

Investigation of photophysical processes in biscyanine dyes

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Results of investigation of influence of the four-biscyanine dyes chromophore interaction on triplet states and basic characteristics of the long-time luminescence are presented. The values of quantum yields of intercombination conversion $S_1 \sim \rightarrow T_1$ for two biscyanines were determined by the pulse photolysis method. Based on the long-time luminescence spectra and kinetics measurements, the coefficients characterizing the efficiency of formation of triplet states of four biscyanine dyes were determined. It was found that increase of the S_1 electronic level splitting of biscyanines conditioned by the efficiency of chromophore interaction results in a decrease in the singlet–triplet splitting and, as a consequence, in increase of intercombination conversion quantum yield.

It is known that the polymethines free of heavy atoms and containing no substituents in the polymethine chain, have low values of fluorescence quantum yields and intercombination conversion (ICC), that is mainly conditioned by photoisomerization processes.¹ At the same time, in biscyanine dyes, being the polymethine dyes with two covalently connected chromophores, a splitting of the S -level proceeds due to the chromophore interaction followed by energy gap reduction between the lower split S and T levels. This leads to increase in the ICC quantum yield.^{2–5} Besides, the biscyanine dyes have more rigid structure, characteristic of dimers, in comparison with the initial monomeric dye, which also favors the quantum yield increase.

In Refs. 6 and 7 we reported the studies of spectral-luminescent properties of four new biscyanine dyes I–IV synthesized on the basis of the dimethylbenzobistiozols, which are the polymethine dyes with two equivalent chromophores. The given dyes differ in the angle between the chromophores and the degree of their conjugation (Fig. 1).

It has been established that a change in the above characteristics leads to regular changes in the biscyanine spectral-luminescent properties. In particular, the increase in degree of conjugation between the chromophores results in the spectrally observable increase in splitting of the excited singlet level S_1 , the maximum value of which belongs to dye IV (Ref. 6). With changing angle between the chromophores, the

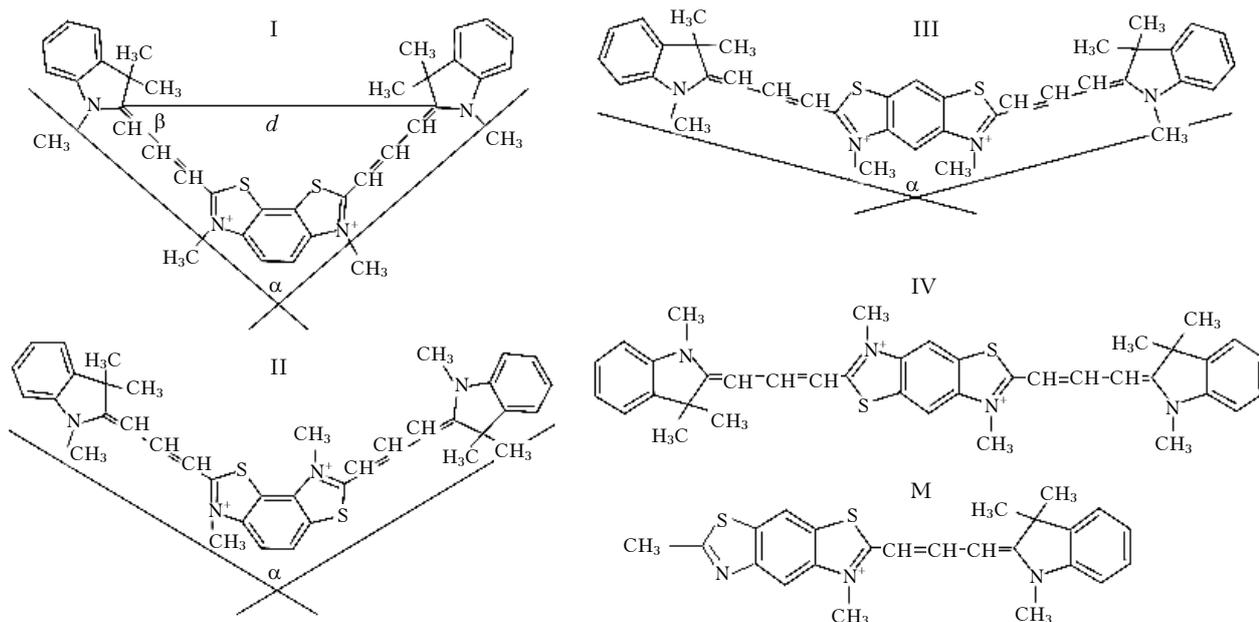


Fig. 1. Structural formulas of the biscyanine molecules I–IV and the corresponding parent dye M.

intensity ratios between the short-wave and long-wave absorption bands, as well as quantum yields of the biscyanine fluorescence change regularly, that can be qualitatively well explained based on the exciton model of the molecular aggregates.⁸ On the base of the given biscyanine properties it is possible to generate the nanostructures with predetermined spectral and luminescent characteristics.

This paper presents the investigation results on the influence of I–IV biscyanine chromophore interaction on their triplet states and basic characteristics of the long-time luminescence. Spectral-luminescence properties of biscyanines were investigated in ethanol solutions with a dye concentration of $1 \cdot 10^{-5}$ mol/l.

To measure fluorescence and absorption spectra, the spectral computer complex KSVU-23 was used. The quantum fluorescence yield ϕ_{fl} was determined by the relative method.⁹ At ϕ_{fl} determination, the eosine aqueous solution was used as a reference [$\phi_{fl} = 0.16$ (Ref. 9)]. The triplet states were studied on the pulse photolysis setup. Photoexcitation of dyes was carried out via the light filter ZS-1. The flash time was equal to 10^{-5} s. Before the measurements, the solutions were degassed up to a residual pressure of 10^{-4} mm Hg. The ICC quantum yields for the dyes III and IV were determined by the Medinger and Wilkinson method.¹⁰ As a suppressor of fast fluorescence, the ethyl iodide (C_2H_5I) was chosen, the concentration of which in the ethanol solutions of the dye III changed between 0.0125 and 0.05 mol/l, and of the dye IV – between 0.5 and 1.5 mol/l.

Figure 2 presents the scheme of molecular energy levels with one and two chromophores. It was shown in Ref. 6 that the magnitude of the splitting $\Delta E_{S_1' S_1'}$ of the biscyanine dyes I–IV S_1 -level is determined by the dipole–dipole (exciton) and resonant interaction of chromophores⁶ and increases in a series of dyes II, I, III, IV. At the same time, energies of triplet levels T_1 of physical and chemical dimers differ insignificantly from energies of monomer levels.^{3,11,12} Therefore, for the same biscyanine series, the difference of energies between the triplet and lower singlet sublevels decreases, which should lead to a corresponding increase in quantum yields of ICC dyes. To check this assumption, triplet states of the dyes I–IV were investigated.

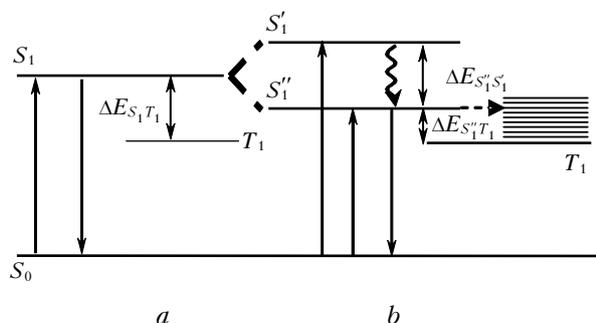


Fig. 2. The scheme of molecular energy levels with one (a) and two (b) chromophores.

Consider the investigation results by the example of dyes III and IV. In the first series of the experiments, spectra of triplet–triplet (T – T) absorption of biscyanines III and IV were measured. The obtained curves were rather wide and structureless. The wavelengths (λ_{max}^{T-T}) of spectra maxima are presented in Table 1.

Table 1. Spectral characteristics of ethanol solutions of the biscyanines III and IV

Dye	λ_{max}^{T-T} , nm	τ_T , ms		ϕ_{ICC}	$\Delta E_{S_1' S_1}$, cm^{-1} (experiment)	$\Delta E_{S_1' T_1}$, cm^{-1} (computation)
		start	end			
III	670	1.5	3.7	0.13	3710	8328
IV	680	1.4	7.3	0.27	4036	6804

As is known, the decay kinetics of the T – T luminophore absorption under conditions of monomolecular decomposition is described by the exponential function⁹

$$D^T(t) \sim D^T(0)\exp(-t/\tau), \quad (1)$$

where $D^T(t)$, $D^T(0)$ are the optical densities of the T – T absorption in the moment of observation time t and initial moment ($t = 0$ s), respectively; τ is the lifetime of the triplet state.

The decay kinetics of the T – T absorption for the dyes III and IV is not exponential through the entire observation time (Fig. 3).

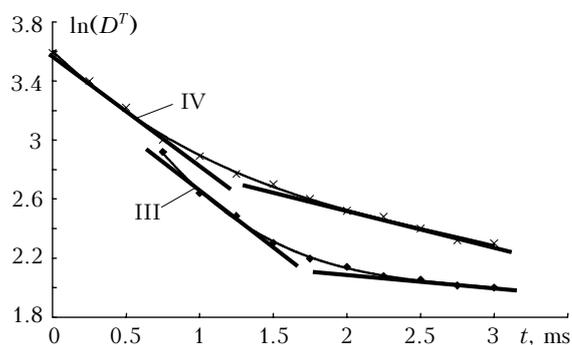


Fig. 3. Time dependence of decay intensity logarithm of the T – T absorption for dyes III and IV.

The logarithmic dependence $\ln(D^T)$ consists of two linear parts, which can be conditioned by formation of additional absorption centers due to decomposition of dye molecules. The obtained lifetimes of triplet states τ_T of biscyanines III and IV are presented in Table 1.

It is well known that if some compound, containing heavy atoms, is added to the luminophore, then the luminophore quantum yield ϕ_{ICC} increases owing to amplification of the spin–orbit interaction in the molecules, while the quantum yield ϕ_{fl} correspondingly decreases. The connection between two these processes can be presented quantitatively by the following relation¹⁰

$$\phi_{fl}^0 / \phi_{fl} = \phi_{ICC}^0 (\phi_{fl}^0 / \phi_{fl} \cdot D^T / D_0^T - 1) + 1, \quad (2)$$

where ϕ_{fl}^0 and D_0^T are the fluorescence quantum yield and the optical density of the T – T absorption in the absence of heavy atoms, respectively.

In the process of constructing the dependence of ϕ_{fl}^0/ϕ_{fl} on $(\phi_{fl}^0/\phi_{fl} \cdot D^T/D_0^T - 1)$ for dyes III and IV, the experimental straight lines were obtained, tangent of the angle of which equaled to ϕ_{ICC} , i.e., to the absolute ICC quantum yield in an unperturbed molecule. The obtained values of ϕ_{ICC} (see Table 1) are in agreement with assumption about the chromophore interaction influence on the efficiency of the biscyanine triplet generation, i.e., the dye IV with a greater $\Delta E_{S_1^*T_1}$ as compared to the dye III (see Table 1), has the ϕ_{ICC} magnitude also exceeding the corresponding magnitude for biscyanine III. It is interesting that the ϕ_{ICC} values for the dyes III and IV obtained by the pulse photolysis method, are close to those determined in Ref. 13 for the same dyes by the nonlinear fluorimetry method. In this work, we have carried out the quantum-chemical computations of electronic structure for molecules III and IV in approximation of Parisier–Parr–Pople (Ref. 14). The energy difference ($\Delta E_{S_1^*T_1}$) of S_1^* , T_1 levels for the dye III exceeds $\Delta E_{S_1^*T_1}$ of the dye IV (see Table 1), that corresponds to the scheme in Fig. 2 as well.

At pulsed irradiation of the deoxygenated dye solutions I–IV, we have registered a moderate fluorescence (MF), the spectrum of which coincided with the spectrum of usual dye fluorescence. A fall in temperature led to the MF intensity reduction. Decay times τ_{MF} of dyes III and IV, obtained from the kinetic measurements, coincided within the error limits with initial times of the T – T -absorption kinetics decay (Tables 1 and 2).

Table 2. Spectral characteristics of ethanol solutions of the biscyanines I–IV

Dye	τ_{MF} , ms	k	$\Delta E_{S_1^*T_1}$, cm ⁻¹ (experiment)	$\Delta E_{S_1^*T_1}$, cm ⁻¹ (computation)
I	1.1	5.7	3672	7192
II	1.0	2.1	2601	8472
III	1.4	84.4	3710	8328
IV	1.3	126.7	4036	6804

It has been assumed that the MF has a thermoactivation character and refers to the E type (Ref. 9). The kinetics of the biscyanines I–IV MF decay is exponential all over the time domain. The decay times of the biscyanine MF are presented in Table 2. When comparing the kinetic curves of the T – T absorption and MF signals, it is possible to suppose that the long-time part of the biscyanine III and IV T – T absorption kinetics is stipulated by their decomposition products, which are not characterized by a long-time fluorescence.

Based on measurements of the dye MF, it is possible to determine the coefficients proportional to their ICC quantum yields. The MF intensity I_{MF} is proportional to the fast fluorescence quantum yield

(ϕ_{FF}), the absorbed radiation intensity (I_{abs}), the ICC quantum yield (ϕ_{ICC}), the rate constant ($k_{T_1S_1^*}$) inverse to ICC ($S_1 \leftarrow \sim T_1$), and the exponential dependence on $\Delta E_{S_1^*T_1}$ (Ref. 9)

$$I_{MF} \sim \phi_{FF} I_{abs} \phi_{ICC} k_{T_1S_1^*} \exp(-\Delta E_{S_1^*T_1}/RT), \quad (3)$$

where R is the universal gas constant; T is the absolute temperature.

Division of I_{MF} by $\phi_{FF} \cdot I_{abs}$ yields the k value, proportional to $\phi_{ICC} k_{T_1S_1^*} \exp(-\Delta E_{S_1^*T_1}/RT)$. The values of ϕ_{ICC} and $k_{T_1S_1^*}$ have equal tendency to variation. An increase in $\Delta E_{S_1^*T_1}$ leads to reduction of $\exp(-\Delta E_{S_1^*T_1}/RT)$. At the same time, the ICC quantum yields also decrease. And, on the contrary, the reduction of $\Delta E_{S_1^*T_1}$ leads to the increase in $\exp(-\Delta E_{S_1^*T_1}/RT)$ and ICC quantum yields. Thus, the coefficient k , equal to $I_{MF}/(\phi_{FF} I_{abs})$, changes monotonically with changing ϕ_{ICC} .

The MF intensity was determined as the sum of areas under kinetic decay curves of the entire MF spectral range. The quantum yield of the fast fluorescence, as it was noted earlier, was determined by the relative method. Radiation intensity absorbed by the dye was determined taking into account the spectral distribution of the flash lamp, spectral characteristic of the optical light filter, and absorption spectrum of the dye. The computed k values and the values of S_1 -level splitting for biscyanine dyes, as well as computed $\Delta E_{S_1^*T_1}$ values, describing the energy difference between the lower singlet and triplet states, are given in Table 2. As is seen, with $\Delta E_{S_1^*T_1}$ increase k increases and $\Delta E_{S_1^*T_1}$ decreases.

Generalization of the obtained data allows a conclusion that the spectral-luminescent properties of the biscyanine dyes I–IV are determined by their spatial structure. The chromophore interaction efficiency depending on the angle between chromophores and the degree of their conjugation, determines the fluorescence quantum yields for biscyanine molecules, the efficiency of their transition into the triplet state, and the MF intensity. Increase in splitting of the biscyanine electronic level S_1 , conditioned by the chromophore interaction, leads to reduction of the singlet–triplet splitting $\Delta E_{S_1^*T_1}$ and, as a consequence, to increase in the ICC quantum yield.

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