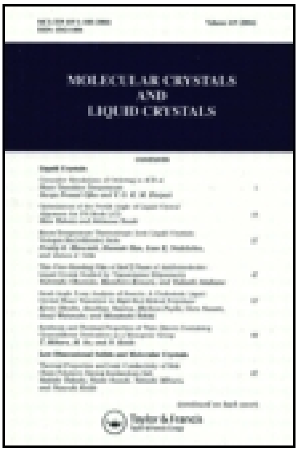

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The Investigation of Relaxation Paths in Dioxaborine Anionic Polymethine Dyes Detected by Low-Temperature Time-Resolved Fluorescence

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The Investigation of Relaxation Paths in Dioxaborine Anionic Polymethine Dyes Detected by Low-Temperature Time-Resolved Fluorescence

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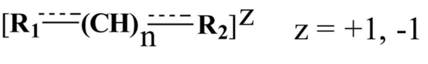
The simultaneous quantum-chemical and spectral investigation of two anionic polymethine dyes derivatives of dioxaborine was carried out. It is shown that there are two paths of relaxation in the excited state: a) cyanine-like path with equalizing the bond lengths and a symmetric charge distribution; b) polyenic path with the considerable bond length alternation and the symmetry breaking in a charge distribution. This assumption is confirmed by the existence of two components in the time-resolved fluorescence spectra measured at low temperatures.

Keywords Charge wave; excited state; low-temperature time-resolved fluorescence; polymethine dyes; quantum-chemical calculation

Introduction

According to the current views [1], the charge (electron or hole) injected to the highly polarized collective system of π-electrons of the ions of linear conjugated molecules **1** is not located



$$\overset{\pi\text{-electrons}}{[R_1 \text{- - -} (CH)_n \text{- - -} R_2]^Z} \quad z = +1, -1$$

Address correspondence to Svitlana V. Vasylyuk, Taras Shevchenko National University of Kyiv, 64, Volodymyrska Str., Kyiv 01680, Ukraine. Tel.: (0038044) 5262445; Fax: (0038044) 5264036; E-mail: bladewalker@ukr.net at any atom or delocalized uniformly over the whole π-system, but is self-localized in the form of a charge wave, i.e., as a kink or soliton (see, for example, reviews [1–3] and references therein).

The quantum-chemical calculations have shown that a charge wave has finite length, approximately 15–17 carbon-carbon bonds ($\approx$25 Å). Simultaneously with a charge wave, a solitonic-like wave of alternating bond lengths is generated. It is the so-called geometrical or topological soliton. The locations of charge and bond length waves in the equilibrium ground state coincide.

According to the definition of soliton as a lone self-located wave, its shape does not depend on the length of a conjugated chain, which is confirmed by quantum-chemical studies [3].

When the length of molecules **1** exceeds the dimension of the solitonic wave, the soliton becomes mobile and can move along the conjugated chain without change of the total energy of the molecule.

Since the speed of solitonic waves (by A.S. Davydov) is approximately $\approx$1 km/s, the time needed for a soliton to pass a whole typical linear system (polymethine chain or polyenes) is 5–10 ps.

It is worth noting that the optimization of a molecular geometry of symmetric molecules by any quantum-chemical method results in that the centers of the charge and topological waves are located at the center of a polymethine chain.

The movement of solitonic waves can be caused by the introduction of terminal groups, for example, into the symmetric cationic polymethine dyes (**1**, $R_1 = R_2$, $n = 2m+1$) with a comparatively long chromophore which absorbs in the near-IR spectral region. It was previously shown [3–5] that the movement of solitonic waves in the cyanine dyes with terminal groups can lead to the breaking of symmetries of the electron density distribution and the equilibrium molecular geometry.

The symmetry breaking results in a drastical broadening of the near-IR absorption bands for dyes, which can be explained by the co-existence of two molecular forms with symmetric and asymmetric charge distributions in the ground state.

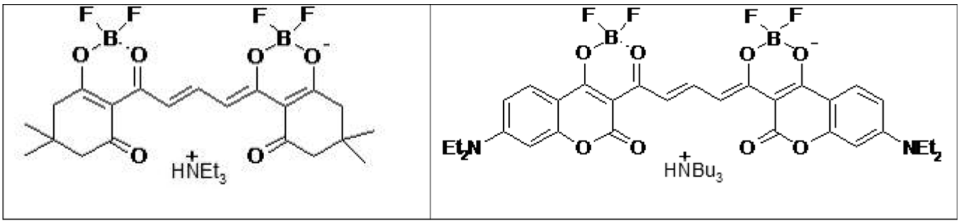
The similar movement of a charge wave in the chromophore of a polymethine chain was found also in its excited state. In this case, the dimension of a solitonic wave becomes smaller, and therefore, the symmetry breaking effect can occur at the shorter polymethine chain. This fact was confirmed experimentally by measuring the low-temperature time-resolved fluorescence: two components with different lifetimes were observed in the spectra of cationic thiacarbocyanines [6]. Basing on the spectral and quantum-chemical investigations, it was assumed that the relaxation in the excited state can leads to two forms of the dye molecules: with the symmetric and asymmetric charge distributions.

This paper presents the results of the combined quantum-chemical and experimental investigation of the relaxation of a molecular geometry and a charge distribution in the first excited state of anionic polymethine dyes – analogs of the cationic dyes with the same length of a polymethine chain, but with the opposite total charge in the collective π-electron system.

Objects and Methodology

The dyes under study are as follows (Scheme 1):

Synthetic procedure for the compounds **2–3** was described earlier: [7,8].



2 (ZK-280) **3** (G-37)

Scheme 1. Anionic dioxaborine dyes **2** and **3**.

UV-Vis absorption spectra were recorded on a Shimadzu UV-3100 spectrophotometer in CH_2Cl_2, acetonitryle, DMSO (spectral grade).

Types of spectra are presented in Figure 1.

Fluorescence spectra. Researches have been performed at temperatures 295 and 77 K. To excite PL, we used the radiation of a nitrogen laser ($\lambda_e = 337.1$ nm, exciting pulse time $t_I = 9$ ns, peak power $N = 5$ kW, pulse repetition frequency $f = 100$ Hz), the fundamental harmonic of a Nd:YAG laser ($\lambda_e = 1064$ nm, $t_I = 10$ ns, $N = 0.05$–1.00 MW, $f = 50$ Hz), and the second harmonic of a Nd:YAG laser ($\lambda_e = 532$ nm, $N = 0.1$–0.5 MW, $f = 50$ Hz). The time-resolved PL spectra at one- and two photon excitations were recorded with a stroboscopic system [15], in which the investigated signal from a photodetector through a delay line was supplied onto the stroboscopic oscilloscope connected with a computer.

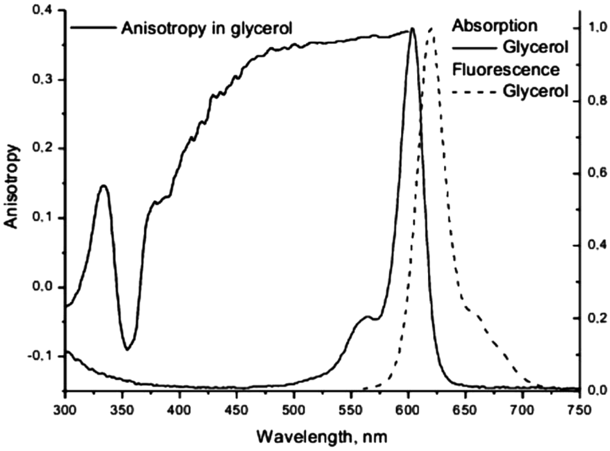
The measurement technique allowed us to register the shapes of PL pulses and the laser radiation reflected from the investigated sample at an identical optical way. From the analysis of the convolution of these signals, it was possible to define the PL lifetime. The time resolution of the system was about 0.1 ns for determining the PL lifetime and 0.7 ns for measuring the PL spectra. To record the PL spectra, we used an MDR-12 monochromator. The spectral slit width for measuring the PL spectra was 0.2–0.4 mm. The spectral setup was used to record the spectra of absorption, reflection, *R*, and PL excitation. The used spectral setup allowed us also to perform the researches of PL spectra, absorption and reflection in a wide interval of temperatures 4.2–300 K. The spectra are presented in Figures 1 and 2.

Fluorescence Excitation Anisotropy Spectra

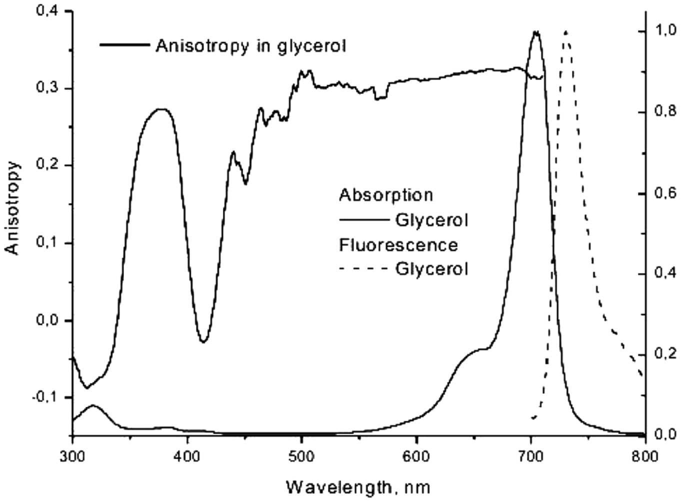
Excitation anisotropy measurements are performed using a CM 2203 spectrofluorimeter (Solar, Belarus) in glycerol solutions to reduce the rotational reorientation and at low concentrations ($C \approx 10^{-6}$ M) to avoid the re-absorption of fluorescence. The anisotropy calculated by the formula $r(\lambda) = \frac{I_{II}(\lambda) - G \times I_{\perp}(\lambda)}{I_{II}(\lambda) + G \times 2 \times I_{\perp}(\lambda)}$ is measured by setting the emission wavelength, typically near the fluorescence maximum, with a fixed polarization. Then, the fluorescence intensity is recorded as a function of the excitation wavelength λat the polarizations parallel ($I_{II}(\lambda)$) and perpendicular ($I_{\perp}(\lambda)$) to the emission polarization. A *G*-factor expresses the sensitivity ratio of the detection system for light which was polarized perpendicularly and in parallel.

The measured spectra of dyes **2** and **3** in the UV and visible regions are shown in Figure 1 and Figure 2(a,b,c).

The quantum-chemical calculations of dyes **2** and **3** in both the ground and excited states were performed by the same AM1 semi-empirical method (package



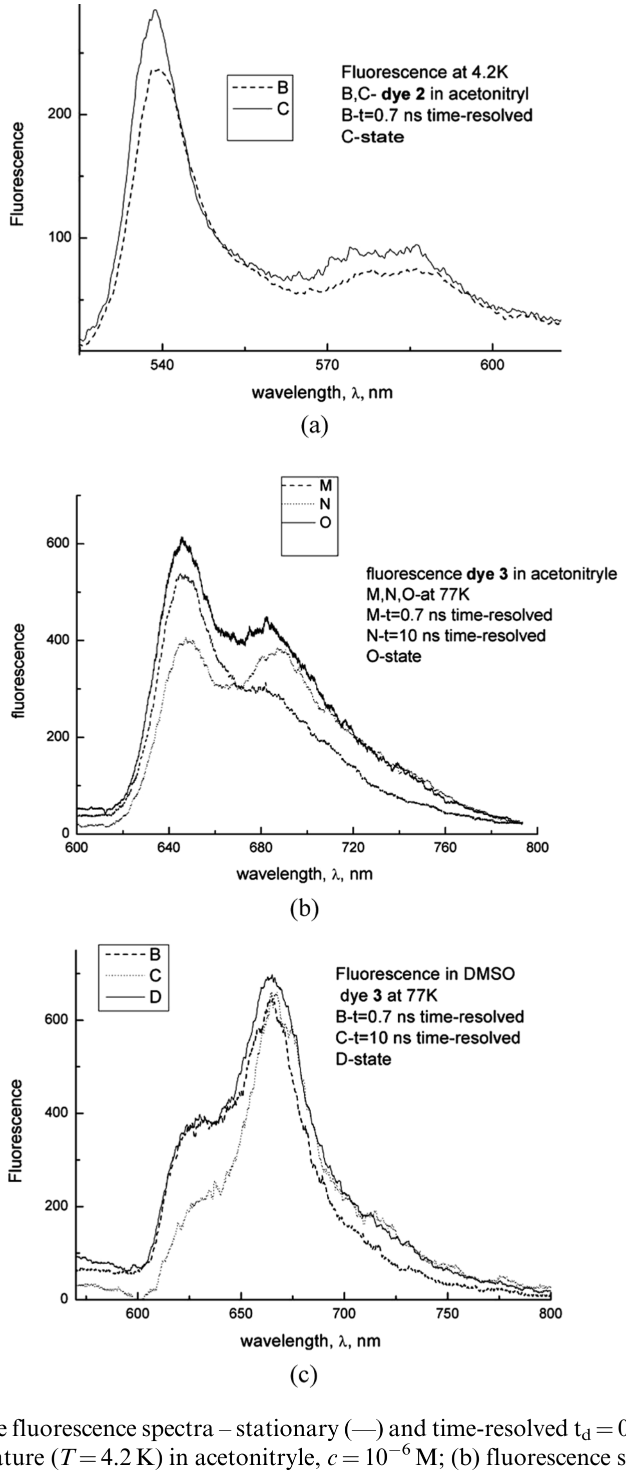
(a)



(b)

Figure 1. The absorption spectra (—), fluorescence (---), fluorescence excitation anisotropy (—) at room temperature (a – dye **2**, b – dye **3**), $c = 10^{-6}$ M.

HyperChem). It was shown earlier that the charge distributions and bond lengths in the polymethine dyes obtained by the semi-empirical AM1 method and the non-empirical *ab initio* method are close and give the same regularities in the movement of solitonic waves [3]. For the excited state, the traditional ZINDO/S method cannot be used, because this approximation does not provide the parameterization for a boron atom. The procedure of the optimization was stopped at an energy gradient of 0.01 kcal/mol. The characteristics of the electronic transitions were calculated using 25 single excited configurations. Of course, there is a substantial divergence between the calculated and experimental wavelengths of the electronic transitions, but the central goal of our work was to establish the nature of the first and higher transitions in dyes **2** and **3** and, hence, to explain correctly the observed phenomena in their fluorescence spectra.



(a)

(b)

(c)

Figure 2. (a) The fluorescence spectra – stationary (—) and time-resolved $t_d = 0,7$ ns (- - -) of dye **2** at low temperature ($T = 4.2$ K) in acetonitryle, $c = 10^{-6}$ M; (b) fluorescence spectra – stationary (—), time-resolved (- - -) $t_d = 0.7$ ns and (●●●●) $t_d = 10$ ns of dye **3** at a low temperature ($T = 77$ K) in acetonitryle, $c = 10^{-6}$ M; (c) fluorescence spectra – stationary (—), time-resolved (- - -) $t_d = 0.7$ ns and (····) $t_d = 10$ ns of dye **3** at a low temperature ($T = 77$ K) in DMSO, $c = 10^{-6}$ M.

Results and Discussion

The absorption spectra of the solutions of both investigated compounds are presented in Figure. 1a. One can see, first at all, the typical high intensive and narrow selective spectral band which corresponds to the lowest electronic transition: $\mathbf{S_0} \rightarrow \mathbf{S_1}$. On the short-wave shoulder of this band, the local peak appears. It is connected with the vibronic transition $0 \rightarrow 1'$, not the next electron transition. The fluorescence excitation anisotropy spectra show that the $\mathbf{S_0} \rightarrow \mathbf{S_2}$ transition, whose polarization is perpendicular to that of the first transition, should be considerably shifted to the short-wave side: by 165 nm for dye **2** and by 180 nm for dye **3**. Because of a low intensity, it does not practically exhibit itself in the absorption spectrum (see Fig. 1 a,b).

A large distance between the first and second electronic transitions was predicted also by the quantum-chemical calculations. Although the AM1 method with a relatively small configuration space gives the higher values of the transition energies, the analysis shows, nevertheless, that the lowest electron transition, $\mathbf{S_0} \rightarrow \mathbf{S_1}$, involves practically only the frontier orbitals: the highest occupied (HOMO) and lower unoccupied orbital (LUMO), whereas the second and third transitions in dye **3** are mixed, although the dominant contributions are given by the configurations with the next vacant MO, respectively (see Table 1): LUMO + 1 and LUMO + 2. In dye **2** with the simple chromophore, both higher transitions, $\mathbf{S_0} \rightarrow \mathbf{S_2}$ and $\mathbf{S_0} \rightarrow \mathbf{S_3}$, are described practically by one configuration.

Table 1 shows also that the oscillator strength, f_i, decreases sharply for the transitions in the higher excited states, which agrees with the same sharp decrease in the absorption intensity in the short-wave part of the spectra. The calculated distance between the transitions of different symmetries, $1A_1 \rightarrow 1A_1$ and $1A_1 \rightarrow 2A_1$, is ~142 nm (dye **2**) and 131 nm (**3**), which is comparable with the experimental values. Such spectral characteristics are typical of polymethine dyes: both cations and anions (see, for example, review [10]).

Moreover, the fluorescence spectra of dyes **2** and **3** measured at room temperature [7,8] are typical; Stokes shifts seen from Figure. 1a,b are relatively small, which indicates a minimal change of the equilibrium molecular geometry upon the relaxation of that component which corresponds to the ordinary fluorescence.

To quantitatively estimate the relaxation of the bond lengths in the excited state (providing the same planar configuration), we have used the well-known correlation between the bond length, $R_{\mu\nu}$, and the bond order, $p_{\mu\nu}$: $R_{\mu\nu}(\text{Å}) = 1.58 - 0.13\, p_{\mu\nu}$ [9]. The lengths of the carbon-carbon bonds in the main chromophore of dye **2** obtained

Table 1. Calculated wavelengths (λ) and oscillator strengths (f) of the lowest electron transitions of dyes **2** and **3**

Dye	Transition	λ, nm	f	Symmetry	Main configurations
2	$S_0 \rightarrow S_1$	437	1.200	$A_1 \rightarrow B_1$	0.95 |H → L>
	$S_0 \rightarrow S_2$	296	0.034	$A_1 \rightarrow A_1$	0.79 |H → L + 1>
	$S_0 \rightarrow S_3$	293	0.099	$A_1 \rightarrow B_1$	0.82 |H → L + 2>
3	$S_0 \rightarrow S_1$	443	1.607	$A_1 \rightarrow B_1$	0.81 |H → L>
	$S_0 \rightarrow S_2$	312	0.083	$A_1 \rightarrow A_1$	0.67 |H → L + 1> − 0.52 |H − 1 → L>
	$S_0 \rightarrow S_3$	287	0.258	$A_1 \rightarrow B_1$	0.57 |H → L + 2 > + 0.52 |H − 1 → L + 1>

in this way are presented in Figure 3 (the plots for dye **3** are practically the same). One can see that the bond lengths of both dyes **2** and **3** are similarly equalized in the ground state $\mathbf{S_0}$ and the symmetrically relaxed state $\mathbf{S_1}$(S-R).

It is worth to note that the fluorescence quantum yields of dyes are relatively low, especially in the polar solvent. The lengthening of a conjugated chain is accompanied by an appreciable increase in the fluorescence efficiency: up to 85%, independently of the solvent polarity, as has been shown in [7,8]. Thus, we can assume that there is an additional channel of the degradation of the excitation energy in the dye molecules with a short polymethine chain.

Based on the careful analysis of results of the detailed parallel quantum-chemical and spectral study presented in [10], the authors have suggested that the relaxation of the excited state can occur in two ways, leading to two isomers:

1. isomer with a symmetric equilibrium geometry: the state S_1 (S-R);
2. isomer with a broken symmetry: the state S_1 (U-R).

Note that the vibration relaxation occurs in the picosecond range of lifetimes of the excited state; only thereafter, the conformational transformation with the rotations of molecular fragments, in principle, around any bond in the open polymethine chain could occur [11].

The symmetric isomer corresponds to that component in the excited state which exhibits the normal fluorescence with a small Stokes shift, independently of the nature of a solvent. The possible conformational transformations could reduce the fluorescence quantum yield of this component; although, due to the equalization of bond lengths, the barriers for a rotation must be relatively high.

In the asymmetric way of the relaxation, the considerable alternation of the lengths of neighboring bonds in the polymethine chain appears, so that the length of one of the extreme bonds near the terminal group can be significantly increased, which should be accompanied by a reduction of the conformational transformation barrier around this bond. As a result, the asymmetric isomer becomes non-fluorescent at high temperatures.

The conformational transformation is impossible, when the fluorescence spectra are measured at low temperatures. This situation was simulated in the calculations of an optimized geometry in the excited state by blocking the torsion and bond angles. The direct calculation has given the asymmetric form – with the considerable

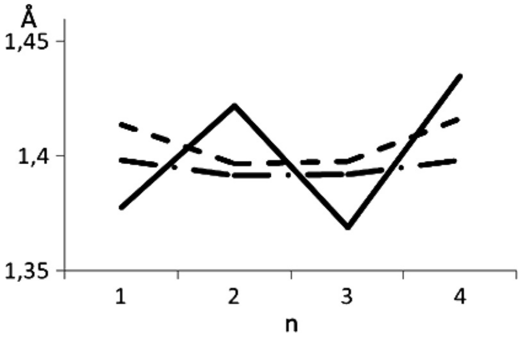


Figure 3. Optimized bond lengths in the main chromophore of dye **2**: ground state (– · –), symmetric relaxed (- - -) and asymmetric relaxed (—) excited states.

polyenic-like bond length alternation, as one can see from Figure. 3. The estimation of a change of bond lengths by the formulae $R_{\mu\nu}(\text{Å}) = 1.58 - 0.13\ p_{\mu\nu}$ (using the calculated bond orders for the excited state) leads to the form with the equalized bond lengths (nearly the Franck–Condon excited state). The existence of two components or forms in the excited state is presented in Figure 4.

It seems likely that there is an appreciable barrier between the symmetric and asymmetric forms, similarly to the ground state [12]. This is confirmed by the holding of the fluorescence band shape with decrease in the temperature. In this case, only the quantum yield increases.

At low temperatures, the influence of a solvent should be stored, because a reorientation of molecules impossible in the rigid matrix. As the asymmetric form of a dye has its dipole, then it is more sensitive to the solvent polarity. A polar solvent can reduce the barrier and the amount of transitions to the asymmetric form, as well as it can simply increase the population of the asymmetric form, additionally stabilizing it.

In view of the fact that the conformational transformation as a channel of the degradation of the excitation energy is blocked at low temperatures, then the asymmetric component could exhibit the appreciable fluorescence. The emission should occur from the asymmetrically relaxed state $\mathbf{S_1}$(U-R) to the unstable state $\mathbf{S_0}$(U-R) with an asymmetric molecular geometry and, hence, with the asymmetric charge distribution which is positioned higher than the equilibrium ground state $\mathbf{S_0}$ (Fig. 4b).

Consequently, the fluorescence of the asymmetric component/form (measuring by the time-resolved spectroscopy at a low temperature) should manifest a number of features:

1. it would appear at longer wavelengths; (E[$\mathbf{S_1}$(U-R)] < E[$\mathbf{S_1}$(FC)]; E[$\mathbf{S_0}$(U-R)] > E[$\mathbf{S_0}$]);

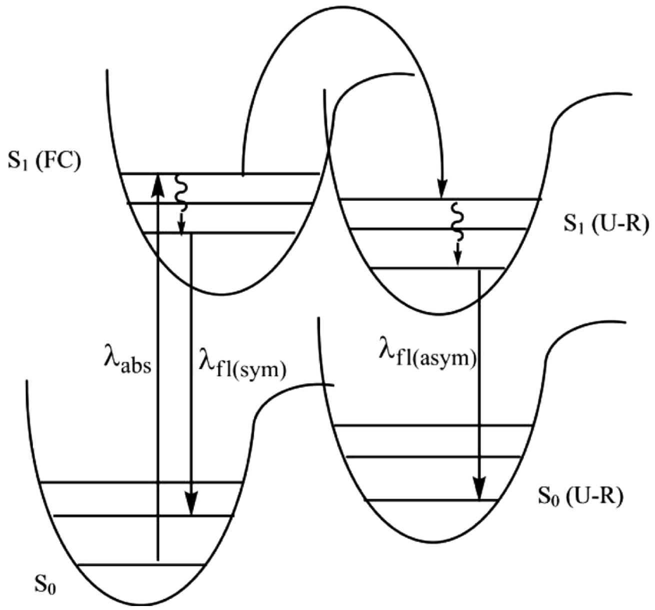


Figure 4. Scheme of electron transitions and relaxation paths in dyes **2** and **3** at low temperatures: left – symmetric form, right – asymmetric form.

2. its intensity would increase with time, because the displacement of bond lengths (vibronic relaxation) is a temporary process;
3. it is sensitive to the solvent polarity, since the asymmetric form has a dipole moment.

One can see from Figure 2 a, b, c presenting the impulse fluorescence spectra of both dyes at a low temperature that the all expected spectral effects are reliably confirmed. Besides the main fluorescence band revealing a small Stokes shift, which is positioned somewhat hypsochromically relative to the maximum of the band at a high temperature (Fig 1a, b), there appears an additional band in the long-wave region, whose intensity increases with time. The increase of the solvent polarity upon going from MeCN to DMSO causes an increase in the intensity of the second component, the intensity of the asymmetric component becoming prevalent for dye **3**, as seen from Figure 2c.

As the main result based on the simultaneous quantum-chemical and spectral studies, we can propose that there are two paths of relaxation in the excited state of anionic dyes **2** and **3**: a) cyanine-like path accompanied by equalizing the bond lengths; b) polyenic path leading to the considerable bond length alternation. Both paths manifest themselves spectrally as two components in the time-resolved fluorescence spectra measured at low temperatures.

Conclusion

Thus, the analysis of low-temperature time-resolved fluorescence spectra, when molecules of the investigated dyes are in a rigid matrix, and the comparison of these spectra with the corresponding spectra measured at room temperature confirm the hypothesis about two ways of relaxation of anionic polymethine dyes in the excited state. The ratio of the symmetric and asymmetric forms of the excited state depends on the solvent polarity and on the lifetime of the excited state.

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