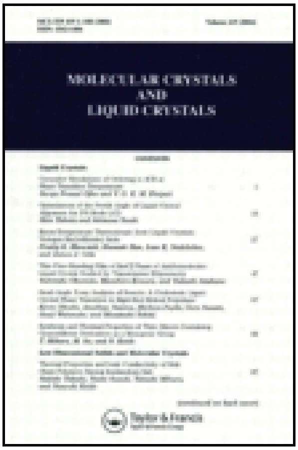

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Investigation of Conformational and Electron Properties of Biscyanine Dyes

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Investigation of Conformational and Electron Properties of Biscyanine Dyes

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The spectral and luminescent characteristics of four biscyanine dyes and corresponding monomer dye in ethanol solutions and in polyvinyl butyral have been investigated. The influence of angle between chromophores of biscyanine molecules on splitting and intensity of absorption bands has been discussed. It has been shown that the splitting of the biscyanine excited electron level S_1 is caused both dipole and resonant chromophor interactions. It has been found that the fluorescence quantum yields of the biscyanines in ethanol at room temperature are 0.005–0.02. The introduction of biscyanines in a polymer matrix, which provides rigidity of a polymethine chain, results in reduction of molecules trans-cis isomerization and consequently increase of fluorescence quantum yields.

Keywords: biscyanine dyes; covalently linked dimer; exciton splitting; fluorescence

INTRODUCTION

The investigation of photophysical processes in molecules of polymethine dyes is great an interest in connection with their wide use as photosensitizing dyes in photographic process, as laser media, in new means of information recording, and also in other areas [1].

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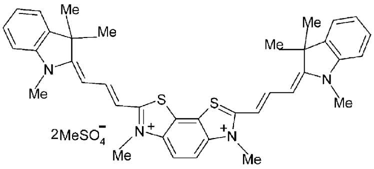
Biscyanine dyes are the class of polymethine dyes with two covalently linked chromophores. They are unique objects as one can purposefully control their spectral and luminescent characteristics by changing mutual chromophores position (angle and distance between them) in molecule [2,3].

In this paper we present the results of influence of chemically linked chromophores interaction on the position and intensity of absorption and luminescence bands and also deactivation of excited singlet states of the biscyanine dyes. The obtained results have been discussed on the basis of exciton model of molecular aggregates [4].

EXPERIMENTAL METHODS

In the paper the spectral and luminescent properties of four biscyanine dyes (1–4) and corresponding dye with one chromophore (monomer) (M) have been investigated. The biscyanines 1–4 are isomers and have two equal chromophores in their structure. Purified ethanol was used as a solvent, and polyvinyl butyral was selected as a



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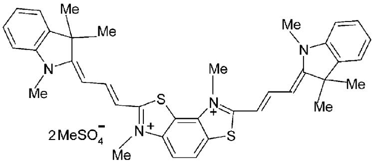

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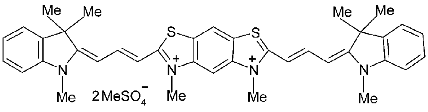

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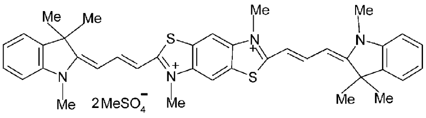

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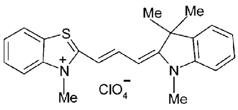

M

polymer matrix. Dye concentration in ethanol was 10^{-5} mol/l, in polyvinyl butyral – $5 \cdot 10^{-3}$ mol/l. Absorption and fluorescence spectra of samples were recorded using a KSVU-23 spectral universal setup equipped with a computer.

Fluorescence quantum yields (φ_f) were determined according to the method of Reference [5] using a water solutions of eosin ($\varphi_f = 0,16$) [5] and methylene blue ($\varphi_f = 0,01$) [6].

The quantum-chemical calculations of the biscyanines were performed by semiempirical method AM1 with standard parameters. The calculation was made taking into account the interaction of the singly excited configurations conditioned by all possible electronic transitions from five higher occupied molecular orbitals to five lower unoccupied molecular orbitals. Preliminarily, the molecular geometry optimization was made by AM1 with the use restricted Hartree-Fock method and Polak-Ribiere algorithm with accuracy 0.001 kkal/(A·mol). Also quantum-chemical calculations of the biscyanines were performed in approximation of Pariser-Parr-Pople with singly exited configuration interactions. The Komarov parameters were used in the calculations [7].

RESULTS AND DISCUSSION

The conformational analysis of the structure of the biscyanine molecules 1–4 and monomer molecule M was performed by method of molecular mechanics in force field MM2. On the basis of the analysis the distances d_{theor} and angles α_{theor} between chromophores were found (Table 1). From the table it is seen that the angle (α) between directions of polymethine chromophores of biscyanines (from one auxochrome to other) is varied from 90° in biscyanine 1 to 180° in biscyanine 4.

Absorption spectra of the dyes 1–4 in the ethanol were measured (Fig. 1). The position of the maximum of monomer M absorption band is marked with dotted line. One can see from Figure 1 that the absorption spectra of the biscyanines consist of two bands shifted to short- and long-wavelength regions with regard to monomer absorption band. The

TABLE 1 Geometrical Parameters of Biscyanine Molecules

Dye	d_{model}, nm	β_{model}, degree	α_{model}, degree	α_{exper}, degree
1	0.942	45	90	87
2	0.100	44	101	119
3	0.115	20	140	140
4	0.116	14	152	156

ratio of the intensities of these bands depends on the angle between chromophores of the bis-dyes. With increase of angle between chromophores of dyes 1–4 the intensity of short-wavelength absorption band increases, and the intensity of short-wavelength absorption band decreases (Fig. 1). In Table 2 wavelengths (λ_{max}) and extinction coefficients (ε_{max}) of maxima of short-wavelength (SW) and long-wavelength (LW) absorption bands of 1–4 and M dyes are shown.

One can explain the observed spectral properties of the biscyanines on the basis of exciton model of molecular aggregates [4].

According to this model the dimers have splitting of the excited S_1 level into two levels S_1' and S_1'' with higher and lower energies respectively (Fig. 2). Therefore chromophore interaction of the biscyanines causes in their absorption spectra two bands appearance: short-wavelength ($S_0 \rightarrow S_1'$) and long-wavelength ($S_0 \rightarrow S_1''$). The intensity of bands depends on the mutual orientation of chromophores transition moments. If the angle between transition moments is 0°, the short-wavelength transition is allowed, if the angle is 180°, the long-wavelength is allowed, in the case of intermediate values of angle ($0° < \alpha < 180°$) both transitions are allowed. When $\alpha = 90°$ the transitions $S_0 \rightarrow S_1'$ and $S_0 \rightarrow S_1''$ are equality probability and the absorption bands corresponding them have equal intensity [8].

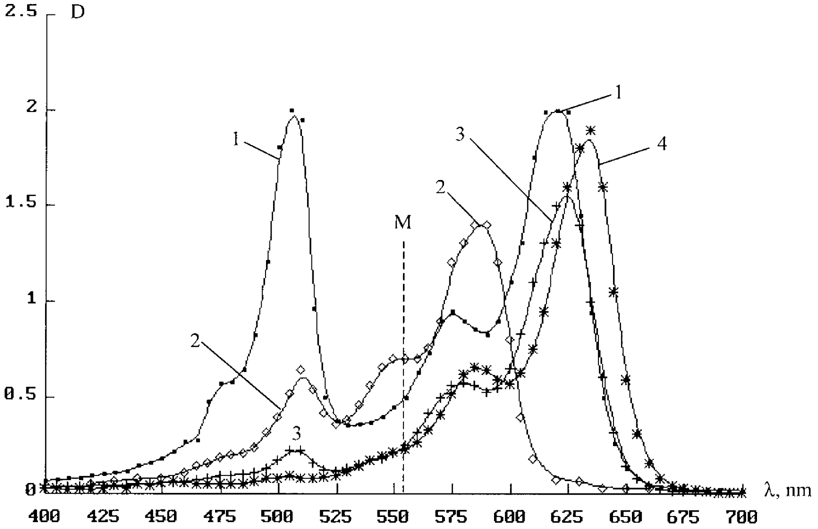

FIGURE 1 Absorption spectra of biscyanine dyes 1–4 in ethanol solutions ($C = 1{\cdot}10^{-5}$ mol/l).

TABLE 2 Parameters of Absorption and Fluorescence Spectra of Ethanol Solutions of Biscyanines 1–4 and Monomer dye M

	$\lambda_{max,}$ nm		$\varepsilon_{max} \times 10^{-4}$, $M^{-1}cm^{-1}$		f		$\Delta E_{exp,}$ cm^{-1}	θ	$\lambda^{fl}{}_{max,}$ nm	φ_{fl}	
Dye	SW	LW	SW	LW	SW	LW				SW	LW
M	554		–		1.44		–	–	583	0.004	
1	509	626	20	20	1.19	1.18	3672	270	643	0.002	0.005
2	516	596	6	14	0.13	1.68	2601	0	612	0.0025	0.007
3	510	629	2.2	16	0.03	2.09	3710	327	650	0.003	0.009
4	508	639	0.9	19	3.10^{-6}	2.28	4036	413	658	0.007	0.02

For the investigated dyes the transition moments lie in the plane of chromophores and are oriented along their long axis [9]. Therefore the probabilities of electron transitions from S_0 ground nonexcited singlet state to S_1' or S_1'' excited states of dimers are the functions of angle α between chromophores. Dipole moments of electron transitions of short- (μ_{SW}) and long-wave (μ_{lW}) absorption bands is connected with angle α, formed by chromophore in the dimer, by Eq. (1) [10]:

$$\frac{\mu_{SW}}{\mu_{1W}} = \frac{1 + \cos\alpha}{1 - \cos\alpha}, \tag{1}$$

where

$$|\mu|^2 = 1,09 \cdot 10^{-19} \int \varepsilon(\nu) d\nu \tag{2}$$

$\varepsilon(\nu)$ – absorption spectrum of corresponding band.

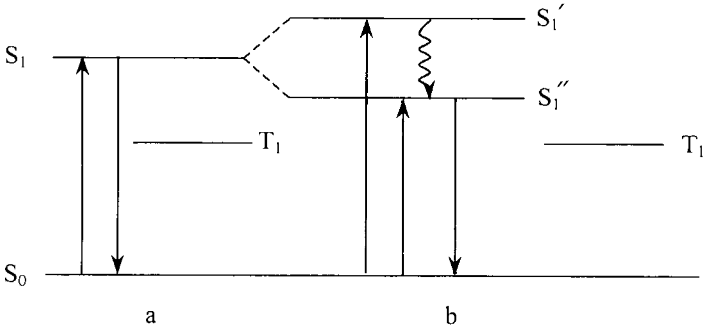

FIGURE 2 Scheme of energy levels of molecules with one (a) and two (b) chromophores.

Oscillator strength (f) is connected with transition moment (μ) in the following way (equation (3)):

$$f = \frac{8\pi^2 m_e c\nu |\vec{\mu}|^2}{3he^2} \tag{3}$$

where ν- frequency in cm^{-1}, m_e, e – electron mass and charge.

The values of the angles α_{exper} and f, obtained on the basis of experimental results and Eq. (1) – (3) are given in Tables 1 and 2.

The value of exciton splitting ΔE determines the degree of chromophores interaction in a molecule. According to exciton model of molecular aggregates in a point dipole approximation ΔE is determined by following expression [10]:

$$\Delta E = \frac{2|\vec{\mu}|^2}{d^3}(\cos\alpha + 3\cos\beta_1\cos\beta_2) \tag{4}$$

where $\vec{\mu}$ – transition dipole moment of chromophore, d–the distance between chromophores centres, α – angle between chromophores, β_1 and β_2 – angles between chromophores directions and segment d (for symmetrical biscyanines 1–4 $\beta_1 = \beta_2 = \beta$). By formula (4) the ΔE values for biscyanines 1–4 were calculated, the necessary geometrical parameters were obtained from conformational analysis of molecular structure in strength field MM2 (Table 1). It was proven that the ΔE value in the sequence of dyes 1–4 should increase. However, experimental values ΔE_{exper}, obtained as distance between short-wave and long-wave maxima of biscyanines absorption spectrum bands do not correspond to exciton model (Table 2). In the work [11] along with dipole (exciton) interaction the resonant interaction between chromophores of bis-dyes is taken into consideration. The value of resonant interaction depends on the structure of the central core linking chromophores. The resulting splitting is determined by both kinds of interactions. For the characteristic of resonant interaction the value θ can be used, which is determined as follows [11]:

$$\theta = \Delta E_{mid1} - \Delta E_{mid2}, \tag{5}$$

where $\Delta E_{mid} = (\nu_{sw} + \nu_{lw})/2$ (ν – frequency of absorption band maximum in cm^{-1}), and the indexes 1 and 2 relate to two dyes. If $\theta > 0$, the resonant interaction for dye 2 is larger than for dye 1, and the more θ, the stronger this difference is. In the table 2 the values θ for biscyanines 1–4 are given. θ with least ΔE (dye 2) is selected as zero. Table 2 shows that in the series of compounds 2, 1, 3, 4 resonant interaction increases.

From the quantum-chemical calculation by AM1 method it is seen that though the absolute values of absorption maxima and oscillator strengths of biscyanines 1–4 differ essentially from the corresponding experimental values they qualitatively correctly transmit the tendencies in their change at chromophore interaction (Table 3). For example, for all biscyanines the calculation forecasts appearance of two new absorption bands–short-wavelength and long-wavelength in comparison with band of monomer dye M. Distance between them, as well as in experiment, increases in the sequence of biscyanines 2, 1, 3, 4. Moreover, their absolute values are close to experimental. The calculation also forecasts oscillator strength decrease of short-wavelength band and its increase for long-wavelength one in the sequence of biscyanines 1–4. The increase of configurations number in calculation increases numerical values of absorption maxima. The similar effect is achieved at the use of molecule geometry optimized by Hartree-Fock unrestricted method. Using such approximations it is possible to achieve good coincidence of numerical values of theoretical and experimental absorption maxima. However, it was not the purpose of the present paper.

The calculation performed with Pariser-Parr-Pople method, also qualitatively correctly forecasts spectral regularities observed for biscyanines 1–4 (Table 3). However, absolute values of wavelengths, oscillator strengths, values of exited electronic levels splitting, which calculation by Pariser-Parr-Pople method gives, differ even more from experimental ones in comparison with data calculated with AM1 method. The considerable discrepancy of spectral characteristics is caused by insufficient number of the configurations considered in calculation.

TABLE 3 Results of Quantum-Chemical Calculations by AM1 and PPP Methods

	AM1 λ_{max}, nm		AM1 f		PPP λ_{max}, nm		PPP f		AM1 ΔE_{exper}, cm^{-1}	AM1 ΔE_{theor}, cm^{-1}
Dye	SW	LW	SW	LW	SW	LW	SW	LW		
M	513		1.431		411		1.865		–	–
1	448	535	1.069	1.603	383	469	1.959	1.634	3629	4788
2	456	525	0.595	1.949	394	435	0.922	2.702	2863	2392
3	449	539	0.055	2.388	387	438	0.480	3.230	3733	3009
4	442	541	0.000	2.490	379	469	0.010	3.249	4140	5063

In fluorescence spectra of biscyanines 1–4 at excitation in short-wavelength and long-wavelength absorption bands it is observed only one band with small shoulder (Table 2), which corresponds to long-wavelength electron transition $S_1^{'}\rightarrow S_0$. It testifies that fast nonradiative relaxation from higher to lower sublevel of splitted dimer exited state takes place. The shoulder on fluorescence band has vibrational structure. The values of fluorescence quantum yields (φ_{fl}) of biscyanine dyes at excitation in short-wavelength absorption band are on average in 2.5–3 times are less than at excitation in long-wavelength band (Table 2). It is a consequence of nonradiative losses due to internal conversion $S_1' \rightarrow S_1''$. The tendencies in change of φ_{fl} do not depend on excitation wavelength.

Polymethine chains of biscyanine dyes 1–4 are not rigid. Therefore take place processes of trans–cis isomerization. It causes very low fluorescence quantum yields of the dyes (≤ 0.02). The increase of φ_{fl} at increase of angle between chromophores in the sequence of compounds 1–4 (Table 2) is connected with the probability of electronic transition $S_0\rightarrow S_1^{''}$ increases according to exciton model and experimentally observed results (see f in the Table 2).

To increase φ_{fl} of biscyanines one can put them, for example, in polymer matrix, which provides sufficient rigidity of molecules to reduce the polymethine chain isomerization. Therefore in the present work the spectral and luminescent properties of biscyanines in polyvinyl butyral were investigated. The maxima of the absorption bands in polymer matrix are shifted to the long-wavelength range on average on 2–7 nm in comparison with ethanol solutions (Table 4). It is connected with larger value of polymer refraction index than of alcohol. Therefore dispersion interaction in polyvinyl butyral amplify. The form of spectra does not vary even when the dye concentration in polyvinyl butyral is $5{\cdot}10^{-3}$ mol/l. This suggests to absence aggregation of the dye molecules. It is well known [9], that in solutions of low-polarity (in particular in polymers) cyanine dyes effectively form associates, which results in distortion and deterioration of their spectral and fluorescent properties.

The absence of aggregation processes of biscyanines in polyvinyl butyral is probably caused by cation dyes (1–4) undergoing to nucleophilic solvation as the polyvinyl butyral contains strongly nucleophilic groups [9]. Fluorescence spectra of coloured polymer films like ethanol solutions consist of one band and do not depend on a wavelength of exciting radiation. However, as it was expected, in polyvinyl butyral the increase of fluorescence quantum yield of biscyanines takes place in comparison with their ethanol solutions (Table 4). Temperature decrease to 77 K results to small increase of fluorescence intensity in

TABLE 4 Parameters of Absorption and Fluorescence Spectra of Biscyanines 1–4 in Polyvinyl Butyral

	$\lambda_{\max}$, nm			
Dye	SW	LW	$\lambda^{\mathrm{fl}}{}_{\max}$, nm	φ_{fl}
1	514	633	660	0.063
2	518	598	620	0.065
3	518	634	670	0.070
4	510	646	680	0.131

polymers. Thus, polymer matrix reduces processes of polymethine chain isomerization much more than the temperature decrease. Temperature decreases practically does not influence on the given process. Therefore nonradiative deactivation of biscyanines exited electronic state in polymer matrixes is mainly caused by processes of internal conversion and intersystem crossing.

CONCLUSION

Thus, for biscyanine dyes 1–4 the value of S_1 electronic level splitting is caused by dipole – dipole and resonant interactions. In biscyanines fluorescence spectra in contrast to the absorption spectra only one long-wavelength band at excitation both in short-, and long-wavelength absorption bands is present. In polyvinyl butyral the values fluorescence quantum yields of biscyanines increase in comparison with their ethanol solutions due to decrease of trans–cis isomerization processes.

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