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Synthesis and Spectral Properties of Merocyanine Dyes Based on Polynitrofluorenes

I. V. Kurdyukova[a], A. A. Ishchenko[a], and D. D. Mysyk[b]

[a] *Institute of Organic Chemistry, National Academy of Sciences of Ukraine,*
ul. Murmanskaya 5, Kiev 02094 Ukraine
e-mail: alexish@i.com.ua
[b] *Donetsk National Technical University of Ukraine, ul. Artema 58, Donetsk, 83000 Ukraine*

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Abstract—The di-, tetra- and hexamethinemerocyanines derived from di-, tri- and tetranitrofluorene, containing heterocyclic indolylidene residue were synthesized and their absorption spectra in the solvents of different polarity were investigated. A quantum-chemical analysis of the electronic structure of the synthesized merocyanines was performed and the types of electronic transitions in their molecules were calculated using DFT and TDDFT methods with the B3LYP/6-31G(d,p) basis. It was shown that with increasing electron-acceptor properies of the fluorene core the electronic structure of the merocyanines can change from a neutral polyene to an ideal polymethine, which significantly affects the position, intensity and shape of the absorption bands, as well as vinylene shifts and deviations.

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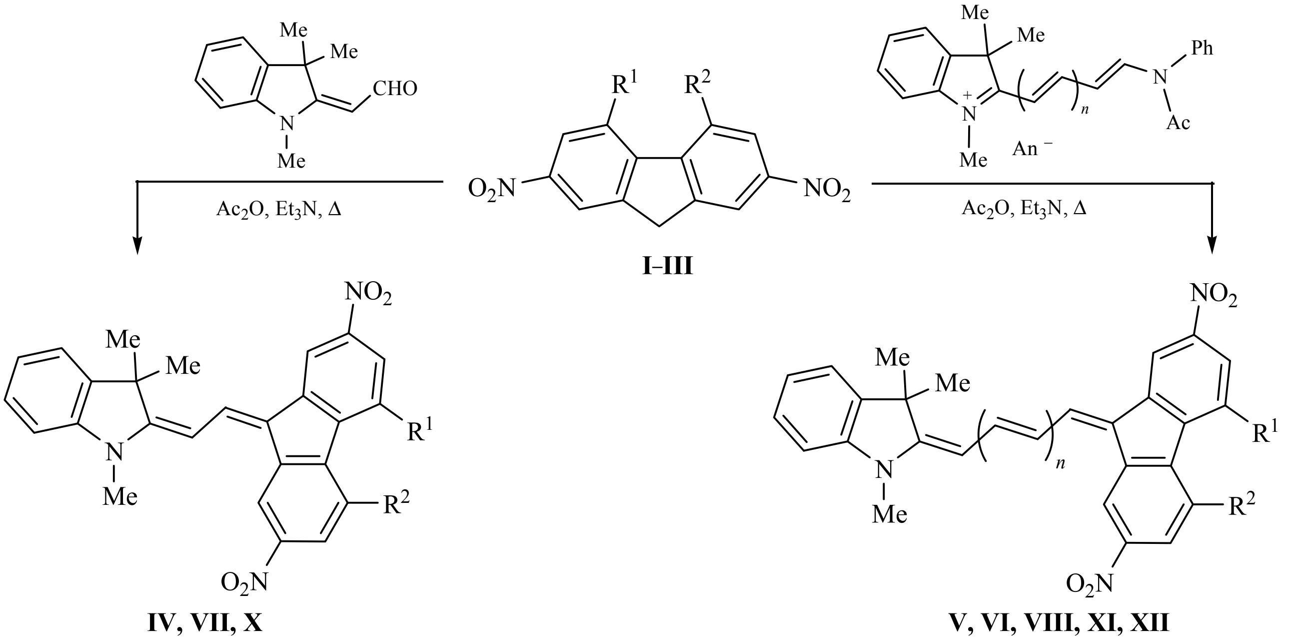
In recent years the interest increased to the donor–acceptor systems containing either a strong donor or a strong acceptor. Due to intramolecular charge transfer such compounds are very promising for the development of organic semiconductor materials, sensitizers of photothermoplastic holographic [1–6], photovoltaic [7], and electroluminescence [8] media. Many works in this field are devoted to the donor–acceptor systems

Scheme 1.

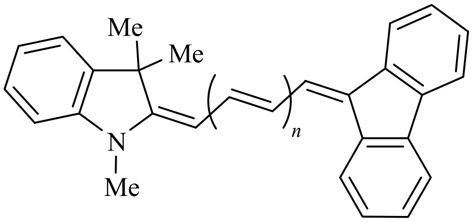


$R^1 = R^2 =$ H (**I, IV–VI**), $R^1 = NO_2$, $R^2 =$ H (**II, VII–IX**), $R^1 = R^2 = NO_2$ (**III, X–XII**); *n* = 1 (**V, VIII, XI**), 2 (**VI, IX, XII**).

based on tetranitrofluorene [9–11]. But more often this compound is used as a component of mixed complexes with polymers or other donor compounds. Therefore it was of interest to obtain the intramolecular donor–acceptor systems based on polynitrofluorene. Previously some representatives of these compounds have been synthesized [2, 4], but no focused and systematic research in this area was carried out. The aim of this work is the synthesis of a number of merocyanines based on the 2,7-dinitrofluorene [12], 2,4,7-trinitrofluorene, and 2,4,5,7-tetranitrofluorene [13] containing a heterocyclic fragment of indolylidene and the study the regularities in their color.

The introduction of strong electron-acceptor, like nitro group, to the fluorene core makes these compounds more prone to the cyanine condensation at the methylene group, in contrast to the unsubstituted fluorene [14]. Polynitrofluorenes **I–III** react with the aldehyde and hemicyanines based on the indolylidene core under standard conditions of the cyanine condensation to afford the merocyanines **IV–XII** (Scheme 1)

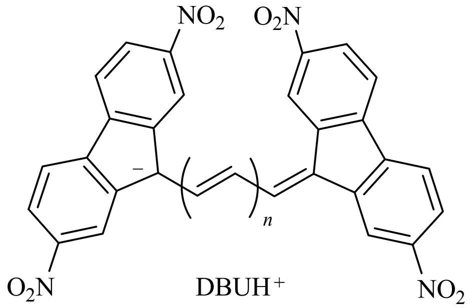
Table 1 lists the spectral characteristics of compounds **IV–XII** including absorption maxima (λ_{max}), deviation of the maxima D_λ, and molar extinction coefficients (ε). Table 1 includes for comparison the same characteristics of the merocyanines **XIII–XV** with unsubstituted fluorene core [14].



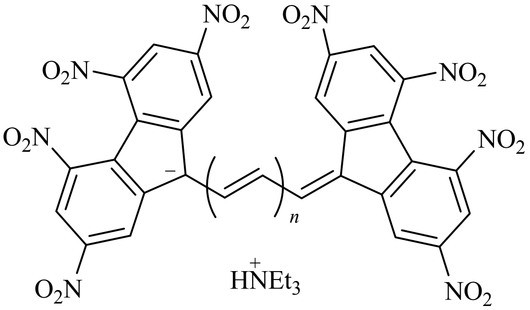
XIII–XV

$n = 0$ (**XIII**), 1 (**XIV**), 2 (**XV**).

To calculate the values of D_λ for the merocyanines **VI, X–XII** we considered compound **XVI–XIX** as the anionic dyes [15] and **XX–XXII,** as the cationic dyes [16].

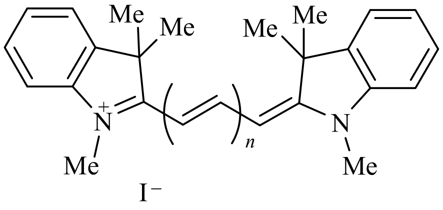


XVI



XVII–XIX

DBU – 1,8-Diazabicyclo[5.4.0]undec-7-en.



XX–XXII

$n = 0$ (**XVII, XX**), 1 (**XVIII, XXI**), 2 (**XVI, XIX, XXII**).

The absorption spectra of merocyanines **IV–XII**, in contrast to their counterparts with unsubstituted fluorene nucleus **XIII–XV** and containing sulfoester substituents [14], show several absorption maxima, like the corresponding symmetrical anionic dyes based on the polynitrofluorenes [15] (Fig. 1). Note that the compound **IV–XII**, despite the well-developed π-system of the chromophore and the presence of strong acceptor auxochromic groups, absorb in a fairly short wavelength region of the spectrum (Fig. 1 and

Table 1. Spectral characterisrics of merocyanines **IV–XII**

Comp. no.	Toluene		CH_2Cl_2			DMF		
	λ_{max}, nm	$\varepsilon\times10^{-4}$, $l\ mol^{-1}\ cm^{-1}$	λ_{max}, nm	$\varepsilon\times10^{-4}$, $l\ mol^{-1}\ cm^{-1}$	D_λ, nm	λ_{max}, nm	$\varepsilon\times10^{-4}$, $l\ mol^{-1}\ cm^{-1}$	D_λ, nm
IV	534	2.42	543	2.11		548	2.07	
	465	3.52	470	3.93		475	3.85	
	347	1.98	350	2.09		351	1.97	
			287	2.40		285	2.67	
V	575	4.48	594	4.13		598	4.09	
	516	3.27	533	3.80		548	4.07	
	350	1.95	355	2.05		356	2.12	
	288	2.35	288	3.17		295	2.18	
VI	612	5.71	621	5.36		623	5.01	166.5
	346	2.35	350	2.54		351	2.40	
	292	5.71	290	3.48		297	2.48	
VII	570	2.36	589	2.00		594	1.94	
	490	3.65	497	3.89		500	3.67	
	370	2.12	372	2.17		373	2.01	
	298	1.44	285	3.06		290	2.16	
VIII	643	4.59	653	4.93		653	4.65	
	548	3.40	565	4.64		585	4.68	
	361	1.64	363	2.20		366	1.94	
	289	2.52	294	3.07		298	2.59	
IX	705	3.55	707	3.83		708	3.54	
	659	3.88	355	1.64		354	1.54	
	354	1.23	290	3.14		298	2.28	
	299	1.17						
X	640	1.99	655	1.71	6	673	1.56	–15
	612	1.99	515	5.49	30	524	4.85	19.5
	502	5.23	381	2.24		390	2.25	
	381	2.06						
XI	696	4.31	718	3.42	54	731	2.76	33
	566	4.43	597	5.59	35	613	6.50	9
	369	1.86	376	1.72		392	1.77	
XII	773	5.90	805	6.33	76	810	5.20	59.5
	627	3.87	675	4.99	44.5	706	6.13	6.5
	372	1.57	377	1.66		397	1.71	
			298	2.36		299	2.39	
XIII	441	4.91	447	6.10	106.5	451	5.32	102.5
	460	4.34						
XIV	485	5.94	491	6.85	151	496	6.30	141.5
XV	509	5.62	516	7.17	232.5	520	6.91	223

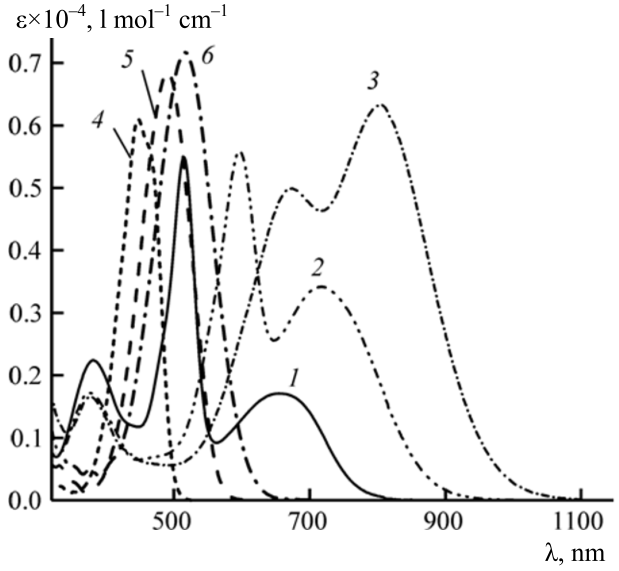


Fig. 1. Electron absorption spectra of merocyanines (*1*) **X**, (*2*) **XI**, (*3*) **XII**, (*4*) **XIII**, (*5*) **XIV**, and (*6*) **XV** in CH_2Cl_2.

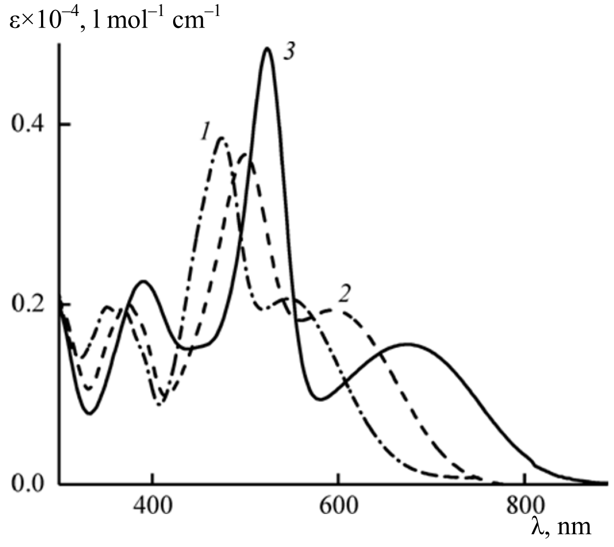


Fig. 2. Electron absorption spectra of merocyanines (*1*) **IV**, (*2*) **VII,** and (*3*) **X** in DMF.

Table 1). The maxima of their longwave absorption bands exhibit a red shift as compared to similar merocyanines with sulfoester groups by only 20–30 nm [14]. They absorb in the fairly high region, almost the same as the malononitrile based merocyanines [16] having a much shorter π-system.

In the spectra of merocyanines **IV–XII** the increasing acceptor properties of the polynitrofluorene core at the successive increase in the number of nitro groups in the core result in a red shift of the absorption bands (Figs. 2–4). The shape and intensity of the most shortwave band suffer a slight change, whereas in the two long-wave bands they change essentially; the shortwave band increases in intensity and narrows, while the the effect on the longwave bands is opposite (Figs. 2–4). These effects are less expressed at the lengthening of the polymethine chain and at decreasing the solvent polarity (Figs. 1 and 5). Thus, in the spectra of dye **VI** in low-polar dichloromethane, and dye **IX** even in the strongly polar DMF the bands in the visible spectral range completely overlap (Figs. 2–4).

In the spectra of dyes **IV–XII** based on di-, tri-, and tetranitrofluorenes the increase in the solvent polarity leads to a small red shift of the absorption bands (Table 1 and Fig. 5), that is, they are characterized by a weak positive solvatochromism.

With increasing length of the polymethine chain the solvatochromic shifts change very little, in the range of 1–5 nm (20–168 cm^{-1}) for the merocyanines **IV–IX**, and of 5–18 nm (77–408 cm^{-1}) for the dyes **X–XII**.

The values of vinylene shift of the longwave band in the spectra of compounds **IV–XII** are less than those of the shortwave bands. The former approach the values characteristic of carotenoids, and the latter are typical of the classical symmetric polymethines. Thus, the first vinylene shift in the spectrum of merocyanine **XI** in DMF is 58 nm for the longwave band, and 83 nm for the shortwave band. As the number of nitro

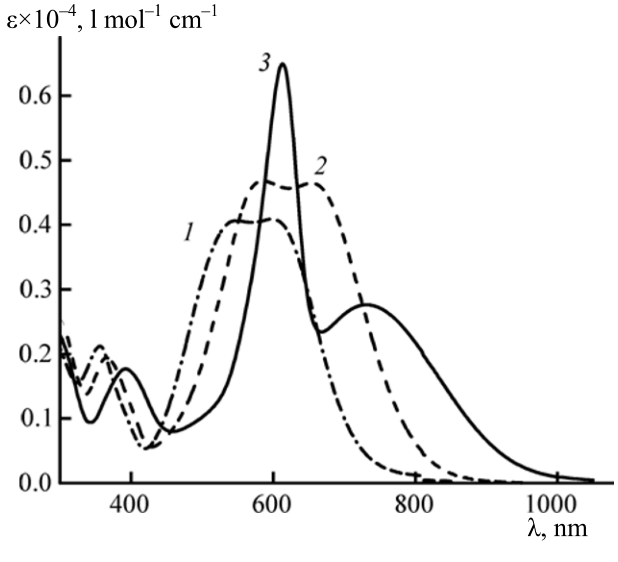


Fig. 3. Electron absorption spectra of merocyanines (*1*) **V**, (*2*) **VIII,** and (*3*) **XI** in DMF.

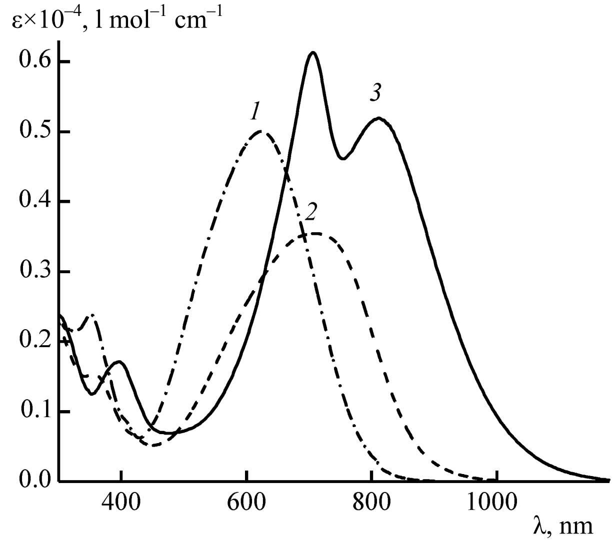


Fig. 4. Electron absorption spectra of merocyanines (*1*) **VI**, (*2*) **IX**, and (*3*) **XII** in DMF.

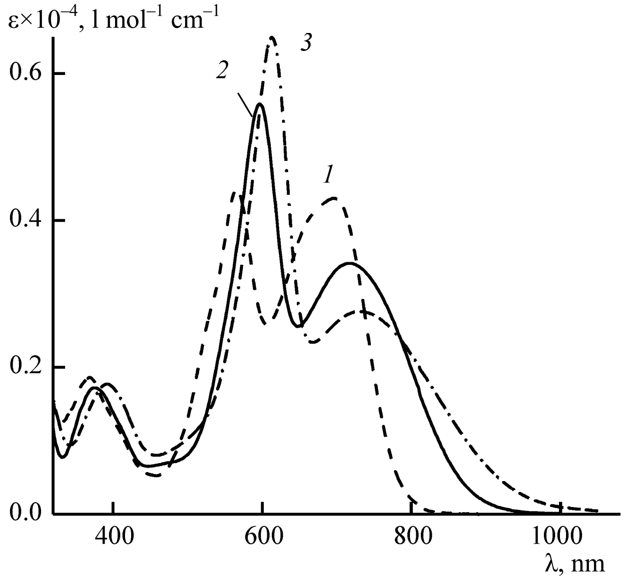


Fig. 5. Electron absorption spectra of merocyanine **XI** in (*1*) toluene, (*2*) CH_2Cl_2, and (*3*) DMF.

groups in the fluorene core increases, a tendency of increasing vinylene shift is observed, and this is more pronounced in the shortwave band (Table 1).

The values of deviations calculated for the maxima of the longwave bands are significantly larger than those calculated for the maxima of the shortwave bands (Table 1). The introduction of nitro groups in the fluorene fragment reduces both longwave and shortwave D_λ values of the merocyanine bands (Table 1). The replacement of CH_2Cl_2 by more polar and nucleophilic DMF increases vinylene shift and decreases D_λ. Based on the analysis of the values of vinylene shifts and deviations a conclusion can be reached that the increase in the number of nitro groups in the fluorene core increases the uniformity of the bond orders in the merocyanine chromophore by transforming their electronic structure from the neutral polyene toward polymethines.

Table 2 shows the data of quantum-chemical calculations of the absorption maxima $\lambda_{\text{max, theor.}}$, oscillator strength $f_{\text{theor.}}$, and dipole moment μ in the ground and excited states of compounds **IV–XV**. The non-empirical quantum-chemical calculations showed that the theoretical absorption spectra are determined by π–π* electron transitions, and the large number of the calculated absorption bands is due to the appearance of additional levels localized on the nitro group, as in the case of anionic dyes on the basis of symmetric polynitrofluorenes [15].

In the calculated spectra of all merocyanines there is the most shortwave band due to the interaction of the orbitals localized on the fluorene core and the nitro groups. It practically coincides with the experimental shortwave band in the absorption spectra (Tables 1 and 2). One of the higher electronic transitions, for example, $S_0 \rightarrow S_7$ in the spectrum of merocyanine **XII** is responsible for its appearance.

According to quantum-chemical calculations, the next shortwave band with respect to that considered above is caused by the polymethine transition into one of the higher excited states. The increase in the length of the polymethine chain results in transition to more low-lying excited states. So, in merocyanines **V, VI, XI,** and **XII** it is the $S_0 \rightarrow S_2$ transition, in the compound **IV**, $S_0 \rightarrow S_3$, while in the dyes **VII, VIII,** and **X,** the $S_0 \rightarrow S_4$ transition. The main contribution to the $S_0 \rightarrow S_2$ transition makes the transfer of electron density from the HOMO to the LUMO+1 (72–85%), the transition $S_0 \rightarrow S_3$ is also determined by the interaction of these orbitals (93%), and the transition $S_0 \rightarrow S_4$ is due to the transfer of electron density from the HOMO to the LUMO+3 (60–86%).

The shortwave transition is determined by the transfer of electron density between neighboring atoms of the polymethine chain, as well as by the displacement of the electron density of polymethine chains and the heterocyclic fragment on the nitro groups and the fluorene core (Fig. 6a). The consecutive

Table 2. The results of quantum-chemical calculation of the theoretical absorption maxima, oscillator strength, and dipole moments in the ground and excited states of merocyanines **IV–XV**

Comp. no.	Transition type	$\lambda_{\max}^{\mathrm{theor}}$, нм	f_{theor}	μ, D				
				S_0	S_1	S_2	S_3	$\boldsymbol{S_4}$
V	$S_0 \rightarrow S_1$	572	0.12	5.73	21.39		11.62	
	$S_0 \rightarrow S_3$	412	0.94					
	$S_0 \rightarrow S_4$	360	0.30					
V	$S_0 \rightarrow S_1$	599	0.22	7.87	29.04	16.93		
	$S_0 \rightarrow S_2$	455	1.35					
	$S_0 \rightarrow S_4$	370	0.14					
VI	$S_0 \rightarrow S_1$	630	0.37	9.67	36.59	22.83		
	$S_0 \rightarrow S_2$	496	1.72					
	$S_0 \rightarrow S_7$	337	0.25					
VII	$S_0 \rightarrow S_1$	606	0.11	10.63	28.89			18.03
	$S_0 \rightarrow S_2$	470	0.16					
	$S_0 \rightarrow S_4$	405	0.83					
	$S_0 \rightarrow S_5$	364	0.31					
VIII	$S_0 \rightarrow S_1$	644	0.18	13.20	37.04			29.97
	$S_0 \rightarrow S_2$	501	0.49					
	$S_0 \rightarrow S_3$	455	0.41					
	$S_0 \rightarrow S_4$	441	0.62					
	$S_0 \rightarrow S_6$	370	0.24					
IX	$S_0 \rightarrow S_1$	684	0.28	15.38	45.11	42.11		
	$S_0 \rightarrow S_2$	535	1.04					
	$S_0 \rightarrow S_3$	483	0.72					
	$S_0 \rightarrow S_4$	462	0.17					
	$S_0 \rightarrow S_6$	376	0.17					
X	$S_0 \rightarrow S_1$	635	0.13	15.18	33.54			24.81
	$S_0 \rightarrow S_2$	455	0.28					
	$S_0 \rightarrow S_4$	401	0.70					
	$S_0 \rightarrow S_7$	367	0.25					
XI	$S_0 \rightarrow S_1$	676	0.20	18.27	42.00	36.47		
	$S_0 \rightarrow S_2$	489	0.85					
	$S_0 \rightarrow S_4$	434	0.63					
	$S_0 \rightarrow S_7$	373	0.25					
XII	$S_0 \rightarrow S_1$	722	0.28	20.97	50.46	39.55		
	$S_0 \rightarrow S_2$	529	1.46					
	$S_0 \rightarrow S_3$	471	0.15					
	$S_0 \rightarrow S_4$	460	0.41					
	$S_0 \rightarrow S_7$	378	0.22					
XIII	$S_0 \rightarrow S_1$	405	1.10	4.0	9.9			
XIV	$S_0 \rightarrow S_1$	446	1.64	5.2	14.2			
XV	$S_0 \rightarrow S_1$	485	2.11	6.1	18.7			

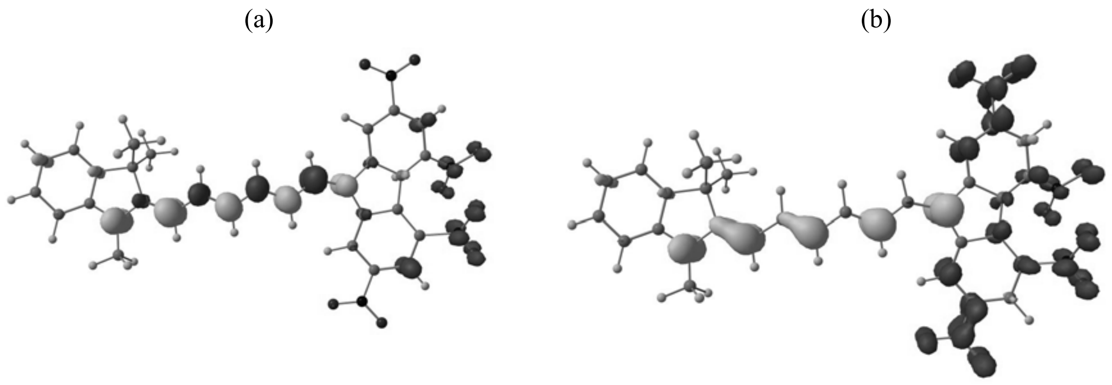


Fig. 6. Change in the electron density of dye **XII** at (a) $S_0 \rightarrow S_2$ and (b) $S_0 \rightarrow S_1$ transitions. Here and hereinafter, dark color shows the increase in the electron density, light color, the decrease in the electron density. The value of isosurface lines is 0.003.

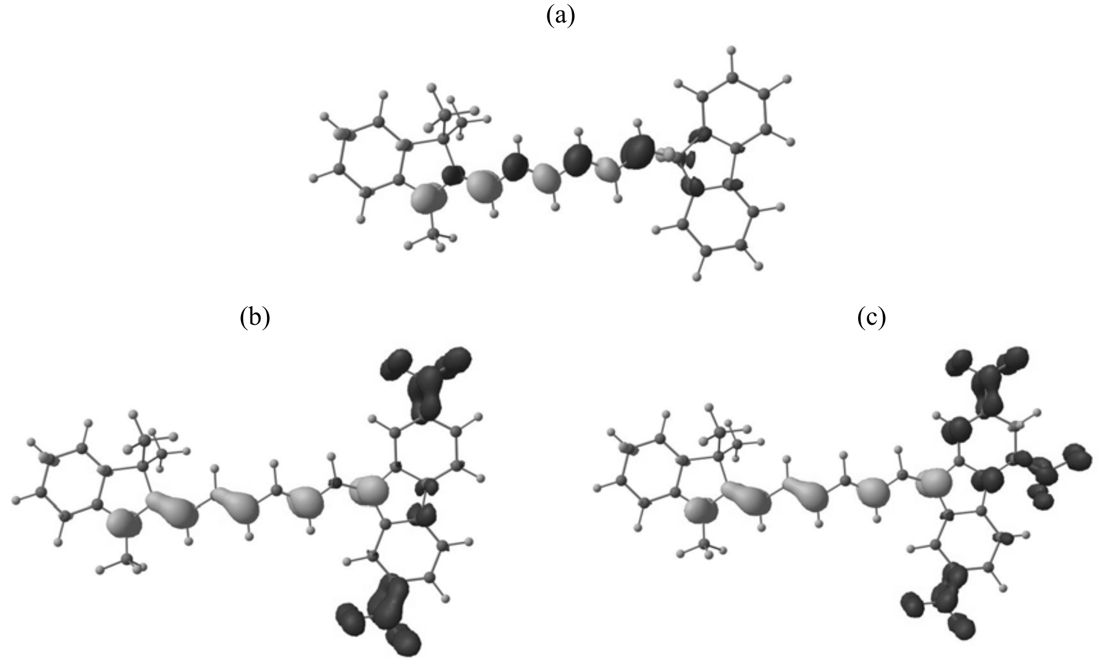


Fig. 7. Change in the electron density of dyes (a) **XV**, (b) **VI**, and (c) **IX** at the transition $S_0 \rightarrow S_1$.

increase in the number of nitro groups in the fluorene fragment of merocyanines **IV–XII** reinforces this trend, resulting in an increase in the alternation of positive and negative charges and lower orders of the formal alternation of simple and double bonds in the polymethine chain. Therefore the merocyanines get close to the ideal polymethine state, resulting in an increase in intensity, narrowing, and the red shift of the experimental shortwave absorption band in going from di- to tri- and tetranitro-substituted merocyanines (Table 1 and Figs. 2–4).

The most longwave band of all merocyanines **IV–XII** is due to the transition $S_0 \rightarrow S_1$, which at 82–96% occurs between the HOMO and LUMO orbitals. A significant contribution to it also makes the interaction of the HOMO and the LUMO+1 orbitals. This transition is characterized by the transfer of electron density from the heterocyclic core and the polymethine chains on the fluorene moiety and the nitro groups (Fig. 6b), while in the compounds **XIII–XV** this transition is localized on the polymethine chain (Fig. 7). It has a lower energy and a greater bond orders alternation in chromophore than in polymethine, therefore its absorption band should be at longer wavelengths, and of lower intensity and selectivity than the polymethine band. This fact is in agreement with the experiment.

In going from the merocyanines **XIII–XV** with unsubstituted fluorene core to the derivatives of di-, tri-and tetaranitrofluorene **IV–XII** the energy of both HOMO and LUMO levels regularly decreases, and the energy gap becomes narrower. These data are consistent with the changes in experimental longwave absorption maxima in going from merocyanines **XIII–XV** to their counterparts **IV–XII** (Tables 1 and 2).

The calculation also indicates an increase in dipole moment upon excitation in both the first and the higher excited states of the merocyanines **IV–XII** (Table 2), which is consistent with the positive solvatochromism of the corresponding electronic transitions.

The values of μ and μ^* for dyes **IV–XII** are greater than those of merocyanines **XIII–XV**. This fact, as well as the above described trends in vinylene shifts and deviations, indicates an increase in the contribution of the structure of ideal polymethine in the electronic structure of merocyanines **IV–XII** compared with the **XIII–XV**. These effects grow with increasing solvent polarity, as it contributes to the redistribution of charges both in the polymethine chain and between the end groups.

Thus, the color of merocyanines based on polynitrofluorenes is determined by the presence of three absorption bands, in contrast to the analogous dyes derived from the unsubstituted fluorene. All of them are caused by π–π^* electron transitions. The most shortwave band is due to transitions localized on the fluorene core. It has a low intensity and is mainly located on the border between the near UV and visible regions, and therefore has little effect on the color. The most longwave band is a band of charge transfer, and intermediate band has the polymethine nature. These two bands are responsible for the color of the merocyanines **IV–XII**. The ratio of intensities of these bands depends on the number of nitro groups, the length of the polymethine chain, and the solvent polarity. The changes in their shape allow to judge on the polyene–polymethine electronic relaxation in merocyanines.

EXPERIMENTAL

The absorption spectra were recorded on a spectrophotometer "Shimadzu UV-3100" in 1-cm cells at concentrations of the solute 1×10^{-5} mol l^{-1}. Solvents were purified by known methods [17]. Dichloromethane was stabilized by adding 1% of anhydrous ethanol. The purity of dyes was monitored by TLC (Silufol UV-254, eluent acetonitrile). ^{1}H NMR spectra were recorded on a Varian VXR-300 (299.945 MHz) and a Jeol Eclipse-400 (400.18 MHz) spectrometers, internal reference TMS. Melting/decomposition points were measured in open capillary and are corrected.

The quantum-chemical calculations were performed within the software package PC Gamess/Firefly by nonempirical DFT method in the B3LYP/6-31G(d,p) basis with a preliminary optimization of the geometry of the ground state in the same basis. The calculation of the electronic transitions was performed using the TDDFT method. The calculated spectra were described taking into account electronic transitions with oscillator strength greater than one-tenth of the transition intensity with the largest oscillator strength. Hexamethinecyanines are best fit for the description, as their chain is long enough to avoid effects due to the close proximity of terminal cores, and their planar structure allows to evaluate the transition polarized along the chromophore main axis.

(2*E*)-1,3,3-Trimethyl-2-[(2*E*)-2-(2,7-dinitro-9*H*-fluoren-9-ylidene)ethylidene]indoline (IV). (*E*)-2-(1,3,3-trimethylindolin-2-ylidene)acetaldehyde, 20 mg (0.1 mmol), mixed with 2,7-dinitro-fluorene (**I**), 25 mg (0.1 mmol), was heated for a few minutes in acetic anhydride. At cooling a precipitate separated. It was filtered off, washed with acetic acid and then with a large amount of ethanol. Yield 42 mg (95%). Found, %: C 70.89, H, 4.70; N, 9.33. $C_{26}H_{21}N_3O_4$. Calculated, %: C 71.06, H, 4.82; N, 9.56. ^{1}H NMR spectrum, δ, ppm (DMSO-d_6): 1.788 s [6H, C(CH$_3$)$_2$], 3.541 s (3H, NCH$_3$) 6.453 d (1H, J = 12.3 Hz, H1), 7.083 t (1H, J = 7.2 Hz, ArH), 7.197 d (1H, J = 8.1 Hz, ArH) 7.327 t (1H, J = 8.1 Hz, ArH), 7.511 d (1H, J = 7.2 Hz, ArH), 8.114 d (1H, J = 8.4 Hz, ArH), 8.206 d (1H, J = 8.4 Hz, ArH), 8.237 d (1H, J = 12.3 Hz, H^2), 8.276 d (1H, J = 8.4 Hz , ArH), 8.361 d (J = 8.4 Hz, 1H, ArH), 8.801 s (1H, ArH), 8.842 s (1H, ArH).

(2*E*)-2-[(2*E*)-4-(2,7-dinitro-9*H*-fluoren-9-ylidene)-but-2-enylidene]-1,3,3-trimethylindoline (V). 1,3,3-trimethyl-2-[(1*E*,3*E*)-4-(*N*-phenylacetamido)buta-1,3-dien-1-yl]-3*H*-indol-1-ium perchlorate, 45 mg (0.1 mmol), mixed with 2,7-dinitrofluorene (**I**), 25 mg (0.1 mmol), was heated for a few minutes in acetic anhydride in the presence of triethylamine. The precipitate formed was filtered off, washed with acetic acid and then with a large amount of ethanol. Yield 41 mg (88%). Found, %: C 72.09, H, 4.73, N 8.90. $C_{28}H_{23}N_3O_4$. Calculated, %: C 72.24, H 4.98, N 9.03. ^{1}H NMR spectrum, δ, ppm (DMSO-d_6): 1.678 s (6H, $C(CH_3)_2$), 3.374 s (3H, NCH_3), 6.086 d (1H, J = 13.5 Hz, H^1), 6.988 t (1H, J = 7.2 Hz , ArH), 7.047 d (1H, J = 8.1 Hz, ArH), 7.187 t (1H, J = 12.9 Hz, H^3), 7.259 t (J = 7.2 Hz, 1H, ArH), 7.430 d (1H, J = 7.2 Hz, ArH), 7.930 t (1H, J = 12.9 Hz, H^2), 8.180 d (1H, J = 9.0 Hz, ArH), 8.253 d (1H, J = 9.0 Hz , ArH), 8.334 d (1H, J = 13.2 Hz, H^4), 8.342 d (1H, J = 8.7 Hz, ArH), 8.407 d (1H, J = 8.7 Hz, ArH), 8.869 s (1H, ArH), 8.903 s (1H, ArH).

(2*E*)-2-[(2*E*,4*E*)-6-(2,7-dinitro-9*H*-fluoren-9-ylidene)hex-2,4-dienylidene]-1,3,3-trimethylindoline (VI) was synthesized similar to **V** from 47 mg (0.1 mmol) of 1,3,3-trimethyl-2-[(1*E*,3*E*,5*E*)-6-(*N*-phenylacetamido)hexa-1,3,5-trien-1-yl]-3*H*-indol-1-ium perchlorate and 25 mg (0.1 mmol) of 2,7-dinitrofluorene (**I**). Yield 35 mg (71%). Found, %: C 73.11, H 4.98, N 8.27. $C_{30}H_{25}N_3O_4$. Calculated, %: C 73.30, H, 5.13; N, 8.55. ^1H NMR spectrum, δ, ppm (DMSO-d_6): 1.591 s [6H, $C(CH_3)_2$], 3.247 s (3H, NCH_3), 5,696 d (1H, J = 12.9 Hz, H^1), 6.554 t (1H, J = 11.4 Hz , H^2), 6.915 t (1H, J = 7.8 Hz, ArH), 6.944 d (1H, J = 7.8 Hz, ArH), 7.210 t (1H, J = 7.8 Hz, ArH), 7.342 d (1H, J = 7.8 Hz, ArH), 7.222–7.431 m (3H, H^{3-5}), 8.008 d (J = 12.0 Hz, 1H, H^6), 8.201 d (1H, J = 8.7 Hz, ArH), 8.273 d (1H, J = 8.7 Hz, ArH), 8.313 d (1H, J = 8.7 Hz, ArH), 8.374 d (1H, J = 8.7 Hz, ArH), 8,817 s (2H, ArH).

(2*E*)-1,3,3-Trimethyl-2-[(2*E*)-2-(2,4,7-trinitro-9*H*-fluoren-9-ylidene]indoline (VII). 2,4,7-Trinitrofluorene (**II**), 30 mg (0.1 mmol), and (*E*)-2-(1,3,3-trimethylindolin-2-ylidene)acetaldehyde, 20 mg (0.1 mmol), was dissolved at heating in a minimum amount of pyridine. Triethylamine was added, and the mixture was heated for several minutes. As soon as the precipitate began to form, the heating was stopped. After cooling, the precipitate was filtered off and washed with several portions of ethanol. Boiling in chloroform was performed to wash out all impurities. Yield 40 mg (83%). Found, %: C 64.22, H 4.01, N 11.50. $C_{26}H_{20}N_4O_6$. Calculated, %: C 64.46, H, 4.16; N, 11.56. ^1H NMR spectrum, δ, ppm (DMSO-d_6): 1.825 s [6H, $C(CH_3)_2$], 3.703 s (3H, NCH_3), 6.689 d (1H, J = 14.0 Hz, H^1), 7.179 t (1H, J = 7.6 Hz, ArH), 7.272 d (1H, J = 8.0 Hz, ArH), 7.386 t (1H, J = 8.0 Hz, ArH), 7.533 d (1H, J = 8.0 Hz, ArH), 8.208 br.s (3H, ArH), 8.534 d (1H, J = 14.0 Hz, H^2), 8.585 br.s (1H, ArH), 9.039 br.s (1H, ArH), 9.118 br.s (1H, ArH).

(2*E*)-1,3,3-Trimethyl-2-[(2*E*,4*E*)-4-(2,4,7-trinitro-9*H*-fluoren-9-ylidene)but-2-enylidene]indoline (VIII). 1,3,3-trimethyl-2-[(1*E*,3*E*)-4-(*N*-phenylacetamido) buta-1,3-dien-1-yl]-3*H*-indol-1-ium tetrafluoroborate, 44 mg (0.1 mmol), and 2,4,7-trinitrofluorene (**II**), 30 mg (0.1 mmol), was dissolved at heating in a minimum amount of pyridine. Triethylamine was added, and the mixture was heated for several minutes. The precipitate obtained after cooling was filtered off and washed with ethanol. Yield 40 mg (78%). Found, %: C 65.70, H 4.19, N 10.81. $C_{28}H_{22}N_2O_6$. Calculated, %: C 65.88, H 4.34, N 10.97. ^1H NMR spectrum, δ, ppm (DMSO-d_6): 1.717 s [6H, $C(CH_3)_2$], 3.491 s (3H, NCH_3), 6.206 d (1H, J = 13.2 Hz, H^1), 7.079 t (1H, J = 7.6 Hz, ArH), 7.113 d (1H, J = 8.0 Hz, ArH), 7.264 t (1H, J = 13.2 Hz, H^3), 7.308 t (J = 7.6 Hz, 1H, ArH), 7.440 d (1H, J = 7.2 Hz, ArH), 8. 093 t (1H, J = 12.8 Hz, H^2), 8.170 br.s (2H, ArH), 8.455 d (J = 12.8 Hz, 1H, H^4), 8.585 br.s (1H, ArH), 8.955 s (1H, ArH), 9.167 s (1H, ArH).

(2*E*)-1,3,3-Trimethyl-2-[(2*E*,4*E*,6*E*)-6-(2,4,7-trinitro-9*H*-fluoren-9-ylidene)hex-2,4-dienylidene]-indoline (IX). 1,3,3-trimethyl-2-[(1*E*,3*E*,5*E*)-6-(*N*-phenylacetamido)hexa-1,3,5-trien-1-yl]-3*H*-indol-1-ium tetrafluoroborate, 46 mg (0.1 mmol), was dissolved at heating in pyridine. Triethylamine was added and the mixture was brought to boil. After the formation of precipitate, the mixture was cooled, and precipitate was filtered off and washed with ethanol. After drying, it was treated with hot chloroform. Yield 40 mg (75%). Found, %: C 67.03, H 4.28, N, 10.11. $C_{30}H_{24}N_4O_6$. Calculated, %: C 67.16, H, 4.51; N, 10.44. ^1H NMR spectrum, δ, ppm (DMSO-d_6): 1.620 s [6H, $C(CH_3)_2$], 3.356 s (3H, NCH_3), 5,843 d (1H, J = 12.0 Hz, H^1), 6.609 t (1H, J = 11.6 Hz, H^2), 6.985 t (1H, J = 7.2 Hz, ArH), 6.985 d (1H, J = 7.6 Hz, ArH), 7.248 t (1H, J = 7.6 Hz, ArH), 7.345 d (1H, J = 7.2 Hz, ArH), 7.507 t (1H, J = 12.0 Hz, H^5), 7.520 t (1H, J = 12.0 Hz, H^3), 8.116–8.316 m (3H, H^6, ArH), 8.626 s (1H, ArH), 8.900 s (1H, ArH), 9.112 s (1H, ArH).

(2*E*)-1,3,3-Trimethyl-2-[2-(2,4,5,7-tetranitro-9*H*-fluoren-9-ylidene)ethylidene]indoline (X). [(*E*)-2-(1,3,3-trimethylindolin-2-ylidene]acetaldehyde, 20 mg (0.1 mmol), and 2,4,5,7-tetranitro-fluorene (**III**), 35 mg (0.1 mmol), was heated for a few minutes in acetic anhydride. The precipitate formed was filtered off, washed with acetic acid and a large amount of acetone. Yield 52 mg (98%). Found, %: C 58.73, H 5.36, N 13.01. $C_{26}H_{19}N_5O_8$. Calculated, %: C 58.98, H

5.62, N 13.23. ^{1}H NMR spectrum, δ, ppm (DMSO-d_6): 1.856 s [6H, $C(CH_3)_2$], 3.827 s (3H, NCH_3), 6.907 d (1H, J = 14.4 Hz, H^1), 7.281 t (1H, J = 6.8 Hz , ArH), 7.422 d (1H, J = 6.8 Hz, ArH), 7.430 s (1H, ArH), 7.449 t (1H, J = 7.2 Hz, ArH), 7.619 d (1H, J = 7.6 Hz, ArH), 8.568 d (1H, J = 1.6 Hz, ArH), 8.738 d (1H, J = 14.4 Hz, H^2), 9.341 d (2H, J = 1.6 Hz, ArH).

(2*E*)-1,3,3-Trimethyl-2-[2-(2,4,5,7-tetranitro-9*H*-fluoren-9-ylidene)but-2-enylidene]indoline (XI). 2-[(1*E*,3*E*)-4-(*N*-Acetyl-*N*-phenylamino)buta-1,3,5-trienyl]-1,3,3-trimethyl-3*H*-indolinium perchlorate, 45 mg (0.1 mmol), and 2,4,5,7-tetranitrofluorene (**III**), 35 mg (0.1 mmol), was heated for a few minutes in acetic anhydride in the presence of triethylamine. The precipitate formed was filtered off, washed with acetic acid and then with a large amount of acetone. Yield 55 mg (99%). Found, %: C 60.40, H 3.68, N 12.89. $C_{28}H_{21}N_5O_8$. Calculated, %: C 60.54, H 3.81, N 12.61. ^{1}H NMR spectrum, δ, ppm (DMSO-d_6): 1.755 s [6H, $C(CH_3)_2$], 3.640 s (3H, NCH_3), 6.524 d (1H, J = 13.6 Hz, H^1), 7.216 t (1H, J = 7.6 Hz, ArH), 7.310 d (1H, J = 7.6 Hz, ArH), 7.391 t (1H, J = 14.4 Hz, H^3), 7.389 t (1H, J = 7.6 Hz, ArH), 7.556 d (1H, J = 7.6 Hz, ArH), 8.312 t (1H, J = 12.8 Hz, H^2), 8.532 s (2H, ArH), 8.704 d (1H, J = 13.2 Hz, H^4), 9.316 s (2H, ArH).

(2*E*)-1,3,3-Trimethyl-2-[(2*E*,4*E*)-6-(2,4,5,7-tetranitro-9*H*-fluoren-9-ylidene)hexa-2,4-dienyliden]indoline (XII). 1,3,3-trimethyl-2-[(1*E*,3*E*,5*E*)-6-(*N*-phenylacetamido)hexa-1,3,5-trien-1-yl]-3*H*-indol-1-iumperchlorate, 47 mg (0.1 mmol), and 2,4,5,7-tetranitrofluorene (**III**), 35 mg (0.1 mmol), was heated in acetic anhydride with triethylamine for 3 min. The filtered off precipitate was washed with acetic acid and a large amount of acetone. Yield 44 mg (76%). Found, %: C 61.75, H 3.73, N 11.90. $C_{30}H_{23}N_5O_8$. Calculated, %: C 61.96, H 3.96, N 12.04. ^{1}H NMR spectrum, δ, ppm (DMSO-d_6): 1.668 s [6H, $C(CH_3)_2$], 3.527 s (3H, NCH_3), 6,166 d (1H, J = 13.2 Hz, H^1), 6.776 t (1H, J = 12.4 Hz, H^2), 7.144 t (1H, J = 7.2 Hz, ArH), 7.192 d (1H, J = 7.6 Hz, ArH), 7.646 t (1H, J = 7.2 Hz, ArH), 7.387 t (1H, J = 12.8 Hz, H^3), 7.698–7.895 m (2H, $H^{4,5}$), 8.412 d (1H, J = 14.0 Hz, H^6), 8.545 s (2H, ArH), 9.271 s (2H, ArH).

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