The Electric Dipole Moments of Methine Dyes — Comparison of Experimental Results with Theoretical Predictions

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Z. Naturforsch. **37a**, 1024—1026 (1982); received April 13, 1982

Absorption and emission spectra of methine dyes in polar and nonpolar solvents were measured. From the Stokes shift as a function of solvent polarity the dipole moments of excited singlet states have been estimated and compared with the quantum chemical predictions. Also the π-electronic charge distribution in the ground and first excited singlet electronic states and bond orders of the dyes were calculated. All investigated methines showed an increase in dipole moment upon excitation to the first excited emitting state.

Introduction

Methine dyes have attracted interest for their possible application in display devices [1]. Unfortunately, there is a lack of experimental and theoretical data on the spectral properties of methines.

Recently it was found that the electronic spectra of the methine dyes are very sensitive to the polarity of the solvents [2, 3]. The solvent effects are particularly pronounced in the fluorescence spectra. Previous results have shown that in polar solvents some methines emit a dual fluorescence [2, 3].

From the dependence of the fluorescence spectrum on the dye concentration it has been suggested that excimer formation is responsible for the second band of fluorescence [3]. It was also shown [3] that the sulphur atom in a dye molecule is mainly responsible for the excimer formation. Therefore, in this paper we have used two types of dye molecules. One of these is showing the excimer band of fluorescence in polar solvents whereas the second one does not.

The aim of the present work was to get further information about the electronic properties of the ground and singlet excited states. That was done by comparison of their experimentally determined and calculated dipole moments and charge distribution.

Materials and Methods

The two types of methine dyes:

A)

2[4(N, N-dimethyloamino) α styrylo] benzothiazol

B)

2[4(N, N-dimethyloamino) α styrylo] benzoksazol

were synthetized as already described [4].

The compounds were chromatographically purified. The absorption spectra were recorded on an UV—VIS spectrophotometer. The fluorescence spectra were measured with an apparatus described elsewhere [5]. The fluorescence was excited at 405 nm through an interference filter (5.5 nm bandwith).

The Pariser-Parr-Pople SCF-MO-CI method with the Mataga-Nishimoto integral approximation [6] and with the parametrization of Kwiatkowski [7, 8] were used. The molecules were taken to be planer with bond length 1.397 Å and angles 120° and 108°. The resonance integrals β between given atoms were taken as follows:

$$\beta_{\mathrm{CC}} = -2.294\ \mathrm{eV}\,,$$
$$\beta_{\mathrm{CO}} = -2.1\ \mathrm{eV}\,,$$
$$\beta_{\mathrm{CS}} = -1.6\ \mathrm{eV}\,,$$
$$\beta_{\mathrm{CN}} = -2.1\ \mathrm{eV}\,.$$

The trans-configuration of both molecules was assumed. Such configuration can theoretically exist in two different conformational states obtained by internal rotation via $C_2 - C_{10}$ bond (Figure 1). To decide which conformational state appears in practice one should compare the total π electronic energies (E^{tot}) in both states. In our case the results

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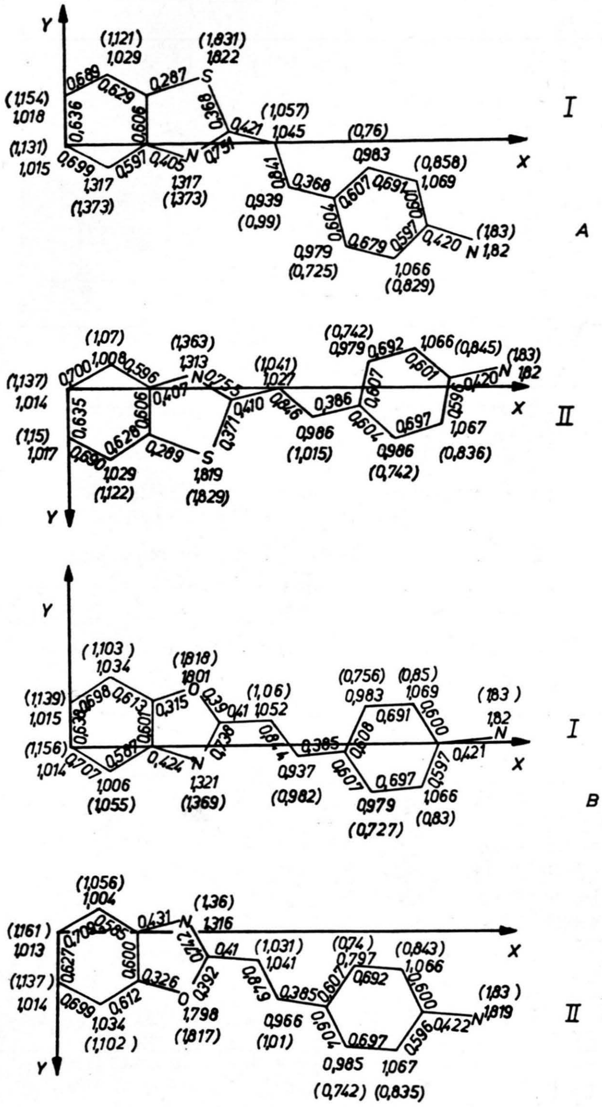

Fig. 1. Calculated values of π-electronic charge distribution in the ground and first excited singlet states (in brachets) and bond orders of used dyes.

are as follows:

$$E_{\mathrm{AI}}^{\mathrm{tot}} = -651.455\,\mathrm{eV}\,, \quad E_{\mathrm{AII}}^{\mathrm{tot}} = -649.771\,\mathrm{eV}\,,$$

$$E_{\mathrm{BI}}^{\mathrm{tot}} = -668.769\,\mathrm{eV}\,, \quad E_{\mathrm{BII}}^{\mathrm{tot}} = -669.672\,\mathrm{eV}\,.$$

The results indicate a small preference of AI and BII conformations. It should be pointed out that the difference in the total π-electronic energy between respective states is small, and therefore the results presented in this work were calculated for both states.

Results and Discussion

The dipole moments in the excited states were estimated according to approximate solvent shift theories. To elucidate the charge distribution and dipole moments we used a PPP-SCF-MO-CI calculation. Figure 1 shows the π-electronic charge distribution in both ground and excited single states and the bond orders.

The solvent effect on the electronic spectrum of a solute molecule is correlated with the solvent dielectric constant ε and the refractive index n. Quantitative correlations of the spectral shift of absorption and fluorescence with the polarity of the solvent have been proposed in several theoretical treatments [9, 10, 11, 12, 13, 14, 15, 16]. The equations [14, 15]

$$\tilde{\nu}_{\mathrm{a}} - \tilde{\nu}_{\mathrm{f}} = S_1 \left(\frac{\varepsilon - 1}{\varepsilon + 2} - \frac{n^2 - 2}{n^2 + 2} \right) \frac{2\,n^2 + 1}{n^2 + 2}\,, \quad (1)$$

where

$$\left. \begin{aligned} S_1 &= \frac{2\,(\mu_{\mathrm{e}} - \mu_{\mathrm{g}})^2}{a^3\,h\,c}\,, \\ F_1 &= \left(\frac{\varepsilon - 1}{\varepsilon + 2} - \frac{n^2 - 2}{n^2 + 2} \right) \frac{2\,n^2 + 1}{n^2 + 2} \end{aligned} \right. \quad (1\mathrm{a}$$

and

$$\frac{\tilde{\nu}_{\mathrm{a}} + \tilde{\nu}_{\mathrm{f}}}{2} \quad (2)$$

$$= S_2 \left(\frac{2\,n^2 + 1}{2\,n^2 + 2} \left(\frac{\varepsilon - 1}{\varepsilon + 2} - \frac{n^2 - 2}{n^2 + 2} \right) + \frac{3\,n^4 - 1}{2\,n^2 + 2} \right),$$

where

$$S_2 = \frac{-\,2\,(\mu_{\mathrm{e}}{}^2 - \mu_{\mathrm{g}}{}^2)}{a^3\,h\,c}\,, \quad (2\mathrm{a})$$

$$F_2 = \left[\frac{2\,n^2 + 1}{2\,n^2 + 2} \left(\frac{\varepsilon - 1}{\varepsilon + 2} - \frac{n^2 - 2}{n^2 + 2} \right) + \frac{3\,n^4 - 1}{2\,n^2 + 2} \right]$$

have been adopted in the present treatment, where $\tilde{\nu}_{\mathrm{a}}$ and $\tilde{\nu}_{\mathrm{f}}$ are the 0 — 0 absorption and emission frequency, respectively, μ_{g} and μ_{e} are the permanent dipole moments in the ground and excited emitting states, a = Onsager cavity radius (17,5 Å and 16,5 Å for dyes A and B, respectively). The correlations between absorption and emission maxima as functions of the solvent parameters, plotted according to (1) and (2), are given in Figs. 2 and 3. The slopes S_1 and S_2 of these plots can be evaluated.

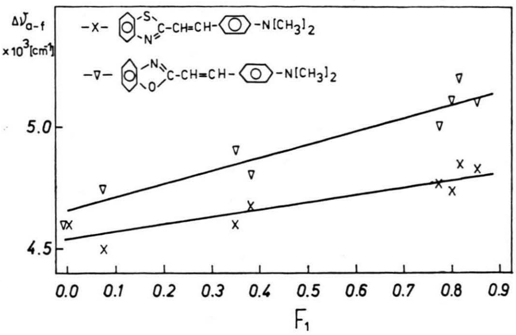

Fig. 2. Spectral shift as a function of solvent parameters according to (1).

Having the slopes, the excited state dipole moments (μ_e) can then be calculated [17] using either: a) (1) and (1a) and the values of μ_g obtained from theoretical calculations giving $\mu_e{}^a$, or b) substituting the actual value of S_1 and S_2 into the equation

$$\mu_e{}^b = \frac{1}{2}\left(\frac{a^3 h c S_2}{2}\right)^{1/2}\left(1 - \frac{S_2}{S_1}\right), \tag{3}$$

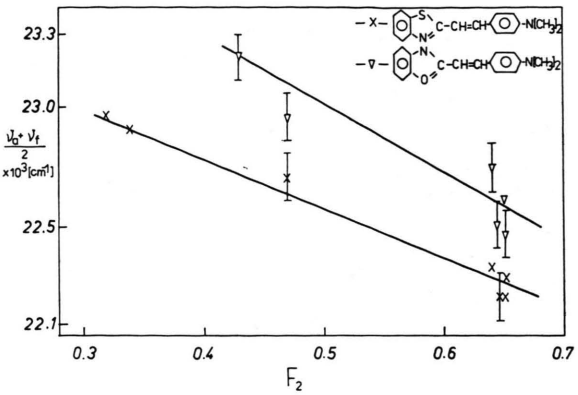

Fig. 3. Spectral shift as a function of solvent parameters according to (2).

which circumvents the use of μ_g. Table 1 lists the values of the dipole moments.

The results from Table 1 indicate that the fluorescent state of methines possesses higher dipole moments than the ground state. Both experimental values of μ_e are lower than the theoretical ones.

Table 1. Values of dipole moments.

Dyes	No. of structure	From PPP calculation						From the solvent shift data	
		μ_{gx}[D)	μ_{gy}[D]	μ_g[D]	μ_{ex}[D]	μ_{ey}[D]	μ_e[D]	$\mu_e{}^a$[D]	$\mu_e{}^b$[D]
A	I	5.80	0.42	5.81	6.705	− 1.995	6.995	5.94	6.03
	II	5.90	1.56	6.11	7.314	− 0.049	7.314	6.24	6.03
B	I	5.51	2.01	5.87	6.939	− 0.201	6.942	6.02	6.30
	II	5.19	3.14	6.07	6.791	1.829	7.033	6.22	6.30

[1] T. Uchida, C. Shishido, H. Seki, and M. Wada, Mol. Cryst. Liq. Ceyst. Lett. **34**, 153 (1977).
[2] Z. Salamon and A. Skibiński, Z. Naturforsch. **35a**, 378 (1980).
[3] Z. Salamon and A. Skibiński, Dyes and Pigments **2**, 256 (1981)
[4] V. Dryanska and C. Iwanow, Tetrahedron Letters **35**, 9 (1975).
[5] Z. Salamon and T. Martyński, Biophys. Chem. **9**, 369 (1979).
[6] K. Nishimoto, Theor. Chim. Acta **7**, 207 (1967).
[7] S. Kwiatkowski, Theor. Chim. Acta **10**, 47 (1968).
[8] S. Kwiatkowski, M. Berndt, and J. Fabien, Acta Physica Polon. **38**, 365 (1970).
[9] E. Lippert, Z. Elektrochem. **61**, 962 (1957).
[10] W. Liptay, Z. Naturforsch. **18a**, 705 (1963).
[11] N. G. Bakhshier, Optika Spektrosk. **10**, 717 (1961).
[12] L. Bilot and A. Kawski, Z. Naturforsch. **17a**, 621 (1962).
[13] L. Bilot and A. Kawski, Z. Naturforsch. **18a**, 10 (1963).
[14] A. Kawski, Acta Physica Polon. **29**, 507 (1966).
[15] M. Sun and P. Song, Photochem. Photobiol. **25**, 3 (1977).
[16] M. Siegmund and J. Bending, Z. Naturforsch. **35a**, 1076 (1980).
[17] A. Chamma and P. Viallet, C. R. Acad. Sci. Paris Ser. C. **270**, 1901 (1970).