CYANINE-LIKE AND POLYENIC RELAXATION PATHS OF MEROCYANINE DERIVATIVES OF MALONODINITRILE IN THE EXCITED STATE DETECTING BY LOW TEMPERATURE TIME-RESOLVED FLUORESCENCE

M.M. SEVRYUKOVA,[1] YU.P. PIRYATINSKI,[1] S.V. VASYLYUK,[2]
V.M. YASHCHUK,[2] O.O. VINIYCHUK,[3] A.O. GERASOV,[3]
YU.L. SLOMINSKII,[3] O.D. KACHKOVSKY[3]

[1]**Institute of Physics, Nat. Acad. of Sci.**
(46, Prosp. Nauky, Kyiv, 03028)

[2]**Taras Shevchenko National University of Kyiv**
(2/1, Academician Glushkov Ave., Kyiv, Ukraine)

[3]**Institute of Organic Chemistry, Nat. Acad. of Sci.**
(5, Murmans'ka Str., Kyiv 03094, Ukraine; e-mail: `adkachkovsky@mail.ru`)

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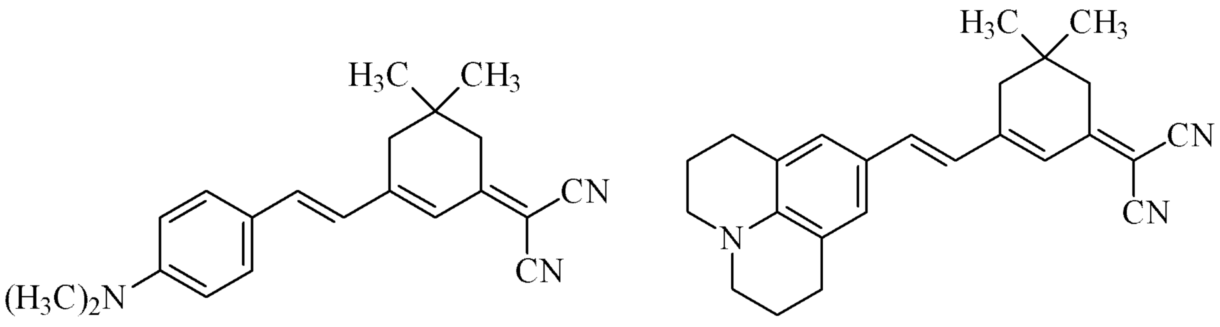
The combined quantum-chemical and spectral study of features of the electron transitions in merocyanines is carried out. It is established that the two lowest transitions are split and involve both donor levels, similarly to symmetric cyanines. The long-wave absorption band has high intensity, while the second transition manifests itself only in the fluorescence excitation anisotropy spectra. In contrast to the ground state, the MO splitting in the excited state leads to the instability. The analysis of the results of theoretical and experimental studies enables us to propose that there are two paths of the relaxation in the excited state: a) cyanine-like one with equalizing the bond lengths; b) polyenic one with the considerable bond length alternation. This assumption is confirmed by the existence of two components in the time-resolved fluorescence spectra measured at low temperatures.

1. Introduction

The merocyanines as donor-acceptor conjugated compounds with the high polarizable collective system of π-electrons are used intensively as non-linear materials [1-3]. The merocyanines containing the nitrogen heterocycles as donor residues and malononitryl or other residues as acceptor terminal groups are well-known among other types of neutral π-systems. They exhibit large dipole moments, high hyperpolarizibilities, comparatively low energy gap, and, hence, absorption and fluorescence in the visible and near IR spectral regions [2]. The chemical constitution of their molecules is comparatively simple; it can be varied regularly and purposefully to obtain the optimal linear and nonlinear characteristics. Under the excitation by light quanta, merocyanine molecules show the considerable intramolecular charge transfer following by a considerable change of the dipole moment, especially in the polar solvents [1, 2, 4]. This factor and large transition dipole moments of the one-photon excited states and the existence of the active two-photon induced excited states provide the high performance for the molecular design of effective nonlinear materials based on merocyanines as high polarizable donor-acceptor organic molecules [1, 3, 5, 6].

On the other hand, it was found that the spectral properties of merocyanines are suitable for the establishment of general relationships between the molecular topology and electronic properties, including the charge transfer upon going to the excited state [4]. It was established that the mobility of a wave of electron density along a chromophore/fluorophore can be detected by the time-resolved low-temperature investigations; so, the existence of two components was observed in the fluorescence spectra of the symmetric cyanine dyes at low temperatures detected as two spectral peaks [7].



1 **2**

Fig. 1. Structural formulae of the merocyanines under study

Based on the spectral and quantum-chemical investigations, it was assumed that the relaxation in the excited state can lead to the formation of two forms of the dye molecules: with the symmetric and asymmetric charge distributions. The similar symmetry breaking of the electron distribution is well-known for the cyanine NIR dyes and was detected by the absorption spectra; this phenomenon manifests itself as a drastic widening of the long-wave spectral band [8, 9].

It is well-known [3, 10–12] that the spectral properties of many merocyanines are close to those of symmetric cyanines, when the so-called “cyanine limit” can exist, i.e. the maximum equalizing of the bond lengths can be reached.

This paper presents the results of joint quantum-chemical and experimental studies of the relaxation of a molecular geometry and a charge distribution in the first excited state of typical merocyanines.

2. Experimental Part

The merocyanines under study can be presented by formulae **1** and **2** (Fig. 1). In dye 2, two trimethylene bridges block the conformational transformation of the disubstituted aminogroup. Introducing the polymethylene bridge in the conjugated chain provides a comparatively high stability of both dyes **1** and **2**.

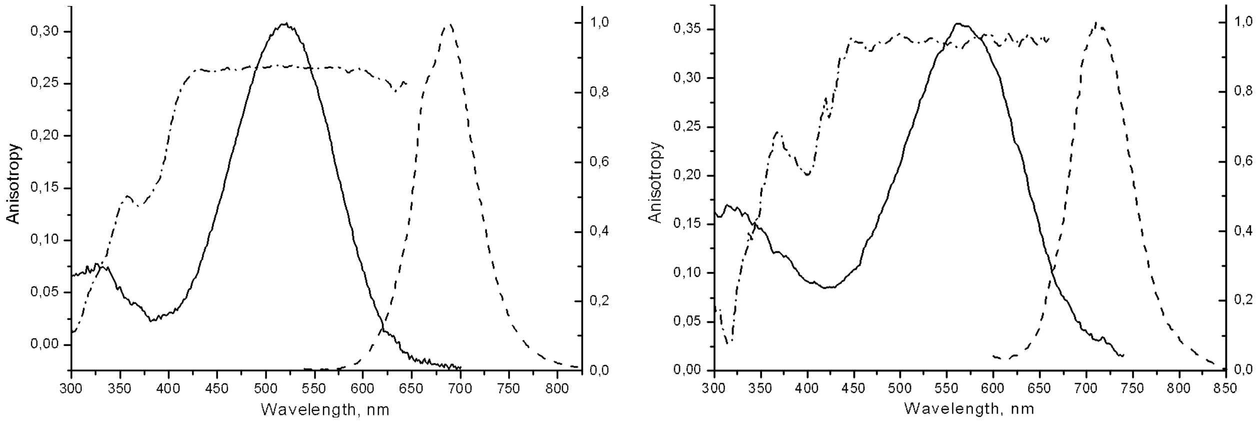
The procedure of synthesis for compounds **1**–**2** was described earlier [13, 14].

UV-Vis absorption spectra were measured by a Shimadzu UV-3100 spectrophotometer in toluene, acetonitrile, and ethylene glycol (spectral grade).

Fluorescence spectra. Researches have been performed at temperatures of 295 and 4.2 K. To excite PL, we used the following excitations: 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) and the second harmonic of a Nd:YAG laser ($\lambda_e = 532$ nm, $t_I = 10$ ns, $N = 0.1$–0.5 MW, $f = 50$ Hz). Time-resolved PL spectra at the one- and two-photon excitations were recorded with a stroboscopic system [15], in which the investigated signal from a photodetector through a line of a delay acted on the stroboscopic oscilloscope connected with a computer.

The measurement technique allowed us to write down the forms of PL pulses and the laser radiation reflected from the investigated sample on the same 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 study PL spectra, we used an MDR-12 monochromator. The spectral slit width in the measurements of PL spectra was 0.2–0.4 mm. The spectra of absorption, reflection R, and PL excitation were recorded with a special setup. It allowed us to perform also the researches of the spectra of PL, absorption, and reflection in a wide range of temperatures 4.2–300 K (the procedure of registration of PL can be found in [15]). It should also be emphasized that the kinetic parameters of signals at the input of an oscilloscope are not determined by a laser pulse (10 ns), but by the steepness of their leading edge and by the stability of a laser pulse.

The excitation anisotropy measurements were performed with the use of a CM 2203 spectrofluorimeter (Solar, Belarus) in viscous solutions to reduce the rotational reorientation and at low concentrations ($C \approx 10^{-6}$ M) to avoid the re-absorption of the fluorescence. The anisotropy calculated by $r(\lambda) = \dfrac{I_{\|}(\lambda) - G \times I_{\perp}(\lambda)}{I_{\|}(\lambda) + G \times 2 \times I_{\perp}(\lambda)}$ was measured by setting the emission wavelength, typically near the fluorescence maximum, with a fixed polarization. Then the fluorescence intensity was recorded as a function of the excitation wavelength λ at the polarizations in parallel ($I_{\|}(\lambda)$) and perpendicularly ($I_{\perp}(\lambda)$) to the emission polarization. The G-factor expresses the



a *b*

Fig. 2. Absorption (—) and fluorescence (---) spectra, and fluorescence excitation anisotropy spectra (-··-) of dyes 1 (*a*) and 2 (*b*) in ethylene glycol

ratio of sensitivities of the detection system for light polarized perpendicularly and in parallel.

The quantum-chemical calculations were performed to study the influence of the electron structure and electron transitions on the molecular constitution. The equilibrium geometry of dye molecules in the ground state was optimized in the AM1 semiempirical approximation (HyperChem package); the procedure was stopped, by attaining the energy gradient of 0.01 kcal/mol. The electron transition characteristics were calculated by the ZINDO/S method. As a rule, all π-electron single excited configurations were used. The empirical parameter OWF (Overlap weight factor) was varied to achieve the best agreement between the calculated and measured spectral energies of the first electron transition. It was enough to correctly analyze the nature of electron transitions, the relaxation of a molecular geometry, and the electron redistribution under the excitation.

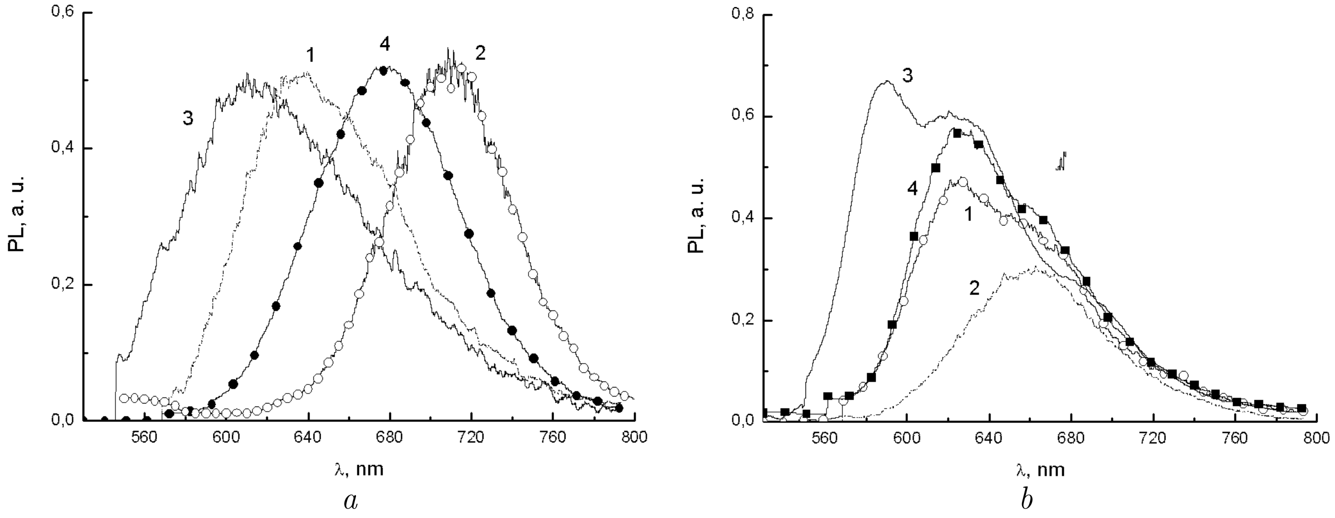
It is found that there is a serious problem concerning the correlation between the calculated and experimental energies simultaneously for both the first and higher electron transitions. In practice, this concerns the parameter OWF in the semiempirical method ZINDO/S, which is connected indirectly with the overestimation of the electron-electron repulsion used in the integrals J_{ij} and K_{ij} in the transition energy: $\triangle E\,(S_0 \rightarrow S_p) = \varepsilon_j - \varepsilon_i + 2K_{ij} - J_{ij}$. It is calculated by the Mataga–Nishimoto's formulas, $\gamma_{\mu\nu} = a/(1 + R_{\mu\nu})$, where a is constant, and $R_{\mu\nu}$ is the distance between the μ-th and ν-th atoms, for the atoms which are removed to a great distance from each other. The same problem of the integrals $\gamma_{\mu\nu}$ has been found to exist even in the simplest PPP approximation taking correctly the electron-electron interaction into account. N.N. Tyutyulkov has proposed to use the modified formula $\gamma_{\mu\nu} = a/(1+tR_{\mu\nu})$, where $t = 10/3$ [16]; then the agreement between the calculated and experimental wavelengths of the first electron transition for the vinylogous series of polymethine dyes has been essentially increased [17]. In this paper, we have used the same OWF parameter for the first and higher electron transitions, by optimistically suggesting that the divergence between the experimental and experimental transition energies is not considerable to establish correctly the order of the transitions of different types (cyanine-like transition or a transition with charge transfer – CT). The central and greatest part of our work was to establish the nature of the first and higher transitions in dyes **1** and **2** and, hence, to explain correctly the main reason for the considerable difference between spectra of these dyes.

3. Results and Discussion

3.1. *Absorption, high-temperature fluorescence, and fluorescence excitation anisotropy spectra*

The measured spectra of merocyanines **1** and **2** are presented in Figs. 2 and 3. The spectral characteristics are summarized in Table 1.

The PL spectra excited by a nitrogen laser (337.1 nm) and an LTI-IF (532 nm) in the spectral region $\lambda > 550$ nm are the same. When excited by a nitrogen laser, the PL spectra contain also the short-wave radiation, whose nature is not considered in the present work. For this reason, the figure indicates only the excitation with a wavelength of 532 nm, which approximately falls in the long-wavelength absorption of dyes. The studies of the



a *b*

Fig. 3. Time-resolved ($t_d = 0.7$ ns) fluorescence spectra ($\lambda_{\text{ex}} = 532$ nm) of molecular solutions ($c = 10^{-6}$ mol/l) of dyes **1** (curves *3, 4*) and **2** (curves *1, 2*) in toluene (*1, 3*) and acetonitrile (*2, 4*) at 295 K (*a*) and 4.2 K (*b*)

PL spectra excited by a nitrogen laser shown that the instant PL spectra measured in the time interval 0–0.7 ns and the stationary spectra coincide. These data show that the relaxation processes in the excited state occur for less than 0.7 ns. A deviation in delay times at low temperatures leads to a spectral resolution of the bands at low temperatures. The kinetics of PL measurements in this spectral region of emission under the excitation at $\lambda_e = 532$ nm shows that the PL pulse and the laser pulse are the same, i.e. the PL decay time is less than 100 ps.

One can see that the separate comparatively intense, but rather wide spectral band is observed in the visible region, which corresponds to the first $\pi \rightarrow \pi^*$ electron transition only. The position of the band maximum is bathochromically shifted upon going from merocyanine **1** to dye **2**. The merocyanines investigated are only slightly sensitive to the polarity of the solvents.

The higher electron transitions manifest themselves in the absorption spectra in the region shorter than 350 nm. Their nature will not be discussed in details in this paper.

Table 1. Experimental characteristics

	Dye **1**		Dye **2**	
	Toluene	Acetonitrile	Toluene	Acetonitrile
$\lambda^{\text{abs}}_{\max}$, nm	494	497	535	540
$\lambda^{\text{fl}}_{\max}$(296 K), nm	610	677	635	710
$\Delta\nu_{\text{S}}$, cm^{-1}	3849	5350	2944	4434
$\lambda^{\text{fl}}_{\max}$(4.2K.),nm	590	625	625	660
	625	660	660	
	670			

Figures 2 and 3 show that the considerable Stokes shifts are observed in the fluorescence spectra of both dyes. The fluorescence excitation anisotropy spectra (Fig. 2) point on the existence of the second electron transition at 350 nm, which is polarized at a considerable angle relative to the first transition. The bathochromic shift of the minimum in the curve of the anisotropy by 30 nm, similarly to the long-wave spectral band in the absorption spectra, is observed going from merocyanine **1** to **2**.

3.2. Low-temperature time-resolved fluorescence spectra

The PL spectra were measured for two solutions (in a polar solvent acetonitrile and a non-polar one toluene).The room-temperature PL spectra showed that, in contrast to the absorption spectra, which are weakly dependent on the solvent polarity, there are significant differences in the PL spectra. These differences are due to a significant change in the dipole moments of molecules in an excited state. It would seem that, as follows from the literature data for many dyes, the PL spectra of molecular solutions at low temperatures should not depend on the polarity of a solvent such as acetonitrile and toluene, because the processes of solvation are insignificant at low temperatures. However, we can see differences in the PL spectra for different solvents.

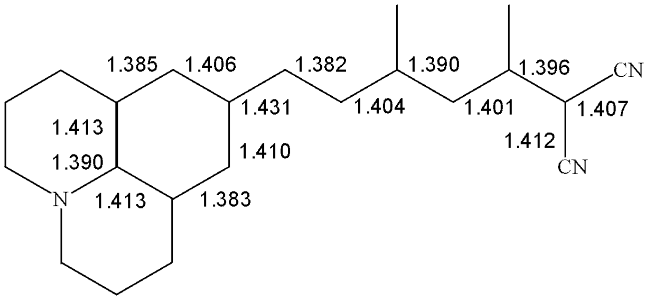


Fig. 4. Time-resolved ($t_d = 0.7$ ns) fluorescence spectra ($\lambda_{\text{ex}} = 532$ nm) of molecular solutions ($c = 10^{-6}$ mol/l) of dyes **1** (curves *3, 4*) and **2** (curves *1, 2*) in toluene (*1, 3*) and acetonitrile (*2, 4*) at 295 K (*a*) and 4.2 K (*b*)

The spectra measured with a temporal resolution of $t < 0.7$ ns and the stationary spectra coincide both at room temperature and at 4.2 K. This means that all the relaxation processes in the molecule in the lowest excited state occur for less than 0.7 ns, and the observed structure in the wavelength region cannot be allowed. The kinetics of PL in this region is also quite fast and almost coincides with that of a laser pulse. In this sense, there is no need to present the kinetic curves.

Figure 3 presents the time-resolved fluorescence spectra of both studied dyes at 4.2 K. The quantum yields increase essentially upon going from room temperature to the lower one.

3.3. Quantum-chemical data

The performed calculations of the equilibrium molecular geometry give the conjugated part of all molecules to be planar, which is typical of π-electron systems [18]. Only one of the methylene groups (CH_2) in the trimethylene bridge in dyes **1** and **2** is out of the plane of the main chromophore. It is seen from Fig. 4, where the optimized molecular geometries of the dyes (within the *ab initio* method) are pictured, that the carbon-carbon bond lengths along the conjugated chain in both dyes are substantially alternated, so that the length of the formally ordinary bond (CH–CH) is approximately 1.45 Å, whereas the bond of the formally double bond (CH=CH) oscillates nearly 1.33–1.35 Å. Unlike, the lengths of the bonds in the aromatic ring are rather equalized: 1.40 ± 0.03 Å. Similarly, the semiempirical method AM1 gives a higher degree of the alternation of bond lengths, than Fig. 5 suggests. In addition, the calculations show that the modification of the chemical constitution of the donor group in dye **2** (introducing the cyclic bridges) is accompanied by a negligible change of the bond lengths in the main chromophore only.

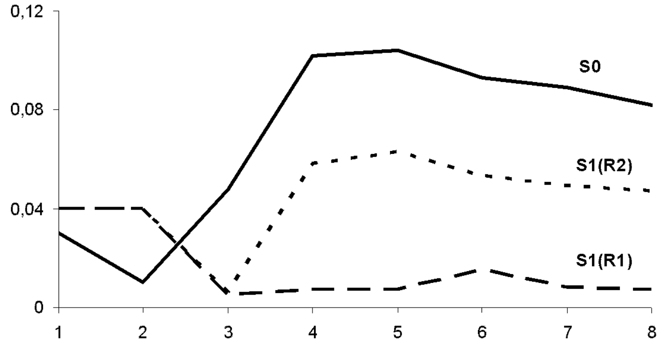


Fig. 5. Bond length alternation, $\triangle l_v$, in the ground (S_0) and excited states: cyanine-like ($S_1(R_1)$), polyenic ($S_1(R_2)$); (*a*) dye **1**, (*b*) dye **2** (AM1 method)

Meanwhile, the calculated dipole moments in the ground and excited states, μ_i, as well as the energies, $\triangle E_{\mu_{0\to i}}$, and dipole moments, $\mu_{0\to i}$, of the lowest electron transitions are presented in Table 2. As asymmetric linear conjugated molecules, dyes **1**–**2** are seen to show the considerable large state dipole moment, which changes essentially under the excitation.

3.4. Cyanine-like nature of Franck–Condon's electron transitions

3.4.4 Generation of the frontier and nearest electron levels

In the traditional theoretical model [2, 3, 10], the merocyanines are considered as conjugated donor-acceptor systems (**3**).

$$\mathbf{D}\text{–}(\text{CH=CH})_n\text{–}\mathbf{A}, \quad \text{or} \quad \mathbf{D}\text{–}\mathbf{C}\text{–}\mathbf{A}. \qquad (\mathbf{3})$$

Here, **D** is a donor residue containing, as a rule, the nitrogen atom with its lone electron pair, which is conju-

Table 2. Calculated characteristics of dyes 1–2 (ZINDO/S, AM1-geometry)

Dye	Transition	λ, nm	f	μ_i, D	$\triangle\mu_i$, D	$\mu_{0\to i}$, D
1	S_0			11.226		
OWF	$S_0 \to S_1$	497	0.994	19.121	7.895	10.244
0.33	$S_0 \to S_2$	355	0.162	16.308	5.082	3.495
	$S_0 \to S_3$	342	0.080	22.899	11.673	2.411
	$S_0 \to S_4$	326	0.224	14.565	3.339	3.939
	$S_0 \to S_5$	277	0.008	11.906	0.680	0.686
2	S_0			11.245		
OWF	$S_0 \to S_1$	540	0.882	19.120	7.875	9.820
0.34	$S_0 \to S_2$	400	0.153	23.137	11.892	3.560
	$S_0 \to S_3$	380	0.082	17.335	6.090	2.556
	$S_0 \to S_4$	345	0.200	16.389	5.144	3.801
	$S_0 \to S_5$	300	0.004	13.165	1.920	0.501

gated with the main chromophore, while **A** is an acceptor group, for example, CH=O, $C(CN)_2$ or more complex residues. Bridge **C** is a polyenic chain. All components are assumed to be strongly conjugated among themselves.

However, the calculations show that there is no "pure" donor or "pure" acceptor local orbital. Quite the contrary, the MOs in, for example, dye **1** are seen from Fig. 6,*b* to be delocalized practically along the π-system on the whole. Although, the shape of the HOMO is, nevertheless, slightly deformed, so the HOMO is shifted to the donor part of the molecule, whereas the LUMO is shifted to the acceptor malononitryl fragment. Other MOs nearest to the frontier orbitals are distributed in the conjugated chromophore more uniformly.

Traditionally, in order to interpret correctly the highly polarizable π-electron structure of donor-acceptor conjugated molecules, they are described in terms of the resonance between a neutral form A and a charge-separated form B, as it is presented in Fig. 7 for merocyanine **1**. The contribution of resonant forms A and B depends on the donor/acceptor strengths of the terminal groups, as well as on the solvent polarity. It was postulated that, providing the equal weights of the two forms, the so-called cyanine-like state is reached. It is characterized, first at all, by the minimum of the bond length alternation in the polymethine chain and a relative narrow and intense absorption band in the long-wave spectral region. It was found in the topological (Hückel) approximation [11] that the alternation of bond lengths (BLA parameter) can be both negative and positive, depending on the donor and acceptor strengths of **D** and **A** residues or, more correctly, on the Coulomb and resonance integrals of the terminal heteroatom in the model donor-acceptor conjugated molecule. It is worth noting that the acceptor group was represented by a single model atom without regard for the relation between the numbers of π-centers and π-electrons in the totally conjugated system (the traditional defect of the Hückel method).

The positive charge is located in resonance form B at the nitrogen atom of the dimethylaminogroup, which is in contrast with the definition of this residue as a donor substituent. Then the location of a positive charge at the carbon atoms in the polymethine chain (resonance forms C and D) is more realistic. On the other hand, the location of a negative charge at the carbon atom of acceptor groups A enables us to consider it as a "donor" substituent in resonance forms B, C, and D. Such a treatment of the merocyanines agrees with the fact that they are electron-excessive π-systems, i.e. their conjugated system contains $N{+}1$ π-electrons delocalized at N atoms or π-centers. The donor properties of residue A are determined by the position of its highest occupied electron level. Consequently, in the first approximation, the merocyanine with a highly positioned level of the acceptor fragment can be described as a π-system with two "donor" fragments and the polymethine chain as an acceptor fragment, which is presented by the resonance structure F in Fig. 6,*a*. Thus, two so-called donor levels positioned comparatively highly exist in the merocyanine. The relative positions of the electron levels of the different types can be estimated for the structure with a distortion of the conjugation between the fragments: **D, C**, and **A**. Such model unconjugated system can be reached providing the both "donor" terminal groups in resonance form F are out of the plane of the main chromophore/fluorophore C. Figure 6 presents the disposition of the frontier and nearest electron levels calculated for the twisted and planar conformations of merocyanine **1**.

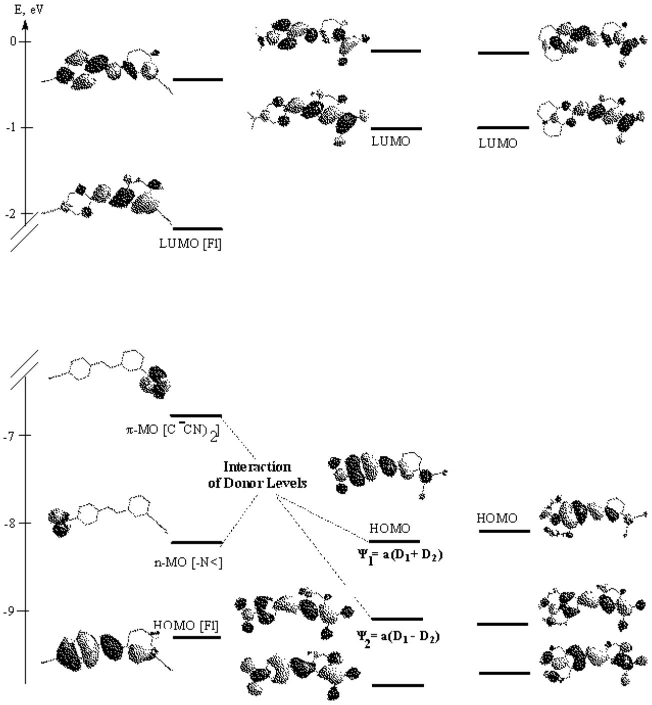


Fig. 6. Generation of frontier and nearest levels in merocyanines **1** (*a*) and **2** (*b*)

One can see that two highest occupied levels are formed by the twisted donor dimethylaminogroup and the twisted acceptor malononitrylgroup, which gives its "donor" level. Moreover, the lowest vacant MO is generated by the main planar part of the molecule. This generation of the frontier levels is similar to that of

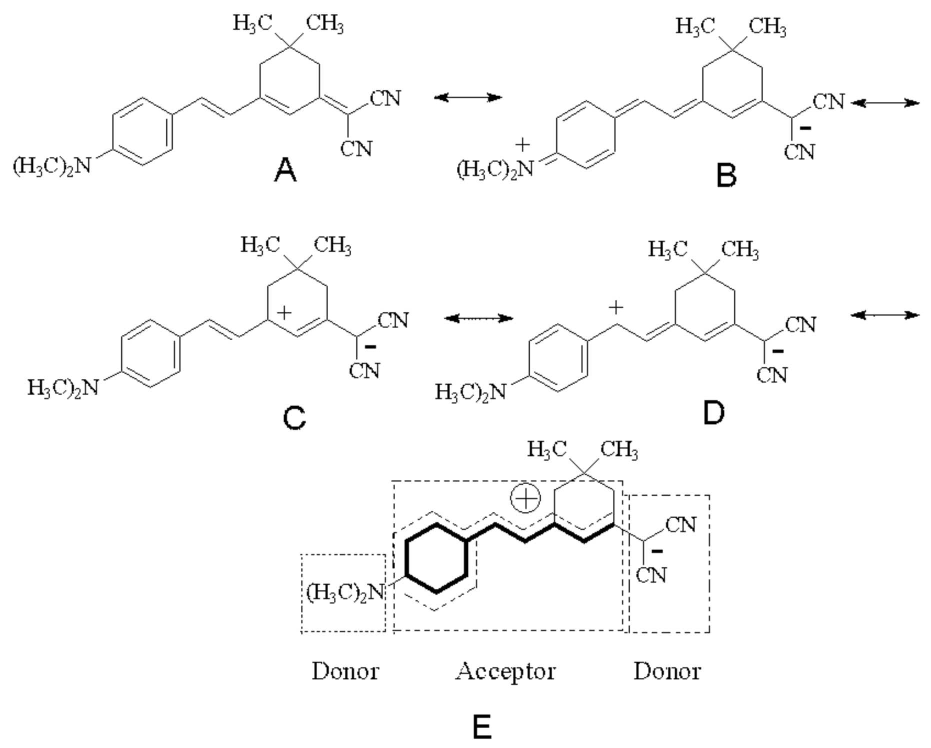


Fig. 7. Resonant structures of merocyanine **1**

symmetric cationic cyanine dyes containing the terminal donor groups with the own extended π-electron system [17]. Such π-electron-excessive conjugated systems can be presented by the following general formulas:

$[\mathbf{D}_1\text{–}\mathbf{C}\text{–}\mathbf{D}_2]^+$ or $\mathbf{D}_1\text{–}\mathbf{C}(+)\text{–}\mathbf{D}_2$.

It is found that each terminal group gives a donor level (degenerated in a symmetric cyanine, when $\mathbf{D}_1 = \mathbf{D}_2$, or non-degenerated in asymmetric dyes), while the polymethine chain gives the lowest vacant level or solitonic-like level of the positive charge [19]. Then, the interaction of both MOs of the two terminal groups, $\phi(D_1)$ and $\phi(D_2)$, leads to the formation of the symmetric and asymmetric linear combinations of these orbitals:

$$\varphi_1 = 2^{1/2}\left\{\phi(D_1) + \phi(D_2)\right\}; \qquad (1)$$

$$\varphi_1 = 2^{1/2}\left\{\phi(D_1) - \phi(D_2)\right\}, \qquad (2)$$

i.e. two corresponding highest occupied levels in the linear conjugated system $\mathbf{D}_1\text{–}\mathbf{C}(+)\text{–}\mathbf{D}_2$ can be interpreted as two splitted specific donor levels. One can see from Fig. 6,*b* that both orbitals, |HOMO⟩ and |HOMO–1⟩, are relatively delocalized regularly along the whole chromophore/fluorophore.

On the other hand, two lowest vacant MOs can be considered as a linear combination of the solitonic-like orbital of the positive charge (delocalized in main chromophore/fluorophore **C** in resonance structure E), $\phi\,[C(+)]$ and the acceptor-like orbital of the acceptor terminal group, $\phi(Ac)$:

$$\varphi_3 = 2^{1/2}\left\{\phi\,[C(+)] + \phi(Ac)\right\}; \qquad (3)$$

$$\varphi_4 = 2^{1/2}\left\{\phi\,[C(+)] - \phi(Ac)\right\}. \qquad (4)$$

As is seen from Fig. 6,*b*, both vacant splitted orbitals, |LUMO⟩ and |LUMO+⟩, are totally delocalized. The comparatively large distances between two lowest vacant levels, as well as between two highest occupied levels, indicate to considerable interactions between the donor orbitals $\phi(D_1)$ and $\phi(D_2)$ and the vacant MOs $\phi\,[C(+)]$ and $\phi(Ac)$.

The other orbitals do not practically take part in the electron transitions corresponding to the absorption spectra in the visible region.

The calculation has shown that the shapes of the frontier and nearest MOs in dye **2** are similar to those in merocyanine **1**.

3.4.5 Electron transitions and absorption spectra

The calculated characteristics of the transitions are summarized in Table 2. The quantum-chemical calculation shows that the first electron transition, $|S_0 \rightarrow S_1\rangle$, connected with the long-wave band peak, involves the frontier orbitals and is practically a "pure" transition: $|S_1\rangle \approx 0.92\Phi_1$, where Φ_1 denotes the excited electron configuration $|\mathrm{HOMO} \rightarrow \mathrm{LUMO}\rangle$. Although both orbitals, $|\mathrm{HOMO}\rangle$ and $|\mathrm{LUMO}\rangle$, are appreciably delocalized, this transition is accompanied by a comparatively large change of the dipole moment, $\triangle\mu = \mu_1 - \mu_0$, which points to a considerable charge transfer under the excitation. The more complete information can be found from the diagrams of charge redistribution at atoms under the excitation [18, 19]. The changes of electron densities upon going to the excited state can be calculated by the relation

$$\delta q_\mu = \left(q_\mu^* - q_\mu^0\right), \qquad (5)$$

where q_μ^* corresponds to the excited state, while the parameter q_μ^0 corresponds to the ground state.

Figure 8 presents the redistribution of electronic densities in merocyanine **1**. One can see that the $|S_0 \rightarrow S_1\rangle$ transition causes mainly the transfer of the electron density in the chromophore from the atoms in the even position of the polymethine chain to neighboring atoms. This is similar to the electron density redistribution upon going to the first excited state in cationic asymmetric cyanine dyes [20, 21]. Then we can treat the first transition in merocyanine **1** similat to that in cyanine dyes from the occupied splitting donor levels and the vacant charge-like (solitonic-like) level. Consequently, this transition has a comparatively large transition dipole moment, $\mu_{0\rightarrow 1} = 10.244$ D, that accords with the comparatively intense spectral long-wave band. In addition, this transition is polarized along the polymethine chromophore/fluorophore similarly to the case of cyanine dyes.

The energies of the next excited configurations, $\Phi_2 = |\mathrm{HOMO} \rightarrow \mathrm{LUMO}+1\rangle$, and $\Phi_3 = |\mathrm{HOMO}-1 \rightarrow \mathrm{LUMO}\rangle$, exceed essentially the first transition energy, because of that the distances between two lowest vacant levels and between two highest occupied levels are rather large. Both configurations Φ_2 and Φ_3 include one from the each pair of the splitting MOs, the involving orbitals being of the opposite signs:

$$\Phi_2 \Rightarrow \phi_1(+) \rightarrow \varphi_4(-);$$

$$\Phi_3 \Rightarrow \phi_2(+) \rightarrow \varphi_3(-).$$

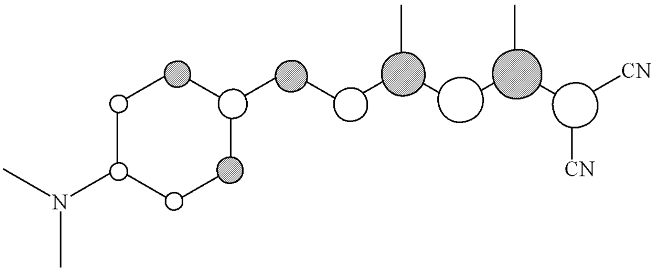


Fig. 8. Diagram of the electron density redistribution under the excitation: colored circle – the electron density increases; uncolored circle – the electron density decreases

The interaction of the excited configurations Φ_2 and Φ_3 leads to the considerable splitting, so that they give the second, $|S_0 \rightarrow S_2\rangle$, and fourth, $|S_0 \rightarrow S_4\rangle$, electron transitions:

$$|S_0 \rightarrow S_2\rangle \approx 0.76\Phi_2 - 0.59\Phi_3;$$

$$|S_0 \rightarrow S_4\rangle \approx 0.76\Phi_2 + 0.74\Phi_3.$$

The change of the corresponding state dipole moments, $\triangle\mu = \mu_2 - \mu_0$ and $\triangle\mu = \mu_4 - \mu_0$, are even lower than the value $\triangle\mu$ for the first transition, which corresponds to the similar localization of the appropriate MOs (compare with Fig. 6,*b*). The calculated oscillator strengths f_2 and f_4 (and, hence, the transition dipole moments $\mu_{0\rightarrow 2}$ and $\mu_{0\rightarrow 4}$) are appreciably lower, as compared with f_1. It is in good agreement with the observed comparatively low-intense absorption bands in the short-wave region.

The calculation gives the third excited state to be described by two configurations concerning the local MO ($|\mathrm{HOMO}-2\rangle$) and both splitting vacant orbitals:

$$|S_0 \rightarrow S_3\rangle \approx 0.74|\mathrm{HOMO}-2 \rightarrow \mathrm{LUMO}\rangle +$$

$$+0.62|\mathrm{HOMO}-2 \rightarrow \mathrm{LUMO}+1\rangle.$$

In contrast to the transitions $|S_0 \rightarrow S_1\rangle$, $|S_0 \rightarrow S_2\rangle$, and $|S_0 \rightarrow S_4\rangle$ considered above, the $|S_0 \rightarrow S_3\rangle$ transition, involving the local MO, is accompanied by a considerable change of the dipole moment. It is evident that this change should be connected with the considerable transfer of the electron density along the chromophore/fluorophore.

One can see from Table 2 that the excited states $|S_2\rangle$, $|S_3\rangle$, and $|S_4\rangle$ give the group with close energies, which are essentially higher than the energy of the first electron transition, so that the next spectral

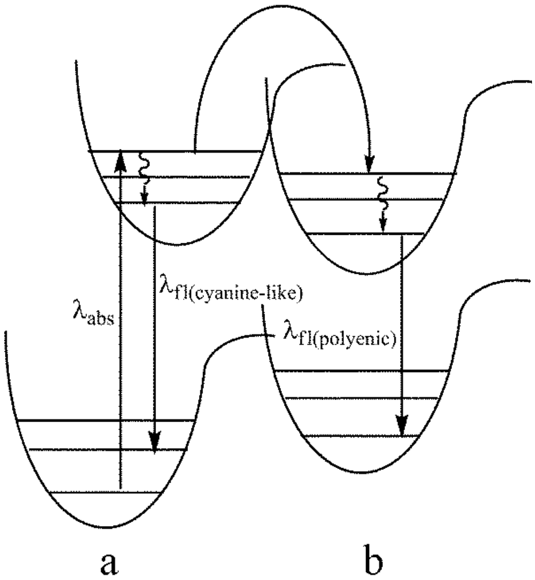


Fig. 9. Scheme of electron transitions at the "cyanine-like" (*a*) and polyenic (*b*) relaxations

band should be shifted hypsochromically by 130–150 nm. Then we can assign the absorption in the short-wave region (to 400 nm) to the electron transitions: $|S_0 \rightarrow S_2\rangle$, $|S_0 \rightarrow S_3\rangle$, and $|S_0 \rightarrow S_4\rangle$ with the comparable oscillator strengths (f_1); whereas no electron transition even with negligible oscillator strength appears in the spectral region between 400 nm and the long-wave band maximum. The fluorescence excitation anisotropy spectra (Fig. 2) show also the existence of electron transitions with distinct polarizations (as compared with the polarization of the $|S_0 \rightarrow S_1\rangle$ transition) in the spectral region at 350–380 nm.

The next excited states form the continuum of higher states; their energies exceed the double excitation energy.

3.5. Cyanine-like relaxation in the excited state and ordinary fluorescence spectra

The considerable redistribution of the electron density within chromophore/fluorophore of the merocyanines at the $|S_0 \rightarrow S_1\rangle$ transition causes, in parallel, the essential changes of the occupancies at the bonds or bond orders, $p_{\mu\nu}$. It is evident that the further direct vibronic relaxation of each bond in the excited state should follow to its order. We mention the well-known relation between the length $R_{\mu\nu}$ and the order $p_{\mu\nu}$ of a carbon-carbon bond in the conjugated system [18]. In the Hückel approximation, it was established that both quantities in the ground state are connected by relation (6). In the semiempirical AM1 approximation, relation (6) slightly transforms to relation (7):

$$R_{\mu\nu}(E) = 1.54 - 0.14p_{\mu\nu}; \tag{6}$$

$$R_{\mu\nu}(E) = 1.58 - 0.13p_{\mu\nu}. \tag{7}$$

In the first approximation, we can optimistically suppose that relation (7) should hold also for the excited state and can be used for the estimation of the geometrical relaxation after the excitation of a molecule.

As an example, the alternation of the bond lengths calculated by formula (7) for merocyanine (*1*) is presented in Fig. 8. One can see that the initial relaxation followed by a change of the occupancies at the bonds (bond orders) leads to the excited state with the considerable equalized bond length in the fluorophore. Such equalizing of the bonds is found to be typical of the cyanine dyes [10, 21]; then we can treat the state $S_1(R_1)$ and the corresponding relaxation as cyanine-like ones. The emission from this excited state appears as an ordinary fluorescence presented in Figs. 2 and 3. The general scheme of electron transitions corresponding to the absorption and the fluorescence, as well as the scheme of the cyanine-like vibronic relaxations, is shown in Fig. 9,*a*. It is particularly to be noted that the emission from the excited state $S_1(R_1)$ takes place to the higher vibronical levels of the global ground state.

One can see from Fig. 2 that the fluorescence band maximum is appreciably shifted to the long-wave region, which points on a substantial change of the equilibrium energy upon the relaxation in the excited state. This is in good agreement with the considerable difference in the molecular geometry (first at all, the difference in the bond lengths) in the ground (S_0) and cyanine-like relaxed excited states $S_1(R_1)$.

It is established [22] that the Stokes shift $\triangle\nu_S$ calculated by formula (8) depends directly on the change of the lengths of bonds in the chromophore, which can be quantitatively estimated by relation (9):

$$\triangle\nu_S = \nu_{\max}(\text{abs}) - \nu_{\max}(\text{fluor}); \tag{8}$$

$$\delta(R_{\mu\nu}) = \sqrt{\sum \left(R^*_{\mu\nu} - R^0_{\mu\nu}\right)^2}, \tag{9}$$

where $R^*_{\mu\nu}$ and $R^0_{\mu\nu}$ are the bond lengths in the excited and ground states; the indices μ and ν run all bonds. The summation runs over all π-bonds.

Taking the correlation between values $R_{\mu\nu}$ and $p_{\mu\nu}$ (6) or (7) into account, it was earlier proposed [23] to replace relation (9) by the equivalent formula

$$\delta(p_{\mu\nu}) = \sqrt{\sum \left(p^{*}_{\mu\nu} - p^{0}_{\mu\nu}\right)^2}. \tag{10}$$

Thus, the quantity $\delta(p_{\mu\nu})$ can be considered as an equivalent integral characteristic of the possible geometrical changes at the relaxation in the excited state (with regard for only the change of the bond lengths in the chromophore/fluorophore, providing the molecule remains planar, and, hence, the fluorescence occurs). Then we can suggest that the parameter $\delta(p_{\mu\nu})$ should correlate with the Stokes shift. The calculated values $\delta(p_{\mu\nu})$ (with regard for the bonds in the open chain and in the benzene ring) are as follows: $\delta(p_{\mu\nu}) = 0.913$ (dye **1**), and $\delta(p_{\mu\nu}) = 0.896$ (dye **2**). These magnitudes exceed considerably the analogous value for the symmetric cyanine dyes: $\delta(p_{\mu\nu}) = 0.120 \div 0.189$ [21].

Similarly, the Stokes shifts in the spectra of the merocyanines ($\triangle\nu_s = 3849$ cm^{-1} in toluene and 5350 cm^{-1} in acetonitrile for dye **1**, as well as $\triangle\nu_s = 2944$ cm^{-1} and 4434 cm^{-1} in the same solvents for dye **2**), are considerably higher than those in spectra of the symmetric cyanines: $\triangle\nu_s = 400 \div 700$ cm^{-1} [21].

It is to be added that the Stokes shift depends also on the solvent. One can see from Fig. 8 that the excitation starts from the solvatic ground state (which is stabilized as compared with the "pure" ground state) to the solvatic excited state which is placed higher than the "pure" excited state (in contrast to the influence of the solvation in the ground state). The next vibronic relaxation to the emission state $S_1(R_1)$ is accompanied not only by a change of the molecular geometry, but simultaneously by a reorientation of the solvent shell. Consequently, the final emission at room temperature is unsolvatic; thereafter, the electron transition, which corresponds to the fluorescence, takes place between the unsolvatic emission state and one of the higher vibronic levels of the unsolvatic ground state. Without any doubt, the energies of the solvation in the ground state and the reorientation of solvent molecules in the excited state depend on the degree of asymmetry of merocyanine molecules and the solvent polarity.

Of course, the scheme in Fig. 9,*a* is somewhat simplified, for the convenience. In fact, there are other channels of the deactivation of the excitation energies, for example, the conformational transformation with the twisting of molecular fragments [15]. Here, we would compare the processes of relaxation and emission at the high and low temperatures.

3.6. Two paths of relaxation and low-temperature time-resolved fluorescence

It is shown that the donor orbital of the donor terminal group and the high-situated quasidonor orbital of the acceptor terminal group are split, both MOs – as two highest occupied orbitals (HOMO and HOMO-1) – being twice fulfilled in the ground state. The excitation causes the jump of the electron from the HOMO to the LUMO; as a result, one of the split MOs becomes single occupied. Thus, although the interaction of the initial donor MOs reaches the additional stabilization of the ground state, the excited state with the split MOs or the cyanine-like excited state $S_1(R_1)$ is not necessarily most stable.

In fact, the direct optimization of a molecular geometry (providing the molecule remains planar) results in another energy minimum, $S_1(R_2)$, with the alternated bond lengths, as one can see from Fig. 5. We propose to call this path of the relaxation in the excited state as polyenic one. The calculation has given that the degree of alternation of the lengths of neighboring bonds in the state $S_1(R_2)$ is rather lower, as compared with that in the ground state, but exceeds significantly the bond length alternation in the cyanine-like relaxed excited state $S_1(R_1)$.

Because of a considerable increase of the length of the bond connecting the chain with the donor residue, the barrier of a conformational transformation should be essentially decreased. Then it is improbable that the emission from the relaxed state $S_1(R_2)$ can be observed. However, if the conformational channel was interlocked, for example, in the frozen matrix, the additional fluorescence can appear in the spectra. It is to be noted that the final state for the emission from the polyenic excited state is seen from Fig. 9,*b* to be the unstable state $S_0(R_2)$ placed higher than the global ground state S_0. As a result, the additional emission should be shifted bathochromically, as compared with the ordinary fluorescence from the emitting state $S_1(R_1)$.

Figure 3 shows that the more complex band is observed in the fluorescence spectra at the low temperature, as compared with the spectral band at room temperature, presented in Fig. 2.

First of all, as would be expected, the fluorescence band maximum obtained in the frozen solution preventing the reorientation of the dye and solvent molecules is shifted hypsochromically. But the main feature of the fluorescence spectra at the low temperature is connected with the shape of a spectral band. One can clearly see from Fig. 3 that the width of the fluorescence curve at 4.2 K exceeds essentially the band width at the high temperature. This is in contrast with the well-known experimentally and well-justified theoretically spectral phenomenon that the band width is usually narrowed down at low temperatures due to a decrease in the vibronic interaction intensity [15]. Based on the discussion above, we can assume that the observed transformation of the spectral band, especially the increase of its width, is connected with the existence of the additional component produced by the polyenic path relaxation in the excited state. Additionally, the time-resolved spectra confirm our assumption. The initial fluorescence band (at 0.7 ns) is seen from Fig. 3 to be narrower (relatively to the integral steady fluorescence); nevertheless, the band tail extends up to 700 nm. In the course of time, the intensity in the long-wave region regularly increases. By subtraction of the fluorescence curves obtained at two time intervals, the new spectral band with a maximum at 650–670 nm appears.

4. Conclusions

Thus, the simultaneous quantum-chemical and spectral studies of the merocyanine indicate that there are two paths of relaxation in the excited state: a) cyanine-like one with equalizing the bond lengths; b) polyenic one with the considerable alternation of bond lengths.

This assumption is confirmed by the existence of two components in the time-resolved fluorescence spectra measured at the low temperature.

1. A. Mishra, R.K. Behera, P.K. Behera, B.K. Mishra, and G.B. Behera, Chem. Rev. **100**, 1973 (2000).
2. F. Meyers, S.R. Marder, and J.W. Perry, *Chemistry of Advanced Materials: An Overview*, edited by L.V. Interrante and M.J. Hampden-Smith (Wiley-VCH, New York, 1998).
3. A.V. Kulinich and A.A. Ishchenko, Usp. Khimii **78**, 151 (2009).
4. Z.R. Grabowski, K. Rotkiewicz, and W. Rettig, Chem. Rev. **103**, 3899 (2003).
5. P.Ch. Ray, Chem. Phys. Lett. **395**, 269 (2004).
6. A. Toutchkine, W.G. Han, M. Ullman, T. Lin, D. Bashford, L. Noodleman, and K.M. Hahn, J. Chem. Phys. A **111**, 10849 (2007).
7. V.G. Nazarenko, Yu.P. Piryatinskii, A.D. Kachkovsky, E.I. Maiboroda, O.A. Zhukova, Yu.L. Slominskii, and A.I. Tolmachev, Teor. Eksp. Khim. **39**, 201 (2003).
8. R.S. Lepkowich, O.V. Przhonska, J.M. Hales, D.J. Hagan, E.W. Van Sryland, M.V. Bondar, Yu.L. Slominski, and A.D. Kachkovski, Chem. Phys. **305**, 259 (2004).
9. A.D. Kachkovski, A.I. Tolmachev, Yu.L. Slominski, M.A. Kudinova, N.A. Derevyanko, and O.O. Zhukova, Dyes Pigm. **64**, 207 (2005).
10. S. Daehne, Science **199**, 1163 (1978).
11. F. Meyers, S.R. Marder, J.W. Perry, and J.L. Bredas, J. Amer. Chem. Soc. **116**, 10703 (1994).
12. A.A. Ishchenko, A.V. Kulinich, S.L. Bondarev, and V.N. Krukshto, J. Phys. Chem. **111**, 13629 (2007).
13. R. Lemke, Chem. Ber. **103**, 1894 (1970).
14. R. Lemke, Synthesis, No.5, 359 (1974).
15. Y.P. Gnatenko, , Y.P. Piryatinski, P.M. Bukivskij, D.D. Kolendryckyj, O.A. Shigiltchoff, and R.V. Gamernyk, J. of Phys.: Cond. Mat. **18**, 9603 (2006).
16. J.R. Lacowicz, *Principles of Fluorescence Spectroscopy* (Plenum, New York, 1983).
17. N.N. Tyutyulkov, A. Gochev, and F. Fratev, Chem. Phys. Lett. **26**, 9 (1969).
18. J. Fabian and R. Zahradnic, Wiss. Z. Techn. Univ. Dresden **26**, 315 (1977).
19. M.J.S. Dewar, *The Molecular Orbital Theory of Organic Chemistry* (McGraw-Hill, New York, 1969).
20. S. Webster, J.Fu, L.P. Padilha, H.Hu, O.V. Przhonska, D.J. Hagan, E.W. Van Stryland, M.V. Bondar, Yu.L. Slominskii, and A.D. Kachkovsky, J. Luminescence **129**, 1927 (2008).
21. A.D. Kachkovsky, Dyes Pigm. **24**, 171 (1994).
22. A.D. Kachkovsky, Usp. Khimii **66**, 715 (1997).
23. E.F. McCoy and I.J. Ross, Austral. J. Chem. **15**, 573 (1962).
24. A.A. Ishchenko, Quant. Electr. **24**, 471 (1994).

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ЦIАНIНОВИЙ ТА ПОЛIЄНОВИЙ ШЛЯХИ РЕЛАКСАЦIЇ МЕРОЦIАНIНIВ, ПОХIДНИХ МАЛОНОДIНIТРИЛУ, У ЗБУДЖЕНОМУ СТАНI, ВИЯВЛЕНI ЗА ДОПОМОГОЮ НИЗЬКОТЕМПЕРАТУРНОЇ, РОЗДIЛЕНОЇ В ЧАСI ФЛУОРЕСЦЕНЦIЇ

М.М. Севрюкова, Ю.П. Пирятинський, С.В. Василюк,
В.М. Ящук, О.О. Вiнiйчук, А.О. Герасьов,
Ю.Л. Сломiнський, О.Д. Качковський

Резюме

Було виконано спiльнi квантово-хiмiчнi та спектральнi дослiдження особливостей електронних переходiв у мероцiанiнах. Встановлено, що два найнижчi переходи роздвоюються, залучаючи обидва донорнi рiвнi подiбно до симетричних цiанiнiв. Крiм того, довгохвильова смуга поглинання дуже iнтенсивна, тодi як наступний за ним другий перехiд виявляється лише в спектрах анiзотропiї збудження флуоресценцiї. На вiдмiну вiд

основного стану, розщеплення МО у збудженому стані приводить до нестійкості. Аналіз результатів теоретичних та експериментальних досліджень дозволяє передбачити, що існує два шляхи релаксації у збудженому стані: а) ціаніновий, з вирівнюванням довжин зв'язків; б) полієновий, із значним альтернуванням довжин зв'язків. Це припущення підтверджується існуванням двох компонент у розділених в часі спектрах флуоресценції, виміряних при низькій температурі.