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Structure and fluorescent properties of merocyanines based on *N*,*N*-diethylthiobarbituric acid

Andrii V. Kulinich [a,*], Nadezhda A. Derevyanko [a], Alexander A. Ishchenko [a],
Stanislav L. Bondarev [b], Valeri N. Knyukshto [c]

[a] *Institute of Organic Chemistry, National Academy of Sciences of Ukraine, Murmanska Str. 5, Kyiv 02094, Ukraine*
[b] *Minsk State Higher Radioengineering College, Nezalezhnasti av. 62, Minsk 220005, Belarus*
[c] *Stepanov Institute of Physics of National Academy of Sciences of Belarus, Nezalezhnasti av. 68, Minsk 220072, Belarus*

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Abstract

Fluorescent properties of a series of positively and negatively solvatochromic merocyanines based on *N*,*N*-diethylthiobarbituric acid containing heterocycles of various electron-donating properties are explored in solvents of various polarity. It is shown, that their solvatofluorochromic range is less than the solvatochromic range. A lengthening of the polymethine chain causes a growth of the vinylene shifts, a decrease of the deviations and a narrowing of the fluorescent spectral bands, as opposed to the absorption ones. The transition to the higher vinylogues is also accompanied by a decrease of the Stokes shifts and an increase of the fluorescent quantum yields. However, a growth of the latter for merocyanines absorbing light in the near-IR range is levelled by an amplification of internal conversion. An absence of a mirror symmetry of the absorption and fluorescence spectra has been revealed. The quantum-chemical analysis of an electronic structure of the merocyanines by the semi-empirical method AM1 is also carried out. The transitions between their ideal electronic states – non-polar polyene, polymethine and dipolar polyene – are investigated. It is shown, that the electronic structure of the fluorescent state of merocyanines approaches the cyanine limit at polymethine chain lengthening.

Keywords: Donor–acceptor systems; Merocyanines; Fluorescence; Solvatochromism; Electronic structure

1. Introduction

Due to their strongly pronounced solvatochromism, abilities to change essentially dipole moment at excitation, and to sensitize various physical and chemical processes, merocyanine dyes are widely used in new materials for optoelectronics, nonlinear optics, and as fluorescent probes for biology and medicine [1–3]. An understanding of the regularities connecting their spectral-fluorescent properties with their chemical structure is important for purposeful search of new practically important merocyanines. By now such regularities have been ascertained for the absorption spectra only [1,4–7]. The fluorescence has mainly been investigated for the dyes found wide practical application [8–10] that does not yield an opportunity to make generalizing conclusions. A maximum of dye fluorescence band λ^{f}_{max} is traditionally used as a reference point, a width and a form of fluorescence band, which display a degree of vibronic (VI) and intermolecular interactions with a solvent (IMI) in the first excited fluorescent state of dyes, were not considered. The purpose of the present work was the understanding of the laws connecting position, intensity and form of merocyanine fluorescence bands with donor–acceptor properties of their terminal groups, polymethine chain length, and the nature of solvent.

Earlier we had studied the absorption spectra of merocyanines **1–9** (Scheme 1), derivatives of *N*,*N*-diethylthiobarbituric acid [7].

The electronic structure of these dyes in the ground state changes from non-polar polyene structure **A1** up to dipolar polyene structure **A3** through the ideal polymethine structure (cyanine limit) **A2** at a variation of donor–acceptor ability of terminal heterocyclic groups, polymethine chain length, and nature of solvent [3,7] (Scheme 2).

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* Corresponding author. Tel.: +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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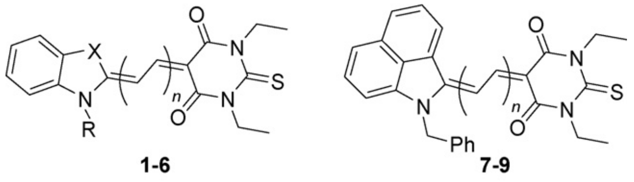
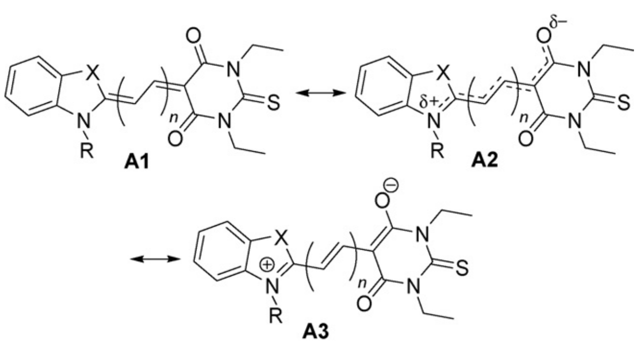


	1	2	3	4	5	6	7	8	9
X	CMe_2	CMe_2	CMe_2	S	S	S	–	–	–
R	Me	Me	Me	Et	Et	Et	–	–	–
n	1	2	3	1	2	3	1	2	3

Scheme 1.



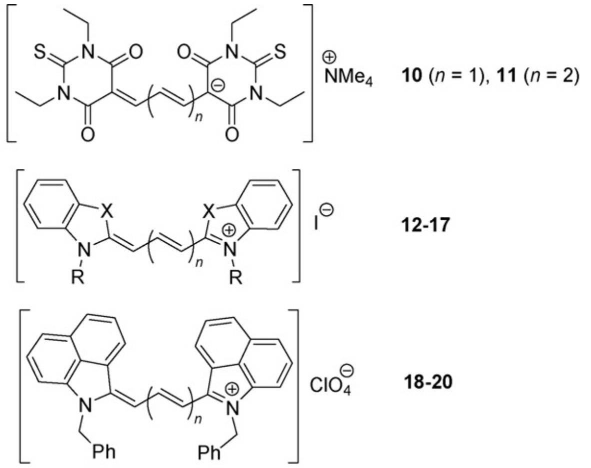
Scheme 2.

The mathematical treatment of fluorescence bands of merocyanines **1**–**9** by the method of moments [7,11] has allowed us to characterize quantitatively their position (M_f^{-1}) and form (σ^f, γ_1^f, γ_2^f, F^f). The parameter M^{-1} reflects the average position of the band (on the wavenumber scale it represents the band gravity centre: $\bar{\nu} = 10^7/M^{-1}$). In contrast to λ_{max}^f, this parameter enables us to make a reliable comparison of the curves of different band shape. The parameter σ^f characterizes a deviation of spectral band points from the gravity centre $\bar{\nu}$. Hence, this parameter allows making a reliable quantitative comparison of the band width regardless of the band shape, that is an advantage over the half-width $\tilde{\nu}_{1/2}$ (the width at half height of the band) traditionally used for this purpose. The asymmetry coefficient γ_1^f, the excess coefficient γ_2^f, and the fine structure coefficient F^f provide additional information on the band shape. The parameters λ_{max}^f, M_f^{-1}, σ^f, γ_1^f, γ_2^f, and F^f, alongside with the fluorescence quantum yields Φ_f, the Stokes shifts SS_λ and SS_M, calculated accordingly on λ_{max}^f, λ_{max}^a and M_f^{-1}, M_a^{-1} (the index a concerns similar characteristics of absorption bands), as well as the deviations D_λ^f and D_M^f (on λ_{max}^f and M_f^{-1}, correspondingly) are collected in Table 1. The deviations have been evaluated with the use of the spectral data of the parent anionic dyes **10**, **11** and cationic dyes **12**–**20** [11] (Scheme 3) measured in three solvents. The data for dyes **12**–**20** are taken from Ref. [11]. The characteristics of dyes **10** and **11** are listed in Table 1.

A disadvantage of many works in the field of solvatochromism is the limited range of solvent polarity. Even such low-polar solvents as arenes influence essentially an electronic structure of molecules with high polarizability [12]. Our purpose was to study the dependence of fluorescence spectra upon the structure of merocyanines in maximal wide range of solvent polarity. Low-polar *n*-hexane and toluene, medium-polar dichloromethane, and high-polar aprotic DMF and protic ethanol, in which the absorption spectra of dyes **1**–**9** [7] had been earlier investigated, have been chosen as solvents (the main characteristics of the chosen solvents are given in Table 2). It should be said, that dichloromethane and DMF were chosen as solvents to compare the spectral band shifts in the pair of solvents with the close values of refractive index n_D and substantially different polarity (permittivity ε_D, nucleophilicity *B*, and electrophilicity *E*).

The aggregation of dye molecules can occur in low-polarity solvents, which results especially in fluorescence quenching. The aggregates are usually nonfluorescent, but can contribute to the absorption spectra and cause deviation from mirror symmetry of the absorption and fluorescence spectra. The absorption spectra of the merocyanines concerned (Ref. [7] in the manuscript) demonstrate that all of them obey Beer's law in a concentration interval of 10^{-6} to 10^{-4} mol/L in toluene and more polar solvents. Moreover, dyes **1**–**3** and **7**–**9** in *n*-hexane also obey Beer's law (up to the concentration 5×10^{-5} mol/L). In fluorescence measurements the maximal optical density of solutions did not exceed 0.2, *i.e.*, the dye concentration was about 2×10^{-6} mol/L. Hence, the aggregation could not influence their fluorescence parameters. Only for strongly dipolar benzimidazole derivatives **4**–**6** in *n*-hexane the pronounced H-aggregation was observed [7]. For this reason, probably, their fluorescence has not been registered. The fluorescence spectra of dyes **7**–**9** in *n*-hexane have not been registered due to the extremely low quantum yields.

An approach of merocyanine electronic structure to one of the theoretical structures **A1**, **A2** or **A3** can be judged on a degree



	12	13	14	15	16	17	18	19	20
X	CMe_2	CMe_2	CMe_2	NPh	NPh	NPh	–	–	–
R	Me	Me	Me	Ph	Ph	Ph	–	–	–
n	1	2	3	1	2	3	1	2	3

Scheme 3.