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Electronic structure and solvatochromism of merocyanines based on *N*,*N*-diethylthiobarbituric acid

Andrii V. Kulinich*, Nadezhda A. Derevyanko, Alexander A. Ishchenko

Institute of Organic Chemistry, National Academy of Sciences of Ukraine, Murmanska Str. 5, Kyiv 02094, Ukraine

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Abstract

A series of merocyanines based on *N*,*N*-diethylthiobarbituric acid containing heterocycles of various electron-donating properties have been synthesized. With the aim of studying the dependence of their electronic structure on the main structural factors (i.e. change of the terminal groups and the length of polymethine chain), and also on the solvation, their solvatochromism has been investigated in a wide range of solvents with different polarity. Moreover, their electronic structure has been studied by NMR spectroscopy and quantum-chemical calculations. It has been found a rather significant influence of the polymethine chain length on the electronic structure of merocyanines in solvents in which the condition close to the ideal polymethine state is not achieved. By analysis of the UV/vis absorption spectra in non-polar *n*-hexane and low-polar toluene the important role of solvation for achievement of the cyanine limit is also shown. Only for dyes with the strong electron-donating group – the benzimidazole end group – a uniformity of bond orders in the chromophore is achieved even in *n*-hexane with minimum participation of the solvent. These conclusions are confirmed by the data of ^{1}H and ^{13}C NMR spectroscopy. Attempts of correlations of the data observed with the results of quantum-chemical calculations appeared unsatisfactory, which seems to be connected to both, the lack of suitable calculation methods, and the neglect of the solvent influence.

Keywords: Donor–acceptor systems; Merocyanines; NMR spectroscopy; Solvatochromism; Electronic structure

1. Introduction

Merocyanines (MC) are a class of donor–acceptor compounds, the interest to which increases permanently. That is connected with the remarkable sensitivity of their electronic spectra to environment polarity [1], to their ability to sensitize silver halide photoemulsions [2] and to the electron–hole conductivity in organic semi-conductor materials [3], as well as to their pronounced NLO properties [4].

Understanding the dependence of the MC electronic structure on their molecular structure and on the polarity of the environment is crucial for an opportunity of purposeful search for MC dyes with the desired properties. The basic approaches to reach this goal are: study of MC solvatochromism [5], quantum-chemical calculations of their molecules [6], NMR spectroscopy investigations [6–8], exploration of their behaviour in an external electric field, and study of their NLO properties [8,9]. The study of the solvatochromism (and solvatofluorochromism) of MC remains the most powerful method till now. The works of Brooker and Keyes and Kiprianov [5] are classical in this field. Many publications in this area have appeared recently [1,4]. However, researchers have not worked with a large series of compounds that have limited opportunities for sweeping generalization. Even in Brooker's work on series of MC, the dyes studied are frequently limited by the length of their polymethine chain, despite of a great variety in their molecular structure. The variety of solvents of different polarity in many publications is also rather small. An important problem for the study of the MC solvatochromism is the decrease in solvent polarity sufficient for the achievement of an electronic state close to those in vacuum. Even such poorly polar solvents as dichloromethane (DCM) and arenes are capable to exert enough strong solvation which essentially influences the electronic structure of MC molecules with high polarizability. The solubility of MC in hydrocarbons is mostly insufficient, even for measurements of electronic UV/vis

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* Corresponding author. Mobile: +380 50 7619303; fax: +380 44 5732643.
E-mail addresses: kulinich@univ.kiev.ua (A.V. Kulinich), alexish@i.com.ua (A.A. Ishchenko).

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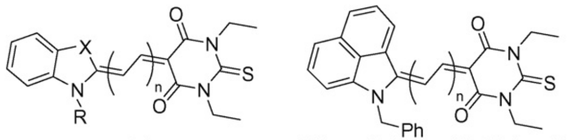


1-9 **10** (n = 1), **11** (n = 2), **12** (n = 3)

	1	2	3	4	5	6	7	8	9
X	CMe$_2$	CMe$_2$	CMe$_2$	S	S	S	NPh	NPh	NPh
R	Me	Me	Me	Et	Et	Et	Ph	Ph	Ph
n	1	2	3	1	2	3	1	2	3

Scheme 1.

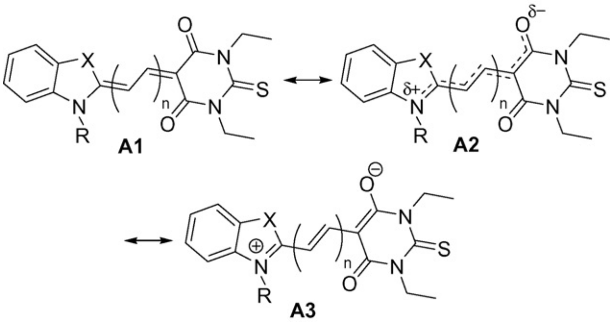
spectra. The aim of the present paper is the investigation of the dependence of the electronic structure and solvatochromism of MC dyes as a function of the main structural factors, the type of the terminal groups, the polymethine chain lengths, and the solvents of different polarity.

As objects of this study the MC dyes **1–12** have been used. They are constructed on the basis of a strong electron-acceptor such as *N*,*N*-diethylthiobarbituric acid and heterocycles with average (**1–6**), strong (**7–9**), and weak (**10–12**) electron-donating properties, as terminal end groups of the polymethine chain (Scheme 1).

The MC **1–3** have been investigated by Brooker and Keyes [5a] and Bublitz et al. [9]. However, in the first work [5a], on the basis of their UV/vis spectra measured only in rather polar solvents, not entirely correct conclusions about the practical absence of solvatochromism have been made. In work [9], conclusions about the positive solvatochromism of these dyes have been made based on Stark-spectroscopy of deep-frozen solutions, the longest vinylogue **3** has been studied only in two solvents, and dyes **1** and **2** have been investigated only in frozen 2-Me-THF. A temperature decrease can essentially influence the spectral-luminescent properties of MC [10]. Dyes **4** [11] and **5** [12] also are known compounds. The MC dyes **6–12** are described for the first time in this work.

Polar ethanol and DMF, medium polar DCM, less polar toluene, and non-polar *n*-hexane were chosen as solvents for this investigation [1].

With the purpose of a visual description of the electronic structure of asymmetrical MC dyes, the model of three limit resonance structures [9,13] suggested by Daehne has been used as shown in Scheme 2 with the mesomeric structure of a neutral polyene (**A1**), an ideal polymethine (cyanine limit) (**A2**), and a charged polyene (**A3**). In the state **A2** the bond orders within the chromophore are as much as possible equalized, hence, it should be characterized by the most long-wavelength band [13] and by the narrowest band due to reduction of vibronic interactions.



Scheme 2.

For the study of solvatochromism the absorption (or fluorescence) band maximum ($\lambda_{\max}$) are traditionally used as a reference point. However, positions of $\lambda_{\max}$ not always objectively reflect spectral regularities as they can be influenced by different vibronic transitions [14]. Moreover, the maximum is determined insufficiently accurate in case of wide, diffuse or strongly structured bands. Such contrast in the change of the band form is more typical for MC, than for corresponding ionic dyes [8]. We have made a mathematical treatment of long-wavelength absorption bands of the investigated MC by the method of moments, [15,16]. It has enabled us to characterize quantitatively not only position (M^{-1}) and intensity (f) of the bands, but also their form (σ, γ_1, γ_2, F), the formulas for calculation of the moments and the given indexes are published in ref. [16]. The parameter M^{-1}, averaged over all vibronic transitions, reflects the average position of the band (on the wavenumber scale, this parameter represents the centre of gravity of the band: $\bar{\nu} = 10^7/M^{-1}$) and, unlike $\lambda_{\max}$, enables one to make a reliable comparison of the curves of different band shape. The integrated absorption intensity (the oscillator strength f) has an analogous advantage over the peak intensity (the extinction coefficient ε). The parameter σ characterizes the deviation (dispersion) of the points belonging to the spectral band from the centre 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. All these parameters as well as the radiation lifetimes (τ_r) of the S_1 state of the MC dyes, calculated according to the equation [15]:

$$\tau_r = \frac{1.5 \times 10^9}{\bar{\nu}^2 f} \tag{1}$$

are collected in Table 1.

The deviations D_λ and D_M (on $\lambda_{\max}$ and M^{-1}, correspondingly) have been evaluated with the use of spectral data of the parent anionic dyes **13**, **14** [5] and the cationic dyes **15–22** (Scheme 3), measured in three solvents. This deviation is a quantitative measure of the electronic asymmetry of the dyes [5]. The data for dyes **15–20** were taken from ref. [15]. The characteristics of other ionic dyes are listed in Table 2.

All first vinylogues of the anionic dyes ($m = 0$) possess an essential bathochromic shift of the absorption band because of internal steric hindrance (leading to deviation from planarity) that reduces the reliability of the deviations calculated from its electronic spectra. In non-polar *n*-hexane and toluene ionic dyes

Table 1
Characteristics of the long-wavelength vis absorption bands of MC **1**–**12**, measured in *n*-hexane, toluene, DCM, DMF, and ethanol at 293 K

Dye	Solvent	λ_{max} (nm)	D_λ (nm)	$\varepsilon \times 10^{-4}$	M^{-1} (nm)	D_M (nm)	f	τ_r (ns)	σ (cm^{-1})	γ_1	γ_2	$F \times 10^{-2}$
1	Hexane	481	–	12.90	466.1	–	0.932	3.5	1015	1.36	2.9	7.4
	Toluene	492	–	12.72	477.2	–	0.934	3.7	976	1.27	2.6	6.1
	DCM	493	–	12.32	478.0	–	0.944	3.7	964	1.20	2.3	5.5
	DMF	493	–	11.23	476.0	–	0.933	3.7	1024	1.20	2.2	5.6
	EtOH	492	–	11.27	474.4	–	0.971	3.5	1037	1.16	2.1	5.3
2	Hexane	560; 526	–	13.38; 7.63	537.9	–	1.133	3.9	1128	1.03	1.7	4.7
	Toluene	584	–	16.95	565.3	–	1.171	4.1	990	1.44	3.4	7.3
	DCM	593	6	21.04	577.8	5.1	1.226	4.1	835	1.56	4.2	8.0
	DMF	593	−1	20.53	576.6	−1	1.207	4.2	883	1.70	4.9	8.9
	EtOH	590	0	20.89	573.2	1.3	1.266	3.9	921	1.68	4.7	8.8
3	Hexane	630; 589	–	9.57; 9.05	585.4	–	1.211	4.3	1344	1.06	1.9	4.8
	Toluene	664; 620	–	11.88; 8.35	625.8	–	1.274	4.6	1282	1.20	2.4	5.6
	DCM	693	8.5	22.56	666.9	13.3	1.480	4.6	1016	1.75	4.9	9.7
	DMF	693	1	25.08	670.7	−4.7	1.449	4.7	978	1.97	6.3	11.5
	EtOH	690	0	24.81	665.8	−2	1.470	4.6	1037	2.01	6.4	12.2
4	Hexane	501	–	–	485.9	–	–	–	910	1.52	3.8	8.3
	Toluene	507	–	14.75	492.8	–	0.847	4.3	859	1.41	3.1	7.5
	DCM	504	–	13.38	488.6	–	0.849	4.2	909	1.38	3.1	7.1
	DMF	501	–	11.16	482.7	–	0.844	4.2	1055	1.42	3.3	7.5
	EtOH	498	–	10.69	478.8	–	0.840	4.1	1065	1.36	3.0	7.2
5	Hexane	580; 544	–	–	553.3	–	–	–	1293	1.48	3.7	7.6
	Toluene	602	–	18.95	585.2	–	1.113	4.6	885	1.54	3.7	8.3
	DCM	603	2.5	22.83	589.8	0.7	1.177	4.5	782	1.78	5.5	9.0
	DMF	597	4	17.51	578.0	6.4	1.137	4.4	1002	1.75	5.0	9.7
	EtOH	593	6	16.00	569.0	13.5	1.167	4.2	1143	1.76	4.9	10.2
6	Hexane	655; 610	–	–	608.6	–	–	–	1374	1.16	2.3	5.2
	Toluene	691; 641	–	15.51; 8.39	653.9	–	1.355	4.8	1209	1.37	2.9	7.3
	DCM	708	−0.5	29.66	689.2	−1.4	1.486	4.8	854	2.02	6.6	11.6
	DMF	700	3.5	19.54	666.1	7.3	1.404	4.8	1227	1.84	5.2	11.7
	EtOH	695	6.5	16.33	648.9	23.8	1.429	4.6	1480	1.78	4.8	11.8
7	Hexane[a]	480	–	–	–	–	–	–	–	–	–	–
	Toluene	481	–	11.60	468.8	–	0.863	3.8	970	1.19	2.4	5.0
	DCM	473	–	9.25	455.4	–	0.890	3.5	1193	1.18	2.2	5.3
	DMF	466	–	7.30	444.9	–	0.869	3.4	1371	1.15	2.1	5.0
	EtOH	463	–	6.10	438.5	–	0.844	3.4	1508	1.15	2.1	5.0
8	Hexane[a]	583	–	–	–	–	–	–	–	–	–	–
	Toluene	587	–	18.81	575.1	–	1.060	4.7	818	1.70	5.2	7.9
	DCM	571	14.5	13.09	547.6	22	1.130	4.0	1197	1.42	3.1	7.4
	DMF	554	27	8.38	523.0	41.3	1.097	3.8	1485	1.14	1.9	5.2
	EtOH	546	32	6.71	509.2	54.2	1.102	3.6	1712	1.18	2.2	5.5
9	Hexane[a]	686	–	–	–	–	–	–	–	–	–	–
	Toluene	700	–	24.34	684.3	–	1.236	5.7	873	2.26	8.4	12.5
	DCM	668	19.5	14.42	629.6	40	1.409	4.3	1354	1.40	2.9	7.7
	DMF	626	52.5	6.56	579.1	78.2	1.304	3.9	1866	1.10	2.0	4.8
	EtOH	578	101	6.39	557.4	99.7	1.375	3.4	2070	0.98	1.6	4.1
10	Hexane	600; 557	–	6.82; 5.37	560.9	–	0.663	7.2	1275	1.17	2.2	6.6
	Toluene	612; 568	–	7.69; 5.46	574.9	–	0.691	7.2	1229	1.22	2.3	7.1
	DCM	611; 567	–	8.69; 5.60	576.9	–	0.711	7.1	1164	1.20	2.3	7.2
	DMF	613; 569	–	8.41; 5.47	578.6	–	0.706	7.2	1169	1.22	2.4	7.4
	EtOH	610; 566	–	9.29; 5.72	576.4	–	0.724	6.9	1141	1.23	2.3	7.6
11	Hexane	660; 617	–	5.25; 7.53	604.7	–	0.905	6.1	1315	0.84	1.2	3.1
	Toluene	690; 641	–	7.44; 8.10	637.8	–	1.007	6.1	1266	0.94	1.4	3.9
	DCM	702; 649	8.0	10.85; 8.54	654.4	31.2	1.098	5.9	1195	1.12	1.9	5.7
	DMF	707; 653	1.0	13.12; 8.39	663.8	14.9	1.114	6.0	1140	1.19	2.1	6.7
	EtOH	704; 650	−2.5	14.51; 8.16	664.5	11.1	1.111	6.0	1098	1.30	2.6	7.6
12	Hexane	662; 622	–	5.22; 4.70	627.4	–	0.743	8.0	1511	0.93	1.9	3.6
	Toluene	693	–	5.96	666.3	–	0.858	7.8	1505	0.91	1.8	3.3
	DCM	715	32[b]	6.41	698.2	88.6	0.958	7.7	1531	1.01	1.9	4.2
	DMF	806; 732	9.5	6.40; 6.00	718.6	51.0	0.938	8.3	1536	1.19	2.3	6.4
	EtOH	803; 729	4	7.34; 5.90	721.3	47.5	0.928	8.5	1505	1.28	2.7	7.3

[a] *n*-Hexane contains addition of DCM (5%).

[b] The value is calculated from “the first maximum” for estimation of which known distance between maxima in ethanol and DMF was used.

Table 2
Characteristics of the long-wavelength vis absorption bands of dyes **13**, **14**, **21**, **22** in DCM, DMF, and ethanol at 293 K

Dye	Solvent	λ_{max} (nm)	$\varepsilon \times 10^{-4}$	M^{-1} (nm)	f	τ_r (ns)	σ (cm^{-1})	γ_1	γ_2	$F \times 10^{-2}$
13	DCM	546	18.06	532.8	1.038	4.1	871	1.72	5.1	8.7
	DMF	542	19.47	529.3	1.044	4.1	868	1.88	5.9	10.1
	EtOH	540	19.76	526.9	1.106	3.8	906	1.86	5.7	10.2
14	DCM	645	20.92	626.5	1.162	5.1	1016	2.17	7.6	13.1
	DMF	642	22.54	624.9	1.162	5.1	1017	2.46	9.5	14.5
	EtOH	638	21.21	618.3	1.182	4.9	1044	2.28	8.2	14.9
21	DCM	874; 786	25.10; 6.64	838.3	1.127	9.4	808	1.46	2.7	11.1
	DMF	874; 788	19.31; 6.54	828.1	1.051	9.8	942	1.61	3.9	11.5
	EtOH	863; 779	23.20; 7.07	824.3	1.137	9.0	865	1.47	2.9	10.5
22	DCM	991; 884	29.21; 7.95	947.1	1.376	9.9	808	1.46	2.9	10.1
	DMF	989; 885	–[a]	914.2	–	–	1183	1.79	4.9	13.5
	EtOH	976; 876	21.81; 8.20	919.3	1.272	10.0	951	1.49	3.3	9.7

[a] Fast decomposition.

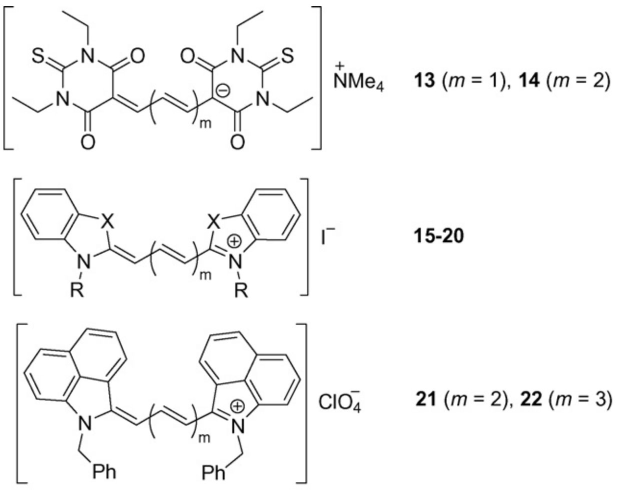
are either insoluble or form close ion pairs that also excludes an authentic calculation of the deviations.

2. Results and discussion

2.1. Electronic structure and solvatochromism

The MC dyes **1**–**3** are constructed on the basis of the nuclei 3*H*-indole and *N*,*N*-diethylthiobarbituric acid. Their narrow (array of σ in Table 1), asymmetric (γ_1), and steep (peaked) (γ_2) long-wavelength absorption bands in DCM, ethanol, and DMF are similar to those of corresponding symmetric dyes. Their low polarizability [9], the small solvatochromic band shifts (Table 1 and [5]) also indicate the high electronic symmetry of these MC dyes. However, in *n*-hexane broadening and symmetrization of their vis absorption bands is observed, and a pronounced vibrational band structure, typical for asymmetrical polyenes, appears (Fig. 1, Table 1) (about three vibrational maxima, distanced on $\Delta\tilde{\nu} = 1150$–$1250\,\text{cm}^{-1}$ can be found, which corresponds to the frequency of full-symmetric oscillation of the C–C-bonds of the polymethine chain [15]). Hence, the non-solvated form of these MC dyes is described by an electronic structure intermediate between **A1** and **A2**. The vinylene shifts in *n*-hexane decrease with an increase in the polymethine-chain length: between MC **1** and **2** the shift equals to $\Delta\lambda = 79$ nm on λ_{max} and $\Delta\lambda = 71.8$ nm on M^{-1}, between dyes **2** and **3** it amounts to $\Delta\lambda = 70$ and $\Delta\lambda = 47.5$ nm, correspondingly. Also, at the transition to the supreme vinylogous dyes a broadening (growth of σ) of the absorption curves is observed, the bands become more symmetric, more sloping, and more diffuse (reduction of γ_1, γ_2, and F for dye **2** in comparison with **1**). This implies that with increasing length of a chain the contribution of structure **A1** to the electronic structure of MC **1**–**3** grows in *n*-hexane, the electronic structure is shifted towards the neutral polyene. Proceeding from this, it is possible to expect for this series of dyes a positive solvatochromism at the transition in going from hydrocarbons to more polar solvents.

In fact, replacement of *n*-hexane by more polar toluene as solvent bathochromic band shifts are observed for the MC dyes **1**–**3**, there is also an increase of the vinylene shifts, intensity, asymmetry, and steepness of the absorption bands (Table 1, Fig. 1). This specifies an approach of the electronic structure of given



	15	**16**	**17**	**18**	**19**	**20**
X	CMe_2	CMe_2	S	S	NPh	NPh
R	Me	Me	Et	Et	Ph	Ph
m	2	3	2	3	2	3

Scheme 3.

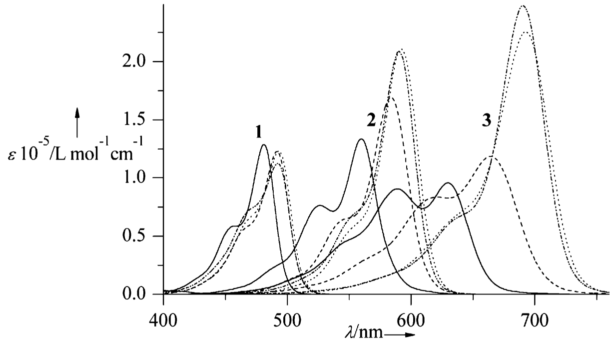


Fig. 1. UV/vis spectra of MC **1**, **2**, **3** in *n*-hexane (—), toluene (- - -), DCM (···), and ethanol (-·-·-).

MC to the ideal cyanine state **A2** in going from *n*-hexane to toluene as solvent which, however, is not achieved, at least for dyes **2** and **3**, on what specify values of vinylene shifts ($\Delta\lambda = 92$ and 80 nm on λ_{max}, $\Delta\lambda = 88.1$ and 60.5 nm on M^{-1}), which are smaller than that typically observed for symmetric dyes, i.e. $\Delta\lambda = 100$ nm [15].

In DCM (more polar than toluene) as well as in strongly polar DMF and ethanol the spectral characteristics of MC **1–3** are very close to each other. Even for the MC dye **3** solvatochromic band shifts are only $\Delta\lambda = 3$ nm, and on the band centres $\Delta\lambda = 4.6$ nm. The vinylene shifts are "classical" with $\Delta\lambda = 100$ nm, and the values of deviations are close to zero. Hence, in all these solvents the electronic structure of dyes **1–3** is close to the cyanine limit **A2**, the polarizability of the dyes is very low which corresponds to literature data [5,9]. However, the application of the method of moments has allowed getting more information from the electronic spectra of these compounds. The analysis of the M^{-1} values, which more rigorously than λ_{max} characterize the position of a band, has shown that the maximal long-wavelength shift of the band for MC **1** is achieved in DCM, and for **2**, **3** in DMF. DCM and DMF possess close refraction indexes n_D^{20} (1.4242 and 1.4303, accordingly), which has also affected the choice of this pair of solvents for this investiganion. Therefore, the influence of n_D^{20} on the position of the absorption band of dyes for this pair of solvents can be neglected. Hence, the maximal approach to electronic state **A2** for dye **1** is achieved in DCM, and for MC **3** in DMF. Final evidence for the correctness of this statement can be received from an analysis of the σ values (Table 1). The band width is defined by both vibronic and intermolecular interactions. One can consider that in all polar solvents the intermolecular interactions almost equally influence the band width [in the case of protic ethanol the influence of H-bonds on band width of dyes **1–3** should differ slightly from the solvation effect in aprotic DMF that is a consequence of the analysis of band widths in the absorption spectra of symmetric dyes **13** and **14** (Table 2)]. For MC **1**, the σ value is minimal in DCM and increase in going to more and to less polar solvents (Table 1). This confirms the conclusion about the achievement of state **A2** in this solvent. This implies that in DMF and in ethanol its electronic structure is already shifted towards **A3**. For MC **2** the band width is also minimal in DCM, and for **3** in DMF. Hence, with the chain lengthening the ideal cyanine state is achieved in more and more polar solvents.

The analysis of dependence of bands width and form on the lengthening of the polymethine chain has shown for series **1–3** (Table 1) that the narrowest and asymmetric bands are achieved for dye **2**. Probably, the transition to the longest vinylogue **3** is accompanied by an amplification or vibronic interactions (larger alternation of bonds orders in chromophore) and intermolecular interactions (due to the increase in the number of charged centres and in chromophore polarizability).

Thus, the analysis of the spectra by the method of moments (viz., the band centres and widths data) has allowed us to draw an univocal conclusion that dyes **1–3** possess an intermediate type of solvatochromism, known as "reverse solvatochromism", though this transition is not so strongly expressed. Besides, their electronic structure depends on chain length (especially in non-polar solvents), being shifted towards **A1** with its growth that contradicts the conclusions made earlier [9].

By the example of MC dyes **4–6** we hoped to see a more precise transition from **A1** via **A2** to **A3** with a change of medium polarity, because the benzothiazole nucleus is more basic than the *3H*-indole nucleus. The solubility of dyes **4–6** in *n*-hexane appeared insufficient for the measurement of quantitative UV/vis spectra, however, it is quite sufficient for qualitative ones. For MC **4–6**, as well as for **1–3**, the polarity of *n*-hexane is too small for an achievement of the ideal polymethine state **A2**. Vinylene shifts are far from $\Delta\lambda = 100$ nm and fade with chain lengthening (Table 1) what specifies the essential electronic asymmetry of their molecules. The contribution of the non-polar structure **A1**, as well as in the series **1–3**, increases with an increase in chain length, the bands of the supreme vinylogues become broader and more symmetric, and additional oscillatory maxima appear.

The increase in medium polarity in going from *n*-hexane to toluene causes the same changes as in the case of MC **1–3**. The contribution of structure **A2** to the electronic structure of dyes **4–6** increases in comparison with *n*-hexane as solvent. The vinylene shifts are larger than for the derivatives of *3H*-indole ($\Delta\lambda = 95$ and 89 nm on λ_{max}; $\Delta\lambda = 92.4$ and 68.7 nm on M^{-1}), and the bands are narrower. Hence, the electronic symmetry of MC **4–6** in toluene is higher than that of MC **1–3**. For compound **4** in toluene, the maximal long-wavelength, shift of the band and the narrowest and most intensive band in the investigated set of solvents is achieved (Table 1). For MC **4** the cyanine limit is observed in less polar solvents as for dye **1**. A further increase in solvent polarity in going to DCM, DMF, and ethanol results in case of dye **4** only in a blue-shift of the band and in a growth in spectral band width. Even in DCM the band width is the same as in *n*-hexane (a little red-shift of the absorption band can be explained by the larger value of n_D^{20} for the first), in DMF and ethanol the bands are even broader and more hypsochromically shifted (Table 1). Hence, the contribution of the electronic structure **A3** in these solvents is even higher than the contribution of **A1** in *n*-hexane.

MC **5** and **6** achieve state **A2** in DCM in which vinylene shifts are equal to $\Delta\lambda = 99$ and 105 nm on maxima and $\Delta\lambda = 101.2$ and 99.4 nm on the centres of bands, the values of deviations are close to zero, and the bands are very narrow, intensive, and asymmetric (Table 1, Fig. 2). The extinction of dye **6** achieves in DCM $\varepsilon = 29.66 \times 10^4$ mol L^{-1} cm^{-1}, such a value is typical

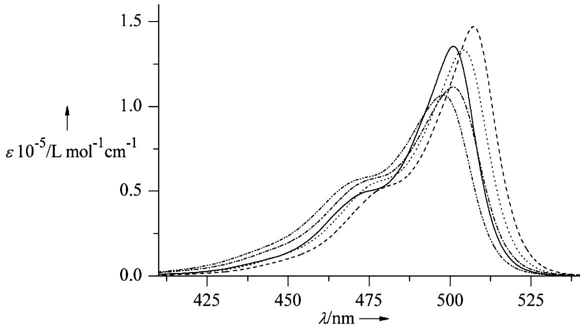


Fig. 2. UV/vis spectra of MC **6** in *n*-hexane (—), toluene (- - -), DCM (···), DMF (-·-·-), and ethanol (-··-··-).

only for symmetrical dyes. In more polar solvents the bands are blue-shifted and essentially broader. These effects are much more well-defined for dye **6** than for MC **3** (Fig. 2).

The benzimidazole nucleus is a considerably stronger electron donor than the 3*H*-indole and benzothiazole nucleus [15]. Therefore, the contribution of the dipolar structure **A3** to the basic electronic state of MC dyes **7–9** should increase strongly. But is this increase enough for the achievement of state **A2** even in non-polar *n*-hexane as solvent?

Dyes **7–9** are practically insoluble in pure *n*-hexane. Quantitative spectra were received only in a mixture of *n*-hexane and DCM (95:5) (Table 1, Fig. 3, concentration of dyes $c = 2.5 \cdot 10^{-6}$ mol L^{-1}). It can be seen that in such a binary solvent mixture their electronic spectra depend critically on the content of DCM: an increase of its concentration within the limits of 2–10% causes a decrease in intensity of the short-wavelength maximum and an increase in intensity of the long-wavelength band at their almost constant position. Moreover, the distance between these maxima does not correspond with the frequency of full-symmetric valent oscillations of C–C-bonds of polymethine chain and, for example, in case of compound **9** amounts to $\Delta\tilde{\nu} = 2060\,\mathrm{cm}^{-1}$. The further increase of the volume fraction of DCM results in a complete vanishing of the short-wavelength maximum (for **7** it is imperceptible even at 5% DCM and it appears only at lower contents of DCM or higher concentration of dye). It can be concluded that MC dyes **7–9** in *n*-hexane/DCM mixture form H-aggregates at low contents of the polar solvent due to strong electrostatic interactions between unlike charges of molecules with electronic structure **A3** at their orientation in a sandwich one above another in opposite directions. However, taking into account the weak dependence of $\lambda_{\max}$ of long-wavelength bands on the DCM concentration at its low content, one can estimate precisely enough the absorption maxima of the monomeric forms of these dyes in pure *n*-hexane. It is necessary to note that dyes **1–6** and **10–12** do not aggregate in *n*-hexane. For the proof of absence of the aggregation of dyes **1–3** and **10–12** in *n*-hexane absorption spectra in the concentration range of $c = 1 \times 10^{-6}$–5×10^{-5} mol L^{-1} have been measured and it is shown that they obey the Lambert–Beer law. Moreover, the spectra of MC **3–6** in a *n*-hexane/DCM (95:5) mixture were registered and it is shown that the addition of the polar solvent does not influence critically the form of bands and the intensity ratio of their maxima, only their normal bathochromic band shifts occur.

For dyes **7–9** the first and the second vinylene shifts in *n*-hexane (calculated on $\lambda_{\max}$) are $\Delta\lambda = 103$ nm. It specifies their high electronic symmetry, an approach to the cyanine limit (structure **A2**) even in such a non-polar solvent, in contrast to that observed for compounds **1–3** and **4–6**. Moreover, lengthening of the polymethine chain in series **7–9** does not cause an increase of the contribution of non-polar polyene structure **A1**.

A change to toluene as solvent for MC **7–9** leads to bathochromic band shift: $\Delta\lambda = 1$ nm (43 cm^{-1}), 4 nm (117 cm^{-1}), and 14 nm (292 cm^{-1}), respectively. The vinylene shifts on $\lambda_{\max}$ (M^{-1}) are somewhat greater than in *n*-hexane: $\Delta\lambda = 107$ nm (106.3 nm) for the first one and $\Delta\lambda = 113$ nm (109.2 nm) for the second one. However, the conclusion about an approach to structure **A2**, that is the positive solvatochromism observed for this pair of solvents, is not quite sure. Toluene has a much greater refraction index ($n_{\mathrm{D}}^{20} = 1.4961$) in comparison with *n*-hexane ($n_{\mathrm{D}}^{20} = 1.3749$), so the Bayliss function $\rho = (n_{\mathrm{D}}^{20} - 1)/(2n_{\mathrm{D}}^{20} + 1)$ has a larger value which causes a long-wavelength shift of the bands. Because of the aggregation of dyes **7–9**, it is impossible to apply the method of moments and to calculate σ in *n*-hexane, and we have estimated the band half-width ($\nu_{1/2}$) for MC **9** in *n*-hexane (with addition of 5% DCM) and in toluene. The value $\nu_{1/2}$ in *n*-hexane (843 cm^{-1}) is less than in toluene (875 cm^{-1}). Hence, in the series of MC **7–9** the cyanine limit is achieved in *n*-hexane. In toluene their electronic structure should deviate a little towards structure **A3**.

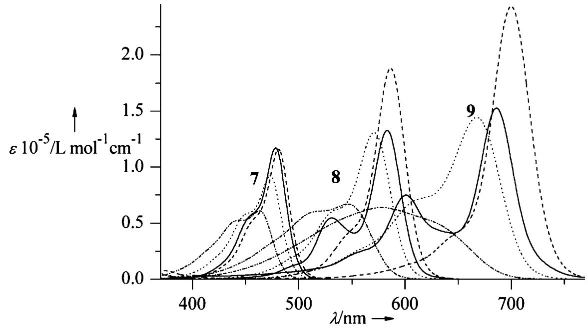


Fig. 3. UV/vis spectra of MC **7**, **8**, **9** in *n*-hexane (+5% of DCM) (—), toluene (- - -), DCM (···), and ethanol (-·-·-·-).

A further increase of solvent polarity by changing from toluene to DCM causes hypsochromic band shifts for dyes **7–9**, for **9** it amounts to $\Delta\lambda = 32$ nm (684 cm^{-1}) on maxima and $\Delta\lambda = 54.7$ nm (1270 cm^{-1}) on the band centres. Vinylene shifts decrease (see Table 1). The values of deviations also specify a small electronic asymmetry, amplifying with lengthening of the chain. Bands become considerably wider, more symmetric, and diffusive (Table 1, Fig. 3). That is, the electronic structure of MC **7–9** shifts towards state **A3**.

Obviously, a further increase of solvent polarity should lead to increasing electronic asymmetry of molecules of MC **7–9**, which is indeed observed in going to strongly polar DMF and ethanol as solvents. In these solvents a further decrease of vinylene shifts occurs, a growth of deviations is observed, and the absorption bands become very wide (for **9** the σ value achieves 2070 cm^{-1} in ethanol), symmetric, sloping, and diffusive (Table 1). Lengthening of the methine chain causes a growth of the band widths of dyes **7–9** in polar solvents, though in toluene the transition from **7** to **8** leads to a narrowing of bands and the transition from compound **8** to **9** causes only a slight broadening. Thus, in strongly polar solvents the electronic structure of dyes **7–9** is close to the charged polyene state **A3** and the relative contribution of **A3** grows with lengthening of the polymethine chain, opposed to that what was observed for MC **1–6**.

In the series of MC **1–9**, the tendency to reducing the lifetime of the S_1 state occurs at the transition from the cyanine limit to both the neutral polyene (see, for example, MC **1–3** in *n*-hexane) and to the charged polyene (MC **7–9** in ethanol and DMF). It is mainly concerned with a hypsochromic band shift at a deviation of electronic structure from the electronic state **A2** (a growth of $\bar{\nu}$ in Eq. (1)).

Dyes **10–12** contain the benzo[*cd*]indole nucleus, the electron-donating ability of which is lower than that of 3*H*-indole [15]. Therefore, a typical positive solvatochromism is expected for dyes **10–12**, with an increase in the contribution of limit structure **A1** in comparison to MC **1–3**. In *n*-hexane, already for tetramethine merocyanine **11** the band form has a pronounced vibronic structure, typical for non-polar carotenoids. For compound **12** the band becomes even more symmetric, sloping, and wide (Table 1). The first and second vinylene shifts in the series **10–12**, calculated from the band centres (a comparison of maxima is not possible because of the strong change of the band form), amount to only $\Delta\lambda = 33.8$ nm and 22.7 nm. The solvent change from *n*-hexane to toluene causes a long-wavelength shift of the bands of MC **10–12**, they become narrower and their intensity as well as the vinylene shifts increase (Table 1). These tendencies even more amplify at replacement of the solvent by DCM, but even in this solvent the vinylene shift between dyes **11** and **12** amounts only to $\Delta\lambda = 43.8$ nm, and the band form is carotenoid-like (Table 1).

In strongly polar DMF and ethanol the absorption bands of dyes **10–12** are displaced even more bathochromically, and the band form comes nearer to the band form of symmetric polymethines. In these solvents the vinylene shifts on maxima are close to “classical” 100 nm, however, based on the band centres the first and second vinylene shifts are $\Delta\lambda = 88.1$ and 56.8 nm, respectively. The band width in polar solvents decreases somewhat on going from dye **10** to **11**, however, a further chain lengthening leads to the same band width as observed in non-polar solvents (Table 1). It can be concluded that even in DMF and ethanol the electronic structure of dyes **11** and **12** deviates from the cyanine limit towards that of non-polar polyene **A1**. MC **10–12** possess the greatest values of τ_r among the investigated dyes. This is caused, first of all, by a significant long-wavelength shift of the bands (decrease of $\bar{\nu}$) and strong decrease in the oscillator strength in comparison with MC**1–9**.

The results received allow making some important conclusions. Firstly, merocyanines with heterocycles of moderate electron-donor properties (series **1–3**, **4–6**) dissolved in solvents of very low polarity (*n*-hexane, toluene), show a rather appreciable solvatochromism, and their electronic structure comes nearer to that of non-charged polyene **A1**. Despite of the high electron-acceptor properties of the diethylthiobarbituric acid residue, for the corresponding MC dyes structure **A2** is achieved only by means of polar solvents. However, a substantial increase of heterocycle donor properties (transition to MC **7–9**) has allowed achieving the cyanine limit even in *n*-hexane. Secondly, the electronic structure of MC depends on the length of the polymethine chain much stronger than it is reported in the literature [9]. So in the series **1–3**, **4–6**, and **10–12** the transition from di- to tetra- and further to hexamethine merocyanine dyes causes an increase of the contribution of structure **A1** in non-polar solvents, whereas for benz[*cd*]indole derivatives even in polar ones. Vice versa, for MC **7–9** in polar solvents a growth of the chain length causes an increase of the contribution of structure **A3**. Only in solvents in which the electronic structure of MC is close to the cyanine limit the influence of chain length on the electronic structure is negligible. And thirdly, not only the analysis of the absorption maxima, but also of the band form, their width and centres allows estimating more precisely the solvatochromic effects, particularly if they are negligible.

2.2. NMR spectroscopy and quantum-chemical calculations

The shifts of signals in NMR spectra are connected with charges around the corresponding atoms. Therefore, studying the electronic structure of MC dyes by this method can give additional information on the distribution of electronic density in a molecule [8,17] (from electronic spectra it is possible to judge authentically only the change of dipole moment on excitation). Therefore, ^{1}H and ^{13}C NMR spectra of dyes **1–3** and **7–9** in $CDCl_3$, and also ^{1}H NMR spectra of MC **3** and **9** in DMSO-d_6 have been analyzed in detail [see Tables 3, 3a, 4 and 4a]. For the unequivocal assignment of signals in case of the more complex compounds **3** and **9** a set of correlation spectra (COSY, HMQC and HMBC) was registered which has allowed, in addition to the assignment of signals, to draw conclusions about the *all-trans* geometry of the polymethine chain.

Table 3
Data of the ^{1}H NMR spectra of dyes **1–3**

Dye	Solvent	CMe_2	NMe	$(CH_2)_2$	$(CH_3)_2$	3-H	4-H	5-H	6-H	10-H	11-H	12-H	13-H	14-H	15-H
1	$CDCl_3$														
	δ	1.744 s	3.608 s	4.592 q	1.328 t	7.094 d	7.319 t	7.253 t	7.309 d	7.711 d	8.730 d				
	J (Hz)			7.0	7.0	7.8	7.8	7.8	7.8	14.6	14.6				
2	$CDCl_3$														
	δ	1.648 s	3.412 s	4.571 q	1.300 t	6.975 d	7.332 t	7.164 t	7.321 d	5.978 m	7.78–7.87 m		8.100		
	J (Hz)			6.9	6.9	7.8	7.8	7.8	7.8	[a]			[a]		
3	$CDCl_3$														
	δ	1.647 s	3.370 s	4.571 q	1.311 t	6.890 d	7.300 t	7.091 t	7.270 d	5.730 d	7.535 t	6.421 t	7.363 t	7.902 t	8.060 d
	J (Hz)			6.9	6.9	7.8	7.8	7.8	7.8	12.8	12.8	12.8	12.8	12.8	12.8
	DMSO-d_6														
	δ	1.651 s	3.527 s	4.436	1.214	7.218	7.325	7.138	7.427	6.113	[b]	6.476 m	[b]	7.813 m	7.890 d
	J (Hz)			6.8	6.8	8.0	7.8	7.8	7.8	13.0					13.0

[a] Probably, because of coincidence of 11-H and 12-H shifts the spectrum of the non-first order has been formed.

[b] The signals of 11-H and 13-H have coincided (multiplet at 7.60–7.71 ppm) that also has caused distortion of other signals of the spectrum.

Table 3a
Data of the ^{1}H NMR spectra of dyes 7–**9**

Dye	Solvent	(Ph)$_2$	(CH$_2$)$_2$	(CH$_3$)$_2$	3-H, 6-H	4-H, 5-H	10-H	11-H	12-H	13-H	14-H	15-H
7	CDCl$_3$											
	δ	7.52–7.59[a]; 7.67–7.75 m	4.405 q	1.165 t	7.01–7.05[b]	7.30–7.35	see[b]	see[b]				
	J (Hz)		7.0	7.0								
8	CDCl$_3$											
	δ	7.50–7.56 m; 7.65–7.72 m	4.412 q	1.170 t	6.97–7.02 m	7.27–7.32 m	5.568 d	6.466 dd	7.367 dd	7.067 d		
	J (Hz)		7.0	7.0			14.5	14.5; 12.1	14.4; 12.1	14.4		
9	CDCl$_3$											
	δ	7.63–7.67 m; 7.73–7.79 m	4.410 q	1.204 t	7.02–7.06 m	7.32–7.36 m	5.478 d	6.209 dd	5.773 dd	6.250 dd	7.389 dd	7.286 d
	J (Hz)		7.1	7.1			14.7	14.7; 12.0	13.2; 12.0	13.2; 12.3	14.4; 12.3	14.4
	DMSO-d$_6$											
	δ	7.75–7.91 m	4.355 q	1.092 t	7.24–7.29 m	7.50–7.54 m	5.861 d	6.232 dd	6.060 dd	6.279 dd	7.217 dd	7.003 d
	J (Hz)		7.0	7.0			15.2	15.2; 11.4	13.6; 11.4	13.6; 11.7	14.5; 11.7	14.5

[a] The intensity of multiplet is 5H, the 11-H signal has got to it.

[b] The intensity of multiplet is 3H, the 10-H signal has got to it.

Table 4
Data of the ^{13}C NMR spectra of dyes **1**–**3** in CDCl$_3$

	CMe$_2$	NMe	2CH$_2$	2Me	C-2	C-3	C-4	C-5	C-6	C-7	C-8
1	28.7	31.1	43.3	12.5	142.4	110.1	128.5	125.1	122.2	141.1	49.3
2	28.1	30.3	42.8	12.5	142.8	109.2	128.4	124.2	122.0	140.2	48.5
3	28.2	29.8	43.0	12.5	143.4	108.5	128.3	123.1	121.9	139.9	47.8

	C-9	C-10	C-11	C-12	C-13	C-14	C-15	C-16	C-17	C-18	C-19
1	177.8	103.0	152.6					99.8	161.2	162.0	178.5
2	171.5	101.3	157.2	122.7	156.9			105.1	160.7	162.0	178.4
3	167.6	100.1	142.6	125.3	160.5	124.7	157.2	107.3	161.6	161.6	178.5

The analysis of regularities in ^{1}H NMR spectra is complicated by the presence of a great number of anisotropic groups in the dye molecules (e.g. phenyl substituents in MC **7**–**9**, carbonyl groups in thiobarbituric residue). The signal of the NMe-group with increasing polymethine chain is shifted to higher fields. Therefore, the electronic density on the nitrogen atom of 3*H*-indole increases. This indicates a reduction of charge separation in the chromophore and an increase in the contribution of the nonpolar limit structure **A1**. On the contrary, replacement of CDCl$_3$ by polar DMSO-d$_6$ leads to opposite signal change. The same regularity is observed for shifts of the 3-H and 5-H atoms which are in *ortho*- and *para*-position to the nitrogen atom. In the series **7**–**9** the shifts of multiplets of the *AA′BB′*-system of the benzimidazole fragment are informative. They are practically constant at increasing chain length, which is in accordance with the conclusion about the stability of their electronic structure at change of chain length in non-polar or low-polar solvents. However, they are shifted to lower fields at replacement of chloroform by DMSO-d$_6$, specifying s decrease in electronic density in the donor nucleus, i.e. a growth of the contribution of structure **A3**.

From ^{13}C NMR spectra one can draw similar conclusions on the approach of dyes **1**–**3** with increasing chain length to the nonpolar polyene state [whereas in the series **7**–**9** with an increase in the polymethine-chain length the electronic structure remains close to the ideal polymethine **A2** (in chloroform)]. The C-9 and C-16 chemical shifts in the series of vinylogues are most informative in this case; the influence of electronic structure changes on their positions should be maximal as they actually

Table 4a
Data of ^{13}C NMR spectra of dyes **7**–**9** in CDCl$_3$

	(Ph)$_2$	2CH$_2$	2Me	C-2 (C-7)	C-3 (C-6)	C-4 (C-5)	C-9
7	127.4; 131.1; 131.3; 133.8	42.5	12.7	133.3	111.1	125.5	147.7
8	127.7; 131.1; 131.3; 133.5	42.7	12.6	133.3	110.9	125.7	148.9
9	127.9; 131.1; 131.2; 133.4	42.7	12.7	133.1	111.1	126.1	148.7

	C-10	C-11	C-12	C-13	C-14	C-15	C16	C-17	C-18	C-19
7	91.1	152.5					97.7	161.2	161.2	177.5
8	94.0	153.7	119.5	149.0			97.8	161.4	161.4	177.1
9	95.6	150.7	121.8	157.1	120.5	146.1	97.6	161.2	161.2	176.4

Table 5
The calculated charge values on the key chromophore atoms of MC dyes **1–3** and **7–9** (in the ground state)

	1	**2**	**3**	**7**	**8**	**9**
N-1	−0.214	−0.219	−0.211	−0.167	−0.155	−0.15
C-9	0.145	0.102	0.075	0.23	0.16	0.13
C-10	−0.313	−0.268	−0.243	−0.326	−0.266	−0.24
C-11	0.112	0.004	−0.04	0.121	0.012	−0.032
C-12		−0.238	−0.198		−0.244	−0.203
C-13		0.084	−0.026		0.09	−0.019
C-14			−0.215			−0.223
C-15			0.076			0.08
C-16	−0.296	−0.268	−0.257	−0.311	−0.276	−0.263

are terminal atoms of an easily polarizable chromophore. At transition from MC **1** to **2** and further to **3** the C-9 signal is shifted to higher field on $\Delta\delta = 10.2$ ppm (see Table 4); almost the same change, but with opposite sign, occurs for the C-16 signal and consequently the contribution of structure **A1** increases with lengthening of polymethine chain. And vice versa, in the ^{13}C NMR spectra of dyes **7–9** signals of these atoms are practically constant (Table 4a).

Results of semi-empirical quantum-chemical calculations of the electronic structure of MC dyes **1–3**, **7–9** (see Tables 5 and 6) are unsatisfactory. In particular, they do not reflect the change of their electronic structure at a variation of their chemical structure. The calculated bond orders (Table 6) correspond to the strongly alternating polyene structure **A1** both for dyes **1–3** and for the considerably more polar compounds **7–9**, which even in non-polar *n*-hexane are close to the electronic structure **A2**. The calculated vinylene shifts do not achieve even $\Delta\lambda = 10$ nm, and for the transition from MC **2** to **3** or from **8** to **9** they are negative. Linear correlations between the calculated charges on the carbon atoms of polymethine chain (Table 5) and their ^{13}C-chemical shifts (Tables 4 and 4a) are unsatisfactory: for dyes **1–3** the correlation coefficient $r = 0.858$ and for dyes **7–9** $r = 0.821$; correlations with ^{1}H chemical shifts of chain protons are lost ($r < 0.5$) that is probably connected with the strong effects of the magnetic anisotropic groups on shifts in ^{1}H NMR spectra. Weak correlation can be explained by the fact that the quantum chemical calculations of the electronic structure of the MC dyes have been performed for gas phase. At the same time, even replacement of non-polar *n*-hexane by low-polar toluene as solvent causes an apparent solvatochromic effect (Table 1, Fig. 1), that specifies the considerable change of an electron density on the chromophore atoms and should be reflected on the chemical shifts. This is of a greater importance for MC dyes which possess the strong negative solvatochromism (the series **7–9**), since the charge separation in a ground state is more essential for them, opposite to the positively solvatochromic ones.

Table 6
The calculated bond orders for the chromophore of MC dyes **1–3** and **7–9** (in the ground state)

	1	**2**	**3**	**7**	**8**	**9**
N-1–C-9	1.129	1.075	1.051	1.070	1.018	1.000
C-9–C-10	1.581	1.668	1.708	1.496	1.624	1.668
C-10–C-11	1.169	1.105	1.083	1.202	1.114	1.089
C-11–C-12	1.599	1.709	1.761	1.560	1.694	1.751
C-12–C-13		1.120	1.082		1.129	1.087
C-13–C-14		1.653	1.740		1.639	1.730
C-14–C-15			1.105			1.110
C-15–C-16			1.673			1.664
BOA	−0.441	−0.577	−0.640	−0.392	−0.565	−0.632

For a more adequate calculation of the electronic structure of these molecules it is necessary to model objectively the influence of the environment in quantum-chemical methods. Some simplified approaches in this direction are illustrated in work described in ref. [18] in which positive tendencies are outlined in the calculations of MC dyes.

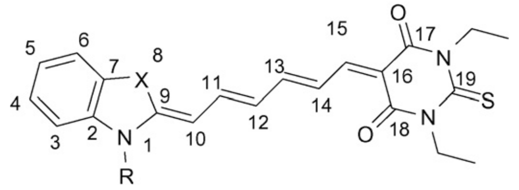
2.3. Conclusions

A complex exploration of the solvatochromism and electronic structure of MC dyes based on *N*,*N*-diethylthiobarbituric acid has been performed by UV/vis spectroscopy, NMR spectroscopy, and quantum-chemical calculations. Both, a detailed examination of the position, intensity, and form of MC absorption bands measured in a wide range of solvent polarity, and the analysis of regular changes of their chemical and electronic structure have been made.

The results allow us to make some important conclusions. Firstly, merocyanines with heterocycles of moderate (series **1–3**, **4–6**) or low (**10–12**) electron-donor properties dissolved in solvents of very low polarity (*n*-hexane, toluene), show a rather appreciable solvatochromism, their electronic structure comes nearer to the non-charged polyene **A1**. Despite the high electron-acceptor properties of the diethylthiobarbituric acid residue, the electronic structure **A2** for them is achieved only with the assistance of polar solvents. However, a substantial increase of heterocycle electron-donor properties (transition to MC **7–9**) has allowed achieving the cyanine limit even in *n*-hexane. Secondly, the electronic structure of MC depends on the length of the polymethine chain more strongly than it is noted in the literature [9]. Thus, in the series **1–3**, **4–6**, and **10–12** transition from di- to tetra- and further to hexamethine merocyanine dyes causes a growth of the contribution of structure **A1** in non-polar solvents, and for benzo[*cd*]indole derivatives **10–12** even in polar ones. Vice versa, for MC **7–9** in polar solvents a growth of chain length causes an increase of the contribution of structure **A3**. Only in solvents in which MC are very close to the cyanine limit the influence of chain length on the electronic structure is negligible. And thirdly, not only the analysis of the absorption maxima, but also of the band form, their width and centres allows to estimating more precisely solvatochromic effects, particularly if they are insignificant.

3. Experimental

The UV/vis spectra were recorded on a spectrophotometer Shimadzu UV-3100. Solvents were purified according to methods given in ref. [19]. Chromatography was carried out on silica gel 60 and aluminium oxide 80 (“Merck”). The purity of the merocyanines was checked by TLC-control (Silufol UV-254, CH_2Cl_2 as the eluent). NMR spectra were measured on a



Scheme 4.

spectrometer Varian Mercury-400 (400.40 MHz for H-atoms), internal standard TMS. The atom numeration is showed at Scheme 4. Melting (decomposition) points were measured in an open capillary and are not corrected.

Quantum-chemical calculations of the electronic structure of the MC dyes have been performed for gas phase by AM1 method with a standard set of parameters [20]. 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.

*3.1. 1,3-Diethyl-5-[(2E,4E,6Z)-6-(3-ethyl-1,3-benzothiazol-2(3H)-ylidene)hexa-2,4-dienylidene]-2-thioxodihydropyrimidine-4,6(1H,5H)-dione (**6**)*

A solution of 3-ethyl-2-methyl-1,3-benzothiazolium tosylate (70 mg, 0.2 mmol) and of *N*-[(1*E*,3*E*)-5-(1,3-diethyl-4,6-dioxo-2-thioxotetrahydropyrimidin-5(2*H*)-ylidene)penta-1,3-dienyl]-*N*-phenylacetamide [5a] (80 mg, 0.2 mmol) in MeCN (5 mL) was refluxed for 3 min with excess of K_2CO_3 (150 mg). After cooling the precipitate was filtered off and washed with water. The product was heated in water (50 mL) and filtered off (50 mg, yield 57%, less than 10% of impurities). Then 6 mg of crude dye was purified by column chromatography (6 g Al_2O_3; DCM/acetone 95:5). After removal of the solvent the product was heated in EtOH (3 mL), filtered off, and dried (4 mg, yield 38%, mp 169–170 °C; bright green lustrous needles). ^1H NMR ($CDCl_3$): $\delta = 1.304$ (t, $^3J(H,H) = 6.9$ Hz 6H; $(CH_3)_2$), 1.450 (t, $^3J(H,H) = 7.0$ Hz, 3H; CH_3), 4.128 (q, $^3J(H,H) = 7.0$ Hz, 2H; CH_2), 4.560 (q, $^3J(H,H) = 6.9$ Hz, 4H; $(CH_2)_2$), 5.955 (d, $^3J(H,H) = 12.6$ Hz, 1H; H^{10}), 6.390 (t, $^3J(H,H) = 12.6$ Hz, 1H; H^{12}), 7.164 (d, $^3J(H,H) = 8.2$ Hz, 1H, H^3,), 7.231 (t, $^3J(H,H) = 12.6$ Hz, 1H; H^{13}), 7.26 (t, $^3J(H,H) = 8.0$ Hz, 1H; H^5), 7.302 (t, $^3J(H,H) = 12.6$ Hz, 1H; H^{11}), 7.416 (t, $^3J(H,H) = 8.0$ Hz, 1H; H^4), 7.565 (d, $^3J(H,H) = 8.0$ Hz, 1H; H^6), 7.831 (t, $^3J(H,H) = 12.6$ Hz, 1H; H^{14}), 7.936 (t, $^3J(H,H) = 12.9$ Hz, 1H; H^{15}); UV/vis: see Table 1; elemental analysis calcd (%) for $C_{23}H_{25}N_3O_2S_2$ (439.6): C 62.84, H 5.73, N 9.56, S 14.59; found: C 62.68, H 5.87, N 9.45.

*3.2. 5-[2-(1,3-Diphenyl-1,3-dihydro-2H-benzimidazol-2-ylidene)ethylidene]-1,3-diethyl-2-thioxodihydropyrimidine-4,6(1H,5H)-dione (**7**)*

A solution of 2-methyl-1,3-diphenyl-3*H*-benzimidazolium chloride (64 mg, 0.2 mmol) and 5-[(dimethylamino)methylene]-1,3-diethyl-2-thioxodihydropyrimidine-4,6(1*H*,5*H*)-dione [5a] (56 mg, 0.22 mmol) in pyridine (2 mL) was heated for 30 min (bath temperature 120 °C). After cooling ethanol (5–7 mL) was added, the precipitate was filtered off, and washed with ethanol (90 mg, yield 91%). After recrystallization from ethanol (45 mL) the purified dye was obtained (80 mg, yield 81%, mp > 280 °C; canary brilliant lustrous needles). ^1H NMR and ^{13}C NMR ($CDCl_3$): see Tables 3a and 4a; UV/vis: see Table 1; elemental analysis calcd (%) for $C_{29}H_{26}N_4O_2S$ (494.6): C 70.42, H 5.30, N 11.33, S 6.48; found: C 70.48, H 5.27, N 11.40.

*3.3. 5-[(2E)-4-(1,3-Diphenyl-1,3-dihydro-2H-benzimidazol-2-ylidene)but-2-enylidene]-1,3-diethyl-2-thioxodihydropyrimidine-4,6(1H,5H)-dione (**8**)*

A solution of 2-methyl-1,3-diphenyl-3*H*-benzimidazolium chloride (48 mg, 0.15 mmol) and *N*-[(1*E*)-3-(1,3-diethyl-4,6-dioxo-2-thioxotetrahydropyrimidin-5(2*H*)-ylidene)prop-1-enyl]-*N*-phenylacetamide [5a] (56 mg, 0.15 mmol) was refluxed in absolute ethanol (3 mL) for 2 min at the presence of Et_3N (≈0.1 mL) and leaved overnight. The product was filtered off (yield 28 mg) and recrystallized from ethanol (35 mL) (24 mg, yield 31%, mp > 280 °C; crimson lustrous stringy needles). ^1H NMR and ^{13}C NMR ($CDCl_3$): see Tables 3a and 4a; UV/vis: see Table 1; elemental analysis calcd (%) for $C_{31}H_{28}N_4O_2S$ (520.6): C 71.51, H 5.42, N 10.76, S 6.16; found: C 71.63, H 5.38, N 10.69.

5-[(2*E*,4*E*)-6-(1,3-Diphenyl-1,3-dihydro-2*H*-benzimidazol-2-ylidene)hexa-2,4-dienylidene]-1,3-diethyl-2-thioxodihydropyrimidine-4,6(1*H*,5*H*)-dione (9). A solution of 2-methyl-1,3-diphenyl-3*H*-benzimidazolium chloride (160 mg, 0.5 mmol) and *N*-[(1*E*,3*E*)-5-(1,3-diethyl-4,6-dioxo-2-thioxotetrahydropyrimidin-5(2*H*)-ylidene)penta-1,3-dienyl]-*N*-phenylacetamide (200 mg, 0.5 mmol) in pyridine (5 mL) (with addition of Et_3N, (≈0.2 mL) was refluxed for 5 min. Then ethanol (15 mL) was added, the product was filtered off, and washed with cold ethanol (100 mg, yield 36%, pure from TLC). For the removal of traces of pyridine it was heated some minutes in ethanol (10 mL) of and filtered off (90 mg, yield 33%, mp 239–240 °C; dark-blue lustrous needles). ^1H NMR and ^{13}C NMR ($CDCl_3$): see Tables 3a and 4a; UV/vis: see Table 1; elemental analysis calcd (%) for $C_{33}H_{30}N_4O_2S$ (546.7): C 72.50, H 5.53, N 10.25, S 5.87; found: C 72.38, H 5.47, N 10.20.

3.4. 5-[(2E)-2-(1-Benzylbenzo[cd]indol-2(1H)-ylidene)ethylidene]-1,3-diethyl-2-thioxodihydropyrimidine-4,6(1H,5H)-dione (10)

A solution of 1-benzyl-2-methylbenzo[*cd*]indolium tetrafluoroborate [21] (70 mg, 0.2 mmol) and 5-[(dimethylamino)methylene]-1,3-diethyl-2-thioxodihydropyrimidine-4,6(1*H*,5*H*)-dione (54 mg, 0.21 mmol) in pyridine (2 mL) was refluxed for 2 min. The product was filtered off, washed with ethanol, and purified by chromatography (6 g SiO_2; $CHCl_3$). The solvent was removed and the residue was heated with EtOH and filtered off (67 mg, yield 72%, mp > 280 °C; dark-brown lustrous stringy needles). ^1H NMR ($CDCl_3$): $\delta = 1.322$ (t, $^3J(H,H) = 7.2$ Hz, 6H; $(CH_3)_2$), 4.589 (q, $^3J(H,H) = 7.2$ Hz, 4H; $(CH_2)_2$), 5.374 (s, 2H; CH_2), 7.086 (d, $^3J(H,H) = 7.8$ Hz, 1H), 7.27–7.38 (m, 5H; Ph), 7.496 (t, ^3J(H,H) = 7.8 Hz, 1H), 7.620 (d, ^3J(H,H) = 8.0 Hz, 1H), 7.795 (t, ^3J(H,H) = 7.9 Hz, 1H), 8.056 (d, ^{3}J(H,H) = 7.8 Hz, 1H), 8.136 (d, ^3J(H,H) = 14.2 Hz, 1H; H^{10}), 8.574 (d, ^3J(H,H) = 7.8 Hz, 1H), 9.293 (d, ^3J(H,H) = 14.2 Hz, 1H; H^{11}); UV/vis: see Table 1; elemental analysis calcd (%) for $C_{28}H_{25}N_3O_2S$ (467.6): C 71.92, H 5.39, N 8.99, S 6.68; found: C 71.80, H 5.43, N 9.04.

*3.5. 5-[(2E,4E)-4-(1-Benzylbenzo[cd]indol-2(1H)-ylidene)but-2-enylidene]-1,3-diethyl-2-thioxodihydropyrimidine-4,6(1H,5H)-dione (**11**)*

To a solution of 1-benzyl-2-methylbenzo[*cd*]indolium tetrafluoroborate (170 mg, 0.5 mmol) and *N*-[(1*E*)-3-(1,3-diethyl-4,6-dioxo-2-thioxotetrahydropyrimidin-5(2*H*)-ylidene)prop-1-enyl]-*N*-phenylacetamide (185 mg, 0.5 mmol) in MeCN (3 mL) Et_3N (≈0.2 mL) was added and the solution was refluxed for 3 min. The dye (it precipitates after some time) was filtered off, washed with a minimum of cold MeCN, and purified by column chromatography (6 g SiO_2; $CHCl_3$). After removal of the solvent the dye was heated with EtOH and filtered off (67 mg, yield 27%, mp = 269–270 °C; dark-bronze lustrous needles). ^{1}H NMR ($CDCl_3$): $\delta = 1.306$ (t, ^3J(H,H) = 6.9 Hz, 6H; $(CH_3)_2$), 4.566 (q, ^3J(H,H) = 6.9 Hz, 4H; $(CH_2)_2$), 5.223 (s, 2H; CH_2), 6.321 (d, ^3J(H,H) = 12.6 Hz, 1H, H^{10}), 6.966 (d, ^3J(H,H) = 7.8 Hz; 1H), 7.221 (d, ^3J(H,H) = 7.8 Hz, 2H), 7.27–7.39 (m, 3H), 7.482 (t, ^3J(H,H) = 7.8 Hz, 1H), 7.532 (d, ^3J(H,H) = 8.0 Hz, 1H), 7.776 (t, ^3J(H,H) = 7.9 Hz, 1H), 7.986 (t, ^3J(H,H) = 12.8 Hz, 1H; H^{12}), 7.991 (d, ^3J(H,H) = 7.8 Hz, 1H), 8.15–8.31 (m, 3H); UV/vis: see Table 1; elemental analysis calcd (%) for $C_{30}H_{27}N_3O_2S$ (493.6): C 73.00, H 5.51, N 8.51, S 6.50; found: C 72.94, H 5.48, N 8.44.

*3.6. 5-[(2E,4E,6E)-6-(1-Benzylbenzo[cd]indol-2(1H)-ylidene)hexa-2,4-dienylidene]-1,3-diethyl-2-thioxodihydropyrimidine-4,6(1H,5H)-dione (**12**)*

Synthesis is analogous to **11**. From of 1-benzyl-2-methylbenzo[*cd*]indolium tetrafluoroborate (170 mg, 0.5 mmol) and *N*-[(1*E*,3*E*)-5-(1,3-diethyl-4,6-dioxo-2-thioxotetrahydropyrimidin-5(2*H*)-ylidene)penta-1,3-dienyl]-*N*-phenylacetamide (195 mg, 0.5 mmol) dye was obtained (50 mg, yield 19%, mp = 176–177 °C; dark-bronze lustrous needles). ^{1}H NMR ($CDCl_3$), $\delta = 1.299$ (t, ^3J(H,H) = 7.2 Hz, 6H; $(CH_3)_2$), 4.550 (q, ^3J(H,H) = 7.2 Hz, 4H; $(CH_2)_2$), 5.181 (s, 2H; CH_2), 6.120 (d, ^3J(H,H) = 12.8 Hz, 1H; H^{10}), 6.557 (t^3J(H,H) = 12.8 Hz, 1H; H^{12}), 6.792 (m, 1H), 7.19–7.48 (m, 8H), 7.712 (t, ^3J(H,H) = 7.8 Hz, 1H), 7.851 (t, ^3J(H,H) = 12.8 Hz, 1H), 7.882 (d, ^3J(H,H) = 7.8 Hz, 1H), 7.963 (t, ^3J(H,H) = 13.2 Hz, 1H), 8.06–8.13 (m, 2H); UV/vis: see Table 1; elemental analysis calcd (%) for $C_{32}H_{29}N_3O_2S$ (519.7): C 73.96, H 5.62, N 8.09, S 6.17; found: C 73.85, H 5.66, N 8.04.

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