Spectral properties and conformations of nonlinear ketocyanines

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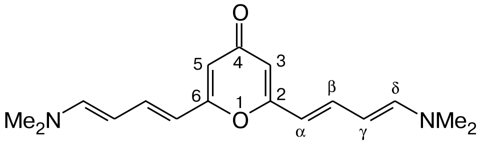
The electronic transitions in molecules of the ketocyanine dyes (polyenic ω,ω´-bisamino ketones) were calculated by quantum chemical methods. Satisfactory agreement was obtained between the experimental bands of the S—S absorption spectra and calculated electronic transitions for the ketocyanine with the central pyranone moiety and the corresponding salt assuming an acute angle between the chromophores and for the ketocyanine with the central pyridone moiety assuming an obtuse angle between the chromophores. Such molecular conformations were confirmed by the gNOESY ^{1}H NMR data for these dyes. The difference in the conformations of the dyes with the pyranone and pyridone moieties is due, most likely, to steric hindrance created by the central methyl groups in the molecules of the latter. The salts corresponding to these dyes have similar conformational differences.

Key words: ketocyanine dyes, 2D gNOESY NMR spectroscopy, quantum chemical calculations, UV spectroscopy.

We have earlier[1—5] studied a series of the ketocyanine dyes (polyenic ω,ω´-bisamino ketones) with the central pyranone or pyridone moiety (**1**, **2**) and the polymethine salts corresponding to these dyes (**3**, **4**).

Molecules of compounds **1** and **2** have simple structures: they consist of two aminopolyenic chromophores of the same length, connected through the carbonyl group, and the central bridge. The replacement of the O bridging atom by the NMe group changes drastically the absorption spectra of the dyes: instead of two bands in the absorption spectrum of the pyranone dye (**1**) caused by the interaction of the chromophores, the absorption spectrum of the dye with the central pyridone moiety (**2**) contains only one broad band lying between the bands of dye **1** (Fig. 1).[1,4] A similar pattern is also observed for the salts corresponding to compounds **1** and **2**: the absorption



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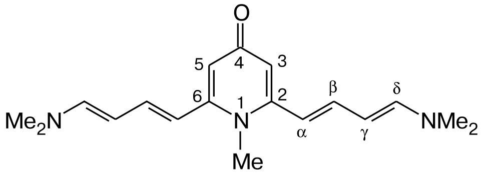

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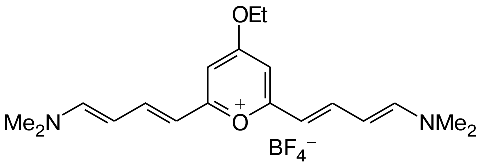

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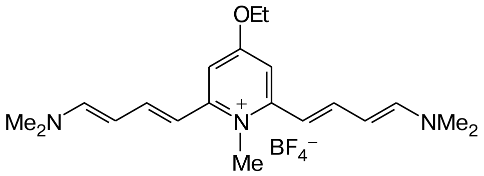

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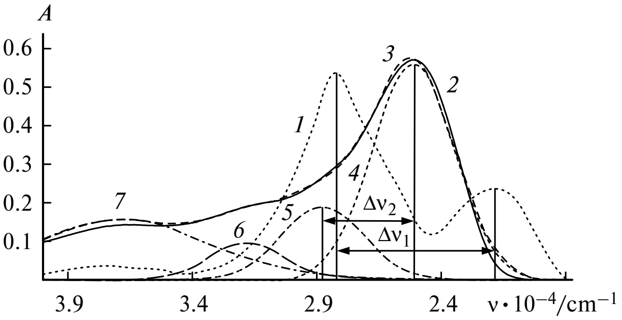


Fig. 1. Absorption spectra of dyes **1** (*1*) and **2** (*2*) in Pr^{i}OH and the expansion of the absorption spectrum of dye **2** to the Gaussian components: *3*, sum of the Gaussian components; *4*, band of the $S_0 \rightarrow S_1$ transition; *5*, band of the $S_0 \rightarrow S_2$ transition; *6*, third Gaussian band; *7*, fourth Gaussian band.

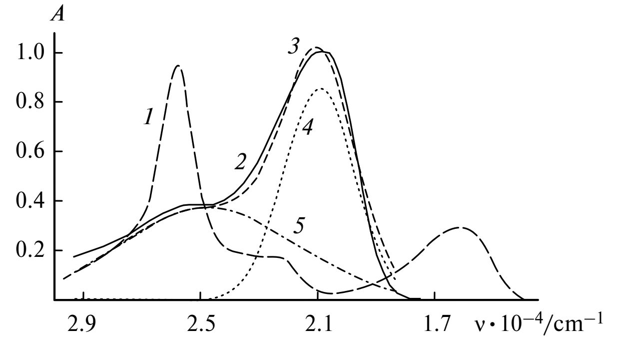
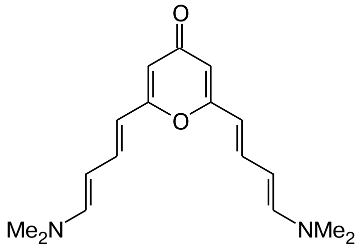


Fig. 2. Absorption spectra of dyes **3** (*1*) and **4** (*2*) in Pr^{i}OH and the expansion of the absorption spectrum of dye **4** to the Gaussian components: *3*, sum of the Gaussian components; *4*, band of the $S_0 \rightarrow S_1$ transition; *5*, band of the $S_0 \rightarrow S_2$ transition.

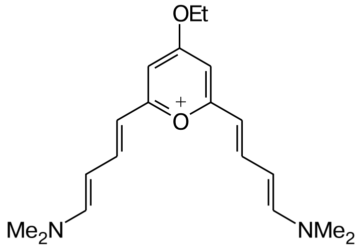
spectrum of pyrilium salt **3** consists of two widely diversed bands, whereas the absorption spectrum of pyridinium salt **4** represents a broad unresolved band, which lies between the bands of salt **3** (Fig. 2).[1,4]

We explained[5] this effect by the perturbation influence of the NMe substituent, which weakens greatly the interaction of the chromophores in molecules of the compounds with the central NMe group. The oscillator strengths for the absorption bands of dyes **1** (totally for two absorption bands) and **2** turned out to be close, being ~1.4. Therefore, two unresolved bands in the absorption spectra of dye **1** run together into one band for dye **2**, indicating the weak interaction of the chromophores in dye **2**.

The spectral properties of the dye can depend on the spatial conformation of the atoms in the molecule, particularly, on the angle between the chromophores.[6,7] Based on the concepts of the theory of chromophore interaction and the experimental ratio of intensities of the long- and short-wavelength bands, we assumed that molecules **1** and **3** exist in the nonlinear conformation (**1′** and **3′**, respectively) in which the chromophores (polyene chains extending between the NMe_2 and carbonyl groups) of the dyes are arranged at an acute angle to each other.[1–3]



1′



3′

The question about the predominant conformation of compounds **2** and **4** remains unanswered, because their absorption spectra consist of a broad poorly resolved band.

This work is devoted to revealing a relationship between the spectral properties of some nonlinear ketocyanines and the spatial conformation of their molecules using quantum chemical methods and 2D gNOESY ^1H NMR spectroscopy.

Experimental

^1H NMR spectra were recorded on a Bruker DRX-500 spectrometer for solutions in $CDCl_3$ at 30 °C using Me_4Si as an internal standard.

Dye **1**, ^1H NMR, δ: 2.87 (s, 6 H, Me_2N); 5.12 (t, 1 H, H_γ, $J_{\beta,\gamma} = J_{\gamma,\delta} = 12.5$ Hz); 5.71 (d, 1 H, H_α, $J_{\alpha,\beta} = 14.7$ Hz); 5.84 (s, 1 H, H(3), H(5)); 6.59 (d, 1 H, H_δ, $J_{\gamma,\delta} = 12.5$ Hz); 7.00 (dd, 1 H, H_β, $J_{\alpha,\beta} = 14.7$ Hz, $J_{\beta,\gamma} = 12.5$ Hz).

Dye **2**, ^1H NMR δ: 2.88 (s, 6 H, Me_2N); 3.56 (s, 3 H, MeN(1)); 5.16 (dd, 1 H, H_γ, $J_{\beta,\gamma} = 11.1$ Hz, $J_{\gamma,\delta} = 13.1$ Hz); 5.83 (d, 1 H, H_α, $J_{\alpha,\beta} = 14.4$ Hz); 6.64 (s, 1 H, H(3), H(5)); 6.65 (d, 1 H, H_δ, $J_{\gamma,\delta} = 13.1$ Hz); 6.93 (dd, 1 H, H_β, $J_{\alpha,\beta} = 14.4$ Hz, $J_{\beta,\gamma} = 11.1$ Hz).

2D gNOESY ^1H NMR spectra were obtained using a standard procedure.[8] The time of mixing was 0.5 s. The quantum chemical calculation for the molecules was performed using a program package based on the method of intermediate neglect of differential overlap (INDO) with spectroscopic parametrization.[9] The molecular coordinates were optimized using the AM1 method (ChemOffice program package).*

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* http://www.camsoft.com

Table 1. Comparison of the experimental data (in the numerator) and calculated results (in the denominator) for dyes **1**, **2**, and **3**

Compound	ν_{max}/cm^{-1} (λ/nm)		$\Delta\nu$/cm^{-1}	I_1/I_2
	1	2		
1	28000 (357)	21700 (461)	6300	2.3
	30700 (326)	24000 (416)	6700	8.3
2*	28770 (347)	25120 (398)	3650	0.34
	29647 (337)	25052 (399)	4600	0.17
3	25800 (388)	16200 (616)	9600	3.1
	27787 (359)	17566 (569)	10200	4.9

* Numerator is the Gaussian expansion of the experimental data.

Results and Discussion

As mentioned above, the absorption spectra of dyes **1** and **3** consist of two bands (λ^1_{max} = 357 nm and λ^2_{max} = 461 nm for **1**; λ^1_{max} = 388 nm and λ^2_{max} = 616 nm for **3** in $\mathrm{Pr^iOH}$), and the short-wavelength band is most intense, which corresponds to an acute angle between the chromophores.[1—3] The ratio of band intensities I_1/I_2 for dyes **1** and **3** is 2.3 and 3.1, respectively (Table 1). The experimental data and results of the quantum chemical calculation of the electronic transitions for molecules **1** and **3**, assuming the molecular conformation with the acute angle between the chromophores, are listed in Table 1. As can be seen from the data in Table 1, the calculated absorption spectra of these dyes exhibit the hypsochromic shift compared to the experimental spectra, which can be due to the solvent effect. However, the calculated spectra of compounds **1** and **3** are qualitatively rather similar to the experiment: the short-wavelength band is most intense and the splitting values between the $S_0 \to S_1$ and $S_0 \to S_2$ transitions practically coincide. Unlike pyranone dye **1** and pyrilium salt **3**, the S—S spectra of pyridone dye **2** and salt **4** represent broad poorly resolved bands (λ_{max} = 395 and 480 nm in $\mathrm{Pr^iOH}$ for compounds **2** and **4**, respectively) arranged between the absorption bands of compounds **1** and **3** (see Figs 1 and 2). The expansion of the broad unstructured bands in the spectra of compounds **2** and **4** to the Gaussian components made it possible to distinguish two bands in the visible spectral region corresponding to the $S_0 \to S_1$ and $S_0 \to S_2$ transitions. In this case, for both compounds the most intense is the long-wavelength band (see Figs 1 and 2). According to the theory of chromophore interaction, this ratio of transition intensities corresponds to the obtuse angle between the chromophores. Since the energy splitting of bands for nonlinear dyes is a measure for the interaction of chromophores, a comparison of the splitting values of the bands $\Delta\nu$ for the pyranone and pyridone dyes confirms our earlier[5] conclusion based on the NMR spectroscopic data about the stronger interaction of the chromophores in compounds **1** and **3** than that in compounds **2** and **4**.

The electronic transitions and their intensities for the pyridone dye were calculated assuming an obtuse angle between the chromophores of the dye. The position and intensity of the bands in the calculated spectrum correlate well with the position and intensity of the Gaussian bands (see Table 1): the long-wavelength band is most intense, and the splitting values $\Delta\nu$ between the calculated and Gaussian bands are close. It is noteworthy that for compound **2** the positions of the calculated electronic transitions and Gaussian bands virtually coincide, although the calculation was performed ignoring the solvent effect. Perhaps, this is due to a weak dependence of the absorption spectra of compound **2** on the solvent nature (λ_{max} = 385, 389, and 395 nm in toluene, chloroform, and $\mathrm{Pr^iOH}$, respectively).

It should be mentioned that the calculated charge values on the carbon atoms of the polyene chain of the chromophores correlate with the chemical shifts of the ^{13}C NMR spectra: higher values of the chemical shifts correspond to greater positive charges. The charges on the corresponding polymethinic carbon atoms change proportionally to the chemical shifts (Table 2).

To confirm our conclusions about different spatial conformation of molecules **1** and **2**, we recorded their 2D ^{1}H NMR (gNOESY) spectra.

As follows from the presented gNOESY ^{1}H NMR spectra (Fig. 3), dye **1** has the conformation with an acute

Table 2. ^{13}C NMR spectra of dyes **1**, **2** (see Ref. 5), and **3** in $CDCl_3$ and the calculated charges on the polymethinic C atoms

Compound	δ (q/e)						
	C_δ	C_γ	C_β	C_α	C(2)	C(3)	C(4)
1	148.54	97.58	137.64	110.1	163.1	108.32	180.36
	(0.113)	(−0.122)	(−0.005)	(−0.081)	(0.192)	(−0.085)	(0.434)
2	147.7	97.6	139.0	111.4	151.9	110.0	177.4
	(0.112)	(−0.121)	(−0.005)	(−0.12)	(0.113)	(−0.08)	(0.433)
3	157.549	96.273	148.32	104.43	167.8	99.919	169.6
	(0.16)	(−0.137)	(0.047)	(−0.119)	(0.244)	(−0.097)	(0.282)

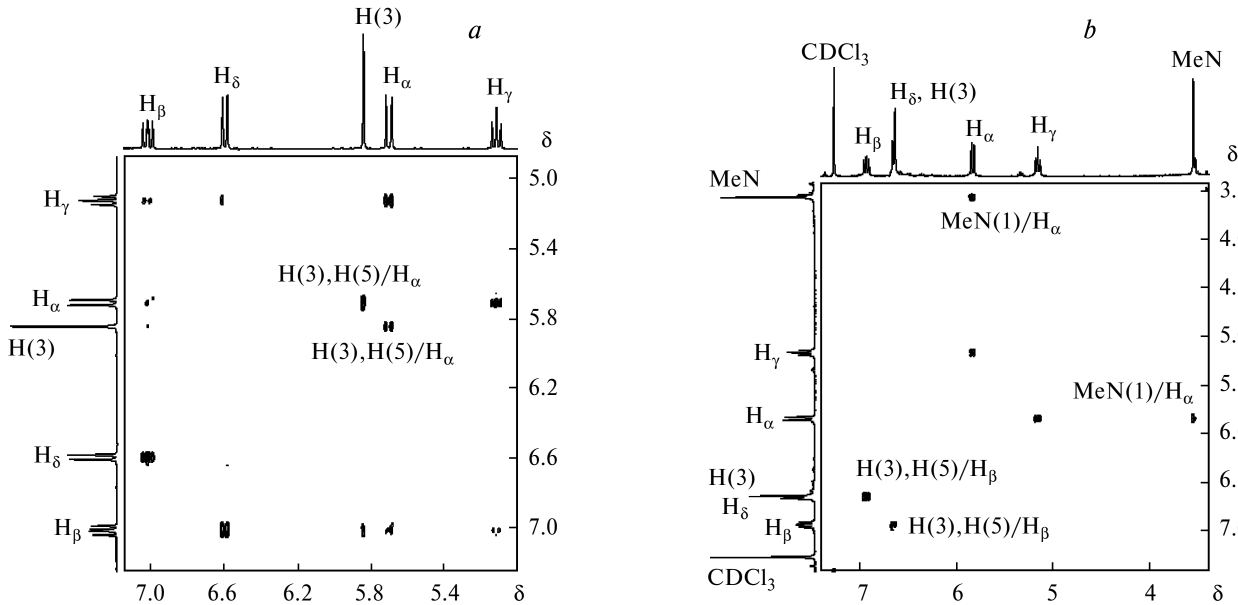
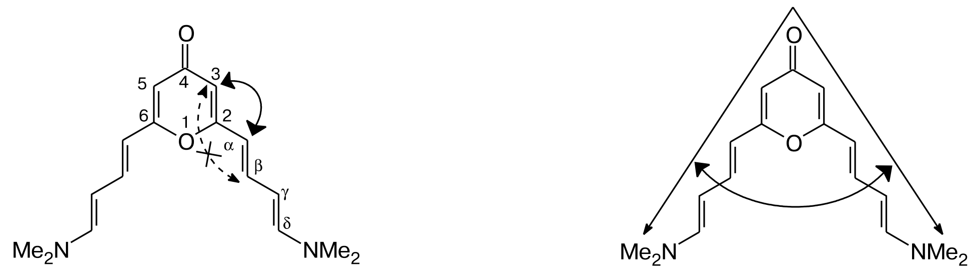


Fig. 3. Fragments of the 2D gNOESY spectra of dyes **1** (*a*) and **2** (*b*). The corresponding 1D spectra are placed along the vertical and horizontal axes.

angle between the chromophores (**1′**), because a correlation between the H(3)/H(5) and H$_\alpha$ protons is observed in the NOESY spectra and no correlation is observed between the H(3)/H(5) and H$_\beta$ protons (**A**). At the same time, for compound **2**, according to the obtuse angle between the halves of the molecule, the protons for the NMe group correlate with the H$_\alpha$ protons but not with the H$_\beta$ protons, whereas the H$_\beta$ protons correlate with the H(3)/H(5) protons. In addition, no correlation is observed between the H$_\alpha$ and H(3) protons (**B**).

The structure similar to compound **2** is typical, most likely, of salt **4** corresponding to this dye, because the spectral features of salt **4** are analogous to the properties of dye **2** (the long-wavelength absorption band is most intense) and, hence, an obtuse angle should also be between the chromophores of salt **4**. The difference in conformations of the dyes and salts with the pyranone and pyridone moieties is related, most likely, to steric hindrance created by the central Me group in the molecules of the latter.



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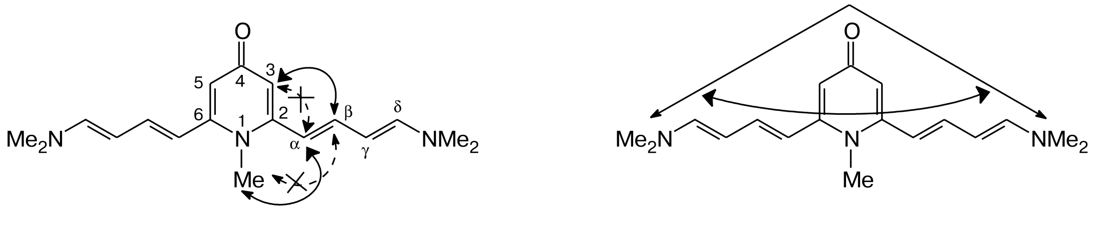

B

In summary, in the present work, the structures of the dyes with the pyranone moiety (**1** and **3**) proposed earlier were confirmed and the structures of the dyes with the central pyridone moiety (**2** and **4**) were determined. It was shown that the spatial conformation of the dyes with the pyranone and pyridone moieties differ dramatically despite similarity in structures: in compounds **1** and **3** the chromophores are arranged at the acute angle to each other, whereas in molecules **2** and **4** such chromophores are arranged at the obtuse angle.

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