Synthesis and spectral properties of malononitrile-based merocyanine dyes

A. V. Kulinich,[a] *N. A. Derevyanko,*[b] *and A. A. Ishchenko*[b]★

[a]*Taras Shevchenko Kiev State University,*
64 ul. Vladimirskaya, 01033 Kiev, Ukraine,
E-mail: kulinich@univ.kiev.ua
[b]*Institute of Organic Chemistry, National Academy of Sciences of Ukraine,*
5 ul. Murmanskaya, 02094 Kiev, Ukraine.
Fax: +380 (44) 573 2643. E-mail: alexish@i.com.ua

Di-, tetra-, and hexamethine merocyanines derived from malononitrile and heterocycles with moderate (dyes **1—6**), strong (**7—9**), and weak (**10** and **11**) electron-releasing ability were synthesized. The electronic structures of merocyanines **10** and **11** are similar to the neutral polyene state, whereas those of **7—9** are similar to the ideal polymethine state. These tendencies become more pronounced with increasing length of the polymethine chain. The merocyanines derived from heterocyclic residues with weak or moderate electron-releasing ability exhibit a positive solvatochromism, whereas those with strong electron-releasing ability show a negative solvatochromism. An increase in the polarity of the solvent makes the former compounds more similar to polymethines, whereas the latter become more similar to polyenes bearing opposite charges on the end groups. The nature of the factors (nonspecific solvation, specific nucleophilic and electrophilic solvation, and vibronic interactions) responsible for the observed characteristic features was analyzed.

Key words: merocyanines, polyene and polymethine states, positive and negative solvatochromism, vibronic and intermolecular interactions.

Merocyanine dyes possess a broad spectrum of practically important properties, such as a pronounced solvatochromism and the ability to change substantially the dipole moment upon electronic excitation and sensibilize various physicochemical processes, due to which they have found increasing use in optoelectronics,[1,2] nonlinear optics,[3] data recording and processing systems,[4,5] medicine, and biology.[6]

To construct merocyanines with desired properties, it is necessary to reveal relationships between the absorption spectra, on the one hand, and the structures of the dyes and the nature of the solvent, on the other hand. Attempts have been made to study these relationships for incomplete series of merocyanines[7—12] with the use of absorption maxima λ_{max} as the reference. However, λ_{max} do not always adequately reflect the spectroscopic features, because they can be associated with various vibronic transitions.[13] In addition, the absorption maxima are determined with insufficient accuracy for broad, diffuse, and highly structured bands. However, these changes in the band shape are more characteristic of merocyanines than of the corresponding ionic dyes. The relationship between the absorption band shape and the structure of merocyanines remained unknown. The band shapes, primarily, the band widths, provide information on the changes in the bond orders and the electron density in the dye molecules upon excitation, which enables one to estimate the direction of the changes in the vibronic and intermolecular interactions, respectively.[14] Hence, these characteristics beneficially supplement the absorption maxima λ_{max}, which primarily characterize the relative arrangement of the electron levels of the ground (S_0) and first excited (S_1) states.

With the aim of revealing general relationships between the electronic absorption spectra of merocyanines, on the one hand, and their structures and the nature of the solvent, on the other hand, in the present study we synthesized and characterized dyes **1—11** derived from malononitrile and containing heterocyclic residues having different electron-releasing properties.

The mathematical processing of the long-wavelength absorption bands of the dyes was performed by the method of moments.[15] This allowed us to reliably and quantitatively characterize not only the positions (M^{-1}) and intensities (f) of the bands but also their shape (σ, γ_1, γ_2, and F). The parameter M^{-1} averaged over all vibronic transitions reflects the average position of the band (on the wavenumber scale, this parameter is the center of

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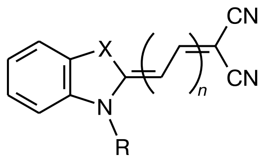
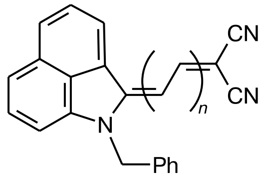


1—9



10, 11

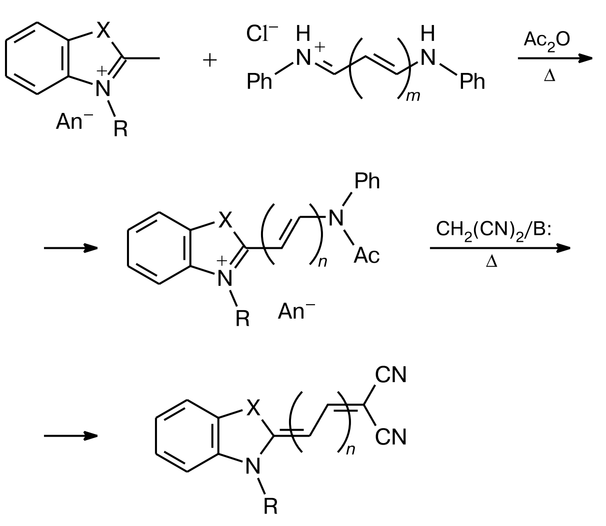
1—3: X = C(Me)$_2$, R = Me; **4—6:** X = S, R = Et;
7—9: X = NPh, R = Ph
1, 4, 7, 10: *n* = 1; **2, 5, 8, 11:** *n* = 2; **3, 6, 9:** *n* = 3

gravity of the band: $\bar{\nu} = 10^7/M^{-1}$) and, unlike λ_{max}, enables one to make a reliable comparison of the curves of different shape. The integrated intensity (the oscillator strength f) has an analogous advantage over the peak intensity (the extinction ε). The parameter σ characterizes the deviation (dispersion) of the points belonging to the spectral band from the center of gravity $\bar{\nu}$. Hence, this parameter allows one to make a reliable quantitative comparison of the band widths regardless of the band shape, which is an advantage over the half width (the width at half height of the band) traditionally used for this purpose. The asymmetry coefficient γ_1, the excess coefficient γ_2, and the fine structure coefficient F provide additional information on the band shape. These coefficients give quantitative estimates of, respectively, the symmetry, the steepness (peakedness), and structurization of the bands. The parameters M^{-1}, f, σ, γ_1, γ_2, and F are listed in Table 1 along with λ_{max} and ε. This table also gives the radiation lifetimes (τ_r) of the S_1 state of the dyes calculated according to the equation[14]

$$\tau_r = 1.5 \cdot 10^9/(\bar{\nu}^2 f). \qquad (1)$$

The synthesis of merocyanines **1—3** has been described earlier.[16,17] Dyes **4—6** and **11** were synthesized according to Scheme 1 (m = 0—2, $n = m + 1$).

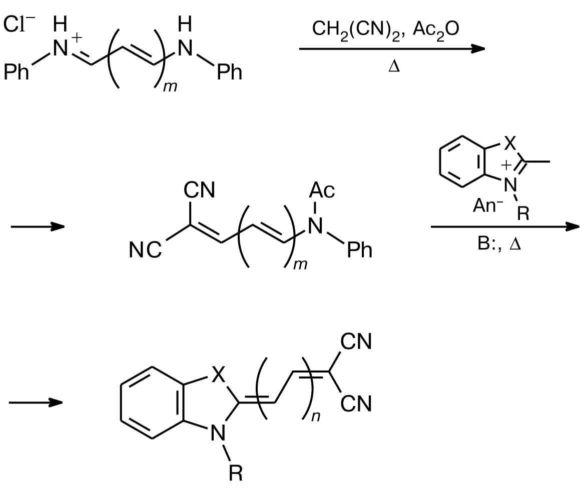
Scheme 1



Intermediate hemicyanines were prepared according to known general procedures.[18]

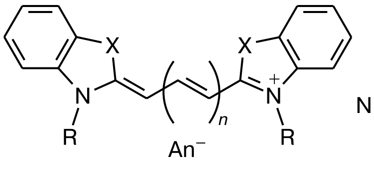
Since this approach proved to be inefficient in the synthesis of dyes **7—10** because of the formation of the corresponding symmetrical both cationic and anionic polymethines, these dyes were prepared with the use of another synthetic sequence (Scheme 2).

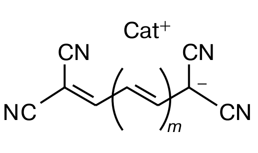
Scheme 2



The synthesis of intermediates has been documented.[16,19]

Merocyanines can be considered as hybrids of two symmetrical dyes, *viz.*, cationic and anionic. In one of them, the polymethine chain is longer than that in merocyanine, whereas the chain in another dye is shorter. In the present study, the deviations were evaluated with the use of **12—22** as cationic dyes[14] and **23—25** as anionic dyes.[16,19]





m = *n* − 1

12—22 **23—25**

The spectroscopic characteristics of cationic cyanines **12—22** were given in the monograph.[14] The corresponding characteristics of anionic cyanines **23—25**, as well as of dyes **1—11**, were determined by the mathematical processing of their spectra by the method of moments (Table 2).

Let us consider merocyanines **1—3** containing the indolylidene moiety with moderate electron-releasing ability. First and foremost, let us determine the sign of the solvatochromism because it reflects the direction of the

Table 1. Characteristics of the long-wavelength absorption bands of merocyanines **1—11** in CH_2Cl_2, ethanol, and DMF

Compound	Solvent	λ_{max}	D_λ	$\varepsilon \cdot 10^{-4}$ /L mol^{-1} cm^{-1}	M^{-1}	D_M	f	τ_r /ns	σ /cm^{-1}	γ_1	γ_2	$F \cdot 10^2$
		nm			nm							
1	CH_2Cl_2	437	12.5	7.25	419.5	14.1	0.89	3.0	1295	1.06	1.8	4.5
	EtOH	435	10.0	7.37	419.2	11.8	0.93	2.9	1311	1.10	2.1	4.6
	DMF	438	10.3	8.18	421.9	10.6	0.99	2.7	1287	1.08	1.9	4.4
2	CH_2Cl_2	527	22.0	8.29	509.5	24.1	0.95	4.1	1244	0.98	1.6	3.3
	EtOH	525	15.5	8.88	504.9	21.0	0.97	4.0	1223	1.11	2.0	4.4
	DMF	530	12.0	9.96	513.5	13.0	1.00	4.0	1175	1.15	2.2	4.6
3	CH_2Cl_2	602	51.5	7.77	573.3	62.0	1.15	4.3	1411	0.93	1.4	3.3
	EtOH	611	30.5	8.60	574.3	44.9	1.30	3.8	1464	0.98	1.4	3.8
	DMF	624	20.5	9.47	585.8	34.0	1.26	4.1	1408	1.05	1.6	4.6
4	CH_2Cl_2	453	1.5	7.82	436.0	7.2	0.73	3.9	1112	1.08	1.6	5.3
	EtOH	451	0.5	8.37	434.7	4.7	0.78	3.7	1092	1.07	1.5	5.1
	DMF	453	1.3	7.39	436.9	4.7	0.68	4.2	1088	1.08	1.6	5.0
5	CH_2Cl_2	545	10.5	12.89	525.3	16.0	1.11	3.8	1083	1.19	2.0	5.6
	EtOH	543	6.5	15.44	526.7	7.2	1.20	3.5	1023	1.26	2.4	6.1
	DMF	548	3.0	14.41	530.4	4.8	1.09	3.9	1014	1.36	3.0	6.4
6	CH_2Cl_2	640	19.5	10.50	602.3	40.7	1.19	4.6	1263	1.07	1.6	4.9
	EtOH	644	9.0	13.19	609.6	18.5	1.23	4.6	1227	1.25	2.1	6.8
	DMF	650	4.0	12.70	618.2	9.0	1.07	5.4	1192	1.38	2.7	7.6
7	CH_2Cl_2	433	4.5	7.54	421.6	5.2	0.71	3.8	1070	0.98	1.6	3.5
	EtOH	428	4.5	8.05	416.0	6.7	0.80	3.3	1104	0.99	1.6	3.5
	DMF	430	3.3	7.37	417.7	7.0	0.73	3.6	1104	1.00	1.7	3.5
8	CH_2Cl_2	532	3.5	15.83	520.6	−0.3	1.08	3.8	894	1.33	3.3	5.8
	EtOH	524	4.5	14.84	510.7	4.1	1.13	3.5	979	1.34	3.2	5.7
	DMF	526	5.0	15.20	512.6	2.5	1.02	3.9	999	1.29	3.0	5.4
9	CH_2Cl_2	638	1.5	21.99	625.2	−0.5	1.31	4.5	822	1.43	3.8	6.0
	EtOH	628	2.5	16.94	609.8	2.7	1.25	4.5	1034	1.50	3.9	6.8
	DMF	630	−1.0	15.44	611.4	−0.4	1.15	4.9	1023	1.48	3.8	6.8
10	CH_2Cl_2	556		3.87	515.7	16.4	0.57	7.1	1446	1.05	1.9	4.7
		520	38	4.10								
	EtOH	555		3.74	514.6	15.7	0.56	7.1	1462	1.07	2.0	4.8
		519	34.5	3.98								
	DMF	558		3.58	518.7	15.1	0.53	7.7	1426	0.99	1.6	4.3
		522	35.5	3.77								
11	CH_2Cl_2	592	69	5.98	577.9	57.8	0.82	6.1	1425	0.89	1.4	3.1
	EtOH	591	62	5.77	577.5	48.9	0.83	6.1	1493	0.99	1.9	3.8
	DMF	598	60	6.03	586.4	43.4	0.85	6.1	1430	0.89	1.4	3.3

Table 2. Characteristics of the long-wavelength absorption bands of anionic symmetrical dyes in CH_2Cl_2, ethanol, and DMF

Compound	Solvent	λ_{max} /nm	$\varepsilon \cdot 10^{-4}$ /L mol^{-1} cm^{-1}	M^{-1} /nm	f	τ_r /ns	σ^a /cm^{-1}	γ_1	γ_2	$F \cdot 10^2$
23	CH_2Cl_2	349	3.24	341.2	0.48	3.7	1557	1.11	2.5	3.9
	EtOH	345	3.11	337.9	0.47	3.7	1595	1.19	2.8	4.4
	DMF	346.5	3.09	339.4	0.46	3.8	1541	1.10	2.4	3.8
24	CH_2Cl_2	446	9.53	434.3	0.84	3.2	1052	1.19	2.3	4.8
	EtOH	441	9.66	429.7	0.87	3.2	1060	1.13	2.1	4.5
	DMF	442	9.61	430.9	0.86	3.3	1072	1.18	2.4	4.6
25	CH_2Cl_2	549	16.73	536.8	1.13	3.8	886	1.37	3.5	5.6
	EtOH	542	17.81	529.1	1.25	3.4	918	1.39	3.6	5.7
	DMF	543	17.74	532.4	1.20	3.6	879	1.35	3.4	5.4

changes in the electronic structure, in particular, in the dipole moment, upon excitation.

The solvatochromism of organic dyes occurs due to nonspecific (universal) and specific interactions between the dye and solvent molecules.[14] The former are determined by macroscopic parameters of the solvent (the refractive index n_D and the permittivity ε_D), whereas specific interactions are determined by microscopic parameters (the nucleophilicity B and the electrophilicity E).[14] The parameters n_D and ε_D characterize the polarizability and polarity of the solvent; the parameters B and E, specific electrostatic (polar) interactions between the distributed positive and negative charges in the dye molecules, on the one hand, and the negatively and positively charged ends of the dipoles of the solvent, on the other hand. Dispersion interactions[14] proportional to n_D (see Ref. 20) make the major contribution to nonspecific solvation of dyes.

A strengthening of dispersion interactions with the solvent (an increase in n_D of the solvent) causes a bathochromic shift of absorption bands. This is associated with the fact that the S_1 state is more polarized than S_0, due to which the energy level of S_1 decreases with increasing n_D of the solvent to a greater extent than the energy level of S_0.

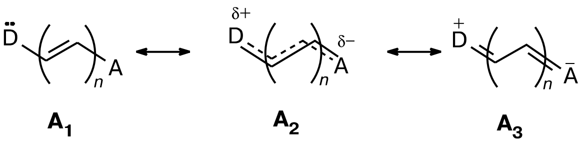
A strengthening of specific electrostatic interactions (nucleophilic and electrophilic solvation), unlike that of dispersion interactions, can lead to both bathochromic and hypsochromic shifts. This is associated with the fact that the solvation is more substantial in the state that is characterized by a larger dipole moment. In the case of merocyanines, this is possible both in the ground and excited states.[20] Consequently, the parameters of nonspecific and specific solvation can influence the absorption band shift both in the same and opposite directions depending on the electronic structures of merocyanines. Hence, to unambiguously determine the type of solvatochromism of merocyanines, it is necessary to compare the spectral shifts of the bands in pairs of solvents, which have similar refractive indices n_D and differ substantially in the macroscopic (ε_D) and microscopic (B and E) polarity parameters. In the present study, we used methylene chloride ($n_D = 1.4242$, $\varepsilon_D = 8.9$, $B = 23$ cm^{-1}, $E = 2.7$) and DMF ($n_D = 1.4303$, $\varepsilon_D = 36.7$, $B = 291$ cm^{-1}, $E = 2.6$)[14] as such solvents. The latter solvent is much more polar and nucleophilic than the former solvent, the values of their n_D and E being similar. Consequently, the observed batochromic shifts of the bands of merocyanines **1—3** on going from CH_2Cl_2 to DMF are directly related to an increase in the polarity of the solvent and are indicative of a positive solvatochromism of these dyes.

In addition to the aprotic solvents CH_2Cl_2 and DMF, we also used ethanol as a typical proton-donor solvent ($n_D = 1.3611$, $\varepsilon_D = 24.3$, $B = 235$ cm^{-1}, $E = 11.6$).[14] First and foremost, ethanol is considered as a solvent, which is potentially prone to strong electrophilic solvation up to hydrogen bonding. At the same time, the spectra of merocyanines **1—3** illustrate the above-mentioned commonly occurring problem of the incorrect determination of the sign of the solvatochromism. For example, in the case of merocyanine **1**, the use of more polar ethanol instead of CH_2Cl_2 causes a hypsochromic shift of λ_{max} and M^{-1} rather than a bathochromic shift, which is observed upon the replacement of the solvent with DMF. It could be concluded that these dyes show a negative solvatochromism. However, this shift is due to the smaller value of n_D of ethanol compared to that of CH_2Cl_2. The hypsochromic shift indicates that this factor dominates over the effects of an increase in ε_D, B, and E on going to ethanol.

The influence of the solvent increases with increasing length of the polymethine chain. For example, λ_{max} and M^{-1} for merocyanine **1** in CH_2Cl_2 differ from those in DMF by 1 nm (52 cm^{-1}) and 2.4 nm (136 cm^{-1}), respectively, whereas these differences for **3** are 22 nm (586 cm^{-1}) and 12.5 nm (372 cm^{-1}), respectively. The solvatochromism of merocyanines **1—3** has a sign opposite to that of the corresponding symmetrical both cationic (**12—22**)[14] and anionic cyanines (**23—25**, see Table 2) and asymmetrical cationic dyes constructed on the basis of various combinations of heterocycles involved in compounds **1—11**.[13]

The electronic structures of merocyanine dyes are clearly described by a superposition of three main canonical structures **A$_1$—A$_3$** (Scheme 3)[21] corresponding to three ideal states, *viz*., neutral polyene (**A$_1$**), polymethine (**A$_2$**), and charged polyene (**A$_3$**).

Scheme 3



D and A are the donor and acceptor ends of the chromophore, respectively

The positive solvatochromism of merocyanines **1—3** indicates that the dipole moment (the contribution of the bipolar canonical structure) in the S_1 state is larger than that in the S_0 state.

The vinylene shifts gradually decrease with increasing length of the polymethine chain. This effect is more pronounced in less polar CH_2Cl_2 than in DMF. For example, the vinylene shifts in CH_2Cl_2 on going from merocyanine **1** to **2** and **3** are, respectively, 90 and 75 nm as related to λ_{max} and 90 and 63.8 nm as related to M^{-1}, whereas these shifts in DMF are 92 and 94 nm for λ_{max} and 91.6 and 74.3 nm for M^{-1}. These data show that the electronic asymmetry of the chromophore for dyes **1—3** in CH_2Cl_2 and, consequently, the bond order alternation are more pronounced compared to those in DMF. This situation should be observed only when the S_0 state of merocyanines **1—3** is similar to the structure $\mathbf{A_1}$. The fact is that the strengthening of polar interactions facilitates the charge separation in this structure, resulting in an increase in the single bond order and a decrease in the double bond order, *i.e.*, in their equalization. In other words, an increase in the polarity of the solvent leads to a decrease in the contribution of the neutral polyene structure $\mathbf{A_1}$ and an increase in the contribution of the polymethine structure $\mathbf{A_2}$ to the S_0 state, which is responsible for an increase in the vinylene shifts. Their values in DMF for merocyanines **1—3** are similar to those for the corresponding symmetrical dyes (~100 nm) (see Table 2 and Ref. 14).

The deviations provide even stronger evidence that the S_0 state of merocyanines **1—3** is similar to the structure $\mathbf{A_1}$. It is known that the deviations serve as a quantitative measure of the electronic asymmetry of dyes, *i.e.*, of the bond order alternation in chromophore.[9] As can be seen from Table 1, the use of both strongly nucleophilic DMF and strongly electrophilic ethanol instead of less polar CH_2Cl_2 leads to a decrease in D_λ and D_M. This indicates that the electronic asymmetry becomes weaker (the bond orders are equalized) with increasing polarity of the solvent. Like the vinylene shifts, this effect is most pronounced in DMF. It should be noted that D_M are more sensitive to the changes in the electronic asymmetry of dyes than D_λ (see Table 1) due to the difference in the band shape of merocyanines **1—3**.

The deviations show that the electronic asymmetry of dyes **1—3** increases in all solvents with increasing length of the polymethine chain. This means that the contribution of the polyene structure $\mathbf{A_1}$ increases in this series of dyes. For example, the parameters D_λ and D_M for compound **3**, which exhibits the largest solvatochromic shifts in the series of merocyanines **1—3**, in DMF are 20.5 nm (510 cm^{-1}) and 34 nm (936 cm^{-1}), respectively, whereas these parameters in CH_2Cl_2 are 51.5 nm (1309 cm^{-1}) and 62 nm (1702 cm^{-1}).

A considerable contribution of the polyene state to the structure of dye **3** is evidenced by the fact that the spin-spin coupling constants of the protons of the polymethine chain in $CDCl_3$ are different, whereas all these constants in DMSO-d_6 are 12.8 Hz. The constants J_{12}, J_{23}, J_{34}, J_{45}, and J_{56} (12.7, 13.3, 12.0, 13.4, and 12.4 Hz, respectively) completely reflect the character of this alternation in the canonical structure $\mathbf{A_1}$. The conformation of dye **3** in DMSO-d_6 differs only slightly from that in $CDCl_3$. The numerical values of the spin-spin coupling constants of the protons of its polymethine chain in both solvents, like those for all other merocyanines, are no smaller than 12.8 Hz, which indicates that the molecules adopt an *all-trans* configuration.

The above-considered directions of the changes in the electronic structures of merocyanines **1—3** should be manifested also in a weakening of vibronic interactions as the polarity of the solvent increases, because a strengthening of the polar interactions with the solvent leads to an increase in the charge separation and equalization of the bond orders in the S_0 state of the polyene canonical structure $\mathbf{A_1}$ (or a nearly resonance structure) due to which it becomes similar to the polymethine structure $\mathbf{A_2}$ (or a nearly resonance structure) observed in the S_1 state. The similarity between the electronic structures of dyes **1—3** in the S_0 and S_1 states will lead to a decrease in the changes in the internuclear equilibrium distances upon excitation and, consequently, to a weakening of vibronic interactions.[22] This should be reflected in the narrowing of the absorption bands with increasing polarity of the solvent. Actually, the use of DMF instead of CH_2Cl_2 as the solvent leads to a decrease in σ for merocyanines **1—3**.

However, it should be noted that the bands are less narrowed than would be expected from the changes in the deviations. In addition, the bands of dyes **1** and **3** in ethanol are even slightly broader than those in CH_2Cl_2. These effects can be attributed to the fact that the influence of the nature of the solvent on the absorption band width is associated with the polar interactions between the solvent molecules and the charges of the dye molecules only in the S_0 state, because, according to the Frank—Condon principle, light absorption is not accompanied by changes in the geometry of this state. Since merocyanines **1—3** are structurally similar to the uncharged polyene state (structure $\mathbf{A_1}$), such interactions in the S_0 state are substantially weakened. Since the contribution of the structure $\mathbf{A_1}$ increases with increasing n, the weakest interactions are present in dye **3**, which is evident from the fact that the difference in σ in DMF is smaller than that in CH_2Cl_2 (see Table 1). In DMF, nucleophilic solvation makes the major contribution to polar interactions. The nucleophilicity of ethanol is smaller, though is rather high, whereas the electrophilicity is substantially larger compared to DMF. Hence, ethanol, unlike DMF, can efficiently strengthen polar interactions with the dye due both to nucleophilic and electrophilic solvation. In merocyanines, whose electronic structures are similar to the neutral structure $\mathbf{A_1}$, the donor fragment D in ethanol will, with higher probability, undergo electrophilic rather than nucleophilic solvation, because a lone pair is located on this fragment. This solvation increases the degree of localization, thus decreasing the electron-releasing ability of D with the resulting increase in the electronic asymmetry and, consequently, in the bond order alternation and vibronic interactions. This is responsible for an anomalous broadening of the absorption bands of dyes **1** and **3** in ethanol compared to CH_2Cl_2.

The deviations reflect not only the changes in the bond order alternation and solvation of the charges in the S_0 state but also the relative arrangement of the energy levels in the ground and excited states. Since the excited state is more bipolar than the ground state, polar interaction play a substantial role in the excited state by decreasing its energy. Hence, the solvatochromic shifts and, consequently, the deviations are very sensitive to changes in the polarity of the solvent even in the case of merocyanines **1—3**, which are structurally similar to neutral polyene.

An increase in the length of the polymethine chain by one vinylene group on going from merocyanine **1** to **2** leads to a narrowing of the absorption bands in all solvents. This situation is analogous to that observed for the corresponding cationic[14] and anionic dyes (see Table 2). A further elongation of the chain (the increase in n from 2 to 3) is accompanied by a substantial broadening of the bands. However, the bands continue to narrow in the spectra of the corresponding symmetrical cationic dyes in CH_2Cl_2 and in the spectra of the anionic dyes in CH_2Cl_2, ethanol, and DMF. This is associated with a weakening of vibronic interactions in the symmetrical dyes of both types with increasing n (a broadening of the bands of their higher vinylogs is associated with a strengthening of specific intermolecular interactions). To the contrary, an increase in the length of the polymethine chain in merocyanines **1—3** should strengthen vibronic interactions because it is accompanied by an increase in the contribution of the polyene resonance structure $\mathbf{A_1}$, which is responsible for an increase in the bond order alternation. Analysis of the changes in the vinylene shifts and the deviations shows that the bond alternation in merocyanine **3** is much more substantial than that in **2**. This is indicative of a strengthening of vibronic interactions, which play the major role in a substantial broadening of the bands in weakly nucleophilic and electrophilic CH_2Cl_2, strongly nucleophilic DMF, and strongly electrophilic ethanol.

The fact that the polyene state tends to be transformed into the polymethine state should be reflected also in the band shape. A decrease in the internuclear equilibrium distances upon excitation, which results in a weakening of vibronic interactions, reduces, according to the Frank—Condon principle, the probability of transitions to the higher vibrational sublevels of the S_1 state (short-wavelength vibronic transitions) and, on the contrary, increases this probability in the 0—0 transition region.[14] Hence, the curve should become not only narrower but also more asymmetrical (due to the presence of the short-wavelength edge), more peaky (sharper), more structured, and more intense. This situation is observed when CH_2Cl_2 is replaced with ethanol and DMF, as evidenced by an increase in γ_1, γ_2, F, ε, and f (see Table 1). The positive sign of γ_1 indicates that the asymmetry of the spectral curve is due to the short-wavelength edge (Fig. 1).

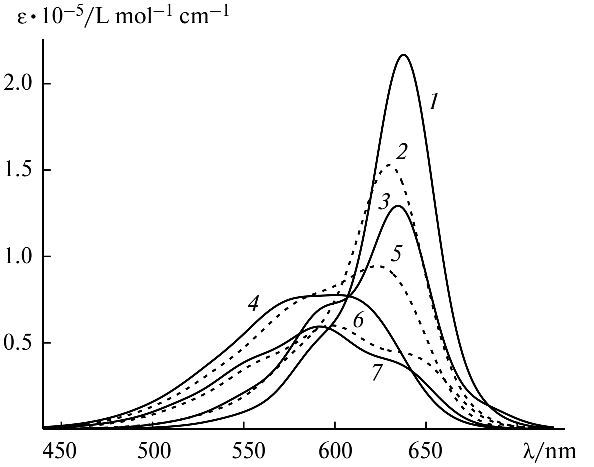


Fig. 1. Electronic absorption spectra of merocyanines **9** (*1—3*), **3** (*4*, *5*), and **11** (*6*, *7*) in CH_2Cl_2 (*1*, *4*, *6*), DMF (*2*, *5*, *7*), and toluene (*3*).

A weakening of vibronic interactions with increasing polarity of the solvent is most pronounced (the largest changes are observed for γ_1, γ_2, F, ε, and f) in dye **2** because, apparently, the effects of short-chain dyes (dye **1**) associated with the closely-spaced end groups[23] are absent in **2**, whereas the partial charges are more pronounced than those in the higher vinylog, *viz.*, merocyanine **3**.

In all solvents, the radiation lifetimes of the S_1 state increase with increasing length of the polymethine chain in the series of dyes **1—3**. On the one hand, an increase in τ_r is retarded by an increase in the oscillator strength, but, on the other hand, it is assisted by a decrease in the wavenumber of the center of gravity of the band. Since the latter parameter is included in Eq. (1) as a square, it has a decisive effect on the change in τ_r. However, the decrease in τ_r in polar solvents compared to CH_2Cl_2 is determined primarily by f, because the solvatochromic shifts $\bar{\nu}$ are substantially smaller than the vinylene shifts.

The electron-releasing ability of the benzothiazolylidene system is higher than that of the indolylidene system. Hence, the canonical structure $\mathbf{A_2}$ bearing the partial positive and negative charges on the fragments D and A, respectively, would be expected to make a larger contribution to the S_0 state of merocyanines **4—6** than to the S_0 state of dyes **1—3**. Hence, the replacement of indolylidene with benzothiazolylidene should lead to a decrease in the electronic asymmetry of these merocyanines due to which they become structurally similar to the polymethine state. This is evidenced by the changes in virtually all main parameters. In merocyanines **4—6**, the larger values are observed for the first and second vinylene shifts as related to λ_{max} and M^{-1} (by 92—95 and 91.6—93.5 nm for the first shifts and by 95—102 and 77—87.8 nm for the second shifts).

There is also a tendency toward a decrease in the solvatochromic shifts of dyes **4—6** compared to **1—3**, but the sign of the solvatochromism remains unchanged. The parameters D_λ and D_M for these dyes are 1.5—2 times smaller than those for the indolylidene derivatives (see Table 1). However, the deviations are also substantially increased with increasing chain length, which is indicative of an increase in the electronic asymmetry.

The fact that the bond orders in dyes **4—6** are more equalized compared to those in **1—3** leads to a weakening of vibronic interactions, which is reflected in the narrowing of the spectral curves of the former compared to the latter. In all cases, their widths are smaller than those for the corresponding indolylidene derivatives, and the difference increases with increasing *n*. For compounds **4—6**, the band width regularly decreases with increasing polarity of the solvent in the series of CH_2Cl_2, ethanol, and DMF. This agrees well with a weakening of vibronic interactions in polar solvents. The influence of the polarity of the solvent on σ of merocyanines **4—6** is associated with a higher degree of bipolarity of their ground state compared to compounds **1—3**, with the resulting increase in nucleophilic and electrophilic solvation of their molecules, which is responsible for a weakening of vibronic interactions. As in the case of **1—3**, the narrowest curves are observed for tetramethine merocyanine **5**. The changes in σ for dyes **4—6** in different solvents show that ethanol acts predominantly as a nucleophilic solvating agent with respect to the fragment D of these dyes. This inverse solvation effect compared to **1—3** is attributed to the higher electron-releasing ability of benzothiazolylidene and, consequently, the larger positive charge on this fragment due to larger delocalization of the lone pair.

The tendency toward a change in the band shape is less pronounced but also noticeable. For dyes **5** and **6**, the coefficients γ_1, γ_2, and F are larger than those for **2** and **3**, which is indicative of an increase in the asymmetry and structurization of their spectra due to a weakening of vibronic interactions.

The fact that the electronic structures of benzothiazolylidene merocyanines are similar to the polymethine state is also evidenced by an increase in the molar extinction coefficients. For example, the peak intensity for merocyanine **5** is, on the average, one-and-a-half times higher than that for **2**, and the oscillator strength is larger by 7—10%.

The electron-releasing ability of the benzimidazolylidene moiety is much higher than that of the benzothiazolylidene fragment. Consequently, the electronic symmetry of merocyanines **7—9** would be expected to be even higher and their structures would be similar to the ideal polymethine state. Actually, the first (96—99 and 94.7—99 nm) and second (104—108 and 98.8—104.6 nm) vinylene shifts as related to λ^a_{max} and M^{-1}, respectively, are not only larger than the analogous shifts for merocyanines **1—6** but also do not decrease with increasing chain length; instead, these shifts are increased and become similar to the value typical of symmetrical cyanine dyes (100 nm). A substantial symmetrization of the electronic states of dyes **7—9** is also evidenced by small D_λ and D_M. The deviations show that these dyes become more symmetrical with increasing length of the polymethine chain. For **8** and **9**, the parameters D_λ and D_M are almost equal to zero. It is also important that the deviations calculated from λ_{max} are virtually equal to those calculated from M^{-1}. This indicates that the band shapes of merocyanines **7—9** are similar to those of the corresponding symmetrical ionic cyanines (see Fig. 1).

These changes in the vinylene shifts and the deviations for dyes **7—9** suggest that their electronic structures in the S_0 state are virtually identical to the ideal polymethine structure, *i.e.*, to the canonical structure $\mathbf{A_2}$. This phenomenon is most pronounced for merocyanine **9** in CH_2Cl_2, as evidenced by the maximum intensity of the color characteristic of this state.[21] Absorption of merocyanine **9** is observed at longer-wavelengths than that of its analog **3**, whereas the inverse situation is observed for the corresponding pairs of lower vinylog, **1** and **7** (in all solvents) and **2** and **8** (in ethanol and DMF) (see Table 1).

The spectra of compounds **7—9**, like the spectra of typical symmetrical dyes, but in contrast to the spectra of indolylidene and benzothiazolylidene **1—6**, show a substantial narrowing of the bands. This narrowing is due to a weakening of vibronic interactions, which typically occurs with increasing chain lengths of symmetrical polymethine dyes.[24] The band width for **9** in CH_2Cl_2 is only 822 cm^{-1}, which is smaller even than that observed for the corresponding symmetrical cationic (1080 cm^{-1}) and anionic (886 cm^{-1}) polymethines. This is possible only for the ideal polymethine state in which the bonds are completely equalized. Actually, the spin-spin coupling constants of the protons of the polymethine chain of merocyanine **9** in $CDCl_3$ are virtually equal to each other (J_{12} = 13.1 Hz and $J_{23} = J_{34} = J_{45} = J_{56}$ = 12.7 Hz). It should be noted that this state is difficult to achieve even in the case of symmetrical dyes because deviations of the electron-releasing (electron-withdrawing) ability of the end groups from the average value in either direction lead to the bond order alternation from the heterocyclic moieties to the center of the chain.

In dyes **7—9**, the sign of the solvatochromism is opposite to that in merocyanines **1—6**. These compounds, like the symmetrical parent dyes (see Ref. 14 and Table 2), exhibit a weak negative solvatochromism, *i.e.*, a hypsochromic shift with increasing polarity of the solvent (see Table 1). This is unambiguously confirmed by the results of the replacement of CH_2Cl_2 with DMF. It is noteworthy that the hypsochromic shifts in ethanol are larger than those in DMF (see Table 1). This is associated with the fact that the macroscopic and microscopic parameters of the solvent have a correlated effect on the shift of the absorption bands of dyes **7—9**, as opposed to **1—6**. The negative solvatochromism signifies that the dipole moments in the S_0 state of **7—9** are larger than those in the S_1 state. Hence, an increase in the polarity parameters in the series of CH_2Cl_2, ethanol, and DMF is accompanied by a decrease in the energy of the ground state. The smaller value of n_D of ethanol compared to those of CH_2Cl_2 and DMF is responsible for weaker dispersion interactions with the solvent molecules in the excited state of the dye. As a result, the level of the S_1 state in ethanol decreases to a lesser extent than that in CH_2Cl_2 and DMF. As a consequence, the hypsochromic shift in the CH_2Cl_2—ethanol pair is larger than that in the CH_2Cl_2—DMF pair.

Based on the negative solvatochromism of merocyanines **7—9** and the fact that the dipole moment of the ideal polymethine structure **A₂** is larger than that of **A₁** and is smaller than that of **A₃**, it can be concluded that the electronic structure of the S_1 state of dyes **7—9** is intermediate between the structures **A₂** and **A₁**. Hence, an increase in the polarity of the solvent is favorable for an increase in the charge separation in the S_0 state, due to which it is intermediate between **A₂** and **A₃**. This would lead to the reverse bond order alternation in the polymethine chain compared to that observed in merocyanines **1—3**. Actually, the constants J_{12}, J_{23}, J_{34}, J_{45}, and J_{56} (the atomic numbering scheme is given in the Experimental section) in the ^{1}H NMR spectrum of dye **9** in DMSO-d_6 are 14.4, 12.0, 14.2, 12.2, and 13.2 Hz, respectively. Consequently, the observed bond alternation is characteristic of the structure of the charged polyene **A₃** (double—single, *etc.*, as opposed to merocyanine **3** in $CDCl_3$ characterized by the following alternation: single—double, *etc.*).

In the case intermediate between **A₂** and **A₃**, an increase in the polarity of the solvent should increase the bond order alternation and the related effects of a decrease in the vinylene shifts, an increase in the deviations, and the band broadening. Actually, the replacement of CH_2Cl_2 with ethanol and DMF leads to a decrease in the first and second vinylene shifts and an increase in σ for merocyanines **7—9**, as opposed to **4—6** (see Table 1). The bands become broader in this series of solvents with increasing chain length, which is indicative of an increase in the role of polar interactions with the solvent. The latter, in turn, causes a strengthening of vibronic interactions. The strengthening of intermolecular interactions is confirmed by an increase in the negative solvatochromism with increasing *n*. For example, in the series of dyes **7**, **8**, and **9**, the hypsochromic shifts of the absorption bands as related to M^{-1} on going from CH_2Cl_2 to DMF are 221, 300, and 361 cm^{-1}, respectively.

It is noteworthy that the replacement of CH_2Cl_2 with less polar toluene, in spite of the fact that it is characterized by the substantially larger value of n_D ($n_D = 1.4969$, $\varepsilon_D = 2.38$, $B = 58$ cm^{-1}, $E = 1.3$),**[14]** as well as the use of more polar ethanol and DMF, are accompanied by a hypsochromic shift, a broadening of the band of merocyanine **9**, and a decrease in its intensity (see Fig. 1). The fact that both an increase and a decrease in the polarity of the solvent lead to changes in the spectral effects in the same direction is additional evidence for the ideal polymethine state of dye **9** in CH_2Cl_2 because deviations from this state toward either neutral or charged polyene are accompanied by an increase in the bond order alternation and, consequently, by an enhancement of the above-described spectral effects.

The maximum similarity between merocyanine **9** and the ideal polymethine state is also evident from the largest increase in the asymmetry and excess coefficients of the bands in the series of the dyes under consideration. Merocyanine **9**, like compounds **7** and **8**, gives a typical absorption band shape with a pronounced vibration maximum near the short-wavelength edge, which is characteristic of symmetrical polymethine dyes (see Ref. 14 and Fig. 1). In addition, the spectra of **9** are narrow due to which this compound is characterized by the largest molar extinction coefficient and the largest oscillator strength. For merocyanine **9** in CH_2Cl_2, $\varepsilon \cdot 10^{-4} = 21.19$ L mol^{-1} cm^{-1} and $f = 1.31$, which are larger than those for all corresponding symmetrical dyes.

The electron-releasing ability of the benzo[*c*,*d*]indolylidene moiety, as opposed to the benzothiazolylidene and benzimidazolylidene moieties, is smaller than that of the indolylidene moiety.**[14]** Hence, the electronic asymmetry of merocyanines **10** and **11** should be larger than that of **1** and **2**, **4** and **5**, and **7** and **8**. Based on this fact, the electronic structures of dyes **10** and **11** would be expected to be even more similar to the polyene state. The larger values of D_λ and D_M for these dyes in CH_2Cl_2 (16.4 nm (598 cm^{-1}) for **10** and 57.8 nm (1573 cm^{-1}) for **11**) compared to those observed for **1** and **2** suggest that this is actually true. The smaller vinylene shifts (70—72 nm for λ_{max} and 62.2—67.7 nm for M^{-1}) additionally confirm this conclusion.

The high electronic asymmetry of these dyes is reflected also in the solvatochromic shifts ($\Delta\lambda_{max}$ and ΔM^{-1} for **11** in CH_2Cl_2 and DMF are 6 nm (169 cm^{-1}) and 8.5 nm (251 cm^{-1}), respectively, whereas the corresponding values for indolylidene analog **2** are as small as 3 nm (107 cm^{-1}) and 2 nm (77 cm^{-1})). The band widths for **10** and **11** are also larger than those for **1** and **2**, the decrease in this value on going to tetramethine merocyanine **11** being much smaller than that observed in the analogous series of indolylidene and benzothiazolylidene dyes.

It should be noted that the more pronounced polyene character of merocyanines **10** and **11** than that of **1—3** leads to a substantial band broadening on going from CH_2Cl_2 to ethanol for the former compounds containing the shorter polymethine chain compared the latter compounds (see Table 1). The parameter σ for tetramethine merocyanine **11** increases by 68 cm^{-1}, whereas this parameter for its analog **2** decreases by 21 cm^{-1}, and it is increased (by 53 cm^{-1}) for hexamethine merocyanine **3**. These data can be interpreted as a result of larger electrophilic solvation of the benzo[*c*,*d*]indolylidene fragment, which is caused by a decrease in the electron-releasing ability, resulting in an increase in the localization of the lone pair.

In addition, the similarity to polyene causes a substantial decrease in the peak and integrated intensities of the bands, a decrease in their asymmetry (a decrease in γ_1) and steepness (a decrease in γ_2), and the appearance of the bell-shaped character (a decrease in F). Besides, the spectra of the compounds, like those of carotinoids, show a vibrational structure both at short and long wavelengths, which is virtually independent of the nature of the solvent (see Fig. 1).

Dyes **10** and **11** are characterized by substantially larger τ_r than merocyanines **1—6**. This is associated primarily with their substantially deeper absorption region. Due to the difference in ν^- of dyes **1—11**, it is difficult to reveal relationships between their molecular structures and τ_r. It can only be stated that these parameters are of the same order of magnitude as the relaxation times of typical polymethine dyes.[14,25]

Therefore, the electronic structures of merocyanines **1—11** can be smoothly varied from neutral polyene to the ideal polymethine state by changing the electron-releasing ability of heteroresidues (from weak to moderate and strong), the polymethine chain length, and the polarity of the solvent. This allows one to invert the spectral effects, *i.e.*, to change the sign of the solvatochromism, to increase or decrease the vinylene shifts and the deviations, and to achieve a narrowing or broadening of absorption bands, an increase or decrease in the asymmetry, steepness, and structurization of the bands, and a strengthening or weakening of vibronic and intermolecular interactions.

Experimental

The absorption spectra were recorded on a Shimadzu UV-3100 spectrophotometer in 1-cm cells. The solvents were purified according to known procedures;[26] CH_2Cl_2 was stabilized by adding 1% of anhydrous ethanol. The addition of ethanol has virtually no effect on the spectroscopic characteristics, as exemplified by strongly solvatochromic dye **3**. The moments of absorption bands were determined by a method described earlier.[15] Chromatography was carried out on silica gel 60 and aluminum oxide 80 (Merck). The purity of merocyanines was checked by TLC (Silufol UV-254, CH_2Cl_2 as the eluent).

The ^1H NMR spectra were measured on a Varian Mercury-400 spectrometer (400.39 MHz) with Me_4Si as the internal standard. Since it was impossible to make unambiguous assignment of the methine protons for compounds **3**, **6**, and **9** based on the usual spectra, the COSY spectra were recorded. The protons in the chains were numbered starting from the heterocyclic moiety.

The melting points were measured in an open capillary tube and are uncorrected.

2-[(2*E*,4*E*)-6-(1,3,3-Trimethyl-2,3-dihydro-1*H*-2-indolylidene)-2,4-hexadienylidene]malononitrile (3). ^1H NMR (DMSO-d_6), δ: 1.565 (s, 6 H, CMe_2); 3.350 (s, 3 H, NMe); 5.824 (d, 1 H, H(1), J = 12.8 Hz); 6.326 (t, 1 H, H(3), J = 12.8 Hz); 6.334 (t, 1 H, H(5), J = 12.8 Hz); 7.034 (t, 1 H, J = 7.8 Hz); 7.104 (d, 1 H, J = 7.8 Hz); 7.275 (t, 1 H, J = 7.8 Hz); 7.417 (d, 1 H, J = 7.8 Hz); 7.475 (t, 1 H, H(4), J = 12.8 Hz); 7.668 (t, 1 H, H(2), J = 12.8 Hz); 7.716 (d, 1 H, H(6), J = 12.8 Hz). ^1H NMR ($CDCl_3$), δ: 1.618 (s, 6 H, CMe_2); 3.290 (s, 3 H, NMe); 5.598 (d, 1 H, H(1), J = 12.7 Hz); 6.210 (dd, 1 H, H(3), J = 13.3 Hz, J = 12.0 Hz); 6.510 (dd, 1 H, H(5), J = 13.4 Hz, J = 12.4 Hz); 6.814 (d, 1 H, J = 8.0 Hz); 7.025 (t, 1 H, J = 7.8 Hz); 7.058 (dd, 1 H, H(4), J = 13.4 Hz, J = 12.0 Hz); 7.228 (d, 1 H, J = 7.8 Hz); 7.268 (t, 1 H, J = 7.9 Hz); 7.344 (d, 1 H, H(6), J = 12.4 Hz); 7.367 (dd, 1 H, H(2), J = 13.3 Hz, J = 12.7 Hz).

2-[2-(3-Ethyl-2,3-dihydro-2-benzothiazolylidene)ethylidene]malononitrile (4). A solution of 3-ethyl-2-[(*E*)-2-methyl(phenyl)carboxamido-1-ethenyl)]-1,3-benzothiazolium iodide[18] (450 mg, 1 mmol) and $CH_2(CN)_2$ (130 mg, 2 mmol) in pyridine (5 mL) was refluxed for 4 min. The product was precipitated with water (20 mL). After 2 h, the precipitate was filtered off, washed, and dried. According to the results of TLC and ^1H NMR spectroscopy, no additional purification of the product was required. The yield was 230 mg (90%), m.p. 197—198 °C. Found (%): C, 66.44; H, 4.47; N, 16.31. $C_{14}H_{11}N_3S$. Calculated (%): C, 66.38; H, 4.38; N, 16.59. ^1H NMR (DMSO-d_6), δ: 1.365 (t, 3 H, $CH_2C\underline{H}_3$, J = 7.1 Hz); 4.303 (q, 2 H, $C\underline{H}_2CH_3$, J = 7.1 Hz); 5.949 (d, 1 H, H(1), J = 13.0 Hz); 7.296 (t, 1 H J = 7.6 Hz); 7.464 (t, 1 H, J = 7.7 Hz); 7.581 (d, 1 H, J = 8.1 Hz); 7.684 (d, 1 H, H(2), J = 13.0 Hz); 7.814 (d, 1 H, J = 7.9 Hz).

2-[(*E*)-4-(3-Ethyl-2,3-dihydro-2-benzothiazolylidene)-2-butenylidene]malononitrile (5). A mixture of 3-ethyl-2-[(1*E*,3*E*)-4-methyl(phenyl)carboxamidobuta-1,3-dienyl)]-1,3-benzothiazolium iodide[18] (240 mg, 0.5 mmol) and $CH_2(CN)_2$ (66 mg, 1 mmol) was heated in pyridine for 5 min. The product was filtered off and twice chromatographed on aluminum oxide (chloroform as the eluent). The yield was 70 mg (40%), m.p. 232—233 °C. Found (%): C, 68.55; H, 4.65; N, 15.09. $C_{16}H_{13}N_3S$. Calculated (%): C, 68.79; H, 4.69; N, 15.04. ^1H NMR (DMSO-d_6), δ: 1.322 (t, 3 H, $CH_2C\underline{H}_3$, J = 7.1 Hz); 4.228 (q, 2 H, $C\underline{H}_2CH_3$, J = 7.1 Hz); 6.221 (d, 1 H, H(1), J = 12.5 Hz); 6.276 (t, 1 H, H(3), J = 12.5 Hz); 7.232 (t, 1 H, J = 7.6 Hz); 7.414 (t, 1 H, J = 7.7 Hz); 7.425 (t, 1 H, H(2), J = 12.5 Hz); 7.467 (d, 1 H, J = 8.0 Hz); 7.585 (d, 1 H, H(4), J = 12.5 Hz); 7.741 (d, 1 H, J = 7.8 Hz).

2-[(2*E*,4*E*)-6-(3-Ethyl-2,3-dihydro-2-benzothiazolylidene)hexa-2,4-dienylidene]malononitrile (6). A mixture of 3-ethyl-2-[(1*E*,3*E*,5*E*)-6-methyl(phenyl)carboxamidohexa-1,3,5-trienyl)]-1,3-benzothiazolium iodide[18] (0.5 mmol) and $CH_2(CN)_2$ (1.5 mmol) was heated over a short period of time

(3—5 min). The product was purified by chromatography (once on silica gel and twice on aluminum oxide) using $CHCl_3$ as the eluent. The yield was 30 mg (20%), m.p. 195—196 °C. Found (%): C, 70.67; H, 4.97; N, 13.93. $C_{18}H_{15}N_3S$. Calculated (%): C, 70.79; H, 4.95; N, 13.76. ^1H NMR (DMSO-d_6), δ: 1.316 (t, 3 H, $CH_2C\underline{H}_3$, J = 7.1 Hz); 4.167 (q, 2 H, $C\underline{H}_2CH_3$, J = 7.1 Hz); 6.039 (d, 1 H, H(1), J = 12.5 Hz); 6.15—6.32 (m, 2 H, H(3) + H(5)); 7.118 (t, 1 H, H(4), J = 12.6 Hz); 7.164 (d, 1 H, J = 7.7 Hz); 7.234 (t, 1 H, H(2), J = 12.6 Hz); 7.357 (m, 2 H); 7.529 (d, 1 H, H(6), J = 12.6 Hz); 7.652 (d, 1 H, J = 7.8 Hz).

2-[2-(1,3-Diphenyl-2,3-dihydro-2-benzimidazolylidene)ethylidene]malononitrile (7). A mixture of 2-methyl-1,3-diphenylbenzimidazolium chloride (**26**)[13] (150 mg, 0.47 mmol) and *N*-(2,2-dicyanovinyl)-*N*-phenylacetamide (**27**)[16] (105 mg, 0.5 mmol) was heated in anhydrous ethanol in the presence of Et_3N for a few minutes. The precipitate was filtered off and washed with ethanol. The yield was 90 mg (50%). The product was chromatographed on Al_2O_3 (CH_2Cl_2 as the eluent). Bright-yellow crystals were obtained, m.p. > 260 °C. Found (%): C, 80.15; H, 4.54; N, 15.70. $C_{24}H_{16}N_4$. Calculated (%): C, 79.98; H, 4.47; N, 15.54. ^1H NMR (DMSO-d_6), δ: 5.078 (d, 1 H, H(1), J = 14.6 Hz); 6.286 (d, 1 H, H(2), J = 14.6 Hz); 6.98—7.08 (m, 2 H, half of an AA´BB´ system), 7.28—7.37 (m, 2 H, half of an AA´BB´ system); 7.66—7.95 (m, 10 H).

2-[(*E*)-4-(1,3-Diphenyl-2,3-dihydro-2-benzimidazolylidene)-2-butenylidene]malononitrile (8). Triethylamine was added to a mixture of salt **26** (150 mg, 0.47 mmol) and *N*-[(1*E*)-4,4-dicyanobuta-1,3-dienyl]-*N*-phenylacetamide[16] (118 mg, 0.5 mmol) in anhydrous ethanol (2 mL) and the mixture was heated for 2 min. The precipitate was filtered off and washed with ethanol. The yield was 58 mg (32%). The product was twice chromatographed on aluminum oxide (CH_2Cl_2 as the eluent). Dark-blue crystals with a metallic luster were obtained in a yield of 44 mg (24%), m.p. 250—251 °C. Found (%): C, 80.76; H, 4.75; N, 14.71. $C_{26}H_{18}N_4$. Calculated (%): C, 80.81; H, 4.69; N, 14.50. ^1H NMR (DMSO-d_6), δ: 5.274 (d, 1 H, H(1), J = 14.4 Hz); 5.583 (dd, 1 H, H(3), J = 13.4 Hz, J = 12.1 Hz); 6.212 (dd, 1 H, H(2), J = 14.4 Hz, J = 12.1 Hz); 6.210 (d, 1 H, H(4), J = 13.4 Hz); 7.03—7.10 (m, 2 H, half of an AA´BB´ system); 7.32—7.38 (m, 2 H, half of an AA´BB´ system); 7.68—7.82 (m, 10 H).

2-[(2*E*,4*E*)-6-(1,3-Diphenyl-2,3-dihydro-2-benzimidazolylidene)-2,4-hexadienylidene]malononitrile (9). A mixture of chloride **26** (160 mg, 0.5 mmol) and *N*-[(1*E*,3*E*)-6,6-dicyano-1,3,5-hexatrienyl]-*N*-phenylacetamide[16] (132 mg, 0.5 mmol) was heated in anhydrous ethanol in the presence of Et_3N for 5 min. The product was twice chromatographed on aluminum oxide (CH_2Cl_2 as the eluent). The yield was 37 mg (18%), m.p. 208—210 °C. Found (%): C, 81.52; H, 4.97; N, 13.55. $C_{28}H_{20}N_4$. Calculated (%): C, 81.53; H, 4.89; N, 13.58. ^1H NMR (DMSO-d_6), δ: 5.367 (d, 1 H, H(1), J = 14.4 Hz); 5.639 (dd, 1 H, H(5), J = 13.2 Hz, J = 12.2 Hz); 5.744 (dd, 1 H, H(3), J = 14.2 Hz, J = 12.0 Hz); 6.198 (dd, 1 H, H(2), J = 14.4 Hz, J = 12.0 Hz); 6.282 (dd, 1 H, H(4), J = 14.2 Hz, J = 12.2 Hz); 6.892 (d, 1 H, H(6), J = 13.2 Hz); 7.05—7.12 (m, 2 H, half of an AA´BB´ system); 7.33—7.40 (m, 2 H, half of an AA´BB´ system); 7.70—7.88 (m, 10 H). ^1H NMR ($CDCl_3$), δ: 5.100 (d, 1 H, H(1), J = 13.1 Hz); 5.649 (t, 1 H, H(5), J = 12.7 Hz); 6.024 (t, 1 H, H(3), J = 12.7 Hz); 6.196 (t, 1 H, H(4), J = 12.7 Hz); 6.260 (dd, 1 H, H(2), J = 13.1 Hz, J = 12.7 Hz); 6.922 (d, 1 H, H(6), J = 12.7 Hz); 6.89—6.94 (m, 2 H, half of an AA´BB´ system); 7.17—7.22 (m, 2 H, half of an AA´BB´ system); 7.53 (d, 4 H, J = 7.7 Hz); 7.67—7.76 (m, 6 H).

2-[2-(1-Benzyl-1,2-dihydrobenzo[*c*,*d*]indol-2-ylidene)ethylidene]malononitrile (10). A mixture of 1-benzyl-2-methylbenzo[*c*,*d*]indolium tetrafluoroborate (**28**)[27] (104 mg) and compound **27** (63 mg) was heated in anhydrous ethanol in the presence of Et_3N for a few minutes. After cooling, the precipitate was filtered off and washed with ethanol and acetone. The product was purified by successive heating with different solvents (acetone, MeCN, and AcOH) and then filtered off. The yield was 32 mg (32%), m.p. > 260 °C. Found (%): C, 82.66; H, 4.58; N, 12.44. $C_{23}H_{15}N_3$. Calculated (%): C, 82.86; H, 4.54; N, 12.6. ^1H NMR (DMSO-d_6), δ: 5.392 (s, 2 H, NCH_2); 6.229 (d, 1 H, H(1), J = 13.3 Hz); 7.26—7.37 (m, 5 H, Ph); 7.389 (d, 1 H, J = 7.1 Hz); 7.557 (t, 1 H, J = 7.7 Hz); 7.618 (d, 1 H, J = 8.2 Hz); 7.788 (t, 1 H, J = 7.7 Hz); 8.105 (d, 1 H, J = 8.1 Hz); 8.591 (d, 1 H, H(2), J = 13.3 Hz); 8.616 (d, 1 H, J = 7.1 Hz).

1-Benzyl-2-[(1*E*,3*E*)-4-methyl(phenyl)carboxamido-1,3-butadienyl]benzo[*c*,*d*]indolium tetrafluoroborate (29). Equimolar amounts of salt **28** and *N*-[(1*E*,2*E*)-3-anilino-2-propenylidene]aniline hydrochloride were heated (bath, 120 °C) in a 1 : 1 Ac_2O—AcOH mixture for 30 min. The product was precipitated with diethyl ether and filtered off. In the next step, the resulting hemicyanine was used without additional purification.

2-[(*E*)-4-(1-Benzyl-1,2-dihydrobenzo[*c*,*d*]indol-2-ylidene)-2-butenylidene]malononitrile (11). A mixture of salt **29** (100 mg, 0.2 mmol) and malononitrile (25 mg, 0.4 mmol) was heated in Ac_2O in the presence of NaOAc for 5 min. The precipitate was filtered off and washed with a minimum amount of Ac_2O and diethyl ether. The product was twice chromatographed on silica gel (CH_2Cl_2 as the eluent). The yield was 11 mg (15%), m.p. > 260 °C. Found (%): C, 83.67; H, 4.82; N, 11.57. $C_{25}H_{17}N_3$. Calculated (%): C, 83.54; H, 4.77; N, 11.69. ^1H NMR (DMSO-d_6), δ: 5.328 (s, 2 H, NCH_2); 6.455 (d, 1 H, H(1), J = 12.8 Hz); 6.595 (t, 1 H, H(3), J = 12.8 Hz); 7.08 (m, 1 H); 7.22—7.37 (m, 5 H, Ph); 7.46 (m, 2 H); 7.748 (t, 1 H, J = 7.7 Hz); 7.974 (d, 1 H, J = 8.0 Hz); 8.118 (d, 1 H, H(4), J = 12.8 Hz); 8.344 (t, 1 H, H(2), J = 12.8 Hz); 8.483 (d, 1 H, J = 7.1 Hz).

References

1. E. Hammam and A. M. El-Nahas, *J. Phys. Chem. A*, 1998, **102**, 9739.
2. F. Wuerthner and Y. Sheng, *Angew. Chem., Int. Ed. Engl.*, 2000, **39**, 1978.
3. R. A. Ganeev, R. I. Tugushev, A. A. Ishchenko, N. A. Derevyanko, A. I. Ryasnyansky, and T. Usmanov, *Appl. Phys. B*, 2003, **76**, 683.
4. S. Nakatsuji, Y. Ogawa, S. Takeuchi, H. Akutsu, J. Yamada, A. Naito, K. Sudo, and N. Yasuoka, *J. Chem. Soc., Perkin Trans. 2*, 2000, 1969.
5. F. Wuerthner, S. Yao, J. Schilling, R. Wortmann, M. Redi-Abshiro, E. Mecher, F. Gallego-Gomez, and K. Meerholz, *J. Am. Chem. Soc.*, 2001, **123**, 2810.
6. A. Mishra, R. K. Behera, P. K. Behera, B. K. Mishra, and G. B. Behera, *Chem. Rev.*, 2000, **100**, 1973.

7. A. I. Kiprianov, *Tsvet i stroenie tsianinovykh krasitelei* [*Color and Structures of Cyanine Dyes*], Naukova dumka, Kiev, 1979, 666 pp. (in Russian).
8. L. G. S. Brooker, G. H. Keyes, and D. W. Heseltine, *J. Am. Chem. Soc.*, 1951, **73**, 5350.
9. G. E. Ficken, in *The Chemistry of Synthetic Dyes,* Vol. **4**, Ed. K. Venkataraman, Academic Press, New York, 1971, p. 212.
10. C. Aliaga, J. S. Galdames, and M. C. Rezende, *J. Chem. Soc., Perkin Trans. 2*, 1997, 1055.
11. Z. Pawelka and L. Sobczyk, *J. Chem. Soc., Faraday Trans. 1*, 1980, **76**, 43.
12. J. A. Soroka and K. B. Soroka, *J. Phys. Org. Chem.*, 1997, **10**, 647.
13. A. A. Ishchenko, V. M. Zubarovskii, G. A. Gromova, and N. A. Derevyanko, *Zh. Org. Khim.*, 1987, **23,** 621 [*J. Org. Chem. USSR*, 1987, **23**, 562 (Engl. Transl.)].
14. A. A. Ishchenko*, Stroenie i spektral´no-lyuminestsentnye svoistva polimetinovykh krasitelei* [*Structures and Spectral Luminescent Properties of Polymethine Dyes*]*,* Naukova dumka, Kiev, 1994, 232 pp. (in Russian).
15. A. A. Ishchenko, N. A. Derevyanko, and V. A. Svidro, *Dyes and Pigments*, 1989, **10**, 85.
16. M. Strell, W. B. Braunbruck, W. F. Fuhler, and O. Huber, *Liebigs Ann. Chem.*, 1954, **587**, 174.
17. M. Strell, W. B. Braunbruck, and L. Reithmayr, *Liebigs Ann. Chem.*, 1954, **587**, 195.
18. F. M. Hammer, *The Cyanine Dyes and Related Compounds*, Intersci. Publ., New York—London, 1964, 790 pp.
19. Yu. L. Slominskii, S. V. Popov, and A. D. Kachkovskii, *Zh. Obshch. Khim.*, 1989, **59**, 459 [*J. Gen. Chem. USSR*, 1989, **59** (Engl. Transl.)].
20. Ch. Reichardt, *Solvents and Solvent Effects in Organic Chemistry*, Wiley-VCH, Weinheim, 2003, 629 pp.
21. G. Bach and S. Daehne, *Rodd's Chemistry of Carbon Compounds*, Vol. **IVB**, Ed. M. Sainsbury, Elsevier Science, Amsterdam, 1997, p. 383.
22. A. A. Ishchenko, *Izv. Akad. Nauk, Ser. Khim.*, 1996, 2194 [*Russ. Chem. Bull.*, 1996, **45**, 2079 (Engl. Tansl.)].
23. A. I. Tolmachev, A. A. Ishchenko, M. A. Kudinova, V. V. Kurdyukov, and S. V. Sereda, *Dyes and Pigments*, 1991, **17**, 71.
24. A. A. Ishchenko, *Izv. Akad. Nauk, Ser. Khim.*, 1994, 1227 [*Russ. Chem. Bull.*, 1994, **43**, 1161 (Engl. Tansl.)].
25. A. N. Tarnovskii, T. K. Razumova, E. P. Shchelkina, and T. V. Veselova, *Optika i Spektroskopiya,* 1993, **74**, 10762 [*Optics Spectr.*, 1993, **74** (Engl. Transl.)].
26. A. J. Gordon and R. A. Ford, *The Chemist's Companion. A Handbook of Practical Data, Techniques and References*, John Wiley and Sons, New York, 1972, 541 pp.
27. A. A. Ishchenko, N. P. Vasilenko, A. G. Maidannik, and L. V. Balina, *Zh. Org. Khim.*, 1989, **25**, 1086 [*J. Org. Chem. USSR*, 1989, **25** (Engl. Transl.)].

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