NOTES

Note on the Association of 3,6-Bis-dimethylaminoacridine in Some Organic Solvents

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(Received June 12, 1964)

The electronic spectra of 3,6-bis-dimethylaminoacridine (BDAA), i. e., of the acridine orange base, have been subjected to numerous investigations. Mataga⁽¹⁾ has examined the absorption spectra of this compound* in various non-aqueous solvents and reached the conclusion that BDAA dissolved in acetone, buthanol, ethanol and methanol is in a marked degree associated forming the dimers. At concentrations of BDAA of the order of 10^{-6} mol. per liter, this author has obtained only one absorption band, with a maximum at about 500 mμ. With an increasing concentration of BDAA, this band diminished and simultaneously a new band with a maximum at 425~430 mμ, was gradually formed.

In connection with our investigations of the mutual interaction between BDAA and some organic acids in non-aqueous solvents,⁽³⁾ we have examined anew the dimerization of BDAA in some solvents and have obtained results differing from those cited above.

BDAA was obtained from acridine orange (G. T. Gurr Ltd., London), and was purified chromatographically by a method given by Zanker,⁽⁴⁾ the melting point (181~182°C) was in keeping with the literature data.⁽⁴⁾ By using proper purification methods⁽⁵⁾ the solvents were obtained free from any traces of acids, bases and moisture.

We have found that the absorption spectrum of BDAA in acetone, dioxane, pyridine, benzene and styrene has only one band visible in all the concentrations between 10^{-6} and 10^{-2} mol./1. The maximum of this band lies in range between 23400 and 23600 cm^{-1} (between 427 and 424 mμ) in the dependence of the used

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1) N. Mataga, This Bulletin, **30**, 375 (1957).

* In the cited work¹⁾ BDAA was described as 2,8-bis-dimethylaminoacridine probably as a result of the use of another sequence of the numeration of atoms in the rings. However, the description of the preparation method of this compound leaves no doubt that in the work of Mataga¹⁾ an acridine orange base was examined. Cf. also.²⁾

2) N. Mataga and S. Tsuno, This Bulletin, **30**, 711 (1957).

3) A. Olszowski and Z. Ruziewicz, *Bull. Acad. Polon. Sci., sér. sci. math. astr. phys.*, in press.

4) V. Zanker, *Z. physik. Chem.*, **199**, 225 (1952).

5) A. Weissberger (Editor), "Technique of Organic Chemistry," Vol. VII, "Organic Solvents," 2nd ed., Interscience Publ., New York (1955).

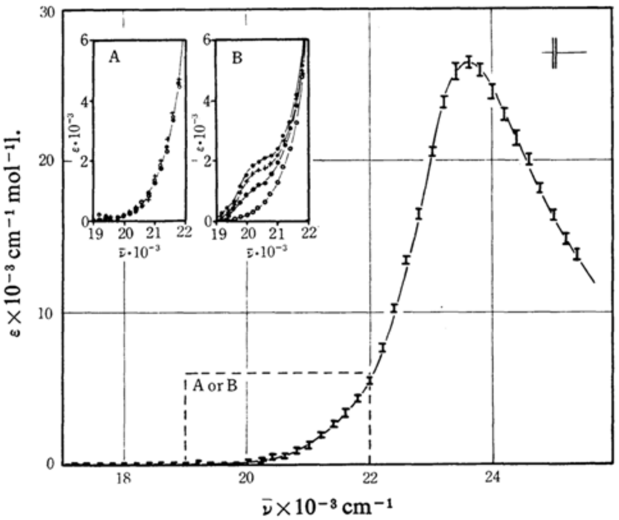

Fig. 1. Absorption spectrum of BDAA solution in acetone.
"A" Part of spectrum in the range of 19000~22000 cm^{-1}; solvent—absolute acetone.
"B" The same part of spectrum, solvent—acetone containing traces of water (<0.1%). Experimental points correspond to the following BDAA concentrations: ●—● 4.0×10^{-6}, +—+ 4.0×10^{-5}, ◐—◐ 1.6×10^{-4}, ○—○ 6.0×10^{-3} mole per liter.

solvent, and its molar absorptivity at a maximum is equal to 25000~29000 mol^{-1} cm^{-1} l. The corresponding results obtained for the acetone solutions are shown in Figs. 1 and 1A. According to the data of Mataga¹⁾ the above band should appear as a result of the BDAA dimers; however, because of the lack of any relation between the molar absorptivity and the concentration, and because of the presence of this band even at low BDAA concentration, we hold that this band is characteristic of the BDAA monomers. We have not found any changes indicating the association of BDAA molecules in the cases mentioned. It should be emphasized that in pyridine, in which, according to Mataga,¹⁾ no association occurs, we have also observed the same band with a maximum at 23400 cm^{-1}.

The band with a maximum at about 20200 cm^{-1} (495 mμ), which according to Mataga should belong to the BDAA monomer, appears when some compounds of strong proton-donor properties are introduced to the solutions of BDAA in non-aqueous solvents. (Cf. Fig. 2, curves 5 and 6). The mutual interaction of BDAA with week proton donors such as methanol (Fig. 2, curve 3) or phenol²⁾ through the hydrogen bond brings about only a weak shift of the 23400 cm^{-1} band towards longer wavelengths. However, under the action of carboxylic acids probably some proton transfer from the acid molecule towards nitrogen in the acridine ring of the BDAA molecule takes place, bringing about the formation of an ionic pair. In our opinion this effect seems to be responsible for the appearance of the 20200 cm^{-1} band. This conclusion is to some extent

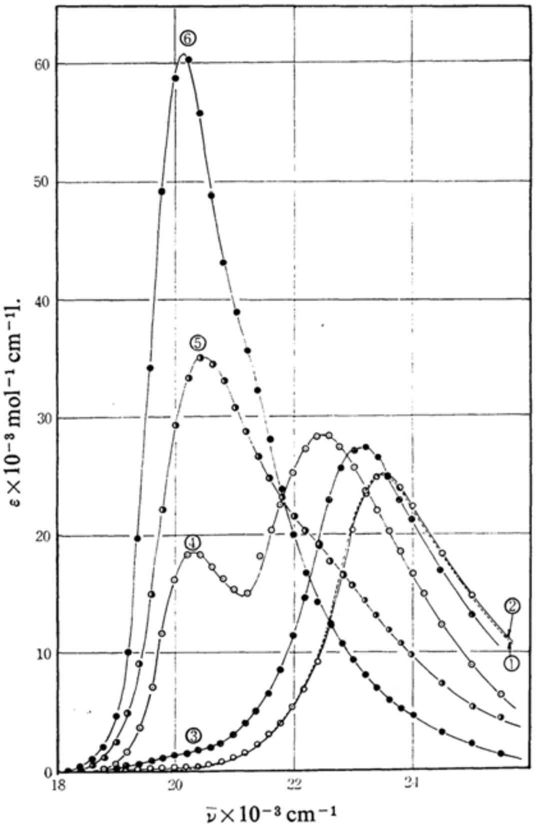

Fig. 2. Absorption spectra of BDAA ($c=4.0\times10^{-5}$) in solutions of benzene.
1: without addition of third component
2: with acetone ($c=2.2\times10^{-1}$)
3: with methanol ($c=2.0\times10^{-1}$)
4: with *p*-hydroxybenzonitrile ($c=1.33\times10^{-3}$)
5: with benzoic acid ($c=1.22\times10^{-3}$)
6: with trichloroacetic acid ($c=1.20\times10^{-4}$)
All concentrations in mole per liter.

confirmed by the fact that an analogous band appears in aqueous and alcohol solutions containing the acridine orange cations, i. e., monocations of BDAA.[4,6] We have also observed an intermediate state by adding *p*-hydroxybenzonitrile to the BDAA solution, thus producing both the shift of the 23400 cm^{-1} band towards red and the appearance of the 20200 cm^{-1} band (Fig. 2, curve 4).

In solvents not sufficiently dried or containing some acidic contaminations besides the 23400 cm^{-1} band, the band at 20200 cm^{-1} appears too. This kind of spectrum was obtained when we used not sufficiently dehydrated acetone (Fig. 1B) or acrylonitrile which we had not succeeded in purifying to a sufficient degree. However, the intensity of the 20200 cm^{-1} band in acrylonitrile does not exceed 15% of the intensity of the 23400 cm^{-1} band, even at very low concentrations of BDAA, and essentially depends on the mode of purifying the solvent. Hence, even in this case we cannot ascertain any association of BDAA.

A more detailed discussion of acidic-basic interaction in BDAA solutions will be published shortly.[3]

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[6] V. Zanker, *Z. physik. Chem.*, **200**, 250 (1952).