acetyl pyridine were refluxed during 3–4 hr. in ethanol. The desired product was precipitated from the reaction mixture by addition of cold ether, the temperature being kept well below zero. The crystals were washed with petroleum ether; they melted sharply at 189° (uncorr.). Reported m.p. 183–185°.[11]

All other chemicals were either available or gifts.

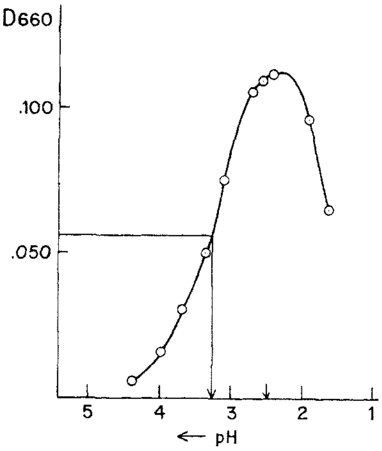
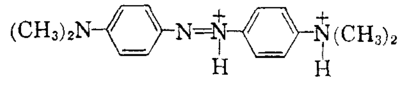


Fig. 3. Intensity of the longer wave length band in the visible spectrum of 4'-N$(CH_3)_2$-DAB *vs.* *p*H. The arrow indicates the limit of the existence of the bipositive cation.

pKa determinations. To ascertain the *p*Ka, the visible spectrum at various acidities in 50% aqueous ethanol was determined. A few representative curves are shown in Fig. 1. The solutions were prepared by adding to 12.5 ml. of aqueous HCl of various strengths, 2 ml. of the alcoholic solution of the dye and completing to 25 ml. with 95% ethanol. Final dye concentration was $8.5 \times 10^{-6}M$. Final *p*H measurements were carried out with a Beckman *p*H meter. Spectra were taken in a Beckman D.U. spectrophotometer at 25°, employing 1-cm. cells. Readings were reasonably constant and reproducible. To calculate the *p*Ka, the optical density at 660 mμ was plotted *versus* the *p*H (Fig. 3). At that wave length there is no absorption whatsoever by the free base. The curve goes through a maximum, a fact clearly to be ascribed to biprotonation; the arrow in Fig. 3 indicates the *p*H at which the red cation starts forming in appreciable amounts. Evidently at this *p*H the curve is already leveling off. This observation allows one to take with reasonable approximation the *p*H corresponding to half maximum intensity as the *p*Ka of the dye.



$$(CH_3)_2N-C_6H_4-N=\overset{+}{\underset{H}{N}}-C_6H_4-\overset{+}{\underset{H}{N}}(CH_3)_2$$

Acknowledgment. The author wishes to thank Prof. J. A. Miller and Prof. E. C. Miller of Wisconsin University for valuable suggestions and also for a sample of 4,4'-bis(dimethylamino)azobenzene. He also thanks Prof. H. Hauptmann for his helpful criticism, and the Rockefeller Foundation as well as the Brazilian Conselho Nacional de Pesquisas for grants.

Department of Chemistry
Faculdade de Filosofia, Ciencias e Letras
Universidade de São Paulo
São Paulo, Brasil

---

[10] A small proportion of a third cation may also be present in the acid solutions of simple monodimethylaminoazobenzenes. Thus, the β-azonium band quite often shows a more or less pronounced shoulder on its longer wave length side. This shoulder can be made much more pronounced by using 1-benzyl-3-acetylpyridinium chloride as the Lewis acid.

[11] A. G. Anderson, Jr., and G. Berkelhammer, *J. Am. Chem. Soc.*, **80**, 992 (1958).