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The nature of electron transitions in anionic dioxaborines, derivatives of aminocoumarin

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Combined quantum-chemical and spectral studies of the features of electron transitions and absorption spectra of symmetrical and unsymmetrical polymethine dyes, derivatives of aminocoumarin, have been performed. It was established that the lowest two electron transitions are splitting transitions, involving solitonic level and two low positioned acceptor levels, in contrast to the cationic cyanine dyes, where two lowest transitions are connected with two splitting donor levels and solitonic level. The considerable interaction between two acceptor levels in symmetrical dyes provides an additional decrease of the first transition energy and hence leads to the relatively deep and intensive color, whereas the second transition with its negligible oscillator strength is practically unobserved. The higher electron transitions involve orbitals located mainly at the coumarin residue; the corresponding spectral bands appear in the short-wavelength region. Introduction of dialkylamino group in coumarin heterocycle shifts bathochromically the long-wavelength absorption band and considerably increases the intensity of $S_0 \rightarrow S_1$ and $S_0 \rightarrow S_3$ electron transitions. Copyright © 2008 John Wiley & Sons, Ltd.

Keywords: polymethine dyes; 4-hydroxycoumarin; 2,2-difluoro-1,3,2-(2H)-dioxaborine; absorption spectra; quantum-chemical calculations

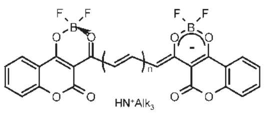
INTRODUCTION

Organic dyes based on 2,2-difluoro-1,3,2-(2H)-dioxaborine (DOB), such as derivatives of biphenyl, fluorene, carbazole, or polymethine dyes, attract considerable and growing attention because of their high two-photon cross-section[1] and large third-order nonlinearities.[2] The anionic polymethine dyes containing terminal DOB residues have been found to show the cyanine-like properties, first of all, the relatively deep light absorption and effective fluorescence; their spectral bands are narrow and intense, similar to those for typical well-known cyanine dyes. Rigidifying of 1,3,2-(2H)-dioxaborine cycle by coumarin or cyclohexanone fragments[3,4] results in the increase of absorption intensity and quantum yield of the fluorescence. To overcome the relatively low stability of the DOB fragment itself, in our previous paper[5] we reported the synthesis and absorption spectra of the polymethine dyes derived from DOBs of 3-acetyl-7-diethylamino-4-hydroxycoumarin and demonstrated that such dyes are among the most stable dioxaborines. Also, it was established that the introduction of dialkylamino groups in the terminal coumarin residues combined with DOB led to the substantial increase of absorption intensity and fluorescence quantum yield, whereas the position of the spectral band was only slightly sensitive to such change of the chemical structure.

In the present work, the results of the simultaneous spectral and quantum-chemical study of the nature of the electron transitions are considered, including the higher transitions connected directly with nonlinear optical properties.

OBJECTS AND METHODOLOGY

The symmetrical and unsymmetrical anionic polymethine dyes of general structures **1–3** were investigated. Also, the electron structure of the cationic indocarbocyanine **4** was calculated to compare the nature of the electron transitions in both anionic and cationic dyes.



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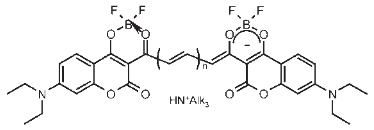

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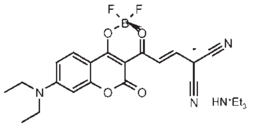

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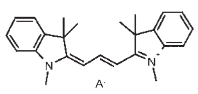

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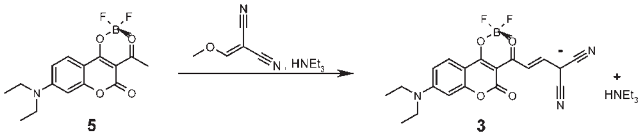
The synthesis of compounds **1** and **2** was described before.[4,5] The unsymmetrical dye **3** was synthesized by the following scheme:



A mixture of **5** (323 mg, 1 mmol), methoxymethylidenemalononitrile (110 mg, 1 mmol), and triethylamine (150 mg,

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1,49 mmol) in dichloromethane (5 ml) was refluxed for 10 min. Dichloromethane was evaporated, the residue was crystallized from acetic acid. Yield 290 mg (58%). M. p. 187–189 °C. ^{1}H NMR (DMSO-d$_6$): δ 1.77 (m, 15H, CH$_3$), 3.10 (q, $^3J_{H,H} = 7.2$ Hz, 6H, NCH$_2$), 3.49 (q, $^3J_{H,H} = 7.2$ Hz, 4H, NCH$_2$), 6.51 (s, 1H, 7-H), 6.78 (d, $^3J_{H,H} = 9.0$ Hz, 1H, 9-H), 7.15 (d, $^3J_{H,H} = 12.9$ Hz, 1H, β-H), 7.69 (d, $^3J_{H,H} = 9.0$ Hz, 1H, 10-H), 8.01 (d, $^3J_{H,H} = 12.9$ Hz, 1H, α-H), 8.86 (br s, 1H, NH$^+$). λ_{max} 492 nm, ε 92 000 (MeCN). Anal. calcd. for $C_{25}H_{31}N_4O_4BF_2$: C, 57.86; H, 4.86; N, 10.21. Found: C, 57.81; H, 4.72; N, 10.23.

Electronic absorption spectra were recorded on Shimadzu UV-3100 spectrophotometer in acetonitrile.

Proton NMR spectra were obtained with Varian VXR-300 instrument (300 MHz) at 25 °C using tetramethylsilane as an internal standard.

Quantum-chemical calculations (the equilibrium geometry of dye molecules in the ground state and electron transition characteristics) were performed in the semi-empirical AM1 approximation (HyperChem package). The procedure of the optimization was stopped upon the energy gradient 0.01 kcal/mol. The shape of the molecular orbitals is defined by the coefficients $C_{i\mu}$ from the equation: $\varphi_i = \sum C_{i\mu}\chi_\mu$ (the standard MOLCAO approximation), where φ_i is an *i*th MO, while χ_μ is a μth atomic orbital. The function of the *p*th excited state ψ_p was written as a linear expansion of single excited configurations, $\Phi_{i\to j}$, so that

$$\Psi_p = \sum T_{i\to j,p}\Phi_{i\to j}\,(\text{Clapproximation}) \qquad (1)$$

The ZINDO/S method cannot be used in the absence of parametrization for the boron (B) atom. The obtained wavelengths of the electron transitions, λ^{calc}, were multiplied by a parameter k to agree the calculated and experimental data: $\lambda_{max} = k\lambda^{calc}$. This correction coefficient, *k*, similarly to the corresponding parameter overlap weight factor (OWF) in the other semi-empirical method ZINDO/S, is connected indirectly with the overestimation of the electron–electron repulsion calculated by Mataga–Nishimoto's formulas, $\gamma_{\mu\nu} = a/(1 + R_{\mu\nu})$, where *a* is constant and $R_{\mu\nu}$ the distance between the μth and νth atoms, for the atoms which are removed to great distance from each other. The same problem of the integrals $\gamma_{\mu\nu}$ has been found to exist even in the simplest PPP approximation correctly taking into consideration the electron–electron interaction. J. Fabian and R. Zahradnic have proposed to use the modifying formulas, $\gamma_{\mu\nu} = a/(1 + tR_{\mu\nu})$, where $t = 10/3$; then, the agreement between the calculated and experimental wavelengths of the first electron transition for the vinylogous series of the polymethine dyes has been essentially increased.[6] The value of *k* was calibrated against the first electron transition. For dyes **1–3**, parameter *k* is somewhat higher than traditional parameter $k = 1.15$ obtaining for the electron transition in the conjugated heterocycles. This seems to be connected with the more great distances between atoms in the linear chromophore of the polymethine dyes containing the extended conjugated chain, so that the overestimation of the electron–electron repulsion by the formulas $\gamma_{\mu\nu} = a/(1 + R_{\mu\nu})$ should be regularly increased, in contrast to the heterocycles with the comparatively short distances between atoms.

As a rule, all π-electron single excited configurations were used in the calculations.

RESULTS AND DISCUSSION

Positions of electron levels and shape of MOs

It was previously shown that the energy gap in the ionic linear π-system is considerably shifted, as compared with the neutral conjugated molecules: down – in cations, and up – in anions.[7] Consequently, there is an essential distinction in the disposition and densities of the vacant and occupied electron levels in the cationic and anionic polymethines.[7] As an example, Fig. 1 presents the positions of the frontier and nearest levels calculated for the dyes **2** ($n = 1$) and **4**. Such shifting of the energy gap in the ionic π-systems is caused by an appearance of the specific charge or soliton level.[7] As shown in Fig. 1a that the lowest vacant level in the cationic indocarbocyanine **4** is situated relatively low and is appreciably separated from the next vacant levels, in contrast to the occupied levels where the distance between two highest levels is smaller. The opposite disposition of the frontier and nearest levels is obtained from calculation for the

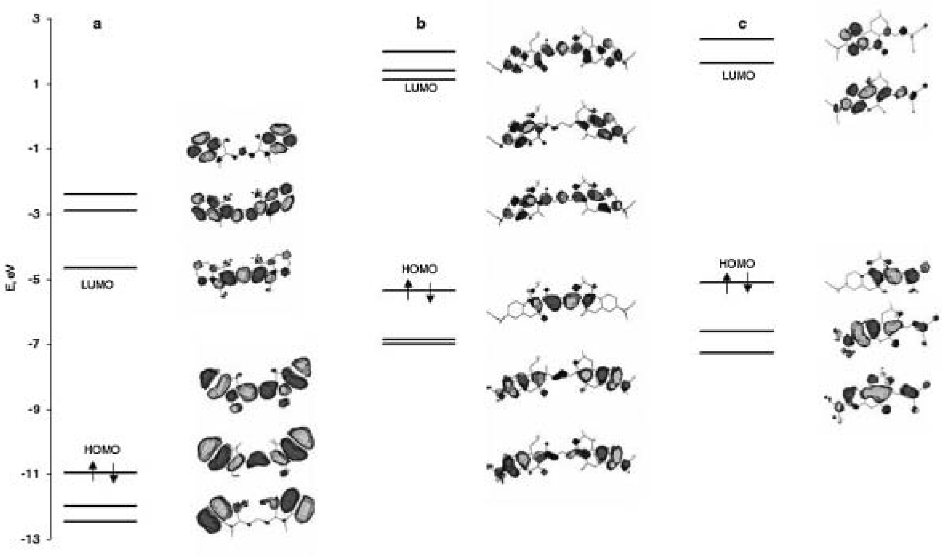

Figure 1. Positions and shapes of frontier and the narrowest electron levels of the dyes: (a) **4,** (b) **2** ($n = 1$)**,** (c) **3**

anionic DOB dye **2** ($n = 1$); the HOMO is orbital of the negative charge (solitonic orbital) and so the corresponding level is separated substantially from the next occupied level, whereas the two lowest vacant levels are relatively close (Fig. 1b).

In the unsymmetrical dye **3** as an anionic π-system, the solitonic level also exists, as can be seen from Fig. 1c. Its position and shape of the corresponding orbital (HOMO) are quite similar to those of the solitonic MO in the symmetrical dye **2** (compare with Fig. 1b). However, there is only one vacant level separated appreciably from the next level in the conductive band (Fig. 1c), in contrast to two close similar levels in the symmetrical anionic trimethine **2** ($n = 1$). This indicates the specificity of such MO. As can be seen in Fig. 1c that LUMO is mainly located at the atoms of the terminal DOB group, so we propose to treat this specific orbital as an acceptor-type MO, whereas the short chain could be considered as an exocyclic conjugated constituent linked with DOB residues. Then symmetrical dyes **2** can similarly be described by the following general structure:

$$\mathrm{A}—\pi(-)—\mathrm{A} \qquad \mathbf{6}$$

where A is an acceptor terminal conjugated system, and $\pi(-)$ negatively charged polymethine chain. Providing the short chain and branched π-system of the acceptor groups A, then two terminal residues give the two lowest acceptor orbitals. They should interact to give two new MOs which can be written as a linear combination of the components $\phi(\mathrm{A}_1)$ and $\phi(\mathrm{A}_2)$:

$$\varphi_1 = (2)^{-1/2}\{\phi(\mathrm{A}_1) + \phi(\mathrm{A}_2)\} \tag{2}$$

$$\varphi_2 = (2)^{-1/2}\{\phi(\mathrm{A}_1) - \phi(\mathrm{A}_2)\} \tag{3}$$

It is seen from Fig. 1b that LUMO corresponds to the function φ_1 (Eqn 2) whereas LUMO + 1 corresponds to the function φ_2 (Eqn 3) Also, the polymethine chain takes part in these MOs as a conjugated component substituent of the DOB residue.

In the same way, the cationic indocarbocyanine **4** could be described as follows:

$$\mathrm{D}—\pi(+)—\mathrm{D} \qquad \mathbf{7}$$

where D is the donor residues. Then, the two highest occupied MOs could be considered as plus- and minus-combinations of both donor orbital of the terminal groups.

Thus, there are practically mirror images of the solitonic and terminal orbitals in the cationic cyanine **4** and related anionic dye **2** (with the same chain length): the whole soliton level and two donor levels in polymethine-cation, and consequently, the electron soliton level and two acceptor levels in polymethine-anion.

The next occupied orbital (HOMO-1) in the unsymmetrical dye **3** is seen from Fig. 1c to be located mainly on the DOB residue and hence could be considered as a local MO. In the symmetrical dye **2** ($n = 1$) with two chemically identical terminal groups, two such specific orbitals exist; they generate the coupled MOs, HOMO-1, and HOMO-2 as the sum-function and minus-function, similarly to the functions φ_1 and φ_2 in Eqns (2, 3). Because of conjugation of the terminal groups with the polymethine chain and interaction between them, both orbitals, HOMO-1 and HOMO-2, are split, although the distance between splitting levels is smaller than similar value between the two splitting lowest vacant levels. Also, it can be seen in Fig. 1b that the next vacant MO, LUMO + 2, is practically delocalized along whole π-system of the dye molecule.

Here we will limit the discussion to MOs referred above, as only they take part in the electron transitions observed in visible and near IR spectral region and can be reliably interpreted.

The gradual lengthening of the polymethine chain is known to be accompanied by a regular increase of the number of π-levels: one vacant and one occupied level per each new vinylene group. As a result, the lowest vacant level shifts down, whereas the highest occupied level shifts up, which could be seen from Fig. 2a. The calculations have shown that solitonic level is also sensitive to the chain length. Also, the splitting of the acceptor levels increases upon increasing of number of vinylene groups *n*, because of the considerable interaction between the corresponding MOs in the polymethine chain which is included in both orbitals as an exocyclic substituent. The next levels (both

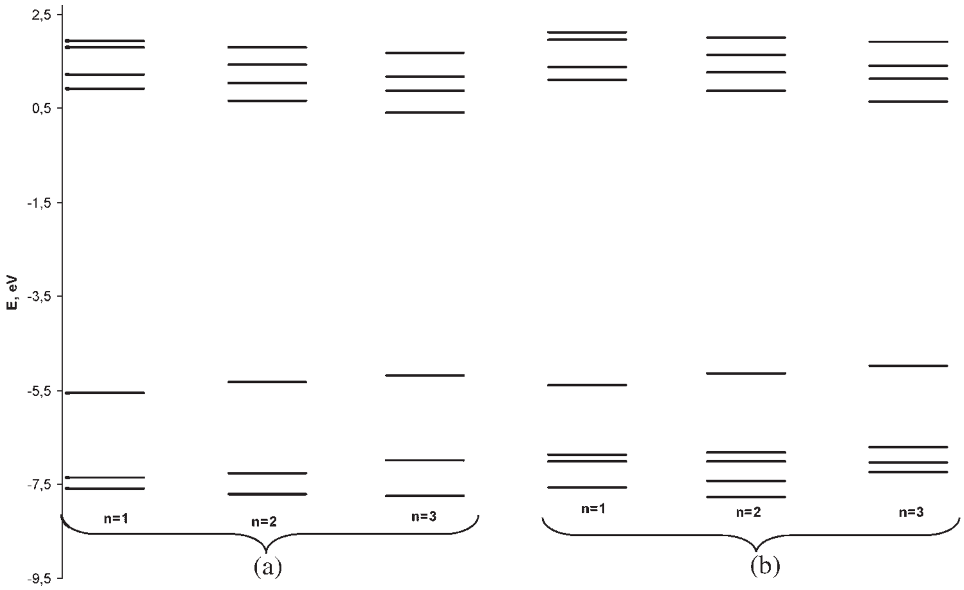

Figure 2. Positions of frontier and the narrowest electron levels of vinylogous series: **1** (a), **2** (b)

vacant and occupied) are seen from Fig. 2 to be also sensitive to the length of the polymethine chain.

Introduction of the donor dialkylamino substituents into acceptor DOB residues decreases the acceptor strengths of terminal groups and hence causes the shifting of both vacant levels up, in comparison with corresponding related dyes **1**, derivatives of coumarin (as shown in Fig. 2b). The solitonic levels are found from the calculations to be also influenced by the amino substituents and shifted up. Because of simultaneous shifting up of both frontier levels, the energy gap appears to be only weakly sensitive to the change of the chemical structure upon going from dyes **1** to related compounds **2**. The level of the nitrogen's electron couple is situated much lower than dye's HOMO and the lengthening of the polymethine chain results in the increased distance between these levels. So, it can be supposed that their interaction in cases of higher vinylogs must be smaller.

The first and second electron transitions

In the Fig. 3, the absorption spectra (long-wavelength absorption band) of the dyes derivatives of the aminocoumarin are presented. The first band maximum in each spectrum is connected with the $S_0 \rightarrow S_1$ electron transition, whereas the second observed peak corresponds to the $0 \rightarrow 1'$ vibronical transition, the distance between maxima to be approximately 1200–1400 cm^{-1}.

In the unsymmetrical dye **3**, the first transition involves the solitonic level and lowest vacant level, as it is schematically shown in Fig. 4a. Taking into account the location of both corresponding MOs (as shown in Fig. 1c), we can suggest that this transition should be accompanied by the transfer of electron density from the polymethine chain to the terminal DOB residue. The diagram of the electron redistribution at the chromophore atoms upon excitation is presented in Fig. 5. It is seen from Fig. 5a that the excitation causes the considerable transfer of the charge mainly from the polymethine chain to the DOB residue: the electron densities decrease most considerably at the carbon atoms in the α- and γ-positions of the chain, whereas maximum increase of the electron densities is obtained for the atoms in the benzene ring and atoms nearest to it; the changes of the charges at the rest of atoms are far much lower. Such transferring of the electron density between the molecular fragments corresponds to the main location of the MOs involved in the first electron transition (compare with the location of the HOMO and LUMO in the Fig. 1c). It should be noted that the boron atom does not participate in the lowest transition, since the corresponding MO is not located at this atom; the boron atom just stabilizes significantly the anionic oxonole-like chromophore.

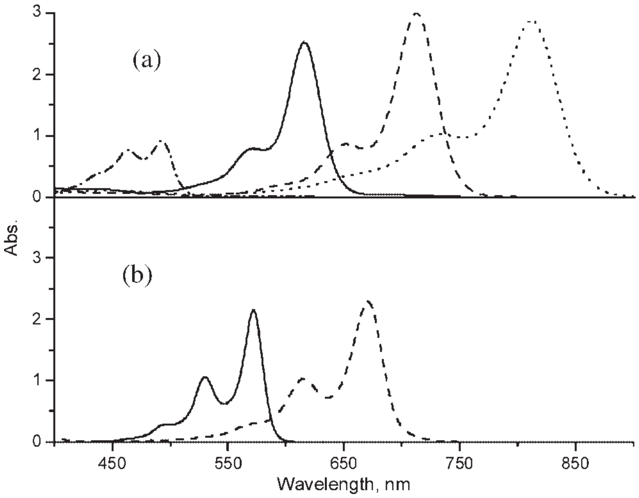

Figure 3. Long-wavelength absorption spectra of the dyes **2** ($n = 1$ – solid, $n = 2$ – dash, $n = 3$ – dot), **3** (dash dot) (a), **1** ($n = 1$ – solid, $n = 2$ – dash) (b) in acetonitrile (1×10^{-5} M)

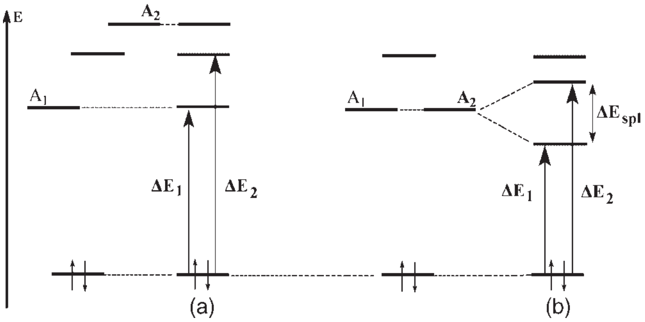

Figure 4. Schematic disposition of delocalized and acceptor (A_1 and A_2) levels and two first electron transition in unsymmetrical dye (a) and symmetrical dye (b); ΔE_{spl} is the splitting energy

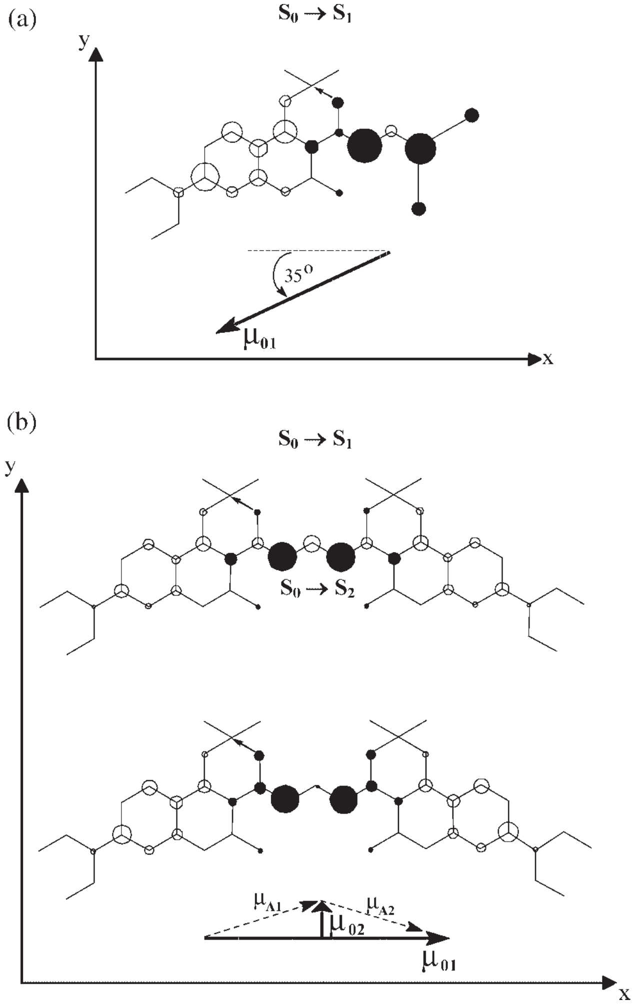

Figure 5. Electron density redistribution diagrams and transition dipole moments (μ_{0i}) of the dyes **3** (**a**) and **2** ($n = 1$) (**b**). ○ – electron density increases; ● – electron density decreases

Also, the performed calculation gives that the $S_0 \rightarrow S_1$ electron transition in the unsymmetrical dye **3** is polarized at an angle 35° (the direction of the transition dipole moment μ_{01}) to the polymethine chain, what is clearly seen from Fig. 5a.

Thus, the first transition is mainly located at the DOB residue and carbon atom in the α-position (and vinylogous γ-position) of the chain, which can be considered as an exocyclic conjugated substituent. So we propose for the sake of convenience (in color theory terms) to treat the terminal acceptor group as a quasi-local or acceptor chromophore. The energy of this transition is relatively high, and hence the corresponding spectral band is positioned in the short-wavelength region, as compared with the absorption band of the symmetrical dye **2** ($n = 1$). It should be taken into consideration that the spectral band maximum undergoes the additional hypsochromic shift because of the considerable alternation of the bond lengths in the polymethine chain of the unsymmetrical dye **3**, in contrast to symmetrical dyes with their equalized bond lengths.

In the same way, we can consider (in the framework of the color theory) the symmetrical dye **2** as a combination of two chemically identical acceptor chromophores, in the strict accordance with the general structure **6**. In this case, the polymethine chain should be treated as a common exocyclic conjugated substituent. This leads to the considerable interaction of both local acceptor chromophores and corresponding acceptor orbitals (in the molecular orbital treatment), as it is shown in the Fig. 4b. As a result, the energy of the first electron transition decreases considerably, in comparison with that in the unsymmetrical dye **3** containing only one such chromophore.

The lengthening of the polymethine chain as a common exocyclic substituent of both acceptor chromophores by introducing vinylene groups in the series **2** ($n = 2$, 3) is accompanied by decreasing of the acceptor levels and hence by decreasing of the $S_0 \rightarrow S_1$ transition with the corresponding bathochromic shift of the spectral band maximum for 90 nm (**2**, $n = 1$, 2) and 102 nm (**2**, $n = 2$, 3).

It is obvious that the second electron transition in the symmetrical dyes also involves acceptor level (more correctly, the second splitting acceptor level), as shown in Fig. 4b. Moreover, the $S_0 \rightarrow S_2$ transition should be treated as the second splitting transition. Thus, both transitions, $S_0 \rightarrow S_1$ and $S_0 \rightarrow S_2$, may be considered as coupled electron transitions obtained upon the interaction of the acceptor chromophores. This specific nature of these transitions is responsible for some their features, first at all, for the polarization and magnitudes of their transition dipole moments.

Since the symmetrical dye contains two virtual acceptor chromophores, its total transition dipole moments are vector sum (Eqn 4) and vector subtraction (Eqn 5) of the dipole moments of both parent quasi-local chromophors (μ_{chr1} and μ_{chr2}):

$$\mu_{01} = \mu_{\text{chr1}} + \mu_{\text{chr2}} \tag{4}$$

$$\mu_{01} = \mu_{\text{chr1}} - \mu_{\text{chr2}} \tag{5}$$

The summation and subtraction of the corresponding vectors are presented graphically in the Fig. 5b. Both vector dipole moments, μ_{01} and μ_{02}, are seen to be mutually perpendicular, so that the first transition is polarized along the polymethine chain, while the second transition is perpendicular to it. Based on the fact that the angle between the dipole moments μ_{chr1} and μ_{chr2} is obtuse, the μ_{01} magnitude exceeds practically twice each dipole moment of the individual local chromophore, whereas the dipole moment μ_{02} is practically negligible. As a result, the interaction of both acceptor quasi-local chromophores in the symmetrical dye increases considerably the dipole moment of the first transition and hence the intensity (or oscillator strength) of the long-wavelength absorption band. This theoretical conclusion agrees with the calculated transition dipole moments (Table 1) and with experimental spectra (Fig. 3). The calculation gives that the distance between the first and second transitions should not be large: approximately 50 nm. Then, we can argue that the intensive high selective long-wavelength band with clear vibronical peak (shifted hypsochromically for 1200–1400 cm^{-1}) is undoubtedly connected with the first splitting transition; in contrast, the second transition, $S_0 \rightarrow S_2$, with too small dipole moment ($\mu_{02} = 0.073$), is not observed in the spectrum, as it is hidden under the vibronical shoulder of the first absorption band. Also, we can suppose that the low intensity spectral peaks in the short-wavelength region are connected with the higher electron transition.

Figure 1b, c shows that the nitrogen atoms of dialkylamino groups practically do not participate in the lowest two electron transitions for the symmetrical dyes. Nevertheless, the long-wavelength band in the spectra of the symmetrical dyes **2** is always shifted bathochromically, in comparison with the related compounds **1**: for 44 nm for $n = 1$ and 37 nm for $n = 2$. Also, the introduction of amino groups into coumarin residue is seen from Fig. 3 upon comparing spectra of the dyes **1** and **2** to somewhat increase the intensity of this spectral band; at the same time, the intensity of the vibronical peak regularly decreases, so that the ratio $I(0 \rightarrow 0')/I(0 \rightarrow 1')$ becomes significantly higher in the derivatives of aminocoumarin **2**, than in the corresponding dyes **1**. It was shown above that the influence of the amino group is the highest in the dye **2** with the shortest chain. Then, it is reasonable that the long-wavelength spectral band is additionally shifted bathochromically; meanwhile, the similar spectral effect in the higher vinylogs should be smaller. As a result, the first vinylene shift, $V = \lambda_n - \lambda_{n-1}$, appears to be somewhat smaller (90 nm for $n = 1$) than this parameter for the next pair of dyes **2** ($V = 102$ nm for $n = 2$, 3), as well as for the related dyes **2** where V ($n = 1$, 2) = 98 nm.

It should be clear that the two lowest electron transitions, $S_0 \rightarrow S_1$ and $S_0 \rightarrow S_2$, in the symmetrical dyes **2** are not described as exact 'pure' excited states, that is, they can not be written by only one configuration. The calculations taking into consideration the configurational interaction show that the coefficient $T_{1,\ \text{HOMO} \rightarrow \text{LUMO}}$ is not equal 1, although it regularly increases upon going to the higher vinylogs: 0.85; 0.89; 0.93 ($n = 1$, 2, 3, respectively). At the same time, the second transitions are described as a combination of two main configurations: $|\text{HOMO-1}\rangle \rightarrow |\text{LUMO}\rangle$ and $|\text{HOMO}\rangle \rightarrow |\text{LUMO+1}\rangle$; the lengthening of the polymethine chain is accompanied by regular increase of contribution of the configuration involved the second splitting acceptor level ($|\text{LUMO} + 1\rangle$): $T_{1,\ \text{HOMO} \rightarrow \text{LUMO}+1} = 0.65$; 0.69; -0.71 ($n = 1$, 2, 3). This fact is likely to be connected with the energies of the configuration $|\text{HOMO-1}\rangle \rightarrow |\text{LUMO}\rangle$ and $|\text{HOMO}\rangle \rightarrow |\text{LUMO} + 1\rangle$ of the same symmetry becoming close and thus the interaction between them should be relatively strong.

In the related dyes **1**, the contribution of the configuration $|\text{HOMO}\rangle \rightarrow |\text{LUMO+1}\rangle$ is seen from Table 1 to be somewhat smaller, so the $S_0 \rightarrow S_2$ transition in the longer vinylog ($n = 2$) is described practically by one configuration: $|S_2\rangle \approx 0.82|\text{HOMO}\rangle \rightarrow |\text{LUMO} + 1\rangle$ with the negligible oscillator strength, $f_2 = 0.001$.

Table 1. Calculated characteristics of electron transitions for the dyes **1–3**[a]

Dye	n	Transition	λ^{calc},nm	λ^{corr},nm	f	Main configuration, $T_{p,i\to j}$
1	1	$S_0 \to S_1$	425	**582**	1.361	$\vert S_1\rangle = 0.88\ \vert H\to L$
	k = 1.37	$S_0 \to S_2$	308	**422**	0.008	$\vert S_2\rangle = 0.78\ \vert H\to L+1$ $0.49\ \vert H\text{-}1\to L$
		$S_0 \to S_3$	282	**386**	0.010	$\vert S_3\rangle = 0.54\ \vert H\to L+2$ $0.47\ \vert H\text{-}1\to L+1$ $-0.55\ \vert H\text{-}2\to L$
		$S_0 \to S_4$	272	**373**	0.724	$\vert S_4\rangle = 0.55\ \vert H\text{-}2\to L+1$ $0.55\ \vert H\text{-}3\to L$
	2	$S_0 \to S_1$	486	**680**	1.703	$\vert S_1\rangle = 0.89\ \vert H\to L$
	k = 1.40	$S_0 \to S_2$	322	**451**	0.0001	$\vert S_2\rangle = 0.82\ \vert H\to L+1$
		$S_0 \to S_3$	294	**412**	0.009	$\vert S_3\rangle = 0.79\ \vert H\to L+2$
		$S_0 \to S_4$	277	**388**	0.62	$\vert S_4\rangle = 0.54\ \vert H\text{-}2\to L+1$ $-0.45\ \vert H\text{-}3\to L$
2	1	$S_0 \to S_1$	432	**626**	1.612	$\vert S_1\rangle = 0.85\ \vert H\to L$
	k = 1.45	$S_0 \to S_2$	313	**454**	0.073	$\vert S_2\rangle = 0.65\ \vert H\to L+1$ $-0.57\ \vert H\text{-}1\to L$
		$S_0 \to S_3$	288	**418**	0.255	$\vert S_3\rangle = 0.51\ \vert H\to L+2$ $-0.58\ \vert H\text{-}1\to L+1$ $-0.54\ \vert H\text{-}2\to L$
		$S_0 \to S_4$	270	**392**	0.372	$\vert S_4\rangle = -0.71\ \vert H\to L+1$
	2	$S_0 \to S_1$	489	**714**	1.935	$\vert S_1\rangle = 0.89\ \vert H\to L$
	k = 1.46	$S_0 \to S_2$	324	**473**	0.026	$\vert S_2\rangle = 0.69\ \vert H\to L+1$ $-0.51\ \vert H\text{-}1\to L$
		$S_0 \to S_3$	296	**432**	0.266	$\vert S_3\rangle = -0.62\ \vert H\to L+2$ $-0.54\ \vert H\text{-}1\to L+1$
		$S_0 \to S_4$	279	**407**	0.250	$\vert S_4\rangle = 0.69\ \vert H\to L+1$ $0.47\ \vert H\text{-}2\to L+1$
	3	$S_0 \to S_1$	533	**815**	2.238	$\vert S_1\rangle = 0.93\ \vert H\to L$
	k = 1.53	$S_0 \to S_2$	334	**511**	0.024	$\vert S_2\rangle = -0.71\ \vert H\to L+1$ $0.49\ \vert H\text{-}1\to L$
		$S_0 \to S_3$	303	**464**	0.233	$\vert S_3\rangle = 0.68\ \vert H\to L+2$ $-0.47\ \vert H\text{-}1\to L+1$
		$S_0 \to S_4$	288	**441**	0.185	$\vert S_4\rangle = -0.66\ \vert H\to L+1$ $-0.52\ \vert H\text{-}1\to L$
3	-	$S_0 \to S_1$	399	**491**	1.154	$\vert S_1\rangle = 0.72\ \vert H\to L$ $0.55\ \vert H\to L+2$
	k = 1.23	$S_0 \to S_2$	325	**400**	0.008	$\vert S_2\rangle = -0.61\ \vert H\text{-}1\to L+1$ $0.58\ \vert H\text{-}3\to L$
		$S_0 \to S_3$	311	**383**	0.107	$\vert S_3\rangle = 0.49\ \vert H\to L+2$ $-0.64\ \vert H\text{-}1\to L$
		$S_0 \to S_4$	270	**332**	0.059	$\vert S_4\rangle = 0.61\ \vert H\to L$ $-0.52\ \vert H\to L+2$

[a] λ^{corr} was calculated from the equation: $\lambda^{corr} = \lambda^{calc}k$, where parameter k was obtained as a ratio of the experimental maximum of the long-wavelength spectral band, λ_{max}, and λ^{calc} for the first transition, so that $k = \lambda_{max}/\lambda^{calc}$.

In the unsymmetrical dye **3,** even the first electron transition is seen from calculation data to be strongly mixed, the contributions of the configurations $|HOMO\rangle \to |LUMO\rangle$ and $|HOMO\rangle \to |LUMO + 2\rangle$ being comparable. As can be seen in Table 1 that these configurations give the pair of electron transitions: $|S_1\rangle$ and $|S_4\rangle$ with the relatively large splitting energy (or the large distance between them). Meanwhile, the second transition in the unsymmetrical anionic dye **3** does not involve the solitonic orbital (HOMO), and so its nature differs from the nature of the splitting $S_0 \to S_2$ electron transition in the symmetrical dyes **1** and **2**.

The higher electron transitions

First, we will consider the nature of the higher transitions in the symmetrical dyes **1** containing the unsubstituted coumarin terminal residues. As can be seen in the Table 1 that the $S_0 \to S_3$ transition in the dye with longer chain ($n = 2$) involves solitonic orbital (HOMO) and the totally delocalized LUMO + 2; the

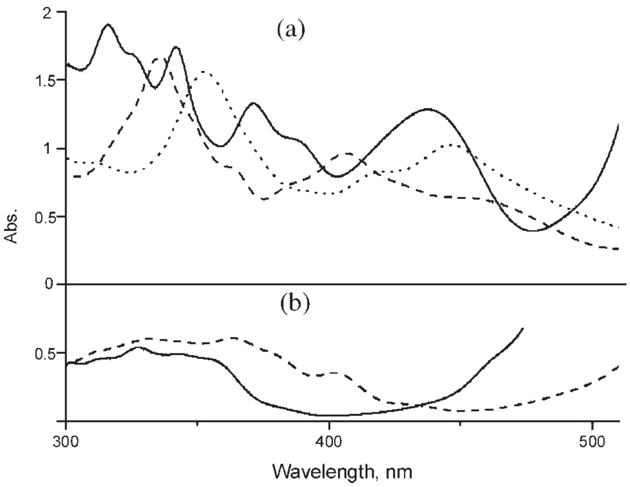

Figure 6. Short-wavelength absorption spectra of the dyes **2** ($n=1$ – solid, $n=2$ – dash, $n=3$ – dot) (a), **1** ($n=1$ – solid, $n=2$ – dash) (b) in acetonitrile (~1×10^{-4} M)

contributions of the other orbitals are significantly smaller: $T_{3,\,i\rightarrow j} < 0.3$. This transition in the dye with shorter chain ($n=1$) is mixed, so that two occupied MOs located mainly at the terminal groups are involved. In both dyes of this series (**1**, $n=1$, 2), the oscillator strength f_3 is relatively small. Thus, the intensity of the corresponding spectral band should be weak, and hence, the $S_0\rightarrow S_3$ transition could not be observed in the spectrum of the dye **1** with the shortest chain. However, the weak separate peak at 400–405 nm in the spectrum of the vinylog **1,** $n=2$ (Fig. 6b) could be assigned to the $S_0\rightarrow S_3$ electron transition.

We propose that the noticeable band in the short-wavelength region of the spectrum at *ca.* 350 nm is connected with the $S_0\rightarrow S_4$ transition, as its oscillator strength is significantly larger: $f_4=0.724$ ($n=1$). As can be seen in Table 1 that two next occupied orbitals, HOMO-2 and HOMO-3, take part in this transition; the splitting vacant MOs are also involved, according to their symmetry.

The calculations predict that the energy of the $S_0\rightarrow S_4$ transition only slightly decreases upon lengthening of the chromophore, and corresponding spectral band should be shifted for 15 nm. It is in a good agreement with the spectral shift of the absorption band from 330–350 nm (**1**, $n=1$) to 370–390 nm (**1**, $n=2$), and does not quite correspond to the peak at 405–410 nm (which is connected with the $S_0\rightarrow S_3$ electron transition). The next electron transitions are considerably more difficult for the correct interpretation, since bands observed in the short-wavelength spectral region are non-selective and low-intense (as shown in Fig. 6b).

The comparison of the spectra of the dyes **1** (Fig. 6b) with the short-wavelength absorption of the related series **2** with the same number of vinylene groups in the chain (Fig. 6a) shows that the introduction of dialkylamino groups in the coumarin residues causes the appearance of the spectral band at 450–470 nm. In the dye **2** with the shortest polymethine chain ($n=1$), this band is shifted strongly (for about 90–100 nm), as compared to the calculated shifts between dyes **1** and **2** of related series: 32 nm for the $S_0\rightarrow S_3$ electron transition, and 19 nm for the next transition. Consequently, we could assume that the band at 450 nm in the absorption spectrum of the dye **2**, $n=1$, corresponds to transition different from that in the related dye **1** with the same chain. As can be seen in Table 1 that the calculated oscillator strength of $S_0\rightarrow S_3$ transition for the dye series **2** exceeds considerably the similar parameter, f_3, for the related dyes **1**, although this transition involves the same MOs. Such essential increase of the transition dipole moment μ_3 and hence the f_3 value allows the $S_0\rightarrow S_3$ transition to become visible in the spectra, in contrast to the dye **1** containing the unsubstituted coumarin residues. As can be seen in Fig. 6a that lengthening of the chromophore causes the regular relatively slight bathochromic shift of the corresponding band, which is in a good accordance with the calculated data. In the dye **2** with the longest chain, this band becomes too wide, without a clear maximum.

CONCLUSION

Combined quantum-chemical and spectral studies of the dyes, derivatives of aminocoumarin, show that the lowest two electron transitions are splitting transitions, involving solitonic level and two low positioned acceptor levels, in contrast to the cationic cyanine dyes, where two lowest transitions are connected with two splitting donor levels and solitonic level. The considerable interaction between two acceptor levels in symmetrical dyes provides an additional decrease of the first transition energy and hence leads to the comparatively deep and intensive color, whereas the second transition with its negligible oscillator strength is practically unobserved. The higher electron transitions involve orbitals located mainly at the coumarin residue; the corresponding spectral bands appear in the short-wavelength region. Introduction of dialkylamino groups in coumarin heterocycle shifts bathochromically the long-wavelength absorption bands and considerably increases the intensity of $S_0\rightarrow S_1$ and $S_0\rightarrow S_3$ electron transitions.

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