

# Structure and fluorescent properties of merocyanines based on *N,N*-diethylthiobarbituric acid

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## Abstract

Fluorescent properties of a series of positively and negatively solvatochromic merocyanines based on *N,N*-diethylthiobarbituric acid containing heterocycles of various electron-donating properties are explored in solvents of various polarity. It is shown, that their solvatochromic range is less than the solvatochromic range. A lengthening of the polymethine chain causes a growth of the vinylene shifts, a decrease of the deviations and a narrowing of the fluorescent spectral bands, as opposed to the absorption ones. The transition to the higher vinyllogues is also accompanied by a decrease of the Stokes shifts and an increase of the fluorescent quantum yields. However, a growth of the latter for merocyanines absorbing light in the near-IR range is levelled by an amplification of internal conversion. An absence of a mirror symmetry of the absorption and fluorescence spectra has been revealed. The quantum-chemical analysis of an electronic structure of the merocyanines by the semi-empirical method AM1 is also carried out. The transitions between their ideal electronic states – non-polar polyene, polymethine and dipolar polyene – are investigated. It is shown, that the electronic structure of the fluorescent state of merocyanines approaches the cyanine limit at polymethine chain lengthening.

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**Keywords:** Donor–acceptor systems; Merocyanines; Fluorescence; Solvatochromism; Electronic structure

## 1. Introduction

Due to their strongly pronounced solvatochromism, abilities to change essentially dipole moment at excitation, and to sensitize various physical and chemical processes, merocyanine dyes are widely used in new materials for optoelectronics, nonlinear optics, and as fluorescent probes for biology and medicine [1–3]. An understanding of the regularities connecting their spectral-fluorescent properties with their chemical structure is important for purposeful search of new practically important merocyanines. By now such regularities have been ascertained for the absorption spectra only [1,4–7]. The fluorescence has mainly been investigated for the dyes found wide practical application [8–10] that does not yield an opportunity to make

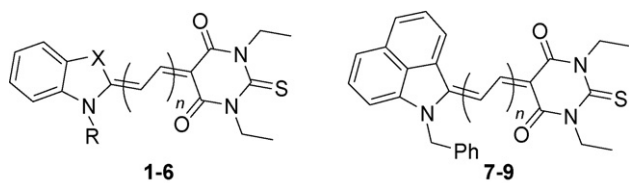
generalizing conclusions. A maximum of dye fluorescence band  $\lambda_{\max}^f$  is traditionally used as a reference point, a width and a form of fluorescence band, which display a degree of vibronic (VI) and intermolecular interactions with a solvent (IMI) in the first excited fluorescent state of dyes, were not considered. The purpose of the present work was the understanding of the laws connecting position, intensity and form of merocyanine fluorescence bands with donor–acceptor properties of their terminal groups, polymethine chain length, and the nature of solvent.

Earlier we had studied the absorption spectra of merocyanines **1–9** (Scheme 1), derivatives of *N,N*-diethylthiobarbituric acid [7].

The electronic structure of these dyes in the ground state changes from non-polar polyene structure **A1** up to dipolar polyene structure **A3** through the ideal polymethine structure (cyanine limit) **A2** at a variation of donor–acceptor ability of terminal heterocyclic groups, polymethine chain length, and nature of solvent [3,7] (Scheme 2).

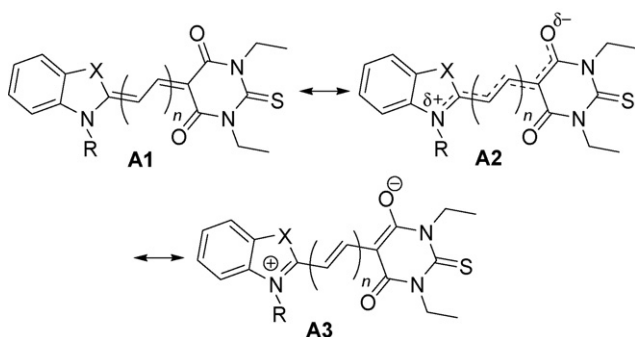
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	1	2	3	4	5	6	7	8	9
X	CMe <sub>2</sub>	CMe <sub>2</sub>	CMe <sub>2</sub>	S	S	S	–	–	–
R	Me	Me	Me	Et	Et	Et	–	–	–
n	1	2	3	1	2	3	1	2	3

Scheme 1.



Scheme 2.

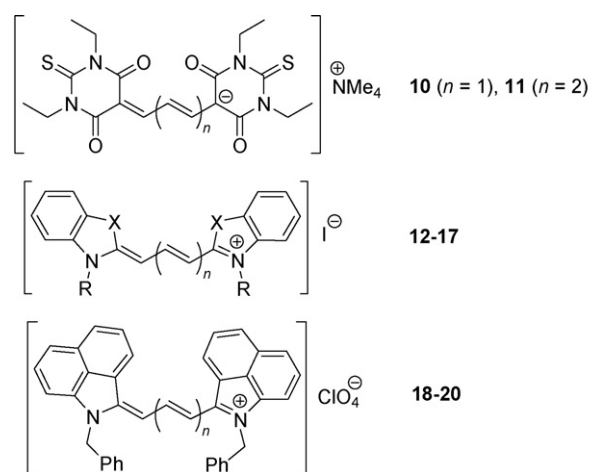
The mathematical treatment of fluorescence bands of merocyanines **1–9** by the method of moments [7,11] has allowed us to characterize quantitatively their position ( $M_f^{-1}$ ) and form ( $\sigma^f$ ,  $\gamma_1^f$ ,  $\gamma_2^f$ ,  $F^f$ ). The parameter  $M^{-1}$  reflects the average position of the band (on the wavenumber scale it represents the band gravity centre:  $\bar{\nu} = 10^7/M^{-1}$ ). In contrast to  $\lambda_{\max}^f$ , this parameter enables us to make a reliable comparison of the curves of different band shape. The parameter  $\sigma^f$  characterizes a deviation of spectral band points from the gravity centre  $\bar{\nu}$ . Hence, this parameter allows making a reliable quantitative comparison of the band width regardless of the band shape, that is an advantage over the half-width  $\bar{\nu}_{1/2}$  (the width at half height of the band) traditionally used for this purpose. The asymmetry coefficient  $\gamma_1^f$ , the excess coefficient  $\gamma_2^f$ , and the fine structure coefficient  $F^f$  provide additional information on the band shape. The parameters  $\lambda_{\max}^f$ ,  $M_f^{-1}$ ,  $\sigma^f$ ,  $\gamma_1^f$ ,  $\gamma_2^f$ , and  $F^f$ , alongside with the fluorescence quantum yields  $\Phi_f$ , the Stokes shifts  $SS_\lambda$  and  $SS_M$ , calculated accordingly on  $\lambda_{\max}^f$ ,  $\lambda_{\max}^a$  and  $M_f^{-1}$ ,  $M_a^{-1}$  (the index a concerns similar characteristics of absorption bands), as well as the deviations  $D_\lambda^f$  and  $D_M^f$  (on  $\lambda_{\max}^f$  and  $M_f^{-1}$ , correspondingly) are collected in Table 1. The deviations have been evaluated with the use of the spectral data of the parent anionic dyes **10**, **11** and cationic dyes **12–20** [11] (Scheme 3) measured in three solvents. The data for dyes **12–20** are taken from Ref. [11]. The characteristics of dyes **10** and **11** are listed in Table 1.

A disadvantage of many works in the field of solvatochromism is the limited range of solvent polarity. Even such low-polar solvents as arenes influence essentially an electronic structure of molecules with high polarizability [12]. Our pur-

pose was to study the dependence of fluorescence spectra upon the structure of merocyanines in maximal wide range of solvent polarity. Low-polar *n*-hexane and toluene, medium-polar dichloromethane, and high-polar aprotic DMF and protic ethanol, in which the absorption spectra of dyes **1–9** [7] had been earlier investigated, have been chosen as solvents (the main characteristics of the chosen solvents are given in Table 2). It should be said, that dichloromethane and DMF were chosen as solvents to compare the spectral band shifts in the pair of solvents with the close values of refractive index  $n_D$  and substantially different polarity (permittivity  $\epsilon_D$ , nucleophilicity  $B$ , and electrophilicity  $E$ ).

The aggregation of dye molecules can occur in low-polarity solvents, which results especially in fluorescence quenching. The aggregates are usually nonfluorescent, but can contribute to the absorption spectra and cause deviation from mirror symmetry of the absorption and fluorescence spectra. The absorption spectra of the merocyanines concerned (Ref. [7] in the manuscript) demonstrate that all of them obey Beer's law in a concentration interval of  $10^{-6}$  to  $10^{-4}$  mol/L in toluene and more polar solvents. Moreover, dyes **1–3** and **7–9** in *n*-hexane also obey Beer's law (up to the concentration  $5 \times 10^{-5}$  mol/L). In fluorescence measurements the maximal optical density of solutions did not exceed 0.2, *i.e.*, the dye concentration was about  $2 \times 10^{-6}$  mol/L. Hence, the aggregation could not influence their fluorescence parameters. Only for strongly dipolar benzimidazole derivatives **4–6** in *n*-hexane the pronounced H-aggregation was observed [7]. For this reason, probably, their fluorescence has not been registered. The fluorescence spectra of dyes **7–9** in *n*-hexane have not been registered due to the extremely low quantum yields.

An approach of merocyanine electronic structure to one of the theoretical structures **A1**, **A2** or **A3** can be judged on a degree



	12	13	14	15	16	17	18	19	20
X	CMe <sub>2</sub>	CMe <sub>2</sub>	CMe <sub>2</sub>	NPh	NPh	NPh	–	–	–
R	Me	Me	Me	Ph	Ph	Ph	–	–	–
n	1	2	3	1	2	3	1	2	3

Scheme 3.

Table 1  
 Characteristics of the fluorescence bands of merocyanines **1–9** and anionic dyes **10, 11** measured in *n*-hexane, toluene, dichloromethane, DMF, and ethanol at 293 K

Dye	Solvent	$\lambda_{\max}^f$ (nm)	$D_{\lambda}^f$ (nm)	$\Phi_f$ (%)	$M_f^{-1}$ (nm)	$D_M^f$ (nm)	$\sigma^f$ (cm <sup>-1</sup> )	$\gamma_1^f$	$\gamma_2^f$	$F^f$ ( $\times 10^2$ )	SS $_{\lambda}$ (cm <sup>-1</sup> )	SS $_M$ (cm <sup>-1</sup> )
<b>1</b>	Hexane	498	–	–	525.0	–	1215	–1.31	3.0	6.9	710	2410
	Toluene	509	–	2.45	534.4	–	1130	–1.35	3.1	7.3	680	2440
	CH <sub>2</sub> Cl <sub>2</sub>	510	–	–	538.2	–	1185	–1.34	3.1	7.2	675	2340
	DMF	510	–	–	539.9	–	1265	–1.28	2.9	6.5	675	2485
	EtOH	507	–	0.8	538.5	–	1285	–1.24	2.5	6.2	605	2510
<b>2</b>	Hexane	580(621) <sup>a</sup>	–	–	619.9	–	1210	–0.91	1.6	4.0	615	2460
	Toluene	611	–	15.0	636.8	–	935	–1.06	2.0	4.4	755	1990
	CH <sub>2</sub> Cl <sub>2</sub>	617	1.5	–	634.3	4.3	805	–1.28	2.7	6.3	655	1540
	DMF	614	1.5	–	632.8	1.1	810	–1.27	2.7	6.3	580	1540
	EtOH	614	–0.5	16.0	635.1	–3.3	830	–1.24	2.5	6.2	660	1700
<b>3</b>	Hexane	652(705)	–	–	720.3	–	1330	–0.89	1.6	4.8	535	3200
	Toluene	706	–	16.0	741.0	–	950	–1.21	2.8	6.7	895	2480
	CH <sub>2</sub> Cl <sub>2</sub>	724	2	–	739.3	5.2	675	–1.43	3.8	7.2	620	1470
	DMF	722	0.5	–	738.7	2.7	680	–1.36	3.3	6.6	580	1375
	EtOH	721	–2	39.0	739.9	–3.1	690	–1.29	3.0	6.5	625	1505
<b>4</b>	Toluene	512	–	1.4	537.2	–	1320	–1.19	2.7	5.8	1260	2715
	CH <sub>2</sub> Cl <sub>2</sub>	506	–	–	532.7	–	1390	–1.16	2.6	5.5	1380	3185
	DMF	505	–	–	529.5	–	1450	–1.12	2.5	5.0	1655	3590
	EtOH	500	–	0.45	525.3	–	1470	–1.02	2.2	4.2	1600	3770
<b>5</b>	Toluene	613	–	51.0	628.8	–	780	–1.26	2.8	5.4	725	1485
	CH <sub>2</sub> Cl <sub>2</sub>	602	12	–	623.7	4.8	900	–1.08	2.1	4.5	900	2230
	DMF	597	14.5	–	619.4	7.5	970	–1.02	2.0	4.0	1300	2975
	EtOH	592	17.5	2.7	616.1	8.1	1010	–0.93	1.6	3.5	1425	3410
<b>6</b>	Toluene	729	–	44.0	744.1	–	620	–1.25	2.7	5.6	570	1175
	CH <sub>2</sub> Cl <sub>2</sub>	711	8.5	–	731.4	5.6	740	–1.18	2.7	4.7	905	2210
	DMF	705	12.5	–	726.8	7.5	830	–0.99	2.2	3.6	1790	3510
	EtOH	701	13.5	25.0	723.6	8.7	860	–1.01	2.3	3.7	3035	4120
<b>7</b>	Toluene	632(681)	–	0.1	693.5	–	1280	–0.61	0.6	2.6	520	2975
	CH <sub>2</sub> Cl <sub>2</sub>	631(681)	–	–	682.8	–	1180	–0.66	0.7	2.7	520	2688
	DMF	631(681)	–	–	681.6	–	1170	–0.68	0.8	3.2	465	2612
	EtOH	623(677)	–	0.5	671.6	–	1180	–0.66	0.7	3.3	340	2459
<b>8</b>	Toluene	720(776)	–	0.05	771.9	–	1000	–0.64	0.6	4.4	1710	2724
	CH <sub>2</sub> Cl <sub>2</sub>	730(776)	1	–	767.7	–17.4	830	–0.74	0.6	4.0	545	2255
	DMF	734(776)	–	–	764.9	–	760	–0.76	0.6	4.1	520	1991
	EtOH	725(776)	–	0.25	751.1	–	750	–0.87	0.7	5.2	410	1735
<b>9</b>	Toluene	(818)885	–	0.07	923.2	–	1260	–0.52	0.5	5.2	3130	4176
	CH <sub>2</sub> Cl <sub>2</sub>	838	1.5	–	907.8	–48.6	990	–0.61	0.6	4.0	2050	3307
	DMF	843	–	–	887.3	–	820	–0.72	0.7	3.8	545	2646
	EtOH	830	–	0.20	864.8	–	810	–0.88	1.0	4.8	405	2300
<b>10</b>	CH <sub>2</sub> Cl <sub>2</sub>	566	–	–	580.8	–	810	–1.28	3.0	6.0	645	1550
	DMF	561	–	–	576.5	–	805	–1.30	3.1	6.1	625	1545
	EtOH	560	–	5.1	574.2	–	810	–1.28	3.1	5.7	660	1565
<b>11</b>	CH <sub>2</sub> Cl <sub>2</sub>	669	–	–	683.6	–	660	–1.27	2.9	5.5	555	1335
	DMF	667	–	–	679.4	–	635	–1.30	3.2	5.7	585	1285
	EtOH	663	–	52.0	676.0	–	635	–1.28	3.2	5.5	590	1380

<sup>a</sup> The less intensive peak positions are typed in parentheses.

of chromophore bond lengths or bond orders alternation [3]. The electronic structure **A2** (the cyanine limit) possesses the longest wavelength absorption (and fluorescence) band, which determines the positive and negative solvatochromic effects for merocyanines lying within the interval **A1–A2** and **A2–A3**, respectively. An increase of bond order alternation in chromophore is accompanied by a decrease of vinylene shifts, an increase of deviations and band width, as well as a change of

band shape [11]. For a quantitative evaluation of bond alternation in donor–acceptor conjugated systems, to which merocyanines belong, the parameters BLA (bond length alternation) and BOA (bond order alternation) [3] are most frequently used. The parameter BLA has the positive values for the neutral polyene **A1** and structures intermediate between **A1** and **A2**, and the negative for **A3** and structures from the interval **A2–A3** [3]. The parameter BOA has inverse signs for these structures. Both

Table 2

The main characteristics of the solvents chosen

Solvent	$n_D^{20}$	$\varepsilon_D$	$B$ (cm <sup>-1</sup> )	$E$	$E_T$ (kJ/mol)	$E_T^N$
<i>n</i> -Hexane	1.3751	1.89	0	0	129.7	0.009
Toluene	1.4961	2.37	58	1.3	142.4	0.099
CH <sub>2</sub> Cl <sub>2</sub>	1.4242	8.9	23	2.7	170.4	0.309
Ethanol	1.3611	24.3	235	11.6	217.3	0.654
DMF	1.4303	36.7	291	2.6	183.4	0.404

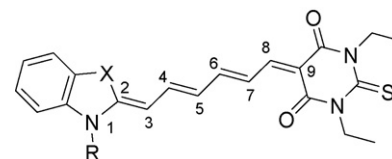
parameters are vanished for structures such as **A2**. The parameter BOA is calculated also for the first excited Franck-Condon  $S_1^{FC}$  state of dye molecules (BOA\*). Nonradiative relaxation from the  $S_1^{FC}$  to the  $S_1$  state is accompanied mainly by an adjustment of a nuclear configuration under electronic configuration changed after absorption of a light quantum [11]. Thus, at the first approximation, it is possible to assume, that bond orders in the  $S_1$  state should be close to those in the  $S_1^{FC}$  state.

Besides BLA and BOA, the values of quadratic changes of bond orders at excitation ( $\delta$ ) for molecules **1–9** are also calculated and listed in Table 3.

$$\delta = \sqrt{\sum_{i=1}^m (P^* - P)_i^2},$$

where  $i$  is the bond number;  $m$  the bond count,  $P^* - P$  a difference of  $i$ -bond orders in the excited and the ground states. The parameter  $\delta$  is proportionate to the internuclear equilibrium distance changes at excitation and is successfully used as the quantitative characteristic for the description of tendencies in change of VI in polymethine dyes [11].

The electrostatic IMI with a solvent depend on a charge alternation in dye molecule [11]. We evaluate this alternation with



Scheme 4.

the help of the integral parameter  $\Delta q_\Sigma$  for ground state  $S_0$  and  $\Delta q_\Sigma^*$  for  $S_1^{FC}$  (Table 3):

$$\Delta q_\Sigma = \sum_i |q_i - q_{i+1}|,$$

where  $q_i$  and  $q_{i+1}$ —charges on the neighbouring atoms. The parameters  $\Delta q_\Sigma$  and  $\Delta q_\Sigma^*$  are calculated for chromophore N-1-C-2...-C-9 (Scheme 4).

## 2. Experimental

Merocyanines **1–9** were refined by chromatography on “Merck” silica gel 60 or neutral aluminium oxide 80. The purity of the merocyanines was checked by TLC-control (Silufol UV-254, CH<sub>2</sub>Cl<sub>2</sub> as the eluent). Solvents were purified according to the known techniques [13]. Solutions of merocyanines were not degassed since the fluorescent characteristics for degassed and non-degassed solutions were shown to be identical. The fluorescence spectra were measured on the large-aperture setup high-transmission spectrometer described in [14]. The moments of the fluorescence and absorption bands were determined accordingly in coordinates  $I_f(\tilde{\nu})/\tilde{\nu}^4$  and  $I_a(\tilde{\nu})/\tilde{\nu}$  ( $I_f$  and  $I_a$ —intensity of fluorescence and absorption,  $\tilde{\nu}$ —wavenumber) in which the law of mirror symmetry [11] is most rigorously obeyed. The fluorescence quantum yields  $\Phi_f$  of merocyanines

Table 3

The results of the quantum-chemical calculation of merocyanines **1–9**, anionic **10**, **11** and cationic **12–20** parent dyes and cyclooctatetraene **21** by method AM1

	BLA (Å)	BOA	BOA*	$\delta_{ch}$	$\delta$	$\Delta\delta$	$\mu$ (D)	$\mu^*$ (D)	$\Delta q_\Sigma$	$\Delta q_\Sigma^*$
<b>1</b>	0.047	-0.421	0.113	0.504	0.538	0.034	7.608	10.04	1.65	0.451
<b>2</b>	0.069	-0.564	0.062	0.742	0.753	0.011	7.689	12.62	1.879	0.581
<b>3</b>	0.079	-0.631	0	0.888	0.894	0.006	7.534	14.61	1.95	0.896
<b>4</b>	0.029	-0.326	0.118	0.418	0.448	0.03	8.498	9.831	1.832	0.35
<b>5</b>	0.064	-0.531	0.067	0.708	0.718	0.01	8.344	12.82	1.975	0.594
<b>6</b>	0.076	-0.608	0.006	0.863	0.876	0.013	8.272	15.31	2.063	0.951
<b>7</b>	0.049	-0.428	0.049	0.451	0.632	0.181	7.259	8.51	1.652	0.124
<b>8</b>	0.072	-0.579	0.004	0.708	0.793	0.085	6.866	10.54	1.731	0.489
<b>9</b>	0.081	-0.637	-0.05	0.851	0.902	0.051	6.737	12.18	1.783	0.781
<b>10</b>	0.002	-0.026	0	0.086	0.373	1.315	0.164	0.614	1.936	0.596
<b>11</b>	-0.004	0.024	0.014	0.068	0.115	0.043	0.815	0.558	2.682	0.956
<b>12</b>	-0.007	0.024	-0.021	0.061	0.258	0.197	2.254	3.711	2.652	0.534
<b>13</b>	-0.001	-0.029	-0.007	0.058	0.165	0.107	1.699	3.639	3.378	1.078
<b>14</b>	0.005	-0.066	-0.013	0.092	0.136	0.044	1.192	3.472	4.064	1.558
<b>15</b>	-0.023	0.135	0.041	0.095	0.243	0.148	0.091	1.023	3.038	0.812
<b>16</b>	-0.015	0.08	0.04	0.075	0.181	0.106	1.081	0.873	3.804	1.55
<b>17</b>	-0.012	0.059	0.048	0.057	0.132	0.075	1.668	0.672	4.492	2.004
<b>18</b>	-0.007	0.043	0.042	0.027	0.342	0.315	1.865	3.443	2.776	0.638
<b>19</b>	-0.002	-0.012	0.041	0.062	0.268	0.206	1.39	3.479	3.472	1.214
<b>20</b>	0.004	-0.049	0.032	0.119	0.237	0.118	0.968	3.423	4.128	1.684
<b>21</b>	0.114	-0.881	0.202	2.02	2.02	0	0	0	0	0

**1–8** were measured for all merocyanines in toluene and ethanol in relation to the  $\Phi_f$  value of cresyl violet in methanol ( $\Phi_f = 65\%$  [15]) and rhodamine 6G in ethanol ( $\Phi_f = 95\%$  [16]), merocyanine **9**—in relation to  $\Phi_f$  value of dye **11** in ethanol ( $\Phi_f = 28\%$  [11]). The values of  $\Phi_f$  were corrected taking into account refractive index changes of the solvent.

The quantum-chemical calculations of the electronic structure of the dye molecules were performed for gas phase by AM1 method with a standard set of parameters [17]. Geometry optimizations with the use of limited Hartree–Fock method and Polak–Ribiere algorithm with an accuracy of  $0.001 \text{ kcal } \text{Å}^{-1} \text{ mol}^{-1}$  had been preliminary carried out.

### 3. Results and discussion

#### 3.1. Electronic structure and solvatochromism

In a series of dyes **1–3** at changing from *n*-hexane to toluene and further to  $\text{CH}_2\text{Cl}_2$  as solvents a bathochromic shift of fluorescence bands both on  $\lambda_{\text{max}}^f$ , and on  $M_f^{-1}$ , *i.e.*, the positive solvatofluorochromism is observed (Table 1). The further increase in solvent polarity, as well as in the case of absorption [7], does not influence noticeably the band position in their emission spectra (Table 1).

The vinylene shifts in the fluorescence spectra of dyes **1–3** are greater, than in the absorption ones, both on the maxima ( $\text{VS}_\lambda^f$ ) and on the band centres ( $\text{VS}_M^f$ ) (cf. Table 1 and [7]). Only in *n*-hexane  $\text{VS}_\lambda^f$  values are substantially smaller than the value of 100 nm typical for the relevant symmetric ionic polymethines [7]. It specifies higher symmetry of an electronic structure in the  $S_1$  state of the given dyes, and thus their greater approach to the theoretical polymethine structure **A2** (cyanine limit) in comparison with their  $S_0$  state.

The deviations  $D_\lambda^f$  and  $D_M^f$  of merocyanines **1–3** are close to zero, they are much less than the relevant values in the absorption spectra and change only a little at chain lengthening (Table 1). This fact also specifies high electronic symmetry of the  $S_1$  state of these dyes.

The maximal  $\sigma^f$  value and the least coefficients  $\gamma_1^f$ ,  $\gamma_2^f$  and  $F^f$ , as well as in the absorption spectra [7], are reached for positive solvatochromic merocyanines **2** and **3** in low-polar *n*-hexane (Table 1), specifying the essential electronic symmetry violation in this solvent. On going from *n*-hexane to more polar toluene the fluorescence bands become essentially narrower, more unsymmetrical and peaked. The further growth of medium polarity is also accompanied by narrowing of the spectral bands (Table 1), and by approach of their shape to those for the relevant symmetric anionic **10**, **11** and cationic **12–20** polymethine dyes [11]. It is significant, that  $\sigma^f$ ,  $\gamma_1^f$ ,  $\gamma_2^f$ , and  $F^f$  values for dyes **1–3** in a set of solvents  $\text{CH}_2\text{Cl}_2$ –DMF–ethanol change very little (Table 1), much less, than the corresponding parameters in the absorption spectra [7]. Consequently, IMI influence slightly dyes' **1–3** fluorescence band width and shape, the latter are defined mainly by VI.

Let us make more detailed analysis of the parameter  $\sigma^f$  changes in a series **1–3** at variation of polymethine chain length and solvent polarity. The transition from dimethinemerocya-

nine **1** to tetramethinemerocyanine **2** causes fluorescence bands narrowing in all solvents, except *n*-hexane, in which  $\sigma^f$  value remains practically constant (Table 1). For the highest vinylogue **3** the value of  $\sigma^f$  grows in *n*-hexane and toluene a little, however in more polar solvents its fluorescence bands become even narrower than for dye **2**, achieving values of  $675$ – $690 \text{ cm}^{-1}$ . At the same time in the absorption spectra an increase of  $n$  is accompanied by a band broadening. The absorption bands get narrower only at transition from short vinylogue **1** to dye **2** in  $\text{CH}_2\text{Cl}_2$ , DMF and ethanol, but  $\sigma^a$  value changes much less, than  $\sigma^f$  at the same transition [7]. A decrease of  $\sigma^f$  and  $\sigma^a$  at chain lengthening indicates a reduction of VI, typical for symmetric polymethine dyes. Hence in the fluorescent state merocyanines **1–3** come nearer to the cyanine limit **A2**. The contribution of the structure **A2** increases for the highest vinylogues. Only in low-polar *n*-hexane and toluene the violation from this tendency is observed.

The violation of mirror symmetry of absorption and fluorescence spectra is observed for dyes **1–3** (Fig. 1), that can also be seen at comparison of parameters  $\sigma^f$ ,  $\gamma_1^f$ ,  $\gamma_2^f$ ,  $F^f$  and  $\sigma^a$ ,  $\gamma_1^a$ ,  $\gamma_2^a$ ,  $F^a$  (see Table 1, [7]). The fluorescence bands of dyes **2** and **3** are narrower than the absorption ones, that is probably concerned with decreasing of VI in the  $S_1$  state, its approach to the ideal polymethine structure **A2**. However, the values of  $\sigma^f$  for dimethinemerocyanine **1** are greater than  $\sigma^a$  in all solvents.

The Stokes shifts  $\text{SS}_\lambda$  and  $\text{SS}_M$  in a series **1–3** slightly vary from a solvent to solvent and at a change of polymethine chain length (Table 1). In *n*-hexane and toluene the values of  $\text{SS}_M$  lie in the range of  $2000$ – $3200 \text{ cm}^{-1}$  and grow at transition from dye **2** to **3**. On the contrary, in more polar solvents the parameter  $\text{SS}_M$  decreases at chain lengthening, achieving for the highest vinylogue **3** values of  $1400$ – $1500 \text{ cm}^{-1}$ , that also indicates high electronic symmetry of both the ground and the excited states of dyes **1–3** in  $\text{CH}_2\text{Cl}_2$ , DMF and ethanol. It is necessary to note, that the parameter  $\text{SS}_M$  is more informative than  $\text{SS}_\lambda$  since it is averaged over all vibronic transitions. For example, some peaks, both in the absorption and fluorescence spectra, are observed for compound **3** in *n*-hexane, and therefore the calculated value  $\text{SS}_\lambda$  depends on  $\lambda_{\text{max}}$  selection.

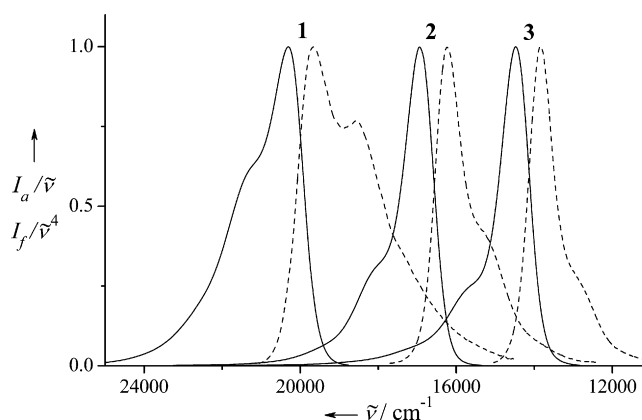


Fig. 1. Normalized UV/vis (—) and fluorescent (---) spectra of merocyanines **1**, **2**, **3** in ethanol.



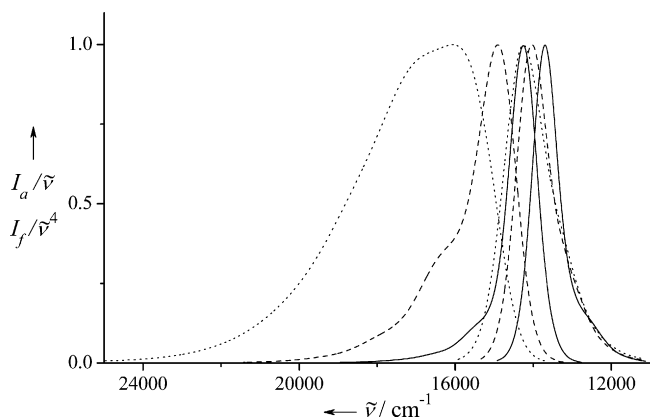


Fig. 2. Normalized UV/vis and fluorescent spectra of merocyanine **6** in toluene (—), dichloromethane (---) and ethanol (···).

So, the regularities in the fluorescence spectra of merocyanines **1–3** are similar to those in the absorption ones [7]. The differences are concerned with a slightly greater contribution of the limit structure **A2** to their excited state, as well as the weakening of IMI with solvent. In all medium- and high-polar solvents dyes **1–3** are very close to the cyanine limit. Since in low-polar *n*-hexane and toluene the electronic structure of the  $S_0$  state of dyes **1–3** lies in the interval **A1–A2** and they have the positive solvatochromism [7], it is possible to suggest that at transition  $S_1^{\text{FC}} \leftarrow S_0$  their electronic structure changes in a direction of an interval **A2–A3** and becomes much more dipolar.

Dyes **4–6**, whose benzimidazole residue is more electron-donating, than *3H*-indole residue in a series **1–3**, are characterized by pronounced negative solvatofluorochromism (Table 1, Fig. 2). The solvatochromic shift values in their fluorescence spectra are much less than those in the absorption ones [7]. For example, for compound **6** shift  $\Delta\lambda_{\text{max}}^{\text{a}}$  ( $\Delta M_{\text{a}}^{-1}$ ) in a pair of solvents toluene–DMF amounts to 74 nm/1690  $\text{cm}^{-1}$  (105.2 nm/2655  $\text{cm}^{-1}$ ), whereas  $\Delta\lambda_{\text{max}}^{\text{f}}$  ( $\Delta M_{\text{f}}^{-1}$ ) amounts to only 24 nm/465  $\text{cm}^{-1}$  (17.3 nm/330  $\text{cm}^{-1}$ ). In a pair of solvents  $\text{CH}_2\text{Cl}_2$ –DMF which, having the close values  $n_{\text{D}}$ , rather strongly differ on polarity (Table 2), differences in values  $\lambda_{\text{max}}^{\text{f}}$  ( $M_{\text{f}}^{-1}$ ) in a series **4–6** do not exceed 6 nm and change a little at chain lengthening (Table 1), whereas in their absorption spectra the solvatochromic shifts for this pair of solvents achieve several tens nanometres and increase substantially for the highest vinylogue [7]. These data specify drastic weakening of IMI with a solvent in the fluorescent state of merocyanines **4–6**.

The first vinylene shifts in a series **4–6** in toluene and  $\text{CH}_2\text{Cl}_2$  as solvents are less in the fluorescence than in the absorption spectra. On the contrary, in high-polar DMF and ethanol, in which the electronic structure of the ground state of these merocyanines is deviated noticeably from the cyanine limit **A2** aside the charged polyene **A3** [7],  $\text{VS}_{\lambda}^{\text{f}}$  and  $\text{VS}_{\text{M}}^{\text{f}}$  are greater than  $\text{VS}_{\lambda}^{\text{a}}$  and  $\text{VS}_{\text{M}}^{\text{a}}$ . The fluorescent vinylene shifts exceed 100 nm in all solvents (Table 1), even in ethanol in which  $\text{VS}_{\lambda}^{\text{a}}$  amounts to only 32 nm. Furthermore, in the fluorescence spectra, in contrast to the absorption ones, the second vinylene shifts exceed the first ones.

The deviations in fluorescence of merocyanines **4–6** (Table 1) are negligible, much less than in their absorption spectra [7].

In a series **4–6** the band widths ( $\sigma^{\text{f}}$ ) increase, and the parameters  $\gamma_1^{\text{f}}$ ,  $\gamma_2^{\text{f}}$ ,  $F^{\text{f}}$  decrease at a growth of solvent polarity (Table 1) that is in agreement with their negative solvatofluorochromism. However, these parameters do not change so considerably, as in the absorption spectra [7]. For example, the value of  $\sigma^{\text{f}}$  for dye **6** amounts in ethanol to only 860  $\text{cm}^{-1}$ , and  $\Delta\sigma^{\text{f}} = 240 \text{ cm}^{-1}$  at transition from toluene to ethanol as solvent, whereas  $\sigma^{\text{a}} = 2070 \text{ cm}^{-1}$  in ethanol, and  $\Delta\sigma^{\text{a}} = 1200 \text{ cm}^{-1}$  in a pair toluene–ethanol. It also indicates that in the excited state dyes **4–6** drop their “solvate coat” substantially. Seemingly, their electronic structure changes from the interval **A2–A3** [7] to the direction **A1–A2** at transition  $S_1^{\text{FC}} \leftarrow S_0$ , getting considerably less dipolar in the excited state that causes a weakening of polar IMI.

The fluorescence spectra of dyes **4–6**, in contrast to the absorption ones, are naturally narrowed at polymethine chain lengthening in all solvents (Table 1). Like merocyanines **1–3**, in a series **4–6** the violation of absorption and fluorescence spectra mirror symmetry is observed. In the case of dimethinemerocyanine **4** the parameter  $\sigma^{\text{f}}$  increases in comparison with  $\sigma^{\text{a}}$ . On the contrary, the fluorescence bands of dyes **5** and **6** become narrower and more asymmetrical than their absorption bands (Table 1, Fig. 2).

For organic dyes with non-rigid chromophore in the absence of steric effects between endgroups  $\sigma^{\text{f}} < \sigma^{\text{a}}$  is more logical [11]. Indeed, besides VI, the solvation processes (IMI) and *trans–cis* isomerization around the polymethine chain bonds make an essential contribution to a band broadening [11]. The IMI result in occurrence of molecules with a different solvation sphere (inhomogeneous broadening). The *trans–cis* torsions bring to a mixture of stereoisomers (conformers). Usually in the emission transition  $S_1 \rightarrow S_0^{\text{FC}}$ , owing to a decrease of IMI, especially for negatively solvatochromic merocyanines, a role of an inhomogeneous broadening is diminished in comparison with the absorption transition  $S_1^{\text{FC}} \leftarrow S_0$  [11].

Independence of fluorescence spectra from excitation and registration wavelengths testifies that only one stereoisomer takes place in light emission and conformational processes do not make determinative influence on the fluorescence band shape of merocyanines **1–6**. Therefore, for an explanation of unusual fluorescence bands broadening of merocyanines **1** and **4** in comparison with the absorption bands it is necessary to assume, that for them the VI in transition  $S_1 \rightarrow S_0^{\text{FC}}$  are larger than in  $S_1^{\text{FC}} \leftarrow S_0$ . For the lowest vinylogues of polymethines the main electronic transition is substantially located in the endgroups and a change of bond orders in the terminal groups makes an essential contribution to VI. And the situation is feasible when the contribution of endgroups into VI is stronger for transition  $S_1 \rightarrow S_0^{\text{FC}}$ , than for  $S_1^{\text{FC}} \leftarrow S_0$ . Quantum-chemical calculation by AM1 method (Table 3) agrees to the assumption, that bond orders of heterocycles in compounds **1** and **4** change at excitation much more strongly, than in the highest vinylogues.

Thus, all the spectral parameters – the negligible deviation values, the vinylene shifts close to 100 nm, and the narrow asymmetric spectral curves – point to an affinity of the electronic

structure of dyes **4–6** in the excited state to the cyanine limit **A2**. The maximal contribution of the ideal polymethine structure, as well as for the ground state, is achieved in low-polar toluene.

Merocyanines **7–9**, derivatives of weak-electron-donating benzo[*cd*]indole, are characterized by distinct positive solvatochromism and high electronic asymmetry in the  $S_0$  state with a significant contribution to them of non-polar polyene structure **A1** [7]. But it is not easy to determine a sign of their solvatochromism. At transition from toluene to  $\text{CH}_2\text{Cl}_2$  and further to DMF a bathochromic shift of  $\lambda_{\text{max}}^{\text{f}}$ , *i.e.*, positive solvatochromism, takes place. However, the replacement of DMF with ethanol as solvent is accompanied with hypsochromic shift, which achieves  $\Delta\lambda = 13$  nm ( $185\text{ cm}^{-1}$ ) for compound **9**. In ethanol the contribution of structure **A2** in the  $S_0$  state of merocyanines **7–9** is maximal [7], in the fluorescent  $S_1$  state situation should be similar. Therefore, the hypsochromic shift of  $\lambda_{\text{max}}^{\text{f}}$  in a series **7–9** at transition from DMF to ethanol is likely concerned with a drastic reduction of medium refractive index  $n_D$ , rather than with an increase of electronic asymmetry of dye molecules. Thus, the signs of solvatochromism and solvatofluorochromism of merocyanines **7–9**, as well as for **1–6**, coincide.

The vinylenic shifts  $\text{VS}_{\lambda}^{\text{f}}$  and  $\text{VS}_{\text{M}}^{\text{f}}$  for merocyanines **7–9** are larger, than the corresponding parameters in their absorption spectra (Table 1, [7]). An especially strong contrast is observed for toluene and  $\text{CH}_2\text{Cl}_2$ .  $\text{VS}_{\lambda}^{\text{a}}$  values amount to a few nanometres, and  $\text{VS}_{\lambda}^{\text{f}}$ —100 nm in these solvents. This fact suggests that in the given series of dyes the  $S_1$  state is also closer to structure **A2**, than the ground  $S_0$  state.

The deviations  $D_{\lambda}^{\text{f}}$  and  $D_{\text{M}}^{\text{f}}$  for dyes **8** and **9** are calculated only in  $\text{CH}_2\text{Cl}_2$ . The values of  $D_{\lambda}^{\text{f}}$  are practically equal to zero, and  $D_{\text{M}}^{\text{f}}$  gets even negative values (Table 1). Taking into account the positive solvatofluorochromism of these merocyanines, one can suggest that in ethanol and DMF their deviations are of the same order or even less than in  $\text{CH}_2\text{Cl}_2$ . The corresponding values  $D_{\lambda}^{\text{a}}$  and  $D_{\text{M}}^{\text{a}}$  in the absorption spectra of compound **9** amount to 8 and 32 nm, respectively [7]. Thus, this parameter specifies the greater contribution of the ideal polymethine structure **A2** to the fluorescent state of merocyanines **7–9**.

The band width in a series **7–9** decreases and the parameters  $\gamma_1^{\text{f}}$ ,  $\gamma_2^{\text{f}}$  and  $F^{\text{f}}$  increase at a growth of solvent polarity (Table 1), confirming positive solvatofluorochromism of these merocyanines. The fluorescence bands of dyes **7–9** get considerably narrowed at transition from di- to tetramethinemerocyanine; the lengthening of the polymethine chain on one more vinylenic group is accompanied by band broadening, however an increase of  $\sigma^{\text{f}}$  in DMF and ethanol is very small. At the same time the parameter  $\sigma^{\text{a}}$  practically does not change in the pair **7–8** and grows essentially at transition from dye **8** to the highest vinylogue **9**. Thus, the fluorescence band width of merocyanines **7–9** in high-polar solvents are close to those for the symmetric anionic **10**, **11** and cationic **12–20** polymethine dyes (Table 1, [7]). Therefore mirror symmetry of absorption and fluorescence spectra is broken due to narrowing of the latter; in the case of dye **9** in DMF and ethanol the band width decreases almost twice (Fig. 3).

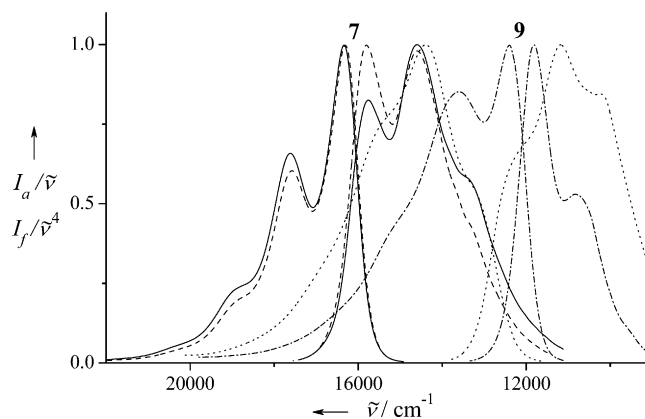


Fig. 3. Normalized UV/vis and fluorescent spectra of dye **7** in toluene (—) and DMF (---) and dye **9** in toluene (···) and DMF (-·-·).

The Stokes shifts in a series **7–9** are of the same order, as for dyes **1–6**. The maximal values of  $\text{SS}_{\lambda}$  also  $\text{SS}_{\text{M}}$  are achieved in low-polar toluene, and minimal—in ethanol.

Thus, all the data points that the fluorescent state of merocyanines **7–9** is closer to the ideal polymethine **A2**, than the ground one. However, the trends in change of  $\sigma^{\text{f}}$  values show, that the contribution of the structure **A2** for them is less, than for dyes **1–6**, even despite the fact that in the  $S_0$  state electronic symmetry of compounds **4–6** in high-polar solvents is essentially violated.

The electronic structure of dyes **7–9** in the  $S_0$  state lies within the interval **A1–A2** [7]. Hence, at transition  $S_1^{\text{FC}} \leftarrow S_0$  their electronic structure changes toward the interval **A2–A3**. Consequently, in the fluorescent  $S_1$  state they approach the structure **A2** from the side of the dipolar polyene **A3**. And the highest contribution of the structure **A2** is achieved in high-polar DMF and ethanol.

Dyes **1–9** contain the residue of *N,N*-diethylthiobarbituric acid with the carbonyl groups solvated efficiently by electrophilic solvents and, in particular, forming H-bonds with molecules of protic solvents like ethanol [18]. As found, EtOH molecules indeed form H-bonds with the C=O groups of the *N,N*-diethylthiobarbituric moiety thus enhancing the dipolarity of merocyanine dye molecules as compared to that in aprotic solvents like DMF. For example, the absorption and fluorescence spectra of negatively solvatochromic dyes **4–6** exhibit the hypsochromic shift, increased band widths, and decreased extinctions in going from DMF to ethanol. However, much smaller changes are observed in the fluorescence than in the absorption spectra. This is consistent with the general conclusion that solvatofluorochromism of merocyanines is weaker than their solvatochromism.

The fluorescence and absorption bands of merocyanines **1–9** mostly demonstrate well-defined fine structure (see Figs. 1 and 3). Its vibronic origin is evidenced by the mirror-image similarity of the absorption and fluorescence spectra and also by a vibrational progression with a frequency of  $1100 \pm 100\text{ cm}^{-1}$  (corresponding to the totally symmetric valence vibration of the polymethine chain in the excited state [11]). Especially well-pronounced vibronic structure is observed

for merocyanines 7–9, the benzo[*cd*]indole derivatives (see Fig. 3) the electronic structure of which is closest to the polyenic resonance structure **A1**.

So well-pronounced vibronic structure of spectral bands allows us to compare the degree to which vibronic interactions contribute to the absorption and emission transitions. For dimethinemerocyanines **1**, **4**, and **7**, the vibronic maxima are more intense in the fluorescence spectra, implying that vibronic interactions are involved more in the emission than in the absorption transition. Thus, the analysis of band vibronic structure enables reliable interpretation of the observed fluorescence band broadening. Formerly this fact, unusual for polymethine dyes (as a rule, fluorescence bands are narrower than absorption bands [11]), was not explained unequivocally in view of several possible mechanisms of band broadening (solvation, *trans*–*cis* isomerization, and vibronic interactions). On the polymethine chain lengthening, the vibronic maxima in the fluorescence spectra of merocyanines 1–9 become less intensive than in the absorption spectra (see Figs. 1 and 3). This also suggests that the dyes are closer to the **A2** structure in the  $S_1$  than in the  $S_0$  state.

For merocyanines 1–3 and 7–9, the intensities of vibronic maxima fall with increasing solvent polarity. On the contrary, negatively solvatochromic dyes 4–6 demonstrate the enhanced bands of higher vibronic transitions (see Fig. 2). These effects confirm the conclusion which follows from the analysis of vinylene shifts, deviations, and band widths: as solvent polarity increases, positively solvatochromic merocyanines approach the cyanine limit **A2** and negatively solvatochromic merocyanines approach the dipolar polyene **A3**.

The fluorescence quantum yields of dyes 1–6 increase at polymethine chain lengthening (Table 1). Seemingly, it is concerned with an increase of the structure **A2** contribution in an electronic structure of their fluorescent state. This assumption is confirmed by the fact that replacement of toluene by more polar ethanol as a solvent causes an increase of  $\Phi_f$  values of positively solvatochromic dyes 1–3 and their falling in a series of dyes 4–6 possessing negative solvatochromism (Table 1). Thus, the well-defined correlation between the contribution of the structure **A2** and the fluorescence quantum yields of merocyanines is traced. A slight decrease of  $\Phi_f$  in toluene at transition from dye 5–6 is concerned, probably, with an approach to IR spectral range, an increase of a contribution of internal conversion in relaxation of the excited state of dyes.

Another interpretation of the  $\Phi_f$  tendencies is also probable. The relative positions of the  $^1(\pi_H\pi_L^*)$  and  $^1(n\pi_L^*)$  levels can significantly influence the fluorescence quantum yields of merocyanines [19]; in turn, they depend essentially on solvent polarity. Formerly we studied the fluorescent properties of di-, tetra-, and hexamethinemerocyanines containing the malononitrile residue and the same heterocyclic nuclei as dyes 1–9 [20]. As was found, the  $^1(n\pi_L^*)$  transitions in such compounds did not play a significant role in the fluorescent state deactivation. At the same time, the trends in fluorescence quantum yields were much the same as for positively solvatochromic dyes 1–3, *i.e.*, the  $\Phi_f$  value increased with the lengthening

of the polymethine chain and/or with rising solvent polarity. One can, therefore, infer that it is just polyene–polymethine transitions that basically govern fluorescence intensity of dyes 1–9. Complete clarification of this issue calls for further research.

The fluorescence quantum yields of merocyanines 7–9 are much less, than for derivatives of 3*H*-indole 1–3 and benzimidazole 4–6 (Table 1). It can be explained by a greater contribution of internal conversion for deep-coloured benzo[*cd*]indole derivatives, and also by the specificity of this heterocycle. Similarly to dyes 1–3 the  $\Phi_f$  values of compounds 7–9 in ethanol are larger than those in toluene.

### 3.2. Quantum-chemical calculations of merocyanines

Let us compare the conclusions about the change of an electronic structure of merocyanines 1–9 at the excitation, obtained after the analysis of experimental data to the results of quantum-chemical calculation of their molecules by method AM1 (Table 3).

The calculated values BLA and BOA of merocyanines 1–9 are considerably less (on absolute value) than similar parameters for cyclooctatetraene **21**, which is used as a model of the ideal neutral polyene **A1** [3], but larger, than those for the corresponding symmetric anionic **10**, **11** and cationic **12–20** dyes (Table 3). It indicates that in gas phase the electronic structure of the merocyanines'  $S_0$  state, corresponding to the interval **A1–A2**, is appreciably displaced aside the structure **A2**.

An essential growth of BLA and BOA values at a polymethine chain lengthening is in good agreement with absorption band broadening and low vinylene shifts of dyes 1–3 and 7–9 in *n*-hexane (see [7]). Polymethine chain bonds of merocyanines 4–6 are more levelled, than in series 1–3 or 7–9 (Table 3), *i.e.*, the contribution of the limit structure **A2** to their electronic structure in the  $S_0$  state should be higher. The smaller values  $\sigma^a$  of the former than of the latter in low-polar toluene agreed with this conclusion [7].

The significant equalization of chromophore bond orders in the excited state of merocyanines 1–9 is clearly traced at the BOA\* values (Table 3). As opposed to the ground state, in the  $S_1^{FC}$  state the electronic asymmetry decreases at chain lengthening, reaching for the highest vinylene values close to those for the corresponding symmetric ionic dyes **10–20** (Table 3, [11]). This result agrees with a growth of vinylene shifts, a decrease of deviations and narrowing of spectral bands at chain lengthening in the fluorescence spectra in comparison with the absorption ones, *i.e.*, with conclusion about approach of the  $S_1$  state of dyes 1–9 to the cyanine limit. The opposite signs of BOA and BOA\* show that in the  $S_0$  and  $S_1^{FC}$  states the electronic structure of merocyanines 1–9 deviates from the cyanine limit **A2** in the opposite directions: aside the neutral polyene **A1** in the ground state and aside the dipolar polyene **A3** in the fluorescent state. In other words, the bond alternation at excitation is complementary to those in the  $S_0$  state.

One can see from Table 3 that  $\delta$  values for merocyanines 1–9 are intermediate between typical for polyene **21** and symmetric



ionic dyes **10–20**, coming nearer to the latter. It is in good agreement with narrowing of the absorption bands in a series: neutral polyene **A1** – merocyanine from the range **A1–A2** – symmetric polymethine **A2**. The  $\delta$  values of merocyanines **1–3** and **7–9** are larger than those for compounds **4–6**. It corresponds to the wider absorption bands of the former in comparison with the latter in low-polar solvents [7]. The  $\delta$  values of merocyanines grow at chain lengthening, as opposed to the corresponding symmetric ionic dyes. This gives the amplification of VI in transition  $S_1^{\text{FC}} \leftarrow S_0$  that should bring to the absorption bands broadening at polymethine chain lengthening in gas phase. It does take place for positive solvatochromic merocyanines **1–3**, **7–9** in *n*-hexane [7].

The parameter  $\delta_{\text{ch}}$  was calculated taking into account only polymethine chain bonds (Table 3). The difference  $\Delta\delta = \delta - \delta_{\text{ch}}$  is much greater for the dimethinemerocyanines than for the higher vinyllogues. This fact correlates with the abovementioned explanation of fluorescence bands broadening for dyes **1**, **4** and **7**.

The parameters  $\Delta q_{\Sigma}$  and  $\Delta q_{\Sigma}^*$  show (Table 3) that charge alternation for merocyanines **1–9** both in the ground and in the excited state is weaker than for the corresponding symmetric dyes **10–20**, but it is much stronger, than those for the neutral polyene **21** (Table 3). Since  $\Delta q_{\Sigma} \gg \Delta q_{\Sigma}^*$  (Table 3), it can be concluded that in the excited state the charges in merocyanine chromophore are more equalized than in the ground one. Therefore solvates, formed owing to nucleophilic and electrophilic solvation in the  $S_0$  state, become less stable in the  $S_1^{\text{FC}}$  ( $S_1$ ) state and should be rebuilt for the excited-state lifetime. Consequently, in the  $S_1^{\text{FC}}$  ( $S_1$ ) state nucleophilic and electrophilic solvation of molecules of dyes **1–9** are weakened in comparison with  $S_0$  that promotes abovementioned weakening of IMI with a solvent in the fluorescent state of merocyanines.

The quantum-chemically calculated dipole moments  $\mu$  and  $\mu^*$  (for gas phase, in the  $S_0$  and  $S_1^{\text{FC}}$  states accordingly) for dyes **1–9** are higher, than those for the corresponding symmetric cationic **12–20** and anionic **10**, **11** dyes (Table 3). It corresponds to stronger solvatochromism of the former in comparison with the latter. Logically we may assert that the values  $\mu$  for merocyanines **4–6** are larger than those for compounds **1–3** and **7–9** (Table 3), since benzimidazole nucleus possesses stronger electron-donating properties than benzo[*cd*]indole and 3*H*-indole.

It should be noticed, that the calculation predicts a growth of the dipole moments at transition from the  $S_0$  state to  $S_1^{\text{FC}}$  ( $\mu < \mu^*$ ) both for positive solvatochromic merocyanines **1–3**, **7–9** and for negative solvatochromic **4–6** (Table 3). So, the theoretical calculation conflicts with the experimental data since negative solvatochromism of merocyanines **4–6** presupposes a reduction of the dipole moments at transition to the excited state. In work [8] by the example of negatively solvatochromic Brooker's merocyanine (4-[2-(1-methyl-4(1*H*)-pyridinylidene)ethylidene]-2,5-cyclohexadien-1-one) it is shown that taking into account solvent polarity in quantum-chemical calculation can result in reduction of the dipole moment at excitation in comparison with gas phase. However there is also other point of view according to which it is nec-

essary to improve calculation methods at their application to merocyanines [21].

#### 4. Conclusions

A study of the fluorescent properties and electronic structure of merocyanines based on *N,N*-diethylthiobarbituric acid has been performed by fluorescent spectroscopy (in a wide range of solvent polarity) and by quantum-chemical calculations.

It has been shown that the electronic structure of typical merocyanines – both positive (**1–3**, **7–9**) and negative (**4–6**) solvatochromic – in the fluorescent state comes nearer to the cyanine limit **A2** in comparison with the ground state. It becomes apparent in a growth of vinylene shifts in their fluorescent spectra, as well as in a decrease of deviations, solvatochromic shifts, band width, and an approach of fluorescence band form to those for the corresponding symmetric polymethine dyes. These facts agree with the results of semi-empirical calculations which predict the levelling of charges and bond orders in chromophore in the excited state of merocyanines.

The essential violation of electronic symmetry in the  $S_1$  state is observed for the positive solvatochromic dyes in low-polar solvents only, *i.e.*, in the case of a significant deviation of their  $S_0$  state aside neutral polyene **A1**.

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