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Synthesis, electronic structure, and absorption spectra of the merocyanines derived from pyranes and benzopyranes

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Abstract

The synthesis, peculiarities of the electron structure and spectral properties of the merocyanine derivatives of the pyranes and benzopyranes with nitrogen-containing heterocycles as donor end groups are presented. It is established that an annelation of the pyrane residue leads to bathochromic shift of the absorption band. Because of the considerable change in the dipole momentum upon excitation, the merocyanines studied show high sensitivity to the solvent polarity.

Keywords: The pyrane and benzopyrane; Merocyanine; Nitrogen-containing heterocycles; NLO properties; Quantum chemical investigation; The dipole momentum

1. Introduction

Merocyanine dyes (MCD) with the chromophore including 2,4-positions of the pyrane or benzopyrane cycle have been known for a long time [1,2]. The dyes of a similar structure were regarded as active laser media [3,4]. Recently the interest in donor–acceptor organic dyes [5] including the mentioned MCD types [6–9] has been highly activated. It is connected with the fact that they exhibit high nonlinear optical (NLO) properties as donor–acceptor π-electron systems [5]. Additionally MCD can be easily sprayed in vacuo giving thin films [10].

The electron properties of the classic donor–acceptor merocyanines $H_2N-(CH=CH)-CHO$, were investigated in details [5], the similar systematic study of the MCD with the chromophore partially including pyrane or benzopyrane cycle has not been carried out yet.

This paper presents the results of the complex spectral and quantum chemical investigations of the electronic structural features in the ground and in the excited state for the MCD series **1–4**. The research also covers the influence of the polymethine chain length and the electron-donor abilities of the terminal residues caused on the electronic characteristics which determine the NLO properties of donor–acceptor conjugated molecules, viz. the transition energies and transition moments, state dipole moments and a change in dipole moments occurring upon excitation [5].

The MCD synthesized contain two types of electron-donor residues, the first being represented by the *p*-*N*,*N*-dimethylaniline group and its analogues. The electronegativity of these groups depends on the substituents at the nitrogen atom (carbazole and julolidine derivatives) as including instead of the *p*-*N*,*N*-dimethylaniline group of corresponding substituted residue of thiophene or furan.

The effect of this substitution results in the mentioned heteroresidues that must lightly transmit a conjugation of dimethylaminogroups owing to reduced energy of resonance stabilization [11]. This was bound to result in increasing hyperpolarisation ability β_0. It should be marked that the

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influence of 2,5-furanilidene bridge on donor–acceptor properties of merocyanines studied was not enough [12]. The comparison of phenylene bridge with its furan and thiophene analogues was not carried out at all. MCD containing residues of heterocycles (derivatives of pyridine, quinoline, benzothiazole) as electron-donor groups were also synthesized. They distinguish each other by their basicity and hence enabling to change the donor strength in a wide range.

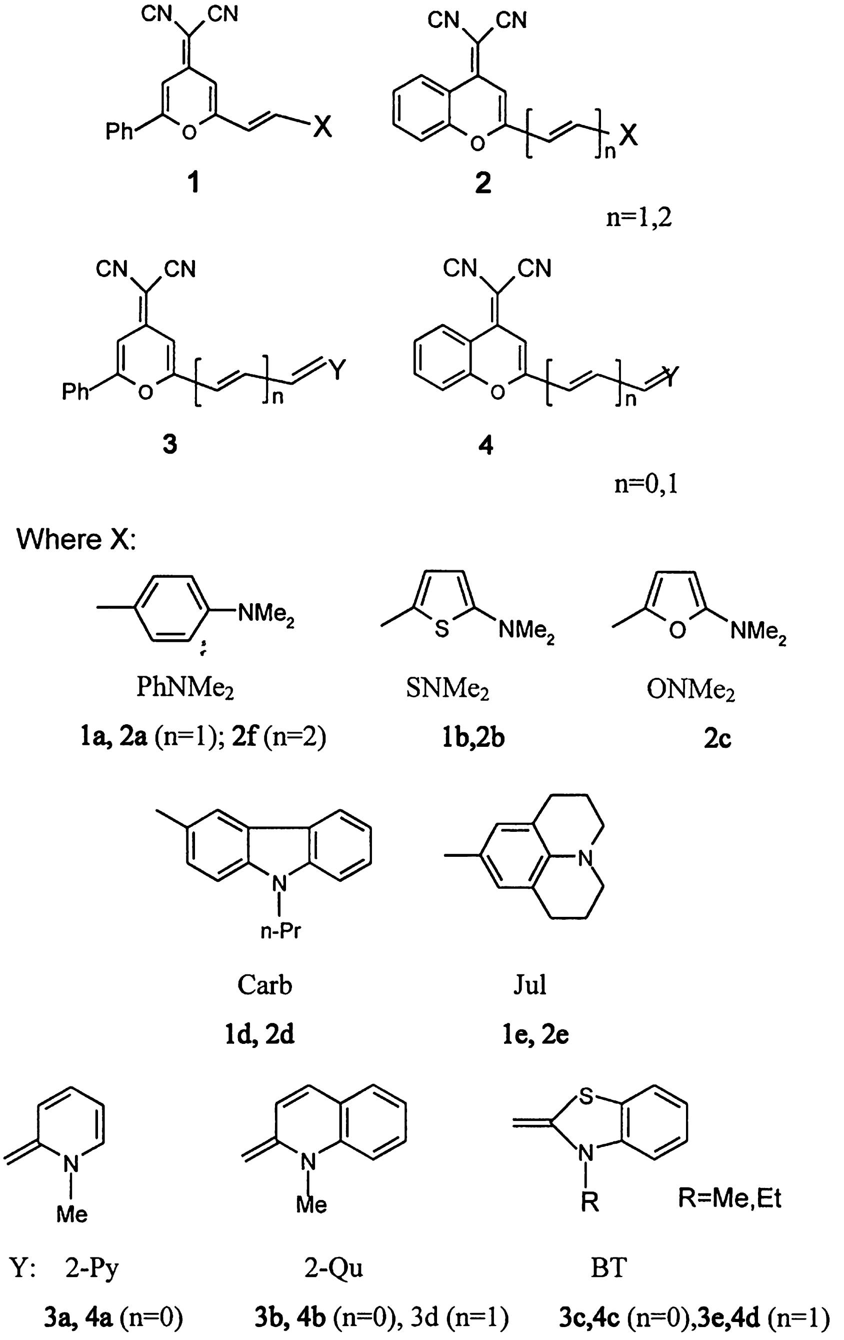
2. Materials

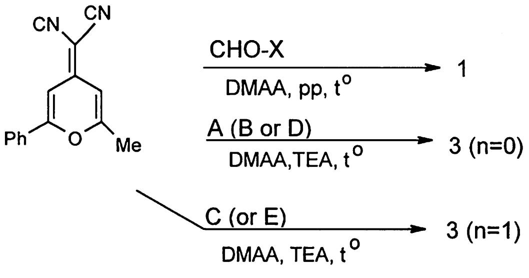
The objects under investigation were MCD containing various heterocyclic residues as terminal groups.

Compounds **1–4** were synthesized by the following Schemes 1 and 2.

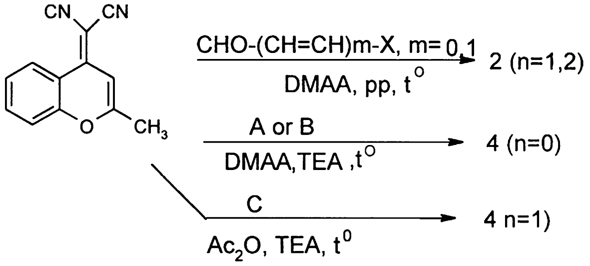
Here DMAA, pp, and TEA denote – dimethylacetamid, piperidine, and triethylamine, respectively.

Merocyanines **2a,f** (X = $PhNMe_2$, $n = 1$, 2) were prepared earlier by the condensation of 2-methy1-4-thiochromone with the corresponding aldehydes [8]. Above Scheme 2 allows these compounds to be obtained more conveniently and in higher yields. It should be noted that the compounds synthesized by us exhibit the long-wavelength spectral bands with somewhat different absorption maximum positions and greater intensity in comparison to those reported previously [8].

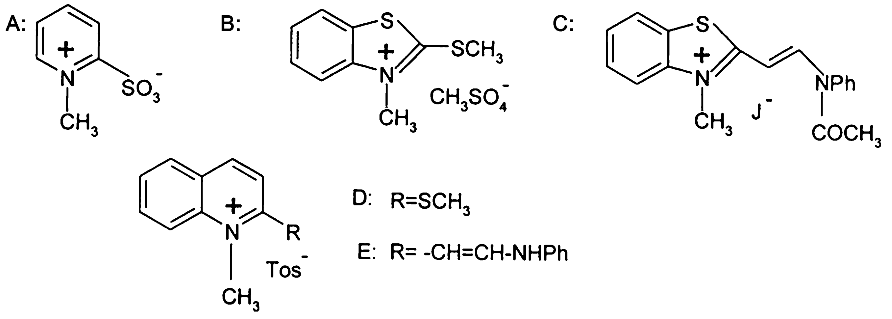




Scheme 1.



Scheme 2.



MCD **3c**, **e** (Y = BT, $n = 0$, 1) was reported in patent of Ref. [1].

A single set of proton signals is observed in ^{1}H NMR spectra of the MCD under study, which implies that the dyes exist in only one conformation. Spin–spin coupling constants for the protons of the polymethine chain varied from 12.0 to 15.9 Hz pointing to its all-*trans* conformation.

3. Experimental

3.1. General

The structure and purity of the synthesized merocyanines **1–4** were supported by ^{1}H NMR spectra, electronic absorption spectra, elemental analysis, and TLC (Merck 6H plates with silica F_{254}). Electronic absorption spectra were recorded on a spectrophotometer Shimadzu UV 3100 in acetonitrile, toluene, and chloroform ($C = 2 \times 10^{-5}$ g mol/1). All solvents were purified by the treatment with dried K_2CO_3 and by distillation before use. ^{1}H NMR spectra were recorded on a Varian VXR-300 at 300 MHz in $CDCl_3$ (or DMSO-d_6), with HMDS as an internal standard. Melting points were measured with capillary tubes and are uncorrected.

The quantum chemical calculations were performed in the AM1 approximation. The equilibrium geometry of the merocyanine molecules in the ground state was optimized up to the gradient of 0.01 kcal/mol. The electron transition characteristics were calculated using the lowest 100 singly excited configurations.

3.1.1. General procedure for the synthesis of **1**, **3**

A mixture of 2.5 mmol 2-methyl-4-dicyanomethylene-6-phenyl-4*H*-pyran [1], 2.5 mmol of the corresponding reagent (see Scheme 1), and 2.5 mmol pp (for **1a**, **b**, **d**, **e**, **3e**) or 2.5 mmol TEA (for **3a**, **b**, **c**) in 3 ml DMAA was heated for 40 min at 100 °C. After cooling in the refrigerator, the solid was filtered and crystallized from the appropriate solvent.

3.1.2. General procedure for the synthesis of **2**, **4**

A mixture of 3 mmol 2-methyl-4-dicyanomethylene-4*H*-chroman and 3.4 mmol of the corresponding reagent (see Scheme 2) in 3 ml DMAA and 3–5 drops of piperidine as catalyst were heated for 1 h at 120–130 °C. In case of **4c**, **d** (Y = BT, $n = 0$, 1) reagents were heated in 3 ml acetic anhydride and 2–3 drops TEA for 15 min at 80–90 °C. After cooling in the refrigerator, the solid was filtered and crystallized from the appropriate solvent.

The yields, melting points, and elemental analysis data for dyes **1–4** are presented in Table 1.

^{1}H NMR ($CDCl_3$/HMDS) for dyes **1** and **2**, **3** (Y = 2-Py, $n = 0$; Qu, $n = 1$; BT, $n = 1$) and **4** (Y = BT, $n = 1$); (DMSO-d_6/HMDS) for dyes **3** (Y = 2-Qu, $n = 0$, BT, $n = 0$) and **4** (Y = 2-Py, $n = 0$; BT, $n = 0$; 2-Qu, $n = 0$), δ: **1a** (X = $PhNMe_2$) 2.99 (s, 6H, NMe_2), 6.40–6.45 (d, 1H, $J = 15.9$ Hz, H-chain), 6.53–6.54 (d, 1H, $J = 2.1$ Hz, β-H), 6.60–6.63 (d, 2H, $J = 9.3$ Hz, Ar–H), 6.94–6.95 (d, 1H, $J = 2.1$ Hz, β′-H), 7.35–7.55 (m, 6H, Ar–H, H-chain), 7.77–7.81 (m, 2H, Ar–H).

1b (X = $SNMe_2$) 3.02 (s, 6H, NMe_2), 5.78–5.80 (d, 1H, $J = 4.5$ Hz, Th–H), 5.95–6.00 (d, 1H, $J = 15.0$ Hz, H-chain), 6.48–6.49 (d, 1H, $J = 1.8$ Hz, β-H), 6.94–6.95 (d, 1H, $J = 1.8$ Hz, β′-H), 7.01–7.02 (d, 1H, $J = 4.5$ Hz Th–H), 7.42–7.47 (d, 1H, $J = 15.0$ Hz, H-chain), 7.45–7.50 (m, 3H, Ar–H), 7.77–7.80 (m, 2H, Ar–H).

Table 1
Yield, melting point and elemental analysis data for merocyanines **1**−**4**

Dye	*n*	X/Y	Yield (%)	Mp (°C)	Empirical formula	Element analysis (% calcd. found)			
						C	H	N	S
1a	−	$PhNMe_2$	64	243	$C_{24}H_{19}N_3O$	78.9	5.2	11.5	
						78.9	5.2	11.8	
1b	−	$SNMe_2$	69	213	$C_{22}H_{17}N_3OS$			11.3	8.6
								11.3	8.9
1d	−	Carb	67	278	$C_{31}H_{23}N_3O$	82.1	5.1	9.3	
						82.0	5.2	9.4	
1e	−	Yul	42	>280	$C_{28}H_{23}N_3O$	80.5	5.5	10.1	
						80.6	5.6	10.1	
2b	1	$SNMe_2$	64	268	$C_{20}H_{15}N_3OS$			12.2	9.3
								12.2	9.3
2c	1	$ONMe_2$	94	220[a]	$C_{20}H_{15}N_3O_2$			12.8	
								12.7	
2d	1	Carb	46	248	$C_{29}H_{21}N_3O$	81.5	4.9	9.8	
						81.6	5.0	10.0	
2e	1	Jul	37	232[a]	$C_{26}H_{21}N_3O$			10.7	
								10.5	
2f	2	$PhNMe_2$	55	192[a]	$C_{24}H_{19}N_3O$			11.5	
								11.4	
3a	0	2-Py	49	243	$C_{21}H_{15}N_3O$	77.5	4.6	12.9	
						77.0	5.0	13.0	
3b	0	2-Qu	47	249	$C_{25}H_{17}N_3O$	80.0	4.6	11.2	
						80.0	4.6	11.3	
3c	0	BT	34	>280[b]	$C_{23}H_{15}N_3OS$			11.0	8.4
								10.9	8.7
3d	1	BT	58	239	$C_{26}H_{19}N_3OS$			10.1	7.6
								9.9	7.6
4a	0	2-Py	47	>270[b]	$C_{19}H_{13}N_3O$	76.2	4.4	14.0	
						76.1	4.2	13.9	
4b	0	2-Qu	55	>290	$C_{23}H_{15}N_3O$	79.0	4.3	12.0	
						78.9	4.2	12.0	
4c	0	BT	84	>290	$C_{21}H_{13}N_3OS$				9.0
									9.0
4d	1	BT	65	>270[c]	$C_{24}H_{17}N_3OS$			10.6	8.1
								10.4	7.8

[a] Solvent for crystallization: CH_3CN.
[b] Solvent for crystallization: **4a** − DMSO.
[c] Solvent for crystallization: **4d** − $CHCl_3$, **4b**,**c** − DMFA.

1d (X = Carb) 0.90−0.95 (t, 3H, *J* = 7.2 Hz, Me), 1.82−1.93 (m, 2H, CH_2), 4.21−4.25 (t, 2H, *J* = 7.2 Hz, NCH_2), 6.66−6.67 (d, 1H, *J* = 2.1 Hz, β-H), 6.71−6.76 (d, 1H, *J* = 15.9 Hz, H-chain), 7.00−7.01 (d, 1H, *J* = 2.1 Hz, β′-H), 7.20−7.25 (t, 1H, *J* = 6.6 Hz, Ar−H), 7.36−7.55 (m, 6H, Ar−H), 7.64−7.67 (dd, 1H, *J* = 8.4 Hz, *J* = 1.2 Hz, Ar−H), 7.65−7.71 (d, 1H, *J* = 15.9 Hz, H-chain), 7.83−7.86 (m, 2H, Ar−H), 8.04−8.07 (d, 1H, *J* = 7.8 Hz, Ar−H), 8.22−8.23 (d, 1H, *J* = 1.2 Hz, Ar−H).

1e (X = Jul) 1.86−1.96 (qv, 4H, *J* = 6.0 Hz, CH_2), 2.68−2.72 (t, 4H, *J* = 6.0 Hz, CH_2), 3.19−3.23 (t, 4H, *J* = 6.0 Hz, N−CH_2), 6.37−6.43 (d, 1H, *J* = 15.9 Hz, H-chain), 6.54−6.55 (d, 1H, *J* = 1.8 Hz, β-H), 6.96 (s, 2H, Ar−H), 6.96−6.97 (d, 1H, *J* = 1.8 Hz, β′-H), 7.29−7.34 (d, 1H, *J* = 15.9 Hz, H-chain), 7.45−7.52 (m, 3H, Ar−H), 7.78−7.82 (m, 2H, Ar−H).

2a (X = $PhNMe_2$, *n* = 1) 3.00 (s, 6H, NMe_2), 6.44−6.50 (d, 1H, *J* = 15.9 Hz, H-chain), 6.60−6.63 (d, 2H, *J* = 9.0 Hz, Ar−H), 6.67 (s, 1H, Ar−H), 7.32−7.36 (td, 1H, *J* = 7.2 Hz, *J* = 1.2 Hz, Ar−H), 7.37−7.40 (d, 2H, *J* = 9.0 Hz, Ar−H), 7.44−7.46 (dd, 1H, *J* = 7.2 Hz, *J* = 1.2 Hz, Ar−H), 7.45−7.51 (d, 1H, *J* = 15.9 Hz, H-chain), 7.61−7.66 (td, 1H, *J* = 7.2 Hz, *J* = 1.2 Hz, Ar−H), 8.80−8.83 (dd, 1H, *J* = 7.2 Hz, *J* = 1.2 Hz, Ar−H).

2b (X = $SNMe_2$, *n* = 1) 3.03 (s, 6H, NMe_2), 5.80−5.81 (d, 1H, *J* = 4.2 Hz, Th−H), 5.97−6.02 (d, 1H, *J* = 14.7 Hz, H-chain), 6.59 (s, 1H, Ar−H), 7.03−7.04 (d, 1H, *J* = 4.2 Hz, Th−H), 7.30−7.35 (td, 1H, *J* = 7.5 Hz, *J* = 1.2 Hz, Ar−H), 7.38−7.41 (dd, 1H, *J* = 7.5 Hz, *J* = 1.2 Hz, Ar−H), 7.53−7.58 (d, 1H, *J* = 14.7 Hz, H-chain), 7.57−7.63 (td, 1H, *J* = 7.5 Hz, *J* = 1.2 Hz, Ar−H), 8.80−8.83 (dd, 1H, *J* = 7.5 Hz, *J* = 1.2 Hz, Ar−H).

2c (X = $ONMe_2$, *n* = 1) 2.99 (s, 6H, NMe_2), 6.06−6.11 (d, 1H, *J* = 15.0 Hz, H-chain), 6.58 (s, 1H, Ar−H), 6.67−6.68 (d, 1H, *J* = 3.6 Hz, Fu−H), 7.06−7.11 (d, 1H, *J* = 15.0 Hz, H-chain), 7.27−7.32 (td, 1H, *J* = 7.2 Hz, *J* = 0.9 Hz, Ar−H), 7.34−7.37 (dd, 1H, *J* = 7.2 Hz, *J* = 0.9 Hz, Ar−H), 7.54−7.60 (td, 1H, *J* = 7.2 Hz, *J* = 0.9 Hz, Ar−H), 8.77−8.80 (dd, 1H, *J* = 7.2 Hz, *J* = 0.9 Hz, Ar−H).

2d (X = Carb, *n* = 1) 0.89–0.94 (t, 3H, *J* = 7.5 Hz, Me), 1.79–1.92 (m, 2H, C–CH_2), 4.17–4.22 (t, 2H, *J* = 7.5 Hz, N–CH_2), 6.68–6.73 (d, 1H, *J* = 15.6 Hz, H-chain), 6.69 (s, 1H, Ar–H), 7.18–7.23 (t, 1H, *J* = 7.5 Hz, Ar–H), 7.30–7.47 (m, 5H, Ar–H), 7.61–7.66 (m, 3H, Ar–H), 7.69–7.75 (d, 1H, *J* = 15.6 Hz, H-chain), 7.99–8.02 (d, 1H, *J* = 7.5 Hz, Ar–H), 8.12 (s, 1H, Ar–H), 8.75–8.78 (d, 1H, *J* = 7.5 Hz).

2e (X = Jul, *n* = 1) 1.87–1.95 (qv, 4H, *J* = 6.3, CH_2), 2.67–2.71 (t, 4H, *J* = 6.3 Hz, CH_2), 3.20–3.23 (t, 4H, *J* = 6.3 Hz, N–CH_2), 6.38–6.44 (d, 1H, *J* = 15.3 Hz, H-chain), 6.64 (s, 1H, Ar–H), 6.96 (s, 2H, Ar–H), 7.30–7.35 (td, 1H, *J* = 8.4 Hz, *J* = 1.5 Hz, Ar–H), 7.37–7.42 (d, 1H, *J* = 15.3 Hz, H-chain), 7.40–7.43 (dd, 1H, *J* = 8.4 Hz, Ar–H), 7.5807.64 (td, 1H, *J* = 8.4 Hz, *J* = 1.5 Hz, Ar–H), 8.79–8.82 (dd, 1H, *J* = 8.4 Hz, *J* = 1.5 Hz, Ar–H).

2f (X = $PhNMe_2$, *n* = 2) 2.97 (s, 6H, NMe_2), 6.13–6.18 (d, 1H, *J* = 15.0 Hz, H-chain), 6.59–6.77 (m, 4H, Ar–H, H-chain), 6.84–6.89 (d, 1H, *J* = 15.0 Hz, H-chain), 7.31–7.44 (m, 5H, Ar–H, H-chain), 7.61–7.66 (t, 1H, *J* = 7.5 Hz, Ar–H), 8.81–8.84 (d, 1H, *J* = 7.5 Hz, Ar–H).

3a (Y = 2-Py, *n* = 0) 3.62 (s, 3H, N–Me), 5.25 (s, 1H, H-chain), 6.18–6.19 (d, 1H, *J* = 1.5 Hz, β-H), 6.52–6.56 (t, 1H, *J* = 6.9 Hz, Ar–H), 6.58–6.59 (d, 1H, *J* = 1.5 Hz, β′-H), 7.44–7.53 (m, 4H, Ar–H), 7.78–7.82 (m, 2H, Ar–H), 7.90–7.95 (m, 2H, Ar–H).

3b (Y = 2-Qu, *n* = 0) 3.62 (s, 3H, N–Me), 5.64 (s, 1H, H-chain), 6.47–6.48 (d, 1H, *J* = 2.1 Hz, β-H), 6.75 (s, 1H, β′-H), 7.19–7.24 (t, 1H, *J* = 7.5 Hz, Ar–H), 7.52–7.60 (m, 6H, Ar–H), 7.63–7.66 (d, 1H, *J* = 9.6, Ar–H), 7.83–7.87 (m, 2H, Ar–H), 7.90–7.94 (d, 1H, *J* = 9.6 Hz, Ar–H).

3c (Y = BT, *n* = 0) 3.55 (s, 3H, N–Me), 6.10 (s, 1H, H-chain), 6.42 (s, 1H, β-H), 6.70 (s, 1H, β′-H), 7.12–7.18 (m, 1H, Ar–H), 7.35–7.38 (m, 2H, Ar–H), 7.56–7.58 (m, 3H, Ar–H), 7.68–7.72 (m, 1H, Ar–H), 7.90–8.02 (m, 2H, Ar–H).

3d (Y = Qu, *n* = 1) 3.44 (s, 3H, NMe), 5.48–5.52 (d, 1H, *J* = 12.0 Hz, H-chain), 5.84–5.88 (d, 1H, *J* = 14.4 Hz, H-chain), 6.40–6.41 (d, 1H, *J* = 1.2 Hz, β-H), 6.90–6.91 (d, 1H, *J* = 1.2 Hz, β′-H), 7.02–7.17 (m, 3H, Ar–H), 7.27–7.29 (d, 1H, *J* = 7.2 Hz, Ar–H), 7.35–7.41 (t, 1H, *J* = 7.5 Hz, Ar–H), 7.48–7.52 (m, 3H, Ar–H), 7.67–7.80 (m, 3H, Ar–H, H-chain).

3e (Y = BT, *n* = 1) 1.29–1.34 (t, 3H, *J* = 7.2 Hz, Me), 3.85–3.93 (q, 2H, *J* = 7.2 Hz, N–CH_2), 5.57–5.61 (d, 1H, *J* = 12.0 Hz, H-chain), 5.76–5.81 (d, 1H, *J* = 14.7 Hz, H-chain), 6.38–6.39 (d, 1H, *J* = 1.8 Hz, β-H), 6.89–6.92 (d, 1H, *J* = 7.5 Hz, Ar–H), 6.91–6.92 (d, 1H, *J* = 1.8 Hz, β′-H), 7.01–7.06 (t, 1H, *J* = 7.5 Hz, Ar–H), 7.22–7.27 (t, 1H, *J* = 7.5 Hz, Ar–H), 7.36–7.45 (m, 2H, Ar–H, H-chain), 7.49–7.52 (m, 3H, Ar–H), 7.79–7.82 (m, 2H, Ar–H).

4a (Y = 2-Py, *n* = 0) 3.74 (s, 3H, NMe), 5.35 (s, 1H, H-chain), 6.26 (s, 1H, Ar–H), 6.72–6.78 (t, 1H, *J* = 7.2 Hz, Ar–H), 7.25–7.33 (m, 1H, Ar–H), 7.56–7.67 (m, 3H, Ar–H), 8.04–8.07 (d, 1H, *J* = 7.2 Hz, Ar–H), 8.26–8.30 (d, 1H, *J* = 7.8 Hz, Ar–H), 8.50–8.53 (d, 1H, *J* = 7.8 Hz, Ar–H).

4b (Y = 2-Qu, *n* = 0) 3.76 (s, 3H, NMe), 5.76 (s, 1H, H-chain), 6.58 (s, 1H, Ar═H), 7.28–7.33 (t, 1H, *J* = 7.2 Hz, Ar–H), 7.40–7.44 (t, 1H, *J* = 7.2 Hz, Ar–H), 7.60–7.83 (m, 6H, Ar–H), 8.28–8.31 (d, 1H, *J* = 9.3 Hz, Ar–H), 8.59–8.62 (d, 1H, *J* = 9.3 Hz, Ar–H).

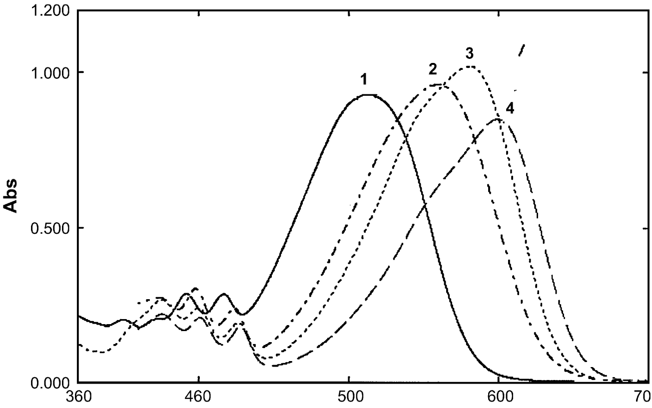


Fig. 1. Absorption spectra of merocyanines in $CHCl_3$ ($C = 2 \times 10^{-5}$ g mol/l), 1 – dye **2a**, 2 – dye **2e**, 3 – dye **2b**, and 4 – dye **2c**.

4c (Y = BT, *n* = 0) 3.60 (s, 3H, NMe), 6.17 (s, 1H, H-chain), 6.41 (s, 1H, Ar–H), 7.17–7.22 (t, 1H, *J* = 7.2 Hz, Ar–H), 7.34–7.45 (m, 3H, Ar–H), 7.59–7.73 m, 3H, Ar–H), 8.50–8.53 (d, 1H, *J* = 7.2 Hz, Ar–H).

4d (Y = BT, *n* = 1) 1.18–1.23 (t, 3H, *J* = 7.5 Hz, Me), 4.09–4.12 (q, 2H, *J* = 7.5 Hz, N–CH_2), 6.01–6.05 (d, 1H, *J* = 12.3 Hz, H-chain), 6.03–6.08 (d, 1H, *J* = 13.2 Hz, H-chain), 6.44 (s, 1H, Ar–H), 6.44 (s, 1H, Ar–H), 7.11–7.17 (m, 1H, Ar–H), 7.3–7.77 (m, 7H, H-chain), 8.58–8.61 (d, 1H, *J* = 7.2 Hz, Ar–H).

3.2. Spectral and calculated results

In the absorption spectra of merocyanines **1–4**, the separated comparatively intensive band is observed in the visible region, which corresponds to the first π → π* electron transition. Some examples are presented in Figs. 1 and 2 while the positions of the maxima of long-wavelength bands in polar and non-polar solvents are summarised in Table 2. One could see that benzopyranic derivatives **2** exhibit relatively wide

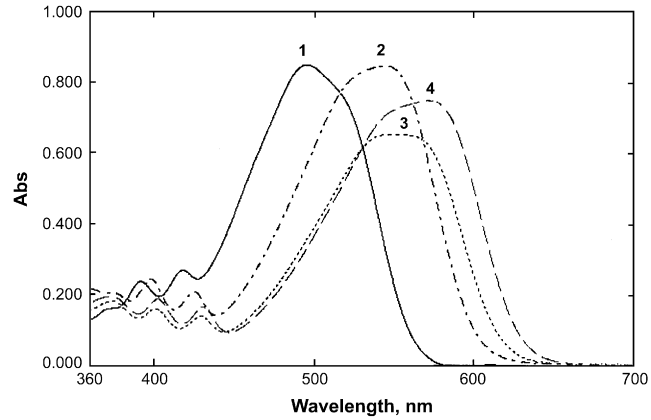


Fig. 2. Absorption spectra of merocyanines in $C_6H_5CH_3$ ($C = 2 \times 10^{-5}$ g mol/l), 1 – dye **2a**, 2 – dye **2e**, 3 – dye **2b**, and 4 – dye **2c**.

Table 2
Absorption spectral data of dyes **1–4**

Dye	n	X/Y	CH_3CN		$CHCl_3$		$C_6H_5CH_3$	
			λ (nm)	$\varepsilon \times 10^{-4}$	λ (nm)	$\varepsilon \times 10^{-4}$	λ (nm)	$\varepsilon \times 10^{-4}$
1a	1	$PhNMe_2$	480	4.15	483	3.41	471	3.73
b		$SNMe_2$	539	4.16	546	3.59	520	3.29
d		Carb	443	3.78	454	3.76	452	3.98
e		Yul	520	–	528	3.37	507	–
2a	1	$PhNMe_2$	507	4.67	513	4.63	495	4.25
b		$SNMe_2$	575	4.98	581	5.10	548	3.26
c		$ONMe_2$	601	–	599	–	571	–
d		Carb	465	4.79	475	4.87	470	4.30
e		Yul	552	4.26	560	4.80	544	4.24
f	2	$PhNMe_2$	516	4.83	530	4.48	518	4.77
3a	0	2-Py	540	5.13	546	4.47	548	–
b		2-Qu	521, 554	5.52, 6.03	522, 556	5.32, 5.16	522, 556	–
c		BT (R = Me)	497	6.72	498	6.49	494	–
d	1	2-Qu	570, 616	–	575, 616	6.5, 5.84	570, 609	–
e		BT (R = Et)	572	–	576	6.61	561	–
4a	0	2-Py	549	–	557	11.24	561	–
b		2-Qu	533, 571	6.02, 10.48	538, 575	6.87, 9.06	540, 577	–
c		BT (R = Me)	521	11.9	524	8.77	517	–
d	1	BT (R = Et)	587	–	605	8.44	607	–

non-structural spectral bands in both polar chloroform (acetonitrile – Table 2) and non-polar toluene (Fig. 1). Vibronical transitions could appear only as a shoulder. Similar shape of the spectral bands is observed also for the phenyl-substituted pyranic analogues, dyes **1**, although the band maxima are usually shifted hypsochromically. Unlike compounds **1–2** that contain the low basic donor residue X, the merocyanines **3–4** with comparatively high basic end group Y show more structural long-wavelength spectral bands (Fig. 3), so that two distinct vibronical maxima are observed, the distance between them being approximately equal to 1100–1200 cm^{-1}. Going from the polar solvents (chloroform) to the non-polar toluene as seen from Figs. 1 and 2 is not accompanied by the essential changes in the shape and positions of the spectral bands, with the exception of the ratio of the vibronical transition intensivities. This should be taken into consideration in the analysis of the spectral effects of the chain lengthening or annelation of the benzene ring instead of the phenyl substituent in dyes of **1** and **2** series as well as in **3** and **4**.

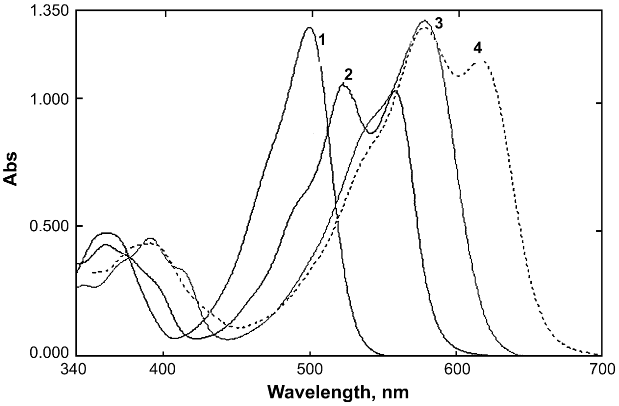


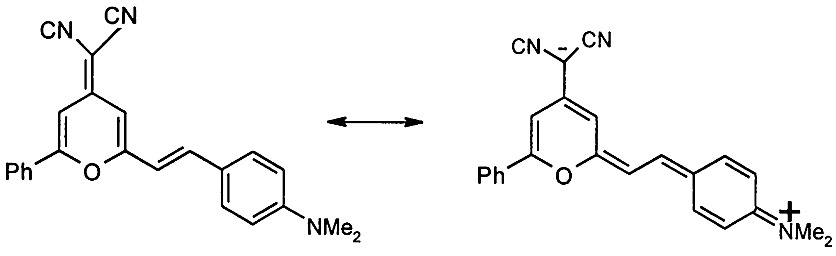
Fig. 3. Absorption spectra of merocyanines in $CHCl_3$ ($C = 2 \times 10^{-5}$ g mol/1), 1 – dye **3c**, 2 – dye **3b**, 3 – dye **3e**, and 4 – dye **3d**.

In Table 3, the calculated wavelengths of the first $\pi \rightarrow \pi^*$ transition and dipole moments for the merocyanines **1–4** are presented. One could see from Tables 2 and 3 that the difference between the calculated and experimental data is about 40–60 nm, which is a typical imperfection of the AM1 method. Of course, increase in the number of configurations upon the calculations of the energy of the excited state slightly improves the convergence between the calculated and spectral results, approximately by 10–15 nm. It was earlier shown [13] that better agreement between the band maxima and calculated wavelengths of the electron transitions can be reached by PPP method, however, π-electron approximation (PPP and HMO) is not suitable to calculate state dipole moments because of the neglect of σ-electrons. Meanwhile, the AM1 method reflects correctly the dependence of the energy of the electron transition on the molecular topology, i.e. the chain lengthening, annelation, nature of the end groups; and hence it can be used also for the calculation of dipole moments, which are necessary for interpretation of the spectral effects in the merocyanines **1–4**.

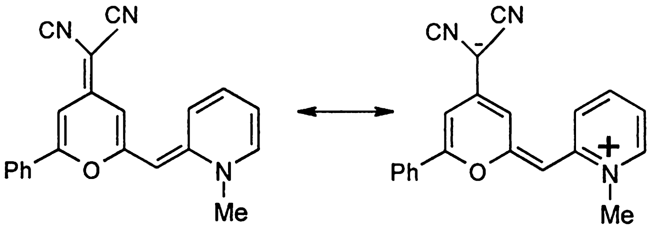
4. Discussion

4.1. Electron asymmetry and dipole moments

As typical donor–acceptor conjugated systems, the merocyanines can be presented by both a non-polar structure (*n*) and a structure with the separated negative and positive charges (*i*). For example, the two valence structure representation of compounds **1** and **3** are as follows:



1a (n) **1a (i)**



3a (n) **3a (i)**

The equilibrium between both the structures depends on the basicity of the end groups X or Y. It is known that residues X in the merocyanines **1** and **2** are low basic, while the end groups Y in dyes **3** and **4** exhibit comparatively high basicity [14,15]. Also, the study of unsymmetrical polymethine dyes and donor–acceptor polyenes has shown that excitation leads to the considerable change in the electron distribution in atoms and hence to the change of a balance between the totally non-polar structure and zwitter-ionic with the couple positive and negative charges.

The electron asymmetry of the merocyanines investigated in the ground and excited states could be quantitatively estimated by their state dipole moments. One could see from Table 3 that the magnitudes of the dipole moments are comparatively large in both the ground state (μ_g) and in the excited state (μ_e). In the merocyanines with low basic donor groups the dipole momentum in the ground state decreases regularly in the series **2**: X = SNMe$_2$, ONMe$_2$, PhNMe$_2$, Carb. The same tendency is observed for the related merocyanines **1**, as well as for both series in the excited state.

Regarding high basic end groups, it is known that the basicity decreases in the series: 2-Py, 2-Qu, BT. One could see from Table 3 that the magnitude of the dipole momentum in the ground state of the merocyanines **3** and **4** decreases in the same manner, however, in the excited state this regularity is broken.

Also, calculations give that replacement of phenyl substituent by the annelated benzene cycle causes decrease in dipole momentum by about 1–1.5 D in the ground state, while in the excited state, effect is essentially less. It is interesting to notice that the chromophore lengthening is accompanied by comparatively small increase in dipole momentum state.

Table 3
Calculated data for dyes **1–4**

Dye	n	X/Y	λ (nm)	μ_g (D)	μ_e (D)	$\Delta\mu$ (D)	μ_{ge} (D)	β_o
1a	1	PhNMe$_2$	458	10.356	11.706	1.350	9.397	98
b		SNMe$_2$	502	12.525	14.437	1.909	10.983	228
d		Carb	441	10.027	10.796	0.742	9.338	49
2a	1	PhNMe$_2$	461	9.043	11.645	2.602	9.804	269
b		SNMe$_2$	517	11.416	13.822	2.406	9.905	316
c		ONMe$_2$	505	9.673	13.311	3.638	10.478	408
d		Carb	444	8.592	10.172	1.580	9.419	108
f	2	PhNMe$_2$	494	9.223	12.315	3.092	11.133	368
3a	0	2-Py	482	10.848	11.549	0.701	8.201	43
b		2-Qu	486	9.862	10.602	0.740	9.234	59
c		BT	478	9.786	10.949	1.163	7.666	61
d	1	2-Qu	530	10.502	12.015	1.513	11.500	221
e		BT	514	10.450	12.883	2.433	10.187	262
4a	0	2-Py	488	9.432	11.406	1.974	8.202	124
b		2-Qu	489	8.588	9.618	1.030	9.266	81
c		BT	482	7.862	10.006	2.144	7.350	109
d	1	BT	525	9.153	11.937	2.784	10.070	306

This can likely be connected with the decrease in contribution of the zwitter-ionic structure.

Also, one can see from Table 3 that the transition moments for all merocyanines are relatively large what agrees with the relatively high intensities (or extinctions ε) of the observed spectral bands (Table 2). The transition moment in MCD **2a**, **b**, **c**, derivatives of dimethylaniline, furan, thiophene increases owing to the rise in molecule polarization ability in the same sequence.

4.2. Spectral effects

At first, we consider the effects caused by the changes in the molecular topology.

4.2.1. Chromophore lengthening

Some examples are presented in Table 4. One could see that increase in the length of the polymethine chain in the merocyanines **2** with the low basic *p*-dimethylaminophenyl residue leads to the small bathochromic shift of the band maximum. On the contrary, the vinylene shift in the merocyanines **3** and **4** containing the high basic quinoline or benzothiazole residues is considerably larger. Decreasing of basicity of donor group upon going from **4b** (Qu) to **4c** (BT) is seen from Table 2 and is accompanied by the increase in the spectral effect. On the other hand, the annelation of dye **4c** (BT) causes decrease in vinylene shift, with respect to the phenyl-substituted merocyanine **3c** (BT).

4.2.2. Annelation of the acceptor group

Annelation of the acceptor group in dyes **4** was compared with merocyanines **3**. One could see from Table 5 that replacement of the phenyl group in dyes **3** by annelation of benzene ring gives rise to only bathochromic shift of the first absorption band. Meanwhile, such spectral effect depends on the basicity of a donor group, chromophore length and solvents. For the low basic residues in the merocyanines **1** and **2**, the shift of the band maximum decreases in the series: SNMe$_2$, Jul, PhNMe$_2$, Carb, independently of solvent polarity.

Unlike merocyanines with low basic residues (**1** and **2**), spectral effect of the annelation in the pairs of dyes **3** and **4** is essentially lower. One can see from Table 5 that decreasing of the basicity in the series 2Py, 2-Qu, BT causes the shift of the band maximum to increase. And also, merocyanines with the longer chain, **4d–3e** (BT, $n = 1$) are more sensitive to replacement of the Ph substituent by annelation; the spectral effects seen in Table 5 reach the maximum (46 nm, in toluene) amongst the dyes investigated.

Table 4
Vinylene shift for dyes **2**, **3**, and **4**

Dye	X/Y	Δλ (nm)		
		CH$_3$CN	CHCl$_3$	C$_6$H$_5$CH$_3$
2f–a	PhNMe$_2$	9	17	23
3d–b	2-Qu	62	60	53
3e–c	BT	75	78	67
4d–c	BT	66	81	90

Table 5
Spectral effects (in nm) of the annelation

Dye	n	X/Y	CH$_3$CN	CHCl$_3$	C$_6$H$_5$CH$_3$
2–1a	1	PhNMe$_2$	27	30	24
b		SNMe$_2$	36	35	28
d		Carb	22	21	18
e		Yul	32	32	37
4–3a	0	2-Py	9	11	13
b		2-Qu	17	19	21
c		BT	24	26	23
4d–3e	1	BT	15	29	46

4.2.3. Effect of solvent polarity

Since merocyanine molecules **1–4** are high-polarizable donor–acceptor π-electron systems with the considerable dipole moments in the ground and excited states, they are sensitive to the polarity of solvents (Table 6). It is seen that the merocyanines **1** and **2** containing low basic heterocycles as a donor group show mainly a positive solvatochromy (except carbazole derivatives **1d** Carb and **2d** Carb). Comparing of the corresponding merocyanines **1** and **2** show that annelation results in decreasing of the solvation effect for the PhNMe$_2$ and SNMe$_2$ derivatives, in contrast to the merocyanines **2d** (Carb). Meanwhile, for dye **2a** (PhNMe$_2$) with the longer polymethine chain ($n = 1$), going to the non-polar solvent causes only negligible bathochromic effect, unlike for the monomethine analogues ($n = 0$).

In contrast, in the spectra of the merocyanines containing the high basic pyridine and quinoline residues, the bathochromic shift of the band maximum is observed upon going from high polar acetonitrile to CHCl$_3$ or C$_6$H$_5$CH$_3$. It should be noted that merocyanines containing benzothiazoline residue

Table 6
Solvation effects: Δλ (nm)

Dye	n	X/Y	CHCl$_3$[a]	C$_6$H$_5$CH$_3$[b]
1a	1	PhNMe$_2$	3	−9
b		SNMe$_2$	7	−19
d		Carb	11	9
e		Yul	8	−13
2a	1	PhNMe$_2$	6	−12
b		SNMe$_2$	6	−27
c		ONMe$_2$	−2	−30
d		Carb	10	5
e		Yul	8	−8
f	2	PhNMe$_2$	14	2
3a	0	2-Py	6	8
b		2-Qu	2	2
c		BT (R = Et)	1	−3
d	1	2-Qu	−1	−7
e		BT (R = Et)	4	−11
4a	0	2-Py	8	12
b		2-Qu	4	6
c		BT (R = Me)	3	−4
d	1	BT (R = Et)	18	20

[a] Δλ (CHCl$_3$ − CH$_3$CN).
[b] Δλ (CH$_3$C$_6$H$_5$ − CH$_3$CN).

show negative solvatochromy, except the trimethine dye **3** (BT) with the longer chain.

Thus, sensitivity to solvent polarity is found to depend on the basicity of the donor group, topology of acceptor residues and length of the chromophore.

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