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Synthesis and spectral properties of cyanine dyes—Derivatives of 10,10-dimethyl-7,8,9,10-tetrahydro-6*H*-pyrido[1,2-*a*]indolium

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ABSTRACT

The electronic absorption spectra of merocyanines and symmetric cationic polymethine dyes based on 10,10-dimethyl-7,8,9,10-tetrahydro-6*H*-pyrido[1,2-*a*]indolium have been investigated in a wide range of solvent polarity. An important feature of these compounds is a cyclic group connecting the nitrogen atom of indole nucleus with the polymethine chain. The explored cationic cyanine dyes, in comparison with the derivatives of 3*H*-indole, are characterized by less bond order and charge alternation in their chromophore in the ground state. It causes a decrease of both vibronic and intermolecular solute–solvent interactions and, consequently, a decrease of their solvatochromic range, a long-wavelength shift, a narrowing, and an increase of the peak intensity of their spectral bands. The synthesized merocyanines get the greater dipolarity of the ground state, as compared to their non-cyclic analogues. It leads to a color deepening and an increase of the absorption band intensity. Besides, it was revealed that the reversion of solvatochromism for merocyanines with *N*,*N*-diethylthiobarbituric moiety containing a cyclic group takes place. The listed regularities fail for the short-chain polymethine dyes. Presumably, it is caused by steric hindrances resulting in non-planarity of their molecules.

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1. Introduction

A partial fixation of the polymethine chain in cyanine dyes with cyclic structures is a general synthetic approach [1–3]. Such modification improves their photo- and thermo-stability [2], and causes an increase of the fluorescence quantum yields due to locking of an important channel of the excited-state energy dissipation—a *trans*–*cis* photoisomerization around the bonds with reduced order [3]. A cyclic group, being actually a substituent in a chain, influences also an electronic structure of polymethines.

Merocyanines, containing cyclic groups in the polymethine chain, are used in non-linear optical materials, photoconducting media, as solvatochromic probes, and also at diagnostics and treatment of cytological abnormalities [1]. The photophysical properties of some practically important merocyanines were investigated in detail. However, as a rule, the regular series of dyes were not researched; more often a single compound (in comparison with the corresponding analogue without a cycle) was the object studied (e.g. [1]). The known merocyanines with the partially cycled polymethine chain contain mainly benzothiazole, benzoxazole, and benzimidazole nuclei (see refs. [1–4]), but not an indole one, though derivatives of the latter possess the important advantage—the substantially better solubility [5], particularly in organic solvents, that is of great importance at creation of functional materials with high dye content.

The compound **1** – 10,10-dimethyl-7,8,9,10-tetrahydro-6*H*-pyrido[1,2-*a*]indolium perchlorate (Scheme 1) – was synthesized for the first time in 1979 [6]. In 1986 the technique of its synthesis was improved essentially [7]. Some symmetrical (**2**–**4**), and only a few asymmetrical polymethine dyes containing this residue were synthesized [6–8]. Nevertheless, the properties of the derivatives of compound **1** are poorly studied.

Thus, the purpose of the present work was the synthesis of series of polymethine dyes based on compound **1** and the investigation of their absorption spectra in a wide set of solvent polarities.

2. Experimental

2.1. Preparation of dyes

The vinylogous series of merocyanines, based on malononitrile (**5**–**7**) and *N*,*N*-diethyl-thiobarbituric acid (**8**–**10**), were synthesized starting from compound **1** (Scheme 1).

The synthetic strategy of dye **8** ($n = 0$) preparation is shown in Scheme 2. The other merocyanines were synthesized in a different

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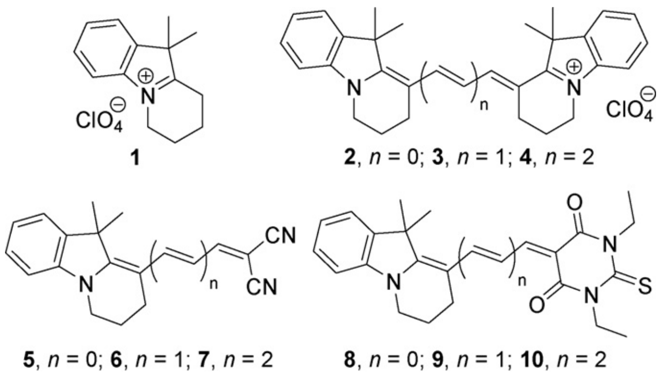


Scheme 1.

way (see an example in Scheme 3). The detailed procedures are described below.

*2.1.1. (9E)-9-[(Dimethylamino)methylene]-10,10-dimethyl-7,8,9,10-tetrahydro-6H-pyrido[1,2-a]indolium perchlorate (**11**)*

Compound **1** (300 mg, 1 mmol) and DMF (0.4 ml) were refluxed in acetic anhydride (4 ml) for 8 h. Then the oily product was precipitated with diethyl ether, decanted and twice washed with new portions of diethyl ether, and used in the next stage, in the same pot, without any additional purification.

*2.1.2. 2-[(10,10-Dimethyl-6,7,8,10-tetrahydropyrido[1,2-a]indol-9-yl)methylene]malononitrile (**5**)*

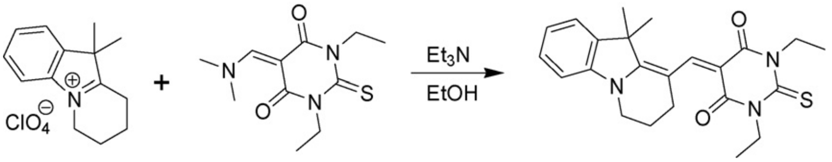
Hemicyanine **11** and malononitrile (200 mg, 3 mmol) were dissolved in pyridine, the reaction mixture was refluxed for 5 min, and then water (20 ml) was added. The next day the product was filtered off, dried, and purified by column chromatography (Al_2O_3; $CHCl_3$; twice). After removal of the solvent the product was heated in EtOH (5 ml), filtered off, and dried (yield 18% (in recount to salt **1**), mp = 243–244 °C; orange needles). ^{1}H NMR, δ ($CDCl_3$, 400 MHz): 1.582 (s, 6H; $(CH_3)_2$), 2.043 (qv, J = 6.0 Hz, 2H; $C^{11}H_2$), 2.897 (t, J = 6.2 Hz, 2H; $C^{10}H_2$), 3.738 (t, J = 5.8 Hz, 2H; $C^{12}H_2$), 6.908 (d, J = 7.8 Hz, 1H, H^{13}), 7.133 (t, J = 7.4 Hz, 1H, H^{15}), 7.259 (d, J = 7.4 Hz, 1H, H^{16}), 7.302 (t, J = 7.6 Hz, 1H, H^{14}), 7.484 (s, 1H, H^4). Anal. calcd for $C_{18}H_{17}N_3$ (275.35): C 78.52, H 6.22, N 15.26. Found: C 78.45, H 6.27, N 15.30.

*2.1.3. (9E)-9-{(2E)-3-[Acetyl(phenyl)amino]prop-2-enylidene}-10,10-dimethyl-7,8,9,10-tetrahydro-6H-pyrido[1,2-a]indolium perchlorate (**12**)*

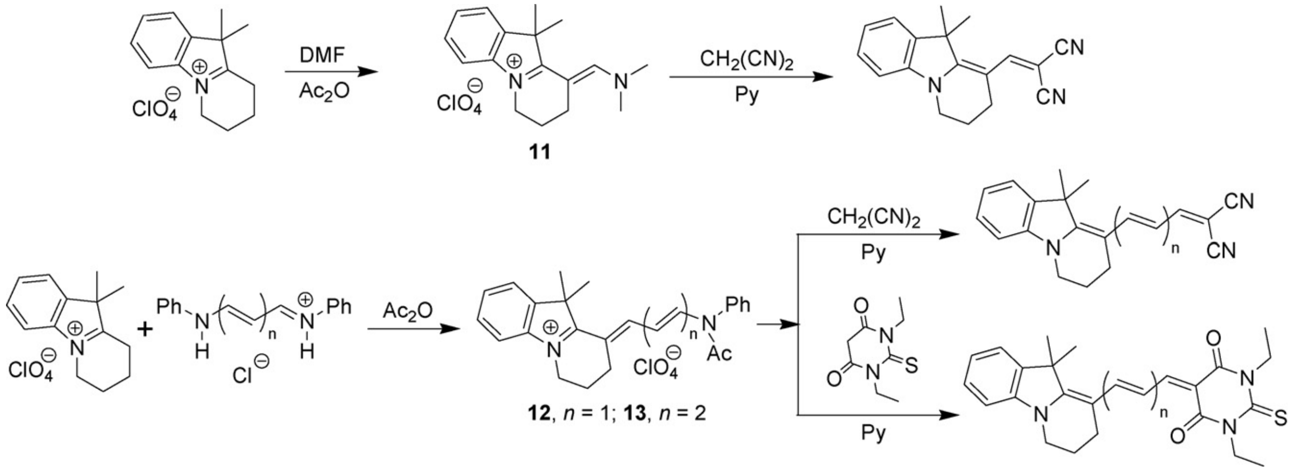
Compound **1** (600 mg, 2 mmol), *N*-[(1*E*,2*E*)-3-anilinoprop-2-enylidene]aniline hydrochloride (520 mg, 2 mmol), acetic anhydride (1 ml), and acetic acid (3 ml) were heated (bath, 120 °C) for 4 h. Then methanol solution (5 ml) of sodium perchlorate (240 mg, 2 mmol) was added to the reaction mixture. 10 min later the reaction mixture was diluted with 30 ml of water and kept overnight in a cooler. The precipitate was filtered off and washed with cooled methanol to yield 55% of dark-brown powder. In the next step, the resulting hemicyanine **12** was used without additional purification.

*2.1.4. 2-[(2E)-3-(10,10-Dimethyl-6,7,8,10-tetrahydropyrido-[1,2-a]indol-9-yl)prop-2-enylidene]-malononitrile (**6**)*

Hemicyanine **12** (140 mg, 0.3 mmol) and malononitrile (40 mg, 0.6 mmol) were dissolved in pyridine (2 ml) and heated in bath (50 °C) for 10 min. Then the product was precipitated with water, filtered off, dried, and chromatographed on SiO_2 and after on Al_2O_3 ($CHCl_3$ as the eluent). The violet crystals of **6** were obtained after solvent evaporation and heating of the residue in 5 ml of ethanol (yield 42%, mp = 200–201 °C). ^{1}H NMR, δ ($CDCl_3$, 400 MHz): 1.600 (s, 6H; $(CH_3)_2$), 2.048 (qv, J = 6.0 Hz, 2H; $C^{11}H_2$), 2.488 (t, J = 6.2 Hz, 2H; $C^{10}H_2$), 3.725 (t, J = 5.9 Hz, 2H; $C^{12}H_2$), 6.310 (t, J = 12.9 Hz, 1H, H^5), 6.845 (d, J = 7.8 Hz, 1H, H^{13}), 7.071 (t, J = 7.6 Hz, 1H, H^{15}), 7.237 (d, J = 7.6 Hz, 1H, H^{16}), 7.271 (t, J = 7.8 Hz, 1H, H^{14}), 7.365 (d, J = 12.6 Hz, 1H, H^6), 7.495 (d, J = 13.2 Hz, 1H, H^4). Anal. calcd for $C_{20}H_{19}N_3$ (301.39): C 79.70, H 6.35, N 13.94. Found: C 79.61, H 6.41, N 13.88.



Scheme 2.



Scheme 3.

*2.1.5. (9E)-9-{(2E,4E)-5-[Acetyl(phenyl)amino]penta-2,4-dienylidene}-10,10-dimethyl-7,8,9,10-tetrahydro-6H-pyrido-[1,2-a]indolium perchlorate (**13**)*

Salt **1** (600 mg, 2 mmol) and *N*-[(1*E*,2*E*,4*E*)-5-anilinopenta-2,4-dienylidene]aniline hydrochloride (570 mg, 2 mmol) were heated in acetic anhydride (3 ml) for 1 h (bath, 120 °C). The product was precipitated with diethyl ether and filtered off (yield 45%).

*2.1.6. 2-[(2E,4E)-5-(10,10-Dimethyl-6,7,8,10-tetrahydropyrido-[1,2-a]indol-9-yl)penta-2,4-dienylidene]malononitrile (**7**)*

To a mixture of compound **13** (100 mg, 0.2 mmol) and malononitrile (33 mg, 0.5 mmol) pyridine (1.5 ml) was added. The reaction ended for 3 min at room temperature. The next isolation and purification of the resulted merocyanine was similar to those for dye **6**. Blue lustrous crystals were obtained (18% yield, mp = 198–199 °C). ^{1}H NMR, δ (DMSO-d_6, 400 MHz): 1.578 (s, 6H; $(CH_3)_2$), 1.939 (qv, J = 5.8 Hz, 2H; $C^{11}H_2$), 2.426 (t, J = 6.0 Hz, 2H; $C^{10}H_2$), 3.775 (t, J = 5.6 Hz, 2H; $C^{12}H_2$), 6.327 (t, J = 12.8 Hz, 1H, H^5), 6.354 (t, J = 12.6 Hz, 1H, H^7), 7.01–7.08 (m, 2H), 7.270 (t, J = 7.6 Hz, 1H, H^{14}), 7.237 (d, J = 7.4 Hz, 1H, H^{16}), 7.504 (t, J = 12.7 Hz, 1H, H^6), 7.570 (d, J = 13.6 Hz, 1H, H^4), 7.620 (d, J = 12.5 Hz, 1H, H^8). Anal. calcd for $C_{22}H_{21}N_3$ (327.42): C 80.70, H 6.46, N 12.83. Found: C 80.71, H 6.50, N 12.78.

*2.1.7. 5-[(10,10-Dimethyl-6,7,8,10-tetrahydropyrido[1,2-a]indol-9-yl)methylene]-1,3-diethyl-2-thioxodihydropyrimidine-4,6(1H,5H)-dione (**8**)*

Compound **1** (90 mg, 0.3 mmol) and 5-[(dimethylamino)-methylene]-1,3-diethyl-2-thioxodihydropyrimidine-4,6(1*H*,5*H*)-dione (77 mg, 0.3 mmol) were refluxed in non-aqueous ethanol (5 ml) in the presence of triethylamine (0.2 ml) for 10 min. The resulted dye was filtered off and crystallized from ethanol (yield 65%, mp = 251–252 °C; salmon crystals). ^{1}H NMR, δ ($CDCl_3$, 400 MHz): 1.263 (t, J = 6.8 Hz, 6H; $(CH_3)_2$), 1.706 (s, 6H; $(CH_3)_2$), 2.004 (qv, J = 5.9 Hz, 2H; $C^{11}H_2$), 2.791 (t, J = 6.0 Hz, 2H; $C^{10}H_2$), 3.849 (t, J = 5.7 Hz, 2H; $C^{12}H_2$), 4.531 (q, J = 6.8 Hz, 4H; $(CH_2)_2$), 7.027 (d, J = 8.2 Hz, 1H, H^{13}), 7.217 (t, J = 7.8 Hz, 1H, H^{15}), 7.30–7.36 (m, 2H), 8.544 (s, 1H, H^4). Anal. calcd for $C_{23}H_{27}N_3O_2S$ (409.55): C 67.45, H 6.65, N 10.26, S 7.83. Found: C 67.39, H 6.62, N 10.20, S 7.80.

*2.1.8. 5-[(2E)-3-(10,10-Dimethyl-6,7,8,10-tetrahydropyrido[1,2-a]indol-9-yl)prop-2-enylidene]-1,3-diethyl-2-thioxodihydropyrimidine-4,6(1H,5H)-dione (**9**)*

Hemicyanine **12** (140 mg, 0.3 mmol) and *N*,*N*-diethylthiobarbituric acid (100 mg, 0.5 mmol) were heated in pyridine (2 ml) in bath (60 °C) for 10 min. Then water (15 ml) was added and the precipitate of dye was filtered off. The product was purified by column chromatography (SiO_2; $CHCl_3$). After solvent removal the dye was crystallized from aqueous (80% EtOH) ethanol (yield 45%, mp > 260 °C; dark-blue crystals). ^{1}H NMR, δ ($CDCl_3$, 400 MHz): 1.255 (t, J = 6.7 Hz, 6H; $(CH_3)_2$), 1.610 (s, 6H; $(CH_3)_2$), 2.036 (qv, J = 6.0 Hz, 2H; $C^{11}H_2$), 2.650 (t, J = 6.2 Hz, 2H; $C^{10}H_2$), 3.777 (t, J = 5.8 Hz, 2H; $C^{12}H_2$), 4.533 (q, J = 6.7 Hz, 4H; $(CH_2)_2$), 6.550 (t, J = 12.5 Hz, 1H, H^5), 7.285 (t, J = 7.2 Hz, 1H, H^{15}), 7.35–7.44 (m, 2H), 7.615 (d, J = 7.5 Hz, 1H, H^{16}), 7.64–7.79 (m, 3H), 8.051 (d, J = 12.9 Hz, 1H, H^4). Anal. calcd for $C_{25}H_{29}N_3O_2S$ (435.58): C 68.93, H 6.71, N 9.65, S 7.36. Found: C 68.97, H 6.91, N 9.59, S 7.38.

*2.1.9. 5-[(2E,4E)-5-(10,10-Dimethyl-6,7,8,10-tetrahydropyrido[1,2-a]indol-9-yl)penta-2,4-dienylidene]-1,3-diethyl-2-thioxodihydropyrimidine-4,6(1H,5H)-dione (**10**)*

The reaction of compound **13** (100 mg, 2 mmol) and *N*,*N*-diethylthiobarbituric acid (80 mg, 0.4 mmol) in pyridine ended in 3 min at room temperature. The ethanol (5 ml) and water (5 ml) were added to the reaction mixture, the precipitate was filtered off, and washed with aqueous ethanol, dried, chromatographed on SiO_2 from CH_2Cl_2, and crystallized from ethanol (yield 40%, mp = 248–249 °C; bright green lustrous needles). ^{1}H NMR, δ (DMSO-d_6, 400 MHz): 1.154 (t, J = 7.0 Hz, 6H; $(CH_3)_2$), 1.664 (s, 6H; $(CH_3)_2$), 2.028 (qv, J = 5.5 Hz, 2H; $C^{11}H_2$), 2.589 (t, J = 5.2 Hz, 2H; $C^{10}H_2$), 4.009 (t, J = 5.7 Hz, 2H; $C^{12}H_2$), 4.410 (q, J = 7.0 Hz, 4H; $(CH_2)_2$), 7.274 (d, J = 8.2 Hz, 1H, H^{13}), 7.217 (t, J = 7.8 Hz, 1H, H^{15}), 7.30–7.36 (m, 2H), 8.544 (s, 1H, H^4). Anal. calcd for $C_{27}H_{31}N_3O_2S$ (461.62): C 70.25, H 6.77, N 9.10, S 6.95. Found: C 70.21, H 6.80, N 9.14, S 6.89.

3. Materials and methods

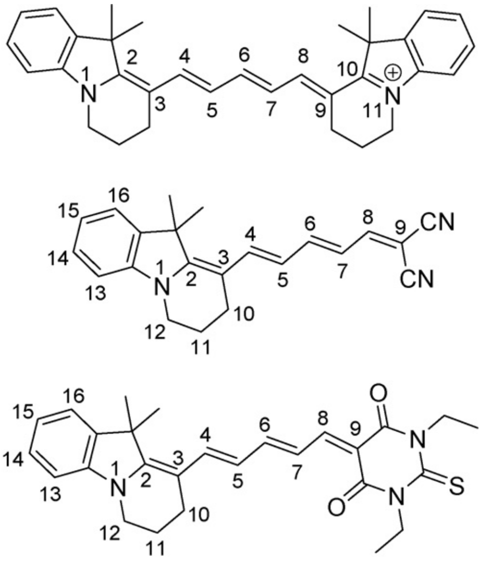
The UV–vis spectra were recorded on a spectrophotometer Shimadzu UV-3100. Solvents were purified according to methods given in ref. [9]. Chromatography was carried out on silica gel 60 and aluminum oxide 80 (“Merck”). The purity of the dyes was checked by TLC-control (Silufol UV-254, $CHCl_3$ or CH_2Cl_2 as the eluent). ^{1}H NMR spectra were measured on a spectrometer Varian Mercury-400 (400.40 MHz for H-atoms) in $CDCl_3$ or DMSO-d_6, internal standard TMS. The COSY spectra were also registered. The atom numeration used in NMR spectra characterization is shown in Scheme 4 (the hydrogen atoms possess the same numbers, as the corresponding skeleton atoms of dye).

Melting (decomposition) points were measured in an open capillary and were not corrected.

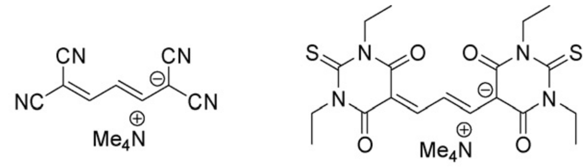
The absorption spectra of merocyanines **5**–**10** were investigated in a maximum wide on polarity set of solvents—*n*-hexane, toluene, dichloromethane, DMF, and ethanol [4]. The spectra of cationic dyes **2**–**4** were explored in dichloromethane, DMF, and ethanol.

The mathematical processing of long-wavelength absorption bands by the method of moments [10] enabled, besides the traditional absorption maxima λ^a_{max} and extinctions ε, to characterize quantitatively the band centers M_a^{-1}, width σ^a, and form γ^a_1, γ^a_2, F^a (these three parameters determine band asymmetry, steepness, and thin structure correspondingly), and also the values of oscillator strength f (the integral band intensity).

The deviations of the absorption spectra of merocyanines **5**–**10** both on the maxima (D^a_λ) and on the band centers (D^a_M) were calculated using the spectral parameters of the parent cationic **2**–**4** and anionic dyes **14**–**18** (Scheme 5) [11,12].



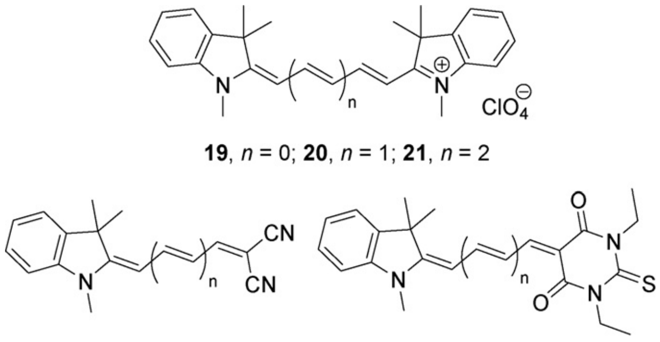
Scheme 4.



14, *n* = 0; **15**, *n* = 1; **16**, *n* = 2 **17**, *n* = 1; **18**, *n* = 2

Scheme 5.

The spectral properties and the electronic structure of dyes **19**–**27** (Scheme 6) were described in refs. [11–13]. The before unpublished characteristics of the absorption spectra of merocyanines **22**–**24** in *n*-hexane and toluene are given in Table 1. These data are necessary for the analysis of the influence of partial rigidization of the polymethine chain on the properties of compounds **2**–**10**.



19, *n* = 0; **20**, *n* = 1; **21**, *n* = 2

22, *n* = 0; **23**, *n* = 1; **24**, *n* = 2 **25**, *n* = 0; **26**, *n* = 1; **27**, *n* = 2

Scheme 6.

Table 1
Characteristics of the long-wavelength vis absorption bands of dyes **2–10**, **19–21** measured in *n*-hexane, toluene, CH_2Cl_2, DMF, and ethanol at 293 K

Dye	Solvent	λ^a_{max} (nm)	D^a_λ (nm)	$\varepsilon \times 10^{-3}$ ($m^2\,mol^{-1}$)	M_a^{-1} (nm)	D^a_M (nm)	f	σ^a (cm^{-1})	γ_1^a	γ_2^a	$F^a \times 10^{-2}$
2	CH_2Cl_2	572	–	13.99	549.7	–	1.02	1080	1.64	4.1	8.7
	DMF	569	–	12.21	546.3	–	0.98	1095	1.48	3.8	7.5
	EtOH	568	–	12.72	544.7	–	1.02	1095	1.45	3.7	7.1
3	CH_2Cl_2	661	–	26.67	641.4	–	1.38	825	1.63	4.3	9.3
	DMF	656	–	23.13	632.9	–	1.34	945	1.70	4.6	10.2
	EtOH	654	–	24.63	631.7	–	1.38	910	1.70	4.7	9.9
4	CH_2Cl_2	767	–	33.69	746.9	–	1.55	760	1.88	5.6	11.1
	DMF	759	–	22.37	720.9	–	1.49	1165	1.90	5.6	12.1
	EtOH	757	–	27.48	726.1	–	1.59	1000	1.89	5.6	11.8
5	*n*-Hexane	433, 413	–	6.15, 4.72	414.5	–	0.692	1280	1.05	1.7	4.6
	Toluene	444	–	6.46	427.3	–	0.699	1245	1.09	1.9	4.7
	CH_2Cl_2	447	13.5	7.18	431.0	14.5	0.769	1210	1.07	1.8	4.3
	DMF	449	8.8	7.10	433.0	9.9	0.762	1225	1.17	2.4	4.8
	EtOH	446	10.5	7.05	430.5	10.8	0.780	1225	1.09	2.0	4.4
6	*n*-Hexane	505 482	–	7.59, 5.99	482.3	–	0.803	1230	1.13	2.2	4.7
	Toluene	526	–	8.74	505.6	–	0.868	1175	1.12	2.2	4.6
	CH_2Cl_2	536	17.5	11.48	517.1	20.8	1.000	1085	1.23	2.4	5.5
	DMF	538	11	11.76	520.3	11.6	0.984	1055	1.32	2.9	6.0
	EtOH	535	12.5	11.42	516.7	14	1.011	1095	1.30	2.8	5.7
7	*n*-Hexane	571 545	–	6.81, 7.83	535.7	–	0.962	1320	1.11	2.1	4.4
	Toluene	596 577	–	7.91, 7.77	567.0	–	1.082	1325	0.96	1.6	3.4
	CH_2Cl_2	626	32	11.70	594.4	47.5	1.312	1245	1.14	2.1	4.8
	DMF	636	15	13.02	604.6	22.1	1.322	1250	1.28	2.6	6.1
	EtOH	628	21.5	12.02	595.4	32.2	1.343	1305	1.22	2.4	5.6
8	*n*-Hexane	495	–	11.08	483.8	–	0.864	990	1.17	2.5	4.5
	Toluene	506	–	11.00	494.2	–	0.860	955	1.16	2.5	4.4
	CH_2Cl_2	508	–	10.91	494.6	–	0.895	1000	1.20	2.6	4.8
	DMF	505	–	9.58	488.7	–	0.859	1070	1.13	2.2	4.6
	EtOH	504	–	8.96	485.2	–	0.878	1070	1.23	2.6	5.3
9	*n*-Hexane	571 535	–	16.86, 6.66	550.5	–	1.087	1020	1.53	3.8	8.8
	Toluene	592	–	20.26	577.1	–	1.162	880	1.72	5.0	9.2
	CH_2Cl_2	599	4.5	23.43	585.8	1.3	1.210	770	1.62	4.3	8.4
	DMF	598	1	21.12	580.2	0.9	1.218	900	1.65	4.4	9.0
	EtOH	595	2	18.95	574.8	4.5	1.191	995	1.70	4.7	9.6
10	*n*-Hexane	643 601	–	11.69, 8.43	603.6	–	1.150	1250	1.21	2.3	6.0
	Toluene	678	–	16.19	645.9	–	1.315	1145	1.40	3.1	7.4
	CH_2Cl_2	702	4	31.30	682.6	4.1	1.679	865	1.98	6.3	11.1
	DMF	699	1.5	27.16	673.3	−0.4	1.582	1030	1.98	6.1	12.4
	EtOH	696	1.5	24.45	664.5	7.7	1.581	1180	1.90	5.5	12.6
22	*n*-Hexane	422 404	–	6.37, 5.55	402.5	–	0.80	1370	1.13	2.2	5.7
	Toluene	435	–	6.41	416.5	–	0.78	1320	1.09	2.0	4.6
23	*n*-Hexane	495 474	–	6.21, 5.94	469.6	–	0.83	1415	1.22	2.6	5.1
	Toluene	516	–	6.92	495.8	–	0.89	1390	1.30	3.1	5.3
24	*n*-Hexane	532	–	6.87	517.4	–	0.90	1505	1.49	4.6	5.8
	Toluene	558	–	6.68	546.6	–	0.97	1455	0.97	1.7	3.4

Table 2
The calculated by the method AM1 parameters of cationic dyes **2–4**, **19–21** and merocyanines **5–10**, **22–27** (for the ground state, gas phase)

	Dye								
	2	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**
BOA	0.039	−0.022	−0.05	−0.57	−0.62	−0.66	−0.477	−0.553	−0.624
Δq_Σ	2.28	3.036	3.734	0.998	1.26	1.39	1.421	1.783	1.905

									Dye
	19	**20**	**21**	**22**	**23**	**24**	**25**	**26**	**27**
BOA	0.024	−0.029	−0.066	−0.546	−0.627	−0.665	−0.421	−0.564	−0.631
Δq_Σ	2.652	3.378	4.064	1.167	1.339	1.441	1.65	1.879	1.95

It is well known that polymethine dyes, both charged and neutral ones, readily aggregate in solvents of low polarity. Earlier we also observed this effect for merocyanines derived from strongly electron donating benzimidazole nucleus [12]. The absorption spectra of the merocyanines **5–10** were shown to obey Beer's law in a concentration interval of 10^{-6}–10^{-4} mol/L in toluene and more polar solvents; for cationic cyanines **2–4** Beer's law holds in all three solvents in which they were studied. Dyes **5–10** in *n*-hexane obey Beer's law up to the concentration 3×10^{-5} mol/L. The final quantitative spectra of all dyes were measured at concentration 3×10^{-6}–10^{-5} mol/L (at which the maximal optical density of solutions did not exceed 1.5 in 1-cm cuvette). Hence, in this concentration interval aggregation could not influence their absorption spectra.

Quantum-chemical calculations of the electronic structure of dye molecules were performed for gas phase by the method AM1 with a standard set of parameters [14]. Geometry optimizations with the use of limited Hartree–Fock method and Polak–Ribiere algorithm with an accuracy of 0.001 kcal Å^{-1} mol^{-1} have been preliminary carried out. The maxima of the electronic absorption bands were determined with allowance for singly excited configurations arising from all possible electronic transitions from five HOMOs to five LUMOs.

For the analysis of bond order alternation in the polymethine chain of dyes the parameter BOA [15] was used. For the calculation of charge alternation in chromophore in the S_0 state we used the formula:

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

where q_i and q_{i+1} are charges on the neighboring atoms of chromophore. The parameter Δq_Σ was calculated for the chromophore N-1–C-2–C-3···–C-10–N-11 for cationic polymethines and N-1–C-2–···–C-9 for merocyanines.

The results of quantum-chemical calculation of dyes **2–10** and their analogue **19–27** are compiled in Table 2.

4. Discussion

4.1. Structure and electronic absorption spectra of cationic dyes 2–4

The spectral properties of dyes **2–4** [7], first of all solvatochromism, have not almost been investigated.

The absorption bands of compounds **2–4** undergo a bathochromic shift in comparison with dyes **19–21** (see Table 1 and [13]), that is in agreement with the Dewar–Knott rule [16]. The long-wavelength shift is maximal for carbocyanine **2** ($\Delta\tilde{\nu} = 600$–$750\,\mathrm{cm}^{-1}$ on $\lambda^{\mathrm{a}}_{\max}$, $\Delta\tilde{\nu} = 720$–$820\,\mathrm{cm}^{-1}$ on M_a^{-1}). The corresponding values for dicarbo- and tricarbo-cyanines **3** and **4** are less and fall within the range of 155–335 cm^{-1}. The greater long-wavelength shift for compound **2** was noticed in ref. [7] and explained by steric hindrances in its molecule (the repulsion of two closely located CH$_2$-groups). This suggestion agreed with the results of our quantum-chemical calculation. The calculated energy of the long-wavelength transition $S_1^{\mathrm{FC}} \leftarrow S_0$ in molecule **19** corresponds to the wavelength $\lambda = 500$ nm, for compound **2** it amounts to $\lambda = 523$ nm. If to set down zero *z*-coordinate for chromophore atoms of molecule **2** at calculation (the planar chromophore), then $\lambda = 515$ nm.

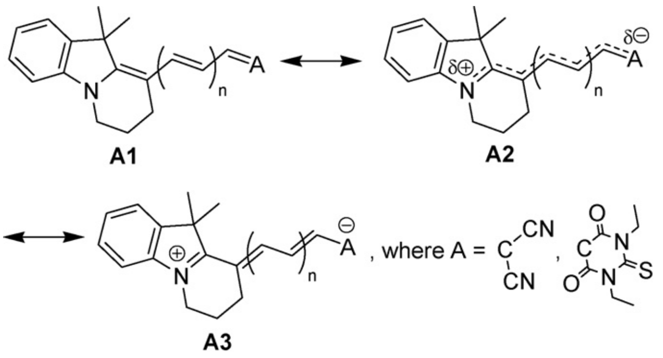
Dyes **2–4**, as well as **19–21**, possess negative solvatochromism (see Table 1), typical for symmetric cationic cyanines [13]. However, the solvatochromic range for the dyes containing cyclic groups is a little bit less. For example, in case of compound **4,** most solvatochromic in this series, the transition from dichloromethane to DMF and ethanol as solvents is accompanied with the short-wavelength shifts of $\lambda^{\mathrm{a}}_{\max}$ equal to $\Delta\tilde{\nu} = 137$ and $\Delta\tilde{\nu} = 172\,\mathrm{cm}^{-1}$ correspondingly. For its analogue **21** the corresponding shifts equal to $\Delta\tilde{\nu} = 211$ and $\Delta\tilde{\nu} = 284\,\mathrm{cm}^{-1}$. Most probably, the cycle as the electron-donating substituent in an odd position of the polymethine chain causes a weakening of nucleophilic solvation by polar solvents of the distributed positive charge in molecules **2–4**. A less solvation stabilization of the ground state causes the smaller hypsochromic shift of the absorption bands of dyes **3** and **4**, as compared to compounds **20** and **21**, at transition from dichloromethane to high-polar solvents (cf. [13] and Table 1). Quantum-chemical calculation (see values of Δq_Σ in Table 2) confirms a decrease of charge alternation in the chromophore of dyes **2–4** in comparison with their analogues **19–21** (Table 2).

The calculated values of BOA are also less for dyes **3** and **4** than for molecules **20** and **21** (Table 2). An increase of BOA in case of compound **2** is probably concerned with a non-planar structure of its chromophore. Hence, the cycle causes the reduction not only of intermolecular solute–solvent interactions (IMI), but also of vibronic interactions (VI) in molecules **3** and **4**. It is expressed in a narrowing of the spectral bands, an increase of their peak intensity (extinction) in comparison with 3*H*-indole derivatives. For example, in dichloromethane the value of σ^a amounts to 760 cm^{-1}, and $\varepsilon = 33.69 \times 10^3$ m^2 mol^{-1} for dye **4** (Table 1), and $\sigma^a = 830$ cm^{-1}, and $\varepsilon = 30.5 \times 10^3$ m^2 mol^{-1} in case of **21** (see ref. [13]). At the same time their integral intensities *f* and the parameters γ_1^{a}, γ_2^{a}, F^{a} are very close.

Thus, the influence of a cycle on the absorption spectra of symmetric cationic dyes **2–4** is mainly expressed in long-wavelength shift, a narrowing, and an increase of extinctions of their long-wavelength bands in comparison with dyes **19–21**. A weakening of solute–solvent IMI results in less solvatochromic range. For compound **2**, these regularities are disturbed by the steric hindrances in its molecule.

4.2. Structure and solvatochromism of merocyanines 5–10

The suggested by Dähne model of the three limit ideal states of donor–acceptor substituted polyenes [non-polar polyene **A1**],



Scheme 7.

[polymethine **A2**] and [dipolar polyene **A3**] [16] is utterly suitable for the analysis of their electronic structure (Scheme 7).

Merocyanines, depending on their chemical structure and solvent polarity, may attain all the limit states or intermediate states between them. 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 approach of a merocyanine to the structure **A2** is accompanied, besides the long-wavelength spectral shift, with the spectral band narrowing (the weakening of the VI), an increase of their intensity, and also with a decrease of the deviations, and a growth of the vinylene shifts [12,16].

The absorption bands of dyes **5**–**7** undergo the long-wavelength shifts (Table 1) as compared to those of their analogues **22**–**24** [11]. This effect is a little bit greater, than that for symmetric cationic polymethines **2**–**4** (counting upon one cyclic group), and is consistent with the Dewar–Knott rule. The corresponding bathochromic shifts are minimal for tetramethinemerocyanine **6** ($\Delta\tilde{\nu} = 300$–$560\,\mathrm{cm}^{-1}$ depending on a solvent). Some irregularity of these shifts at chain lengthening is most probably concerned with the additional long-wavelength shift in case of dye **5**, caused by the interaction of close located terminal groups (cf. with compound **2**).

Merocyanines **5**–**7** demonstrate well defined positive solvatochromism, growing at the polymethine chain lengthening. It points at an increase of the dipole moment (i.e., the dipolar limit structure contribution) in the S_1^{FC} state, as compared to that in the S_0 state. The range of solvatochromism for dyes **5**–**7** is less, than that for their analogues **22**–**24** [11], that is more legibly traced on the absorption band centers M_a^{-1}, than on their maxima (Table 1). For example, for compound **7** at transition from toluene to DMF $\Delta M_a^{-1} = 1095\,\mathrm{cm}^{-1}$, and for **24** $\Delta M_a^{-1} = 1225\,\mathrm{cm}^{-1}$ at the same solvent replacement.

The vinylene shifts in a series **5**–**7** grow with an increase of solvent polarity both on the maxima (VS_λ^{a}), and on the band centers (VS_M^{a}). The parameter VS_λ^{a} changes irregularly at the chain lengthening, however, the value of VS_M^{a} decreases at an increase of *n* in all solvents. Both parameters exceed those of dyes **22**–**24**, but do not achieve the value of 100 nm, typical for symmetric cyanine dyes.

The deviations D_λ^{a} and D_M^{a} of merocyanines **5**–**7** are larger in dichloromethane, than in high-polar DMF and increase at the polymethine chain lengthening.

Thus, all the considered spectral parameters indicate that the electronic structure of dyes **5**–**7** lies within the interval **A1**–**A2**, and the contribution of the non-polar polyene **A1** grows at a decrease of solvent polarity and at transition to the higher vinylogues. Besides, one can conclude that the ideal polymethine **A2** contributes more to the electronic structure of molecules **5**–**7**, than in case of their analogues **22**–**24** with the residue of 3H-indole. This suggestion was confirmed by the analysis of intensity, width and form of their absorption bands (Fig. 1, Table 1).

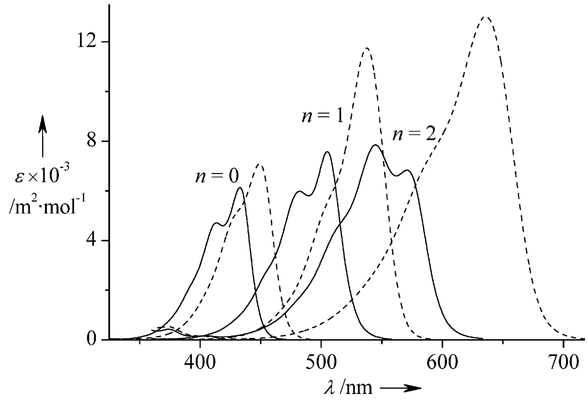


Fig. 1. UV–vis spectra of dyes **5**, **6** and, **7** in *n*-hexane (—) and DMF (- - -).

The band width σ^a in a series **5**–**7** is less, than those in a series **22**–**24** in all solvents. The value of σ^a decreases, and the parameters γ_1^{a}, γ_2^{a}, F^a grow at an increase of solvent polarity (Table 1). However, a strong electrophilic solvation of the non-divided electron pair at the heterocyclic nitrogen atom with molecules of protic ethanol causes, as well as in case of dyes **22**–**24** [11], an increase of the parameter σ^a at transition to this solvent. Such H-bond increases the structure **A1** weight, counteracting to the high polarity of ethanol. The absorption band width for merocyanines **5**–**7** at first decreases, and then grows at the polymethine chain lengthening in all solvents. It is typical for electron asymmetric dyes and points at an increase of the VI for the highest vinylogues.

The narrowing of the absorption bands of dyes **5**–**7** in comparison with the analogous derivatives of 3H-indole causes an increase of their peak intensity at the practically constant oscillator strength *f*. An observed growth of the integral intensity *f* in case of dye **7** is probably concerned with a larger contribution of the ideal polymethine structure **A2**.

Dyes **8**–**10** contain *N*,*N*-diethylthiobarbituric acid residue, whose electron-acceptor ability is much higher, than that for malononitrile [17]. Therefore, *a priori* they should be characterized by a greater dipolarity, as it takes place in a series **25**–**27** [12]. Taking into account the change of π-electron density distribution in their molecules, we expected that the influence of the cyclic group would differ from that for merocyanines **5**–**7**.

In a series **8**–**10**, the cycle does not affect the position of the absorption bands so considerably, as for compounds **5**–**7** (cf. the values of $\lambda_{\max}^{\mathrm{a}}$ and M_a^{-1} in Table 1 and those for dyes **25**–**27** in ref. [12]). Dimethinemerocyanine **8** does not obey this rule; probably, the steric hindrances in case of *N*,*N*-diethylthiobarbituric moiety is greater than those for malononitrile, that results in stronger in-plane distortion in molecule **8** and, hence, in the long-wavelength shift of the absorption band.

As opposed to both the corresponding symmetric dyes **2**–**4** and merocyanines **5**–**7**, the differences of $\lambda_{\max}^{\mathrm{a}}$ and M_a^{-1} between merocyanines **8**–**10** and **25**–**27** decrease at an increase of solvent polarity (Table 1, [12]). In ethanol at transition from dye **27** to **10** the absorption band center undergoes even slight hypsochromic shift ($\Delta\tilde{\nu} = -29\,\mathrm{cm}^{-1}$). What is the reason of such difference?

In a series **8**–**10**, the absorption bands demonstrate long-wavelength shift at transition from low-polar *n*-hexane to toluene and further to dichloromethane. The further growth of solvent polarity is accompanied with the hypsochromic shifts (Table 1, Fig. 2). Thus, as opposed to positive solvatochromic merocyanines **25**–**27**, dyes **8**–**10** possess inverse solvatochromism.

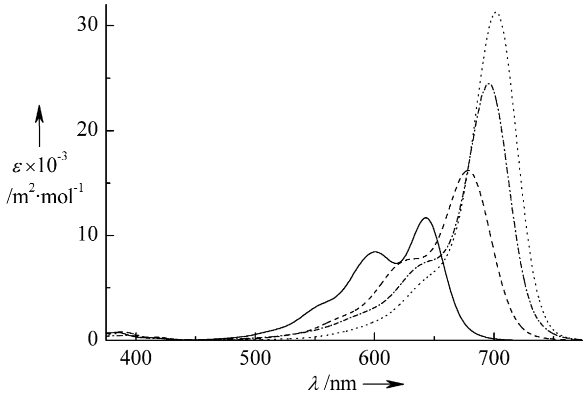


Fig. 2. UV–vis spectra of merocyanine **10** in *n*-hexane (––), toluene (- - -), dichloromethane (· · ·), and ethanol (-·-·-).

The deviations in the absorption spectra of merocyanines **8**–**10** are close to zero both on the maxima, and on the band central positions in a set of solvents dichloromethane - DMF - ethanol (Table 1). These data indicate high electronic symmetry of these compounds in a such set of solvents.

The vinylene shifts in a series **8**–**10** exceed the values of VS_{λ}^{a} and VS_{M}^{a} of malononitrile derivatives **5**–**7**, approaching in solvents more polar than toluene to the value of 100 nm, characteristic for the symmetric cationic [13] and anionic [11,12] polymethine dyes. The maximal value of $VS_{\lambda}^{a} = 103$ nm is observed in dichloromethane in which the coloring of dyes **8**–**10** is the deepest. The first vinylene shifts are a bit smaller, than the second ones that, probably, are concerned with planar distortions in molecule **8**, which cause an additional long-wavelength shift of their absorption bands.

The absorption band width σ^a for merocyanines **8**–**10** is minimal in dichloromethane and increases at any change of solvent polarity (Table 1). The solvent induced changes of the parameter σ^a are maximal in case of the most solvatochromic vinylogue **10**, for which in a pair of solvents *n*-hexane—dichloromethane $\Delta\sigma^a$ amounts to 385 cm^{-1}, and in a pair dichloromethane—DMF $\Delta\sigma^a = 315$ cm^{-1}. The polymethine chain lengthening in a series **5**–**7**, as well as in case of their analogues **25**–**27** [12], is accompanied at first with a narrowing of the spectral bands, and then with their broadening (Table 1). Only in low-polar *n*-hexane the σ^a value also increases at transition from di (**8**) to tetramethinemerocyanine **9** (Table 1).

A transition from dyes **25**–**27** to **8**–**10**, i.e., the insertion of the cyclic group into merocyanine molecules, is accompanied with band narrowing in low-polar *n*-hexane and toluene, and also in medium-polar dichloromethane as a solvent. In high-polar ethanol and DMF the effect is opposite.

The parameters γ_1^a, γ_2^a, and F^a of dyes **8**–**10** was found not informative enough. However, their analysis allowed to reveal the opposite tendencies in a change of band asymmetry, excess and fine structure at the chain lengthening in low-polar and high-polar solvents. In the former the transition from vinylogue **9** to **10** is accompanied with a decrease of the γ_1^a, γ_2^a, and F^a values, and in the latter —with their growth.

The oscillator strength values (*f*) in a series **8**–**10** are comparable to those for symmetric cationic cyanines (Table 1). Along with the narrow absorption bands it gives the unusually high for asymmetrical dyes extinctions of compounds **9** and **10**.

Summarizing the above-stated, we made a conclusion that the electronic structure of merocyanines **8**–**10** in *n*-hexane and toluene lies within the interval of structures **A1**–**A2**, achieves the cyanine limit **A2** in dichloromethane, and gets the interval **A2**–**A3** at the further growth of solvent polarity. However, the contribution of the dipolar polyene **A3** in DMF and ethanol is not that great since it does not result in an essential electronic symmetry violation. The presence of the cycle, as well as in case of malononitrile derivatives **5–7**, results in the greater dipolarity of the S_0 state of compounds **8**–**10** as compared to those of dyes **25**–**27**. Consequently, the reduction of the long-wavelength shift, caused by the cycle, in high-polar DMF and ethanol is concerned with an occurrence of weak electronic asymmetry of these dyes.

The results of quantum-chemical calculation of merocyanines **5**–**10** and **22**–**27** (Table 2) well agreed with the conclusions made on their spectral data. The cycle group causes (with the exception of dimethinemerocyanines **5** and **8** in which the essential chromophore planar distortions take place) a decrease of bond order alternation (BOA) in the polymethine chain. It suggests an increase of the contribution of the ideal structures **A2** to the electronic structure of the considered dyes. One can also infer from Table 2 (cf. the values of Δq_{Σ}) that the charge alternation in the chromophore of merocyanines **5**–**10** is weaker than those for their analogues **22**–**27**. It explains a decrease of the solvatochromic range of the former in comparison with the latter.

5. Conclusion

The saturated cyclic group connecting a terminal heterocycle and the neighboring position of the polymethine chain in cyanine dyes causes an increase of electronic density in the even positions of the chromophore. In case of merocyanines it results in an increase of dipolarity of the ground S_0 state. For symmetric dyes **2**–**4** the cycle causes an equalization of charges and bond orders in the chromophore, that leads to a decrease of the VI and IMI and narrowing of the spectral bands. The effect of the cyclic group is equivalent to a slight increase of the electron-donating properties of the terminal group in comparison with 3H-indole.

The comparison of the spectral properties of merocyanines **5**–**10** with the similar dyes containing other terminal heterocycles [11,12] allowes to conclude that the electron-donating properties of the investigated here terminal group are close to those of benzothiazole.

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