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The Absorption Spectra of Dyes. XI.[1] A Note on the Color Change in Some Azobenzene Dyes with Variation in the Acidity*

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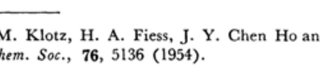
The absorption spectra of azobenzene and its para hydroxy, amino or dimethylamino derivative, and their sodium salts have been determined above 220 mμ in mixed solutions of water and ethanol (7 : 3 in volume) at various acidities. All the samples show characteristic changes in spectra with increase in the acidity, and the respective spectral changes keep well-defined isosbestic points, indicating a binary system spectrally. The wavelengths of the color band peaks and the corresponding spectral species have been determined. Consequently, the following order of the substitution effect has been obtained;

$$\left.\begin{matrix}\text{-NH}_3{}^+\\ \text{-NHMe}_2{}^+\end{matrix}\right)<\text{-H}<\text{-OH}<\text{-NH}_2<\text{-O}^-<\text{-NMe}_2$$

The color change in azobenzene derivatives with a variation in the pH value has been very often studied.[2] The conclusions on the proton addition, however, have not always coincided with one another. Klotz et al.,[3] for instance, have concluded that a first proton goes to the amino group and that a second proton goes to the azo group with an increase in the hydrogen ion concentration:



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[1] Part X of this series: T. Hoshi and Y. Tanizaki, This Bulletin, **39**, 476 (1966).

* Presented partly at the Nagoya Meeting of the Chemical Society of Japan, November, 1964.

[2] G. Cilento, E. C. Miller and J. A. Miller, *J. Am. Chem. Soc.*, **78**, 1718 (1956); E. Sawicki and F. E. Ray, *J. Org. Chem.*, **19**, 1686 (1954); E. Sawicki and D. Gerber, ibid., **21**, 410 (1956); E. Sawicki, ibid., **21**, 605 (1956); **22**, 621, 743, 915, 1048 (1957); F. Gerson, E. Heilblonner, A. Van Veen and B. M. Wepster, *Helv. Chim. Acta*, **43**, 1899 (1960); A. Zenhäusern and H. Zollinger, ibid., **45**, 1882, 1890 (1962).

[3] I. M. Klotz, H. A. Fiess, J. Y. Chen Ho and M. Mellody, *J. Am. Chem. Soc.*, **76**, 5136 (1954).

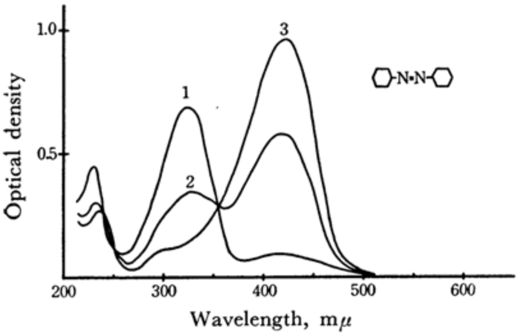


Fig. 1. Absorption spectra of AB.
Concentration of AB = 4.00×10^{-5} mol./l.
1. conc. H_2SO_4 20 ml. + 30% aqueous ethanol in 100 ml.
2. conc. H_2SO_4 40 ml.
3. conc. H_2SO_4 50 ml.

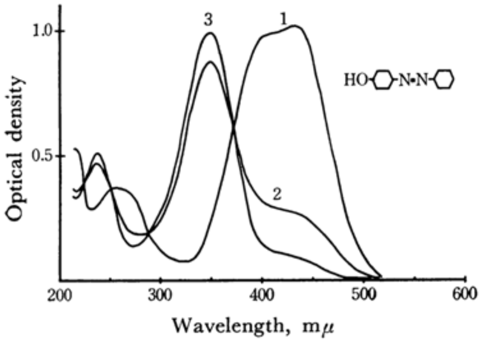


Fig. 2. Absorption spectra of HAB.
Concentration of HAB = 5.15×10^{-5} mol./l.
1. 30% aqueous ethanol
2. 1% HCl 1 ml. + 30% aqueous ethanol in 100 ml.
3. conc. HCl 1 ml.

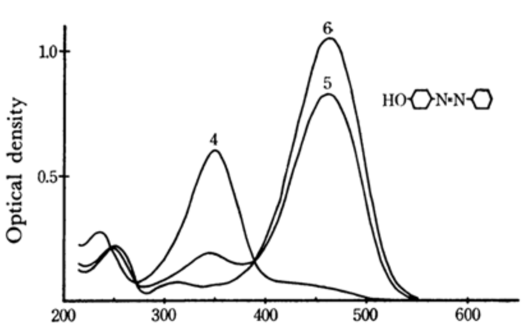


Fig. 3. Absorption spectra of HAB.
Concentration of HAB = 2.75×10^{-5} mol./l.
4. conc. H_2SO_4 5 ml. + 30% aqueous ethanol in 100 ml.
5. conc. H_2SO_4 20 ml.
6. conc. H_2SO_4 40 ml.

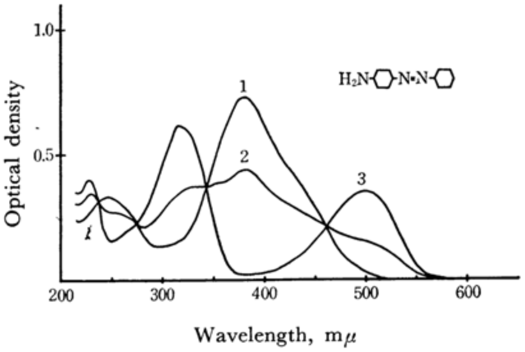


Fig. 4. Absorption spectra of AAB.
Concentration of AAB = 3.42×10^{-5} mol./l.
1. 30% aqueous ethanol
2. 25% H_2SO_4 0.03 ml. + 30% aqueous ethanol in 100 ml.
3. conc. H_2SO_4 1 ml.

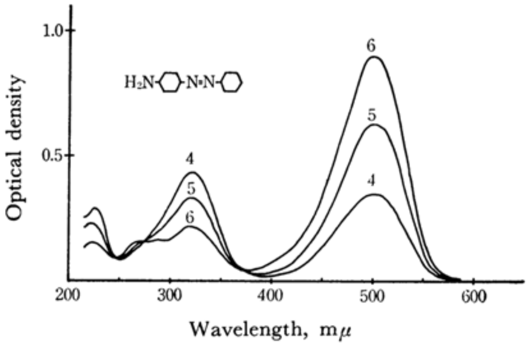


Fig. 5. Absorption spectra of AAB.
Concentration of AAB = 2.61×10^{-5} mol./l.
4. conc. H_2SO_4 8 ml. + 30% aqueous ethanol in 100 ml.
5. conc. H_2SO_4 20 ml.
6. conc. H_2SO_4 30 ml.

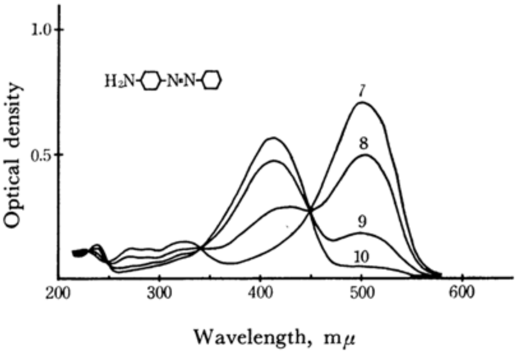
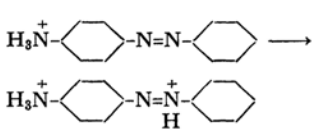
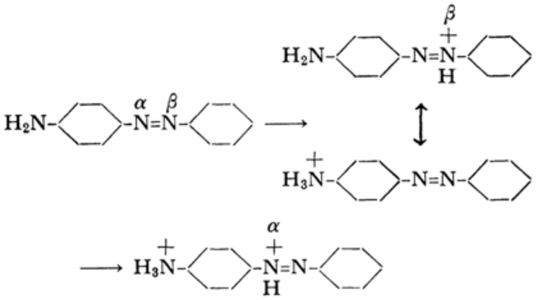


Fig. 6. Absorption spectra of AAB.
Concentration of AAB = 3.90×10^{-5} mol./l.
7. conc. H_2SO_4 35 ml. + 30% aqueous ethanol in 100 ml.
8. conc. H_2SO_4 40 ml.
9. conc. H_2SO_4 45 ml.
10. conc. H_2SO_4 50 ml.



If this is true, the first proton addition must shift the color band to a shorter wavelength, because the electronic theory insists that the protonated amino group cannot conjugate with the ring system because of the loss of the π-type electrons. Therefore, this scheme cannot correspond to the red shift of the color band resulting from the first proton addition. On the other hand, Sawicki[4] has considered the tautomer concept of the proton addition, which is as follows;



According to his scheme, either the first or the second protonation process could involve three spectral species. However, as will be shown later, a careful re-examination will make it evident that, in the course of an increase in the acidity, three kinds of spectral changes appear in turn, when a dicationic species is produced, and that each spectral change has well-defined isosbestic points, thus indicating a binary system spectrally.

In the present paper, a systematic interpretation will be given of the color band peaks with relation to the proton addition to some azobenzene derivatives. At the same time, the order of the substitution effect on neutral azobenzene and azobenzenium ions will be determined.

Experimental

The azo compounds used here were azobenzene (abbreviated to AB), *p*-hydroxyazobenzene (HAB), *p*-aminoazobenzene (AAB) and *N, N*-dimethylaminoazobenzene (DAB) prepared from the special-grade commercial materials by recrystallizations, repeated more than ten times, from the ethanol solution. The melting points of all the applied compounds were in agreement within ±1°C with those in the literature. The other compounds used here were the sodium salts of DAB-*m'*-sulfonic acid, HAB-*m'*-sulfonic acid and HAB-*p'*-sulfonic acid; they were synthesized in accordance with the usual steps and were purified by repeated recrystallizations in the same way as above.

The measurement of the absorption spectra was carried out over the 220—550 mμ region using a Shimadzu QR-50 manual spectrophotometer and a Hitachi EPS-2U recording spectrophotometer.

A mixed solution of water and ethanol (7 : 3 in volume) was used as the solvent.

The samples were carefully dealt with in order to avoid converting them to the cis isomer by light.

Results

The spectral change in various acid concentrations of AB, which is the prototype of the derivatives used here, is illustrated in Fig. 1. The first absorption peak moves from 320 mμ to the long wavelength at 425 mμ with an increase in the acid concentration.

The absorption spectra of HAB are shown in Fig. 2. The spectrum with a peak at 430 mμ in a neutral solution (curve 1) changes into another one with a 350 mμ band in an acid solution (curve 3) through the isosbestic points kept by the spectra in the intermediate solutions. With a further increase in the acid concentration, HAB reveals a new band at 460 mμ and a diminution of the 350 mμ band (Fig. 3).

The spectral changes of AAB are illustrated in Figs. 4, 5 and 6. Figure 4 shows that the intense band at 380 mμ in alkaline or neutral solutions (curve 1) is made to disappear by the addition of dilute sulfuric acid, while instead two new bands appear at 317 mμ and 500 mμ (curve 3). With a further increase in the acidity, absorption curve 3 (Fig. 4) varies as follows, keeping the isosbestic points (Fig. 5): the 317 mμ band decreases, and at the same time the 500 mμ band increases in intensity without a shifting of the peaks. After the almost total disappearance of the 317 mμ band (curve 7 in Fig. 6), the intensified 500 mμ band is moved to the shorter side at 415 mμ by a further-concentrated sulfuric acid, as is shown in Fig. 6.

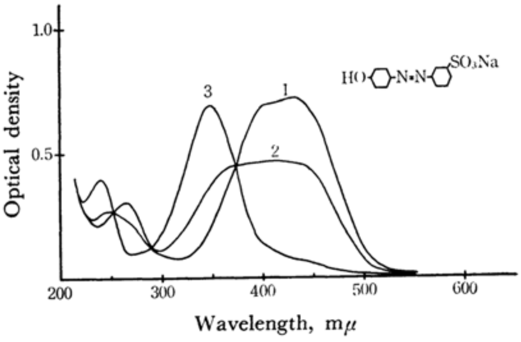


Fig. 7. Absorption spectra of HAB-*m'*-sulfonic acid sodium salt.
Concentration of HAB-*m'*-sulfonic acid sodium salt = 3.25×10^{-5} mol./l.

1. pH 9.70 (solvent water)
2. pH 9.05
3. pH 1.90

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[4] E. Sawicki, *J. Org. Chem.*, **22**, 365 (1957).

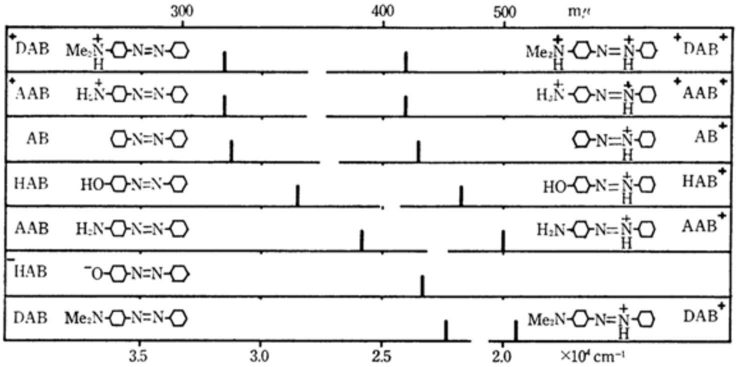

Fig. 8. Absorption maximum of the first band of azobenzene and its derivatives.

DAB behaved like AAB, though the spectral change corresponding to Fig. 5 was not so remarkable as in AAB.

The sulfonic sodium salts of HAB and AAB showed spectral changes quite similar to those of HAB and AAB, indicating essentially no effect of the sulfonic group. The spectral change of HAB - *m'*-sulfonic acid sodium salt is shown as an example in Fig. 7; it can be compared with HAB, which is shown in Fig. 2.

Discussion

The spectral change for the solvent variation in the sodium sulfonate of the azo compound is essentially identical with that of the parent azo compound. Accordingly, the discussion of the mechanism of the color change can be limited to the azo compounds, excluding the sulfonic groups, and the conclusion thus derived is also applicable to the corresponding compounds, including the sulfonic groups.

The proton addition to AB makes the 320 mμ band change to the 415 mμ band by attaching a proton to the electron pairs of one of the azo nitrogen atoms.[5] Let us describe this formally by:

$$\mathrm{AB}(320\ \mathrm{m}\mu) \rightarrow \mathrm{AB}^+(425\ \mathrm{m}\mu) \qquad (1)$$

As it is well known that the phenolic hydroxyl group can easily be dissociated, HAB in alkaline or neutral solutions has to be ionized; the 430 mμ band must be due to the $^-$HAB species. A first proton will go to the oxy-anion part of the $^-$HAB species, and a second one, this time preferentially, to the nonbonding σ electrons of β azo-nitrogen.[4,6] The spectral change of HAB may, therefore, be described as follows:

$$^-\mathrm{HAB}(430\ \mathrm{m}\mu) \rightarrow \mathrm{HAB}(350\ \mathrm{m}\mu) \rightarrow \mathrm{HAB}^+(460\ \mathrm{m}\mu) \qquad (2)$$

Now let us consider the case of AAB. According to Fig. 5, the 317 mμ and the 500 mμ band should be due to spectrally different species, while Fig. 4 indicates that the two bands behave as if they are only one species. This implies that, under such experimental conditions as are indicated in Fig. 4, there is no appreciable change in the amount-ratio of the two species. Since a first proton can be attached to either the amino-group or the β azo-nitrogen atom, representing the respective protonated species as $^+$AAB or AAB$^+$, the 317 mμ and the 500 mμ band may be assigned to the $^+$AAB and the AAB$^+$ species respectively. Therefore, the spectral changes shown in Figs. 4, 5 and 6 can reasonably be explained by the following mechanism. At first, while the AAB species is usable, the amount-ratio of $^+$AAB and AAB$^+$ is unchanged (Fig. 4); in the second step, the spectral change after using up the AAB species continues as a result of the increasing acidity until $^+$AAB is completely converted into AAB$^+$ (Fig. 5); finally, AAB$^+$ is protonated again by the further increase in acidity, thus producing the dicationic $^+$AAB$^+$ species (Fig. 6). Thus, the following scheme is obtained for the protonation processes and the absorption peaks:

$$\mathrm{AAB}(380\ \mathrm{m}\mu) \rightarrow \begin{matrix} ^+\mathrm{AAB}(317\ \mathrm{m}\mu) \\ \mathrm{AAB}^+(500\ \mathrm{m}\mu) \end{matrix}$$
$$\rightarrow \mathrm{AAB}^+(500\ \mathrm{m}\mu) \rightarrow {}^+\mathrm{AAB}^+(415\ \mathrm{m}\mu) \qquad (3)$$

Similarly, scheme 4 may be considered to hold for the case of DAB:

$$\mathrm{DAB}(460\ \mathrm{m}\mu) \rightarrow \begin{matrix} ^+\mathrm{DAB}(317\ \mathrm{m}\mu) \\ \mathrm{DAB}^+(516\ \mathrm{m}\mu) \end{matrix}$$
$$\rightarrow \mathrm{DAB}^+(516\ \mathrm{m}\mu) \rightarrow {}^+\mathrm{DAB}^+(420\ \mathrm{m}\mu) \qquad (4)$$

where the $[^+\mathrm{DAB}]/[\mathrm{DAB}^+]$ amount-ratio seems to be smaller than $[^+\mathrm{AAB}]/[\mathrm{AAB}^+]$.

Correlations among the first band positions of the spectral species appearing in schemes 1—4 are summarized as a pattern in Fig. 8, which reveals quite clearly the order of the substitution effect.

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

6) Cf. M. B. Robin and W. T. Simpson, ibid., **36**, 580 (1962).

The band positions of the left-side and the right-side series in Fig. 8 can be considered in relation to the substitution effect of the *p*-group to azobenzene and azobenzenium ions respectively, and they are understandable in terms of the electronic theory.

Thus we may conclude that the order of the substitution effect at the para position of both neutral and cationic azobenzene is:

$$\left.\begin{matrix}-\mathrm{NH_3}^+\\ -\mathrm{NHMe_2}^+\end{matrix}\right) < \mathrm{-H} < \mathrm{-OH} < \mathrm{-NH_2} < \mathrm{-O^-} < \mathrm{-NMe_2}.$$

The authors are indebted to Dr. Harutada Negoro, Sankyo Co., Ltd., for permission to use that company's Hitachi EPS-2U recording spectrophotometer.