Photodynamics of Polyene−Polymethine Transformations and Spectral Fluorescent Properties of Merocyanine Dyes

Alexander A. Ishchenko,*,† Andrii V. Kulinich,*,† Stanislav L. Bondarev,‡ and Valerii N. Knyukshto‡

Institute of Organic Chemistry, National Academy of Sciences of Ukraine, Murmanska 5, 02094 Kyiv, Ukraine, and Institute of Molecular and Atomic Physics, National Academy of Sciences of Belarus, F. Skaryna Avenue 70, 220072 Minsk, Belarus

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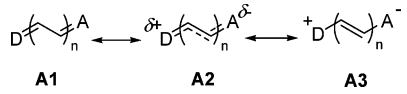
Absorption and fluorescence spectrum band moments (center of gravity, width, asymmetry, excess, and fine structure) have been determined in a wide range of solvents with different polarities for inverse solvatochromic di-, tetra-, and hexamethinemerocyanines derived from 1,3-diphenyl-2,3-dihydro-1*H*-benzimidazole. Juxtaposition of the quantum-chemically calculated (by the semiempirical AM1 method) charges, bond orders, and dipole moments of the merocyanine molecules in the ground and excited singlet states with the experimentally observed spectral fluorescent characteristics suggests that the molecular electronic structure in the two states can vary from a nonpolar polyene via a polymethine to a charge-separated polyene, depending on the length of the polymethine chain and the medium polarity. As shown, solvatofluorochromism gives rise to smaller spectral band shifts than those of solvatochromism. This effect is attributable to weaker intermolecular solute−solvent interactions in the fluorescent excited state due to the more equalized charges as compared to those of the ground state. A lack of mirror symmetry of the absorption and fluorescence spectra has been revealed for di- and tetramethinemerocyanines (broadened fluorescence bands) as well as for hexamethinemerocyanines (narrowed fluorescence bands); the two cases are accounted for by the different behavior of vibronic and intermolecular interactions in the course of absorption and emission. As found for merocyanines, the electronic structure of their fluorescent state approaches the cyanine limit and the ground state becomes increasingly polyene-like with lengthening of the polymethine chain. A close vicinity of the excited state to the cyanine limit causes a dramatic increase in fluorescence quantum yields and a decrease in Stokes shifts observed for higher merocyanine vinylogues.

Introduction

Merocyanine dyes enable a convenient investigation of polyene−polymethine transformations in their chromophore because they can exist in any of the ideal electronic states represented by the resonance structures **A1**−**A3** (Scheme 1) or in an intermediate state, depending on their constitution and the nature of the solvent.[1−3]

For a weak donor D and/or weak acceptor A, the ground state of the merocyanine is close to that of a neutral ideal polyene, with zero atomic π-charges and a maximum π-bond order alternation in the conjugated chromophore, as in structure **A1**. As the donor strength of D and/or the acceptor strength of A increase, the charge separation in the merocyanine molecule becomes more pronounced due to the electron density shift from D to A through the system of conjugated bonds. As a consequence, the bond order increases for single bonds and decreases for double bonds, tending to a value of 1.5 for all bonds between D and A. Such a state referred to as an ideal polymethine state or the cyanine limit is described by structure **A2**, a linear combination of equally weighted **A1** and **A3**. A further increase in the donor/acceptor properties of D and A will lead to an enhanced charge separation and interchanged single and double bonds relative to structure **A1**. Eventually, a polyene structure **A3** arises which is characterized by a maximum separation of the opposite π-charges on the two end groups.

SCHEME 1: Resonance Structures of Merocyanines Corresponding to Their Ideal Electronic States (D and A Are Electron-Donor and Electron-Acceptor Groups, Respectively)



A1 **A2** **A3**

In contrast to structures **A1** and **A3**, the first electronic transition in **A2** (an ideal polymethine) is accompanied by a minimum change in bond orders, only in the range from 1.5 to 1 or 2. Therefore, vibronic interactions (VI) in a polymethine structure are weaker than those in polyenes of both types,[1,4] which results in a narrowing of the spectral bands and an enhancement of their peak intensities (extinctions). Bond order equalization in the polymethine chain of structure **A2** also gives rise to bathochromic shifts of the absorption and fluorescence bands as compared to that of structures **A1** and **A3**.[1]

The polyene−polymethine transformations have been studied hitherto only in the S_0 state.[1−3] The present work addresses such effects in the low-lying fluorescent singlet S_1^f state and in the $S_1^f \leftarrow S_0$ transitions.

* To whom correspondence should be addressed. E-mail: alexish@i.com.ua (A.A.I.); andrii.kulinich@gmail.com (A.V.K.).

† Institute of Organic Chemistry. Tel: (+38) 044-499-4604. Fax: (+38) 044-573-2643.

‡ Institute of Molecular and Atomic Physics.

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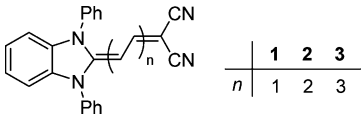
SCHEME 2: Molecular Structures of the Merocyanines Investigated



Objects and Methods of Study

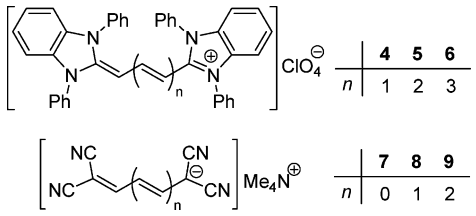
In view of the challenge formulated above, our study involved positively and negatively solvatochromic merocyanines as well as the cases of reverse solvatochromism, so as to cover a wide range of the electronic structures between the cases of **A1**, **A2**, and **A3**, each representing an ideal electronic state. Most of the known merocyanines exhibit positive solvatochromism.[5,6] Such regularity originates from the fact that for a bipolar (charge-separated) structure to be formed, additional energy is required for the charge separation. Since this energy can be provided by light quanta, the charge-separated structure is more readily realized in the excited state. The closer the electronic structure of a merocyanine to the **A1** type, the more difficult it is to transform it into the **A2** and all of the **A3** types in the S_0 state. Transformations of this kind are more plausible for merocyanines bearing strong electron-donating heterocyclic groups, such as the 1,3-diphenylbenzimidazolyl-2 residue in recently obtained dyes **1**−**3** (Scheme 2).[7]

The long-wavelength absorption and fluorescence band shapes of dyes **1**−**3** were analyzed by the method of moments.[8] As a result, a number of characteristics—the band position (M^{-1}), the intensity (f), and the shape (σ, γ_1, γ_2, F)—were derived in addition to the commonly used wavelength at the band maximum (λ_{max}) and molar extinction (ϵ).

The quantity M^{-1} is averaged over all of the vibronic transitions and represents the spectral band center wavelength or the center of gravity of the band in the wavenumber scale, $\tilde{\nu} = 10^7/M^{-1}$. Unlike the quantity λ_{max}, it permits differently shaped curves to be compared correctly and, moreover, is determined an order of magnitude more accurately.[4] The integral intensity (the oscillator strength f) has the same advantage over the peak intensity (extinction ϵ). The quantity σ characterizes a deviation of spectral band points from the band center of gravity $\tilde{\nu}$. It affords, therefore, a quantitative comparison of bandwidths irrespective of their shapes, thus having a special convenience relative to the normally used band half-width (the full width of a spectral band at a height equal to half of the height at the band maximum). Additional evidence about band shapes is provided by the coefficients of asymmetry γ_1, excess γ_2, and fine structure F, which quantitatively estimate the band symmetry, slope (steepness), and level of structure, respectively. In the case when a band maximum shifts only slightly, much more information can be derived from the analysis of spectral band shapes. Band shapes and, first of all, bandwidths give an insight into the changes in bond orders and electron density distribution occurring in the molecule upon excitation (or fluorescence); one can thus judge the respective trends in VI and intermolecular interactions (IMI).[4] The analysis of the bandwidths conveniently complements the use of quantities such as λ_{max} and M^{-1}, which reflect only the relative energies of the equilibrium ground state S_0, the Franck−Condon first excited singlet state S_1^{FC}, the fluorescent (equilibrium) first excited singlet state S_1^f, and the Franck−Condon ground state S_0^{FC}.

The deviations which quantify the dye electronic asymmetry[4,5] were calculated from the positions of band maxima (D_λ) and centers (D_M), with symmetric cationic (**4**−**6**) (Scheme 3) and anionic polymethines (**7**−**9**) involved as parent dyes.[4,7] Due to steric hindrances, dye **7** has a nonplanar structure, which causes additional bathochromic shifts of its spectral bands; hence, the deviation values calculated with this parent dye are somewhat overestimated.

SCHEME 3: Cationic (4−6) and Anionic (7−9) Parent Dyes



The solvatochromism of organic dyes originates from nonspecific (universal) and specific solute−solvent IMI.[4,6] The former are governed by the refraction index n_D and the relative permittivity ϵ_r (macroscopic medium parameters), whereas the latter are determined by the nucleophilicity B and the electrophilicity E (molecular-microscopic medium parameters).[4]

In addition, some integral characteristics of dye polarity are applied.[6] However, they cannot adequately represent all of the above-mentioned IMI types since reference compounds have a different sensitivity toward certain solvent parameters. As an example, the betaine dyes on which Dimroth and Reichardt based their solvent polarity scale of the integral empirical parameter E_T most readily undergo electrophilic solvation (controlled by the parameter E) and even tend to form hydrogen bonds.[6] As a result, the integral quantity E_T does not depict the medium nucleophilicity.[9,10]

Nonspecific solvation resulting from the dipolar, dispersion, and some other less significant forces are mainly contributed by dispersion interactions proportional to the quantity n_D^2.[4,6] As the excited state is more polarizable than the ground state, it lowers to a larger degree with enhanced dispersion interactions (increasing n_D) of the solvent, which leads absorption and fluorescence bands to shift bathochromically. On the contrary, the enhancement of specific electrostatic interactions, that is, nucleophilic or electrophilic solvation, can result both in bathochromic and hypsochromic shifts because it more strongly lowers the energy of the state with a larger dipole moment. As far as merocyanines are concerned, the excited state can be more polar than the ground state and vice versa.[6]

To unambiguously determine the type of solvatochromism for merocyanines, it is necessary to compare the spectral band shifts in pairs of solvents with close values of n_D and substantially different ϵ_r, B, and E. By this criterion, we chose dichloromethane and dimethylformamide (DMF); the latter is much more dipolar and nucleophilic, whereas the values of n_D and E are rather close for the two solvents. In addition, some other low-polar (toluene and chloroform) and high-polar media (ethanol, acetonitrile, dimethylsulfoxide (DMSO), and formamide) were involved. The basic parameters of polarity and viscosity (η) for all solvents used are presented in Table 1.

The closeness of the electronic structure of the chromophore concerned to one of the limiting structures **A1**, **A2**, or **A3** can be judged by the degree of alternation of bond lengths (or orders) and atomic charges. To quantify the electron density distribution over bonds, the parameters of bond length alternation (BLA) or bond order alternation (BOA) are widely used.[3,11−14] They are usually specified as the difference between the average lengths (or π-orders) of the formal single and double bonds in the polymethine chain. The parameter BLA is defined so that it is positive for structures like **A1** and those between **A1** and

TABLE 1: The Polarity and Viscosity Parameters of the Eight Solvents Used (taken from Refs 4 and 6)

solvent	n_D^{20}	ϵ_r	B cm^{-1}	E	E_T kJ/mol	E_T^N	$\eta \cdot 10^3$ mpoise
toluene	1.4961	2.37	58	1.3	142.4	0.099	5.52
$CHCl_3$	1.4459	4.7	14	3.3	163.7	0.259	5.42
CH_2Cl_2	1.4242	8.9	23	2.7	170.4	0.309	3.9
ethanol	1.3611	24.3	235	11.6	217.3	0.654	10.8
MeCN	1.3441	36.2	160	5.2	190.9	0.460	3.45
DMF	1.4303	36.7	291	2.6	183.4	0.404	7.96
DMSO	1.4770	49.0	362	3.2	188.8	0.444	19.8
$HCONH_2$	1.4475	110.0	270	14.5	237.0	0.799	33.0

A2 and takes negative values for **A3** and in the interval of **A2**−**A3**.[11] Accordingly, the parameter BOA has the opposite sign from that of BLA throughout the structure space. Both BLA and BOA reduce to zero for the structures of the **A2** type.[11,12]

Bond order alternation in the chromophore dictates the trends in vinylene shifts, deviations, band shapes, and first of all, their widths. The stronger the BOA, the smaller the vinylene shifts and the larger are deviations and bandwidths.

The total value of the excitation-induced change in bond order alternation was characterized by the quadratic change in bond orders upon excitation, δ, which was calculated according to

$$\delta = \sqrt{\sum_{i=1}^{m} (P^* - P)_i^2}$$

(m is the number of bonds and $(P^* - P)_i$ denotes the difference in the ith bond order between the S_1^{FC} and S_0 states). This quantity is proportional to the change in the equilibrium internuclear separations occurring upon excitation, and it serves as a convenient measure to quantify the trends in VI in polymethine dye molecules.[4]

To estimate the charge alternation in the chromophore, we involved the parameter Δq_Σ

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

where q_i and q_{i+1} are the charges on neighboring atoms.

The structural and electronic parameters of dye molecules were found using the semiempirical AM1 method with a standard parameter set for a vacuum in the restricted Hartree−Fock approximation.[15] The molecular geometry was optimized by the Polak−Ribiere algorithm until the root-mean-square energy gradient was 0.001 kcal/(Å·mol).

Experimental Section

Merocyanines **1**−**3** were purified by multiple chromatographies. The dye purity was controlled by thin-layer chromatography on Silufol UV-254 with the eluent dichloromethane. The solvents were purified by known procedures.[16] The solutions of merocyanines were not degassed because the fluorescent characteristics of the dye solutions under study were found to remain unchanged upon degassing.

Band moments in dye electronic spectra were determined by the previously reported method.[8] Absorption spectra were recorded on a Shimadzu UV-3100 spectrophotometer with the 1 cm path length cuvettes. Fluorescence spectra were measured on a high-aperture optical system described in ref 17. Absorption and fluorescence band moments were calculated in the respective coordinates $I_a(\tilde{\nu})/\tilde{\nu}$ and $I_f(\tilde{\nu})/\tilde{\nu}^4$ (I_a and I_f are absorption and fluorescence intensities, respectively, and $\tilde{\nu}$ is the wavenumber), which provide the most obvious obedience to the law of the mirror symmetry.[4]

Fluorescence quantum yields Φ_f of merocyanines were measured with reference to the Φ_f values of the cresyl violet dye in methanol (65%) and rhodamine 6G in ethanol (95%).[18,19] Solution optical densities at the excitation wavelength were no more than 0.2. In the Φ_f determination, a correction was introduced to make allowance for the change in the solvent refractive index.

^{1}H NMR spectra were recorded on a Varian Mercury-400 instrument at 400.39 MHz with TMS as the internal standard.

Spectroscopic and Computational Results

The parameters of the absorption and fluorescence bands of merocyanines **1**−**3** were derived from the corresponding spectra. The values of M^{-1}, f, σ, γ_1, γ_2, and F as well as λ_{max} and ϵ are listed in Tables 2 and 3 (the superscripts a and f refer to absorption and fluorescence parameters, respectively).

Starting from the computational data for the compounds under study, we obtained the parameters BLA, BOA, δ, Δq_Σ, and μ (dipole moments) listed in Table 4. Likewise, the values of q (π-atomic charges) within the chromophore of dye **3** were found (see Table 5).

Discussion

Electronic Absorption Spectra. The benzimidazole nucleus exhibits high electron-donor ability.[7] Thus, one would expect that the S_0 state of merocyanine molecules **1**−**3** is dipolar enough to approach the interval of **A2**−**A3** in an appropriately chosen medium. As these dyes are insoluble in *n*-hexane, toluene was used as a low-polar solvent, though it is very prone to nucleophilic solvation (see Table 1). The first two vinylene shifts in the absorption spectra of dyes **1**−**3** amount to $\Delta\lambda = 98$ and 102 nm in terms of band maxima or to 95.5 and 91.4 nm in terms of band centers (see Table 2 and Figure 1), that is, they are close to the value of $\lambda = 100$ nm typical for symmetric polymethines.[4] It follows from here that their electronic structure in toluene is very much like that of an ideal polymethine, that is, the **A2** type.

When passing from toluene to the somewhat more polar chloroform, a band narrowing and a bathochromic band shift both in terms of λ_{max}^a and M_a^{-1} is observed for dyes **2** and **3**, despite a smaller n_D value for the latter solvent (see Table 2 and Figure 2). Hence, the polarity of the medium dominates over its polarizability in this instance. For dye **1**, these factors cancel each other so that the replacement of toluene by chloroform causes no influence on the positions of λ_{max}^a and M_a^{-1}. At the same time, dyes **2** and **3** exhibit positive solvatochromism in the two solvents. This inference is consistent with a significant increase in the quantum-chemically calculated molecular dipole moments of these dyes, which occurs in going from the S_0 to the S_1^{FC} state (see the corresponding values of μ and μ^*, the ground- and the excited-state dipole moments, in Table 4). Larger differences between μ and μ^* for dyes **1**−**3**, as compared to those of the corresponding parent symmetric dyes **4**−**6** and **7**−**9**, lead to a more pronounced positive solvatochromism of the former dye series. The bathochromic shift and the narrowing of absorption bands observed for dyes **1**−**3** in going from toluene to chloroform suggest that the contribution of **A2** increases at the expense of **A1** as the solvent polarity rises. Accordingly, both vinylene shifts are larger in chloroform than those in toluene.

TABLE 2: The Parameters of the Long-Wavelength Absorption Bands of Merocyanines 1−3 in Solvents of Varied Polarity

dye	solvent	λ^a_{max}/nm	D^a_λ/nm	M_a^{-1}/nm	D^a_M/nm	$\epsilon \cdot 10^{-4}$	f	σ^a/cm^{-1}	γ^a_1	γ^a_2	$F^a \cdot 10^2$
1	toluene	435		423.6		6.94	0.66	1095	1.01	1.7	3.6
	$CHCl_3$	435		423.6		7.58	0.71	1065	0.99	1.6	3.6
	CH_2Cl_2	433	4.5	421.6	5.2	7.54	0.71	1070	0.98	1.6	3.5
	EtOH	428	4.5	416.0	6.7	8.05	0.80	1104	0.99	1.6	3.5
	MeCN	426		414.4		6.94	0.70	1110	0.98	1.6	3.4
	DMF	430	3.3	417.7	7.0	7.37	0.73	1104	1.00	1.7	3.5
	DMSO	430		417.8		7.20	0.72	1105	0.97	1.6	3.4
	$HCONH_2$	428		415.4		6.53	0.71	1195	1.03	1.8	3.5
2	toluene	533		519.1		13.98	1.08	973	1.21	2.5	4.9
	$CHCl_3$	535		523.6		16.12	1.08	875	1.32	3.2	5.6
	CH_2Cl_2	532	3.5	520.6	−0.3	15.83	1.08	894	1.33	3.3	5.8
	EtOH	524	4.5	510.7	4.1	14.84	1.13	979	1.34	3.2	5.7
	MeCN	521		509.0		13.71	1.06	962	1.25	2.8	4.9
	DMF	526	5.0	512.6	2.5	12.90	1.02	999	1.29	3.0	5.4
	DMSO	526		512.7		12.67	1.03	1020	1.30	3.0	5.3
	$HCONH_2$	523		505.6		10.46	0.98	1180	1.40	3.4	6.4
3	toluene	635		610.5		13.10	1.10	1080	1.17	2.4	4.9
	$CHCl_3$	642		628.9		22.31	1.30	823	1.46	3.9	6.2
	CH_2Cl_2	638	1.5	625.2	−0.5	21.99	1.31	825	1.43	3.8	6.0
	EtOH	628	2.5	609.8	2.7	16.94	1.25	1034	1.50	3.9	6.8
	MeCN	624		605.8		15.95	1.19	1028	1.42	3.7	6.2
	DMF	630	−1.0	611.4	−0.4	15.44	1.15	1023	1.48	3.8	6.8
	DMSO	631		608.9		14.37	1.17	1125	1.57	4.2	7.9
	$HCONH_2$	621		586.1		10.12	1.13	1530	−1.65	4.5	9.0

TABLE 3: The Parameters of the Long-Wavelength Fluorescence Bands of Merocyanines 1−3 in Solvents of Varied Polarity

dye	solvent	λ^f_{max} nm	D^f_λ nm	Φ_f %	M_f^{-1} nm	D^f_M nm	σ^f cm^{-1}	γ^f_1	γ^f_2	$F^f \cdot 10^2$	SS_λ cm^{-1}	SS_M cm^{-1}
1	toluene	471	−	0.19	504.9	−	1880	−1.01	2.0	4.9	1760	3800
	$CHCl_3$	473	−		501.6	−	1700	−1.22	2.7	5.7	1845	3670
	CH_2Cl_2	473	16.5	0.25	499.7	14.2	1700	−1.22	2.7	5.8	1955	3710
	EtOH	469	12	0.28	493.7	17.5	1710	−1.20	2.7	5.6	2045	3780
	MeCN	464	−		491.1	−	1750	−1.16	2.7	5.7	1925	3780
	DMF	471	13	0.33	495.0	20.8	1720	−1.14	2.6	5.2	2025	3740
	DMSO	470	−	0.47	492.4	−	1715	−1.13	2.5	4.3	1980	3630
	$HCONH_2$	469	−		496.5	−	1770	−1.07	2.4	4.3	2040	3930
2	toluene	566	−	0.9	592.8	−	1130	−1.11	2.2	4.6	1095	2395
	$CHCl_3$	566	−		585.7	−	971	−1.24	2.8	5.2	1025	2025
	CH_2Cl_2	562	5.5	4.2	581.0	8.3	975	−1.23	2.8	5.1	1005	1995
	EtOH	555	8	3.4	574.1	9.6	990	−1.18	2.6	4.8	1065	2160
	MeCN	554	−		572.9		995	−1.14	2.4	4.5	1145	2190
	DMF	560	7	4.3	580.1	6.5	1000	−1.16	2.5	4.4	1155	2270
	DMSO	561	−	6.5	580.7	−	995	−1.16	2.5	4.4	1185	2285
	$HCONH_2$	560	−		581.7	−	995	−1.17	2.4	4.5	1260	2585
3	toluene	669	−	2.5	703.9	−	1025	−1.30	2.9	7.0	800	2175
	$CHCl_3$	671	−		690.7	−	750	−1.32	3.2	5.8	675	1422
	CH_2Cl_2	670	2.5	33	689.1	2.4	755	−1.33	3.1	5.7	750	1485
	EtOH	665	1.5	30	682.5	3.2	770	−1.30	3.1	5.4	885	1750
	MeCN	656	−	26	673.1	−	775	−1.23	2.7	5.2	780	1650
	DMF	667	2	43	681.7	6.7	770	−1.25	2.9	5.2	880	1685
	DMSO	669	−	56	687.8	−	760	−1.17	2.6	4.6	900	1885
	$HCONH_2$	664	−		683.1	−	790	−1.24	2.8	5.0	1040	2420

TABLE 4: Some AM1-Calculated Parameters of Dyes 1−9 and Cyclooctatetraene 10 for the S_0 and S_1^{FC} States (See Unstarred and Starred Symbols, Respectively)

	1	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**
BLA	0.059	0.074	0.081	−0.023	−0.015	−0.012	0	0.009	0.013	0.114
BOA	−0.513	−0.603	−0.647	0.135	0.08	0.059	0	−0.085	−0.111	−0.881
BOA*	0.212	0.101	0.015	0.041	0.04	0.048	0	0.101	0.056	0.202
δ	0.683	0.833	0.93	0.243	0.181	0.132	0.387	0.31	0.276	2.02
μ/D	7.397	7.967	8.25	0.091	1.081	1.668	1.89	2.693	3.2	0
μ*/D	8.683	11.28	13.55	1.023	0.873	0.672	0.725	1.122	1.317	0
Δq_Σ	0.888	1.121	1.262	3.038	3.804	4.492	0.73	1.536	2.25	0
Δq^*_Σ	0.461	0.491	0.638	0.812	1.55	2.004	0.872	1.018	1.024	0

As calculated, dyes **1**−**3** have positive BLA and negative BOA values, with their absolute magnitudes smaller than those for cyclooctatetraene **10** used as a model ideal nonpolar polyene (see Table 4).[11,12] It can thus be concluded that the electronic structure of the S_0 state for merocyanines **1**−**3** in a vacuum falls into the range of **A1**−**A2**, being notably shifted toward **A2**. This statement is also in conformity with the fact that the values of Δq_Σ for dyes **1**−**3** are much closer to those for the parent symmetric dyes **4**−**6** and **7**−**9** than to the corresponding values for cyclooctatetraene **10** (see Table 4).

As the polymethine chain of dyes **1**−**3** is lengthened, the difference $\mu^* - \mu$ increases, and hence, the bathochromic band

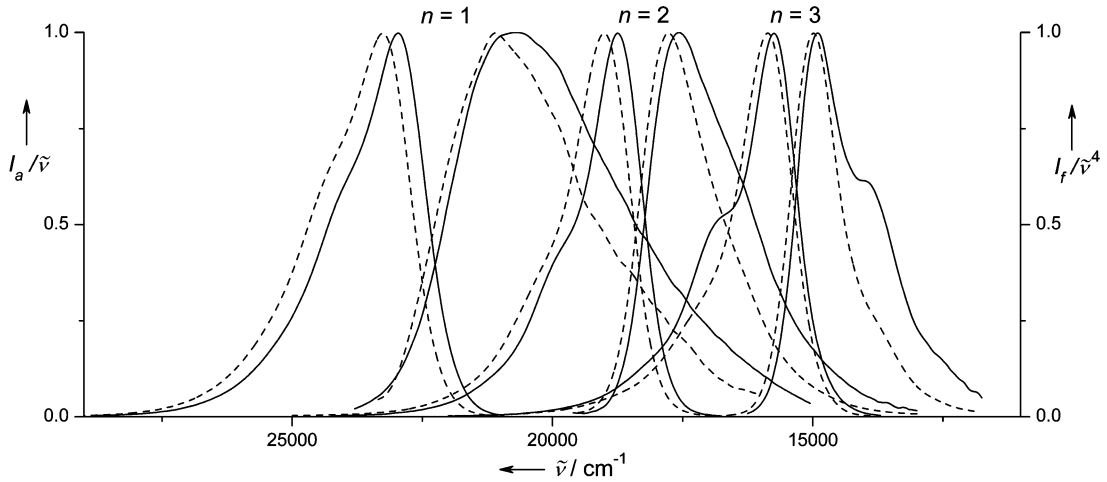


Figure 1. Normalized absorption and fluorescence spectra of dyes **1**−**3** measured in toluene (solid line) and in DMF (dashed line).

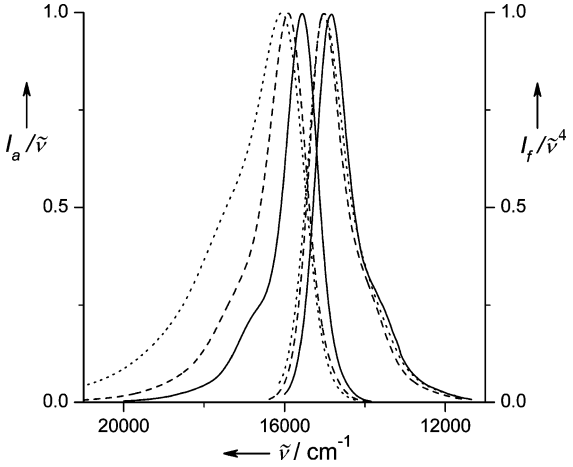


Figure 2. Normalized absorption and fluorescence spectra of merocyanine **3**, measured in chloroform (solid line), ethanol (dashed line), and formamide (dotted line).

shifts occurring in passing from toluene to chloroform should rise, which is indeed the case (if calculated from the positions of band maxima and centers, they amount to $\Delta\tilde{\nu} = 0$, 70, 172 and 0, 166, 479 cm^{-1} for dyes **1**, **2**, **3**, respectively). Thus, the distinction between the electronic structures of dyes placed into these media grows with lengthening of the polymethine chain. Indeed, it is observed that for dyes **1**−**3**, dissolved in toluene, that the second vinylene shift in terms of λ^{a}_{max} ($\Delta\lambda = 102$ nm) is larger than the first one ($\Delta\lambda = 98$ nm), and the opposite is true in terms of M_a^{-1} ($\Delta\lambda = 91.4$ and 95.5 nm, respectively), whereas the second vinylene shift in chloroform solutions exceeds the first one both in terms of λ^{a}_{max} ($\Delta\lambda = 107$ and 100 nm) and M_a^{-1} ($\Delta\lambda = 105.3$ and 100 nm). For toluene solutions of the dye series **1**−**3**, lengthening of the polymethine chain is accompanied by a band narrowing in going from **1** to **2** and broadening in going from **2** to **3**. On the contrary, chloroform solutions exhibit values of σ^a monotonically decreasing from **1** to **3**, as is the case in the series of symmetric cationic dyes **4**−**6** and anionic dyes **7**−**9**.[4] Again, similar to the parent series **4**−**6** and **7**−**9**, the narrowing of the bands in the series **1**−**3** is accompanied by an increase in band integral and peak intensities as well as in their coefficients of asymmetry, excess, and fine structure (see Table 2), which is indicative of VI weakening as the dye structure approaches the **A2** type.

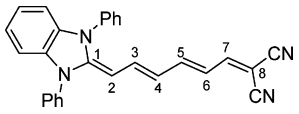
Such trends in the vinylene shifts of absorption maxima and in the bandwidths of dyes **1**−**3** in toluene and chloroform suggest essentially different effects of the chromophore length on the polyene−polymethine relationship, depending on the nature of the solvent. Lengthening of the polymethine chain leads to an increased contribution of structure **A1** to the S_0 state for low-polar media like toluene (which is consistent with an increase in BLA and BOA, as shown in Table 4). By contrast, the S_0 state of the dye series in chloroform is increasingly determined by structure **A2** in going from shorter to longer vinylogues (in agreement with the fact that the molecular dipole moment rises together with the chromophore length).

It is indicative that the bandwidth for dye **3** in chloroform is only 828 cm^{-1}, that is, even narrower than that for the corresponding symmetric cationic dye **6** (1080 cm^{-1}) and the anionic dye **9** (886 cm^{-1}).[4] In addition, such a narrow band is associated with an extremely large molar extinction coefficient ($\epsilon \times 10^{-4} = 22.31$ L·mol^{-1}·cm^{-1} at $f = 1.30$), which exceeds those of the parent symmetric dyes. These characteristic spectral features are only possible if the ideal polymethine state with completely equalized bonds is realized. Indeed, merocyanine **3** in $CDCl_3$ demonstrates the same value of vicinal spin−spin coupling constants ($^3J_{HH} = 12.8$ Hz) for all of the H atoms in the polymethine chain.[20] Hence, it follows that this dye, if dissolved in chloroform, has a ground-state electronic structure very close (or even identical) to that of the **A2** type. It is noteworthy that the cyanine limit is hard to access even in the case of symmetric polymethines because any deviation of the electron-donor (and electron-acceptor) ability of the two heterocyclic nuclei from the middle value results in a bond order alternation extending from the dye end groups to the chain center.[4]

The quantum-chemically calculated values of BLA and BOA for merocyanines **1**−**3** in a vacuum imply that lengthening of the polymethine chain causes an enhanced bond order alternation in the S_0 state in terms of all alternation parameters (see Table 4). Contrastingly, BOA* for the S_1^{FC} state decreases with rising *n*, as seen from Table 4. Their absolute magnitudes are smaller than those for the ground state, thus pointing to a weakening of bond alternation upon the Franck−Condon excitation. The opposite sign of BOA* relative to BOA is indicative of the interchanged positions of single and double bonds in the S_1^{FC} state as compared to that in the ground state.

It is evident from Table 4 that the δ values for merocyanines **1**−**3** are intermediate between those of polyene **10** and symmetric parent dyes (i.e., the cationic **4**−**6** and anionic **7**−**9**), being much closer to the latter. This result conforms well to the experimentally observed decrease in absorption bandwidths, which follows the order nonpolar/low-polar polyene **A1** >

TABLE 5: The AM1-Calculated π-Atomic Charges within the Chromophore of Dye 3 in the S_0 (q) and S_1^{FC} (q^*) States and the Corresponding Difference (Δq)



	C-1	C-2	C-3	C-4	C-5	C-6	C-7	C-8
q	0.125	−0.236	−0.039	−0.197	−0.037	−0.205	0.006	−0.001
q^*	0.001	−0.082	−0.19	−0.046	−0.181	−0.105	−0.076	−0.013
Δq	−0.124	0.154	−0.151	0.151	−0.144	0.100	−0.082	−0.012

merocyanine in the range between **A1** and **A2** > symmetric polymethine **A2**. In contrast to symmetric dyes **4**−**6** and **7**−**9**, the δ value for merocyanines **1**−**3** rises with lengthening of the polymethine chain. One would therefore expect a VI enhancement in the transition $S_1^{FC} \leftarrow S_0$ and hence an absorption band broadening as the polymethine chain becomes longer in the merocyanine series **1**−**3** in vacuum. However, even in toluene, which is closer to vacuum among the solvents involved, the band broadening is observed only when n increases from 2 to 3 (see Table 2 and Figure 1). Thus, a low-polar solvent also provokes substantial reduction of bond order alternation compared to a vacuum.

It is thus clear that despite the high electron-donor ability of the benzimidazole residue, significant bond order equalization in the merocyanines concerned can be realized only by action of a solvent. One can make the same inference correlating the ^{1}H and ^{13}C NMR chemical shifts of the atoms in the polymethine chain with the calculated atomic π-charges in a vacuum. As shown previously,[20] the best insight into the electronic structure of merocyanines is offered by the ^{13}C NMR signals from the carbon atoms of the end groups to which the polymethine chain is bound (the atoms C-1 and C-8 in the formula referring to Table 5). For dyes **1**−**3** in $CDCl_3$, the chemical shifts of these C atoms are nearly independent of the chain length, being much the same as that in the parent symmetric dyes.[20] These data suggest that chloroform makes the electronic structure of the dyes in question very close to that of the ideal polymethine **A2**. However, quantum-chemical calculations provide quite a different picture of the electron density distribution in their molecules. The calculated π-charges on the two mentioned terminal C atoms depend significantly on the chain length. For dyes **1**, **2**, and **3**, the respective differences of the two charges are equal to 0.224, 0.159, and 0.126. It is just such a result that is anticipated for a solvent-free situation which implies a larger contribution of the low-polar polyene structure **A1** and its more pronounced increase with lengthening of the polymethine chain as compared to that of the dyes dissolved in toluene.

When passing from chloroform to the more polar dichloromethane, hypsochromic shifts of the band maxima and central positions are observed for the whole series **1**−**3** (see Table 2). However, this is not a sufficient reason to assume negative solvatochromism of these dyes in the solvent pair of chloroform−dichloromethane (as opposed to how it was inferred that the pair toluene−chloroform provides positive solvatochromism) because going from chloroform to dichloromethane is accompanied by a decrease in n_D, which itself causes an independent hypsochromic band shift. Nevertheless, the inference about weak negative solvatochromism is supported by the fact that both the first and the second vinylene shifts of dyes **1**−**3** are somewhat smaller in dichloromethane than those in chloroform (see Table 2).

The values σ^a demonstrate that dyes **1**−**3** have somewhat broader absorption bands and smaller extinctions in dichloromethane than those in chloroform (see Table 2). Since bandwidths and intensities are practically insensitive to n_D and depend mainly on BOA (responsible for the VI magnitude), it is apparent that the ground-state electronic structure of the dyes deviates from that of the ideal polymethine **A2** toward the charge-separated polyene **A3**. At the same time, this deviation is only slightly pronounced, as evidenced by the band narrowing and the increase in ϵ, f, γ_1^a, γ_2^a, and F^a observed in going from shorter to longer vinylogues throughout the whole series **1**−**3** in dichloromethane (just as in chloroform).

If high-polar solvents are used instead of dichloromethane, the absorption bands of all dyes in the series **1**−**3** are shifted hypsochromically, and the vinylene shifts are reduced, that is, a typical negative solvatochromism is manifested (see Table 2 and Figure 2). In parallel, a band broadening occurs, which corroborates the deviation of the electronic structure from the **A2** toward **A3** type. The offset from **A2** in the ground state remains, however, rather slight, judging from moderate deviations D_λ^a and D_M^a both in aprotic (DMF) and protic solvents (ethanol), the vinylene shifts are close to $\Delta\lambda = 100$ nm (or somewhat smaller in terms of the band center positions), not very large values of σ^a in almost all high-polar solvents (except formamide), and the absorption band shapes are similar to those of symmetric polymethines.

Thus, the structure of the charge-separated polyene **A3** is far from predominating even in such polar solvents as DMF and DMSO. Only formamide, which is distinguished for its extremely high values of both macroscopic (ϵ_r) and microscopic (B and E) polarity parameters, affords a very close approach of merocyanine **3** to structure **A3** and hence the maximum separation of opposite charges in the chromophore. As a result, negative solvatochromic band shifts are observed in passing from other polar solvents to formamide, the first and the second vinylene shifts decrease to $\Delta\lambda = 90.2$ and 80.5 nm (in terms of M_a^{-1}), the absorption band is broadened dramatically, and its peak intensity falls off (see Table 2 and Figure 2).

Interestingly, protic (ethanol) and aprotic (acetonitrile, DMF, and DMSO) polar solvents cause a very similar influence on the spectral characteristics of merocyanines **1**−**3** as shown in Table 2. Thus, hydrogen bonding plays no significant role in the solvation of the dyes under study.

The negative solvatochromism of dyes **1**−**3** in going from chloroform to high-polar solvents is also accompanied by an interchange of single and double bonds in their molecules relative to structure **A1** so that their positions become as those in structure **A3**. The vicinal spin−spin coupling constants in ^{1}H NMR spectra alternate accordingly for the H atoms of the chain; they amount to $^3J_{HH} = 14.4$, 12.0, 14.2, 12.2, and 13.2 Hz for dye **3** in DMSO-d_6 (cf. their equalized value of 12.8 Hz in $CDCl_3$).

The negative solvatochromic behavior of the dyes concerned, which is observed upon the replacement of chloroform by more

polar solvents, is indicative of a larger dipole moment in the ground than in the excited state, as opposed to the situation in a vacuum or low-polar solvents. Therefore, polar solute−solvent IMI in the S_0 state are enhanced as compared to S_1^{FC}. Since the magnitudes of negative solvatochromic shifts increase when passing from shorter to longer vinylogues, it is evident that the difference between the values of μ and μ^* rises with lengthening of the polymethine chain.

Fluorescence Spectra. In going from toluene to chloroform as the solvent for merocyanines **1**−**3**, bathochromic shifts of the fluorescence maxima λ_{max}^f are observed (as in absorption spectra), thus pointing to the positive solvatofluorochromism in this pair of solvents (see Table 3). Consequently, chloroform influences the S_1^f state of the dyes in much the same manner as their S_0 state, that is, it makes the electronic structure closer to the ideal polymethine type. The substantially reduced σ^f values and the increased coefficients γ_1^f, γ_2^f, and F^f in chloroform as opposed to toluene (see Table 3) also evidence the approach of the dyes to structure **A2** in the former solvent. However, one would expect the opposite from the comparison of the M_f^{-1} values in the two solvents as the fluorescence bands are shifted to shorter wavelengths in chloroform (see Table 3). This apparent contradiction can be explained by the fact that the hypsochromic fluorescence shifts in terms of M_f^{-1} are mainly caused by a significant narrowing of the fluorescence bands in chloroform.

In toluene, the first vinylene shift of the fluorescence band in terms of the band maximum positions ($\Delta\lambda = 95$ nm) is a little smaller than that of the absorption band ($\Delta\lambda = 98$ nm), whereas the situation is opposite for the second vinylene shifts ($\Delta\lambda = 103$ and 102 nm, respectively). As the polymethine chain is lengthened, fluorescence bands narrow monotonically, unlike the behavior of absorption bandwidths in toluene (see Tables 2 and 3 and Figure 1). Moreover, it has been found that $\sigma^a \ll \sigma^f$ for dye **1**, $\sigma^a < \sigma^f$ for dye **2**, and $\sigma^a > \sigma^f$ for dye **3**. It is thus clear that the S_1^f state of dyes **1**−**3** in toluene approaches the ideal polymethine structure **A2** rather than moving away from it with the lengthening of the polymethine chain, as opposed to the S_0 state.

Passing from chloroform to dichloromethane as the solvent is accompanied by negligible changes in the fluorescence bandwidths and shapes for merocyanines **1**−**3**. In parallel, bands are shifted hypsochromically, just as in the absorption spectra, that is, the solvatofluorochromism apparently changes its sign. However, this rather slight effect may also be attributable to a smaller n_D value for dichloromethane than that for chloroform.

The sign of the solvatofluorochromism of dyes **1**−**3** on a further increase of medium polarity can be correctly determined by comparing the fluorescence band characteristics for the solvent pair dichloromethane−DMF; the two dyes have close n_D values but much different ϵ_r, B, E, and E_T. The dyes under study display a negative solvatofluorochromic behavior in going from dichloromethane to DMF, thus suggesting that the S_1^f state is less dipolar than the S_0^{FC} (see Table 3). Though the signs of solvatochromic and solvatofluorochromic effects are the same, the latter are essentially weaker. To exemplify, the absorption spectrum of merocyanine **3** demonstrates hypsochromic shifts of $\Delta\tilde{\nu} = 199$ and 361 cm^{-1} (in terms of λ_{max}^a and M_a^{-1}, respectively) when passing from dichloromethane to DMF, whereas the corresponding values for the fluorescence spectrum are $\Delta\tilde{\nu} = 67$ and 158 cm^{-1} (in terms of λ_{max}^f and M_f^{-1}). It is notable that polar solute−solvent IMI in the S_1^f state are weakened so significantly as compared to the S_0 state (even in such a polar solvent as formamide) that the fluorescence maximum positions λ_{max}^f of merocyanines **2** and **3** change only very slightly in going from dichloromethane to formamide.

Upon electronic excitation, a substantial charge redistribution occurs in the molecules of merocyanines **1**−**3**, some atomic charges even changing their sign, as shown in Table 5. Therefore, the solvates resulting from nucleophilic and electrophilic solvation in the ground state become unstable in the S_1^{FC} state and tend to restructure, that is, to relax to the more energetically preferable S_1^f state. The electrostatic IMI are stronger when the charge distribution in the chromophore is more uneven.[4] Since $\Delta q_\Sigma \gg \Delta q_\Sigma^*$, one can infer that the charge is distributed more uniformly, and hence, nucleophilic and electrophilic solvation is weaker in the excited than in the ground state. Also, some solvates can decompose within the excited-state lifetime. As a consequence, fluorescence bands are less sensitive to solvent effects than their counterparts in the absorption spectrum (cf. the respective parameters σ^f, γ_1^f, γ_2^f, and F^f to σ^a, γ_1^a, γ_2^a, and F^a for various solvents based on the data presented in Tables 2 and 3 and Figures 1 and 2).

The fluorescence spectra of dyes **1**−**3** demonstrate that the first vinylene shift is smaller than the second one not only in toluene but also in chloroform as well as in more polar solvents (for chloroform, the first and the second vinylene shifts are $\Delta\lambda = 93$ and 105 nm in terms of λ_{max}^f and $\Delta\lambda = 84.1$ and 105 nm in terms of M_f^{-1}; see Table 3). This effect may be due to the additional bathochromic band shift observed for dimethine-merocyanine **1** (as a result of a twist around the double bond induced by the interaction between the closely spaced end groups). The same reason can account for the strongly broadened fluorescence bands of this compound, especially as compared to its absorption bands (see Tables 2 and 3 and Figure 1). However, this tendency also holds for merocyanine **2**; it diminishes as the solvent polarity rises.

If organic dyes have a nonrigid chromophore structure and are free of steric or transannular effects caused by the end groups, it is normal for them to exhibit $\sigma^f < \sigma^a$, whereas the case of $\sigma^f > \sigma^a$ appears to be most nontrivial. The rationale of this statement is the fact that band broadening is substantially contributed to, in addition to VI, by solvation and cis−trans isomerizations around the bonds of the polymethine chain.[4] The former gives rise to a set of molecules with various solvate environments (responsible, in turn, for inhomogeneous broadening), whereas the latter provide a mixture of stereoisomers and conformers. For negatively solvatochromic compounds, distinguished by their enhanced ground-state polar IMI, solvation prevails in the S_0 state and leads to an additional band broadening in the absorption spectra. All solvates and isomers participate in light absorption; on the contrary, fluorescence originates mostly from the species having the lowest energy of the S_1^f state. Hence, the relationship $\sigma^f < \sigma^a$ is realized, as exemplified abundantly.[4]

An opposite effect revealed by us attracts particular attention because the quantum-chemical data are evidence for notable excited-state bond equalization in the chromophore of dyes **1**−**3** (BOA* is much smaller than BOA, as seen from Table 4). However, this calculated picture does not include the effect of solute−solvent IMI, which can substantially change the bond order alternation both in the ground and excited states.[4]

Light-induced excitation of a positively solvatochromic molecule gives rise to an electron-density transfer from the donor to acceptor moiety (from the 1,3-diphenylbenzimidazolyl-2 residue to the dicyanomethylene group, as far as merocyanines **1**−**3** are concerned). This has the effect of growing dipolarity

(charge separation), that is, the molecular structure in the S_1^{FC} state tends to the **A3** type, in distinction to the S_0 state characterized by the **A1** type. Such a tendency manifests itself by the increased dipole moment and the opposite sign of BOA (interchanged single and double bonds) relative to the **A1** structure, as evidenced by the quantum-chemical calculations (see Table 4).

In the range of positive solvatochromism, the predominant **A1** structure of the S_0 state tends to **A2**, that is, to bond equalization, as the solvent polarity rises. Hence, VI are weakened in the $S_1^{FC} \leftarrow S_0$ transition. As the S_1^f state is more polar than S_0 for positively solvatochromic dyes, the solvent molecules which manage to restructure within the excited-state lifetime will increase the contribution of the **A3** structure to the fluorescent state and accordingly cause the alternation pattern and magnitude to change toward that in **A3**. The radiative transition will result in a decreased dipole moment which is inherent in the **A1** structure mainly contributing to the ground state. The S_0^{FC} state emerges in the energetically disadvantageous (nonequilibrium) solvation sphere of the S_1^f, state and the solvent cannot, therefore, act toward bond order equalization so efficiently as in the S_0 state. It is thus evident that with regard to solvent effects, both S_1^f and S_0^{FC} states will be characterized by more pronounced bond order alternation than that of the S_0 and S_1^{FC} states. As a consequence, VI are much stronger in the $S_1^f \rightarrow S_0^{FC}$ transition than those in $S_1^{FC} \leftarrow S_0$, which accounts for the fluorescence band broadening with respect to absorption bands (as is probably the case with dyes **1** and **2** in toluene).

In the range of negative solvatochromism, rising solvent polarity leads to an increased contribution of the **A3** structure to the S_0 state. Accordingly, absorption of a photon by a dye molecule gives rise to an electron-density transfer from the acceptor to the donor moiety, unlike the case of positively solvatochromic dyes. Hence the transition $S_1^{FC} \leftarrow S_0$ transforms the dye electronic structure so that it falls into the interval **A2** − **A1**; as a result, polar solute−solvent IMI are significantly weakened in the excited state. In the fluorescent state, the solvation sphere decomposes to a considerable degree due to the weakening of solute−solvent IMI; thus, the contribution of the **A1** structure to the S_1^f state should increase as compared to that to S_1^{FC}. The radiative transition $S_1^f \rightarrow S_0^{FC}$ brings the molecular structure closer to the **A3** type, with the dipole moment accordingly increased in the S_0^{FC} state. This state, in distinction to S_0, has an unrestructured solvation sphere of $S_1^{FC}$and, therefore, a smaller contribution of the **A3** structure than that of the equilibrium ground state. As a result, bond order alternation in the equilibrium states, S_0 and S_1^f, is more pronounced than that in the respective Franck−Condon states, S_0^{FC} and S_1^{FC}. If bonds alternate stronger in the S_1^f state than in S_0, then VI are stronger, and correspondingly, the bands are broader in fluorescence as compared to absorption. Conversely, if the bond order alternation is more pronounced in S_0 than in S_1^f, the opposite effect arises. Increasing solvent polarity brings the ground state closer to the **A3** structure and the fluorescent state closer to the **A2** structure, that is, favors absorption band broadening and fluorescence band narrowing. For instance, the values of σ^a and σ^f for merocyanine **2** become closer in going from chloroform to more polar solvents.

As the polymethine chain is lengthened, polar solute−solvent IMI are enhanced in the S_0 state, which is manifested by the broadened absorption bands (see Table 2 and Figure 1). As an example, an increase in $\Delta\sigma^a$ observed when passing from dichloromethane to DMF amounts to $\Delta\nu = 34$, 105, and 198 cm^{-1} for dyes **1**, **2**, and **3**, respectively. Absorption bands of merocyanine **3** are, therefore, much broader than its fluorescence bands. Besides, the S_1^{FC} state, as opposed to the ground state, is characterized by a decrease in absolute magnitudes of bond order alternation with increasing *n*; the BOA* values of the longest vinylogue **3** approach those of the corresponding symmetric polymethines (see Table 4). This result is consistent with decreasing deviations and narrowing bands in the fluorescence spectra as one goes from **2** to **3**, in contrast to the corresponding absorption spectra. The second vinylene shift of the fluorescence band also much exceeds that of the absorption band in various solvents. Such regularities illustrated by Tables 2 and 3 and Figure 1 point to the close approach of the S_1^f state of dye **3** to the cyanine limit. This inference is additionally evidenced by the fact that $\sigma^f \ll \sigma^a$ for merocyanine **3** in all of the solvents, and its fluorescence bandwidth, as well as the band shape parameters (γ_1^f, γ_2^f, and F^f), is practically independent of the nature of the medium (see Figure 2). It should be emphasized that the value of σ^f for dye **3** in DMF is as small as 770 cm^{-1}, that is, even less than for the corresponding symmetric cationic dye **6** (777 cm^{-1}) or anionic dye **9** (903 cm^{-1}).[4] This drastic band narrowing is only possible in the cyanine limit, with the bonds completely equalized. The foregoing shows that the mirror symmetry of the absorption and fluorescence bands of merocyanines can be broken due to increased or decreased σ^f values as opposed to σ^a.

Of special note is a dramatic rise of the fluorescence quantum yield Φ_f when passing from merocyanine **2** to **3**. The latter dye exhibits $\Phi_f = 56\%$ in DMSO, a value which is even larger than that for the corresponding symmetric dyes and resembles the quantum yields of polymethine luminophores with the rigidly fixed conjugated chain.[4] Thus, the main radiationless deexcitation channel, namely, photoisomerizations proceeding via twisting around the bonds of the chain, is likely to be essentially ruled out for dye **3**. This peculiarity may be attributable to the closeness to the cyanine limit achieved not only in the excited state but in the ground state as well; bond equalization with a bond order of 1.5 throughout the conjugated chain hinders isomerization processes. Moreover, the approach of the S_0 and S_1^f states to the **A2** structure provides minimum change of VI in the radiative transition, thus favoring an increased quantum yield. Importantly, the fluorescence quantum yield of merocyanine **3** rises drastically with increasing solvent polarity; it becomes 2 orders of magnitude larger in going from toluene to DMSO (see Table 3). The extremely high sensitivity of the Φ_f value to solvent polarity strikingly illustrates the nature of the polyene−polymethine transformation in the dye electronic structure. The fluorescence quantum yield of dye **3** dissolved in DMF and DMSO is additionally increased due to the higher viscosity of these solvents (see Table 1).

Both in absorption and emission transitions of merocyanines **1**−**3**, VI decay with lengthening of the polymethine chain, as in the case of the parent symmetric cationic **4**−**6** and anionic **7**−**9** dyes.[4] Accordingly, the Stokes shifts, SS_λ and SS_M (in terms of band maxima and centers, respectively), are reduced from shorter to longer vinylogues because absorption and fluorescence bands move closer together (to the region of the 0−0 transition). Since the weakest VI are typical of merocyanines **2** and **3** in chloroform and dichloromethane, where their S_0 and S_1^f states approach closest to the **A2** structure, the smallest Stokes shifts are observed just in these solvents. Going both to less polar (toluene) and more polar (ethanol, acetonitrile, etc.) solvents results in a decreased contribution of the **A2**

structure to the ground and fluorescent excited states, which causes the enhancement of VI and hence an increase in Stokes shifts.

Conclusion

Due to the high electron-donor ability of the benzimidazole end group, dyes **1**−**3** are readily polarized under the action of absorbed light. Depending on the length of the polymethine chain and the medium polarity, the polarization pattern of the ground and excited states varies from a nonpolar polyene via a polymethine to a charge-separated polyene. The variation range in the S_1^f state is much smaller than that in S_0. The place of a merocyanine within a space specified by structures **A1**, **A2**, and **A3** governs the band positions, intensities, and shapes both in absorption and fluorescence spectra as well as the fluorescence quantum yields. The regularities elucidated in the present study enable one to predict the character of the polyene−polymethine transformations of merocyanines and the trends in their spectral fluorescent properties.

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References and Notes

(1) Bach, G.; Dähne, S. Cyanine Dyes and Related Compounds. In *Rodd's Chemistry of Carbon Compounds*; Sainsbury M., Ed.; Elsevier: Amsterdam, The Netherlands, 1997; Vol. IVB, Chapter 15.

(2) Lawrentz, U.; Grahn, W.; Lukaszuk, K.; Klein, C.; Wortmann, R.; Feldner, A.; Scherer, D. *Chem.—Eur. J.* **2002**, *8*, 1573−1590.

(3) Rettig, W.; Dekhtyar, M. *Chem. Phys.* **2003**, *293*, 75−90.

(4) Ishchenko, A. A. *Structure and Spectral Luminescent Properties of Polymethine Dyes*; Naukova Dumka: Kiev, Ukraine, 1994.

(5) Brooker, L. G. S.; Keyes, G. H.; Heseltine, D. W. *J. Am. Chem. Soc.* **1951**, *73*, 5350−5356.

(6) Reichardt, C. *Solvents and Solvent Effects in Organic Chemistry*, 3rd ed.; Wiley-VCH: Weinheim, Germany, 2003.

(7) Kulinich, A. V.; Derevyanko, N. A.; Ishchenko, A. A. *Russ. Chem. Bull.* **2005**, *54*, 2714−2725.

(8) Ishchenko, A. A.; Derevyanko, N. A.; Svidro, V. A. *Dyes Pigm.* **1989**, *10*, 85−96.

(9) Burger, K. *Solvation, Ionic and Complex Formation Reactions in Non-aqueous Solvents*; Elsevier: Amsterdam, The Netherlands, 1983.

(10) Reichardt, C. *Pure Appl. Chem.* **2004**, *76*, 1903−1919.

(11) Meyers, F.; Marder, S. R.; Pierce, B. M.; Bredas, J. *J. Am. Chem. Soc.* **1994**, *116*, 10703−10714.

(12) Bourhill, G.; Bredas, J.; Cheng, L.-T.; Marder, S. R.; Meyers, F.; Perry, J. W.; Tiemann, B. G. *J. Am. Chem. Soc.* **1994**, *116*, 2619−2620.

(13) Ishchenko, A. A.; Svidro, V. A.; Derevyanko, N. A.; Slominskii, Yu. L.; Tolmachev, A. I. *Opt. Spektrosc.* **1989**, *66*, 1302−1306.

(14) Baraldi, I.; Brancolini, G.; Momicchioli, F.; Ponterini, G.; Vanossi, D. *Chem. Phys.* **2003**, *288*, 309−325.

(15) Stewart, J. J. P. *J. Comput.-Aided Mol. Des.* **1990**, *4*, 1−105.

(16) Gordon, A. J.; Ford, R. A. *The Chemist's Companion. A Handbook of Practical Data, Techniques and References*; Wiley: New York, 1972.

(17) Borisevich, Y. A.; Knyukshto, V. N.; Kozyrev, A. N.; Solov'yov, K. N. *Opt. Spektrosc.* **1993**, *74*, 210−218.

(18) Isak, S. J.; Eyring, E. M. *J. Phys. Chem.* **1992**, *96*, 1738−1742.

(19) Magde, D.; Wong, R.; Seybold, P. G. *J. Photochem. Photobiol., A.* **2002**, *75*, 327−334.

(20) Kulinich, A. V.; Ishchenko, A. A.; Groth, U. M. *Spectrochim. Acta, Part A* **2007**, *68*, 6−14.