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The structural criteria of hydrolytic stability in series of dioxaborine polymethine dyes

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ABSTRACT

The structural criteria that affect stability to the alkaline hydrolysis of dioxaborine dyes were analyzed. Dyes with different electron-donor and electron-withdrawing groups conjugated with dioxaborine cycle, and also having some steric effects were analyzed. For this purpose, some new dioxaborine dyes were synthesized. It was shown that electron-donor substituents, unlike electron-withdrawing ones, increase the hydrolytic stability of the dioxaborine dyes. The possible way of the basic hydrolysis of dioxaborine dyes was suggested. The products of the partial hydrolysis of the symmetrical dioxaborine dyes were first obtained.

1. Introduction

Polymethine dyes based on 2,2-difluoro-1,3,2(2H)-dioxaborine (DOB-dyes, structure A, Fig. 1) are noted for their deep colour and intense luminescence [1–15], effective two-photon absorption cross-section [6,16], as well as large second- [2] and third-order [3] hyperpolarizabilities. However, a significant drawback of DOB-dyes on the way to expand their practical applications exists, which are not always acceptable stability and particularly low stability towards hydrolysis of dioxaborine cycle. Notably, the stability of luminophors in alkaline medium (pH ~ 8–9) is an important characteristic of the dyes that are used in biological studies, for example for fluorescent labels of biomolecules. Therefore, it was important to identify and examine the factors that affect the resistance of DOB-dyes to alkaline hydrolysis. In this work we investigated hydrolytic stability for both: new and described in the literature DOB-dyes.

2. Results and discussion

We have recently shown that the introduction of dialkylamino groups to the coumarin nucleus gives rise to the dramatic increase of the absorption, fluorescence intensities and the hydrolytic stability of the DOB-based dyes (**B** and **C**-type structures) [11,12] in comparison with the unsubstituted analogues [10,11]. Improved hydrolytic stability the former dyes was explained by electron-withdrawing properties of DOB-fragment. For better understanding of these factors, which affect the stability, it was our intention to expand the above dye series with some new representatives.

The electron-donor properties are increasing on changing from diethylaminophenyl (type-**B** dyes) to julolidine fragment (derivative **2**, Scheme 1) due to rigidifying of the dialkylamino substituent, and hence increasing the positive mesomeric effect. Dioxaborine **2** was obtained in one step by the acetylation of coumarin **1** [17] with acetic anhydride in the presence of BF_3- etherate (Scheme 1).

The electron-withdrawing properties of type-**B** DOB-fragment are decreased on replacing the coumarin oxygen atom with the less electronegative quinolone nitrogen atom. As the direct introduction of the acetyl group into 3 position of the quinolone **3** [18] did not succeed, dioxaborine **6** was obtained in several steps analogously to published procedure [19] (Scheme 2).

Symmetrical anionic dyes and indolenine merocyanines were synthesized from compounds **2** and **6** by conventional methods (Scheme 3, structures in the Tables 1 and 2).

To estimate the influence of the lactone and lactam fragments on the hydrolytic stability of DOB-dyes based on 4-hydroxycoumarin (dyes **7**–**10**) and 4-hydroxyquinolone (**11a**,**b**) we also analyzed benzoylacetone-based DOB-dyes (**12**–**14**, **20**, Tables 1 and 2). For this purpose new merocyanines **13b** and **14b** were synthesized (Table 2).

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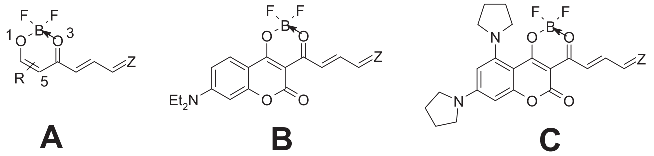


Fig. 1. General types of DOB-dyes.

The methyl group in dioxaborine **19** [20] derived from 4-dimethylaminobenzoylacetone has the very low reactivity in cyanine condensations, so that we were able to synthesize only one non-bridged merocyanine dye **20** (Scheme 4) in addition to **12b** [4].

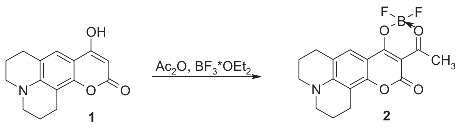
The hydrolytic stability of pyranone **15a**,**b** and pyridone **16a**,**b** dyes [13] was also investigated. For comparison, we measured the resistance to alkaline hydrolysis of known polymethine anionic **17** and cationic dyes **18** (Table 1).

In the reports [14,21] triethylamine and sodium acetate aqueous solutions were used for the study of the hydrolysis of some dioxaborine dyes. In our case, these reagents proved to be inconvenient due to the relatively high stability of the most dyes in these conditions. Consequently, using stronger bases, such as DBU, allowed to reduce the experiment time significantly. In our study a large excess of DBU (1:10000) was used in the acetonitrile-water (9:1) mixture, so that the measurements would only depend on the dye concentration. On the addition of DBU to an aqueous-acetonitrile dye solution the series of the absorption spectra, depending on the reaction time, was obtained (Fig. 2a). The subsequent measurement of the optical density (D) led to kinetic curve (D as function of time), which after the transformation gave the linear dependence shown in Fig. 2b, which allowed for the hydrolytic stability constants of the dyes to be investigated (Tables 1 and 2).

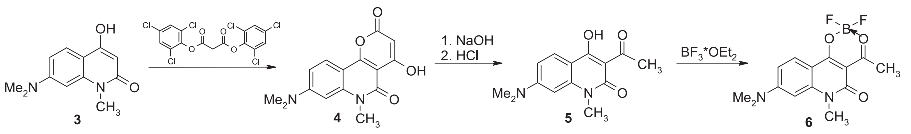
Analysis of the hydrolytic rate constants of the symmetrical DOB-dyes shows that weakening of electron-withdrawing properties of DOB-nucleus significantly increases their stability (Table 1). For example, rigidifying of the chromophore part with the methylene bridge in the case of benzoylacetone derivatives (dye **13a**) leads to a decrease of electron-withdrawing properties of DOB-fragment (compared with **12a**). The reason for this is strengthening of the conjugation between the phenyl nucleus and the DOB-cycle, and the introduction of electron-donating methylene group at the position 5. At the same time, the introduction of the ethylene bridge (dye **14a**) hardly changes electron-donor effect of the substituent at the position 5 of DOB-cycle, but the conjugation with the phenyl fragment distinctly disrupts, because of the distortion of the planarity [7]. Such trends in the electron-withdrawing properties of DOB-fragment are in good agreement with the hydrolytic stability of these dyes, which increases in the series: **12a** < **14a** < **13a**.

On comparison of coumarin dye **7a** with benzoylacetone derivative **12a**, one can see that the formation of the lactone cycle drastically (by more than two orders of magnitude) reduces the hydrolytic stability of these dyes due to the electron-withdrawing effect of the ester group at the position 5 of DOB-cycle. The electron-withdrawing properties of the DOB-fragment are decreased on replacing the lactone fragment (dyes **8a**, **15a**) with the lactam (dyes **11a**, **16a**), which results in the higher hydrolytic stability of the dyes. Introduction of electron-donating dialkylamino groups into the coumarin nucleus (dyes **8a**, **9a**, **10a**) leads to a subsequent increase in the stability to the alkaline hydrolysis (half-lifetime ($t_{0.5}$) is 410 s, 870 s and 26660 s respectively). Thus, the highest stability is reached for the dipyrrolidylcoumarin-based dye (**10a**). The additional factor that affects the stability of this dye could be the steric hindrance (from the second pyrrolidyl-group) to attack at the DOB-cycle by the hydroxyl anion.

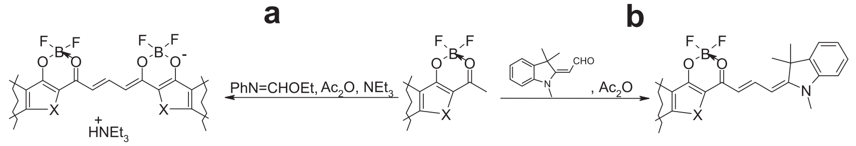
For all investigated symmetrical (**7a**–**16a**) and indolenin-type merocyanine dyes (**7b**–**16b**), (except for **7a**, **7b** and **15a**, **15b** dyes) we noticed the higher stability of symmetrical dyes, caused by the anionic character of the chromophore (Tables 1 and 2). A chromophore charge (positive or negative) significantly affects the resistance to alkaline hydrolysis. This phenomenon is very well exemplified by the conventional cationic (**18**, $t_{0.5}$ = 116 s) and anionic (**17**, $t_{0.5}$ = 7750 s) symmetrical dyes. In addition, the deviation from the symmetrical distribution of electron density, typical of merocyanines, could also be the reason of their lower hydrolytic stability. However, within the dye pairs **7a**–**7b**, and **15a**–**15b** with the strong electron-withdrawing DOB-nucleus, asymmetrical electronic structure of the merocyanines (**7b** and **15b**) results in increasing their hydrolytic stability, compared to their symmetrical analogs (**7a** and **15a**), due to the strong shift of the electron density towards the DOB-cycle.



Scheme 1. Synthesis of boron difluoride complex **2**.



Scheme 2. Synthesis of boron difluoride complex **6**.



X = -OCO-, -(CH$_3$)NCO-, -CH$_2$-, -(CH$_2$)$_2$-

Scheme 3. General method for the DOB-dyes synthesis: a) anionic symmetrical dyes; b) indolenine-based merocyanines (Table 1).

Table 1
Spectral properties and hydrolytic stability parameters of symmetric polymethine dyes.

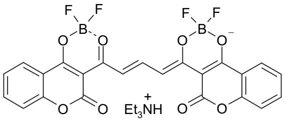
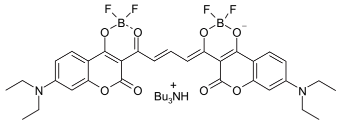
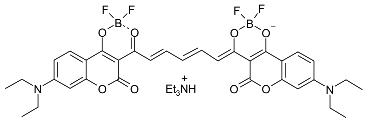
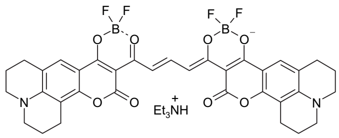
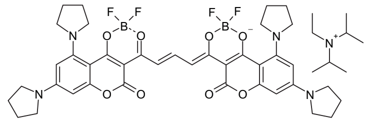
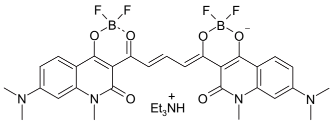
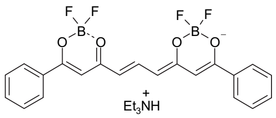
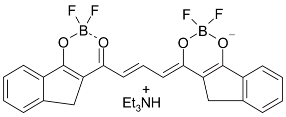
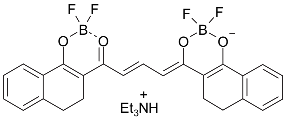
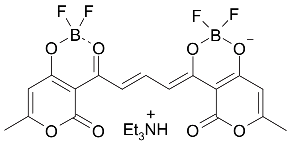
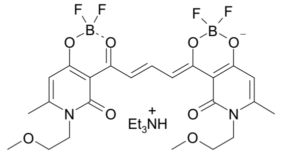
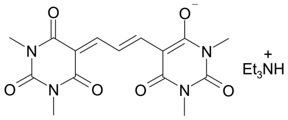
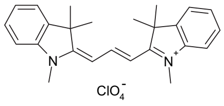
Dye	Structure	λ_{abs}(MeCN), nm ($\varepsilon \cdot 10^{-5}$, M^{-1} cm^{-1})	λ_{em}(MeCN), nm (φ)	$t_{0.5}$, s	k, s^{-1}
7a		572 (2.15)	581(0.04)	13	$5.36 \cdot 10^{-2}$
8a		615 (2.52)	636 (0.86)	410	$1.69 \cdot 10^{-3}$
8c		712 (3.00)	732 (0.66)	60	$1.15 \cdot 10^{-2}$
9a		663 (2.73)	666 (0.11)	870	$7.98 \cdot 10^{-4}$
10a		633 (3.00)	661 (0.29)	26660	$2.60 \cdot 10^{-5}$
11a		617 (1.96)	631 (0.31)	2040	$3.40 \cdot 10^{-4}$
12a		597 (1.14)	618 (0.25)[c]	2330	$2.98 \cdot 10^{-4}$
13a		606 (2.11)	621 (0.50)[c]	11950	$5.80 \cdot 10^{-5}$
14a		619 (2.14)	636 (0.30)[c]	4680	$1.48 \cdot 10^{-4}$
15a		554 (1.55)	560 (0.12)	112	$6.19 \cdot 10^{-3}$

Table 1 (*continued*)

Dye	Structure	λ_{abs}(MeCN), nm ($\varepsilon\cdot10^{-5}$, M^{-1} cm^{-1})	λ_{em}(MeCN), nm (φ)	$t_{0.5}$, s	*k*, s^{-1}
16a		5.68 (1.47)	575 (0.20)	260	$2.67\cdot10^{-3}$
17		495 (1.13)[a]	–	7750	$8.94\cdot10^{-5}$
18		542 (1.38)	568 (0.03)[b]	116	$5.96\cdot10^{-3}$

$t_{0.5}$ – half lifetime. *k* – hydrolytic rate constant.

[a] In $CHCl_3$.

[b] In EtOH.

[c] In CH_2Cl_2.

Merocyanine dye **20** derived from 4-dimetylaminobenzoylacetone shows one of the highest values of the hydrolytic stability ($t_{0.5}$ = 11890 s) within the merocyanine series. However, such a decrease of the electron-withdrawing properties of the DOB-fragment has its drawback: the methyl group in dioxaborine **19** reactivity is considerably decreased, which limits the synthetic versatility of the initial complex.

For diethylaminocoumarin-based merocyanines (**8b**, **8e** and **8f**), the increase in the electron-donor ability of the second heterocyclic residue, gives rise to the increased hydrolytic stability of the dyes. Thus, in passing from indolenine merocyanine **8b** ($t_{0.5}$ = 300 s) to benzothiazole **8e** ($t_{0.5}$ = 1050 s), and quinoline derivatives **8f** ($t_{0.5}$ = 4310 s) the hydrolytic stability increases by more than an order of magnitude, which significantly exceeds the respective characteristic for symmetrical dye **8a** ($t_{0.5}$ = 410 s). This could be explained in terms of the increased electron-donor ability of the heterocyclic residue and hence shifted electron density towards the DOB-cycle.

The influence of the polymethine chain length on the hydrolytic stability of the dyes could be examplified by the vinylogue dyes **8a** ($t_{0.5}$ = 410 s) and **8c** ($t_{0.5}$ = 60 s), as well as **8b** ($t_{0.5}$ = 300s) and **8d** ($t_{0.5}$ = 42 s). On passing from trimethine- to pentamethinecyanine system, the hydrolytic stability is significantly decreased (Tables 1 and 2). For the heptamethinecyanine dye, the solution decolorized immediately after the addition of the base (DBU). Similar conclusions on the influence of the polymethine chain length on the hydrolytic stability of DOB-dyes were drawn in the literature [14].

It is known that merocyanines with DOB-nuclei are hydrolyzed to the corresponding 1,3-dicarbonyl compounds (Scheme 5) [8,11,22,23].

In the case of the symmetrical trimethine DOB-dyes it was expected that the products of hydrolysis would be 1,3,7,9-tetracarbonyl derivatives. But on treating compound **8a** with tetrabutylammonium hydroxide only partially hydrolyzed anionic dye **21** was isolated (Scheme 6).

The singlet at −144 ppm in ^{19}F NMR spectrum of the reaction product confirms the presence of the remaining non-hydrolyzed DOB-cycle. The ^{1}H NMR spectrum of dye **21** reveals the presence of nonequivalent protons from the heterocyclic residues and the chain, which clearly proves the asymmetric character of the molecule (Fig. 3). Elemental analysis of the compound is in good agreement with the proposed structure. Treating of compound **21** with BF_3-etherate in the presence of triethylamine results in the initial dye **8a** (confirmed by the absorption spectrum) (Scheme 2). The stability of dye **21** to the further hydrolysis could be explained in terms of the greater negative charge, localized on the DOB-cycle, than in case of **8a**.

The absorption maximum of dye **21** is only 39 nm higher than that of corresponding dye **8a**, with the significantly lower absorption intensity (Fig. 4). The noticeable broadening of the absorption band could be the result of the asymmetrical distribution of the electron density.

The partial hydrolysis products of the symmetrical dyes **7a** and **12a** were obtained similarly to **8a**. In the case of the large excess of base and more drastic hydrolysis conditions, only products of the complete destruction were observed, and 1,3,7,9-tetracarbonyl derivatives were not obtained.

We assume that the initial step of the reaction of DOB-dye A with base is the addition of the hydroxyl anion to the meso-atom of the polymethine chain with the formation of intermediate D (Scheme 7), accompanied by breaking of the conjugation and hence a loss of the resonance stabilization of the DOB-cycle. Subsequently, the DOB-cycle undergoes the further hydrolysis with the formation of the intermediate E. Upon of the acidification of the reaction mixture, dye A absorption band appears, as well as that of the hydrolyzed product F in the electronic spectrum. Thus, the partial regeneration of the initial dye A through the elimination of the hydroxyl group from intermediate D confirms the suggested mechanism.

3. Experiment

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

NMR spectra were obtained with a Varian VXR-300 instrument (300 MHz) at 25 °C using tetramethylsilane as an internal standard for ^{1}H NMR and $CFCl_3$ for ^{19}F NMR.

Table 2
Spectral properties and hydrolytic stability parameters of merocyanine dyes.

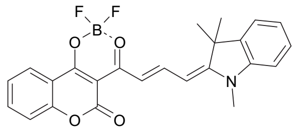
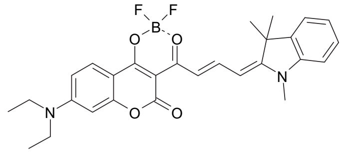
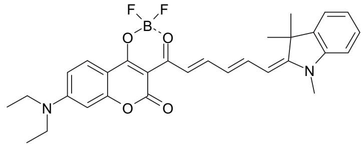
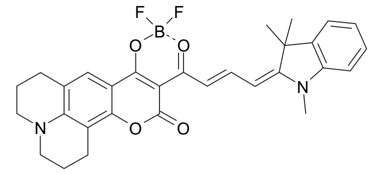
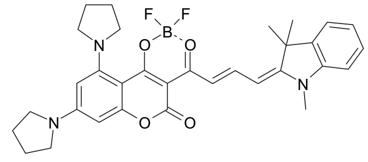
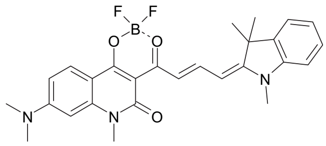
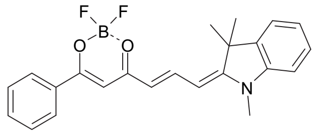
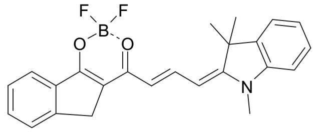
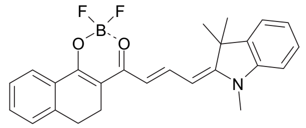
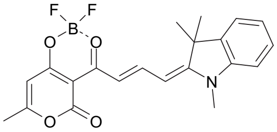
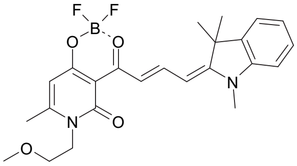
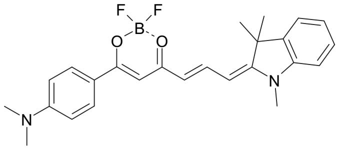
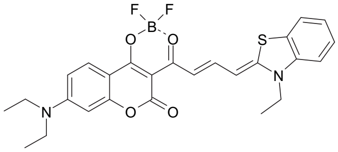
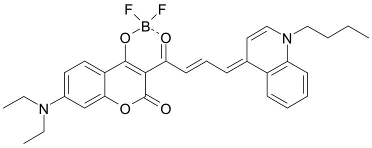
Dye	Structure	λ_{abs}(MeCN), nm ($\varepsilon \cdot 10^{-5}$, M^{-1} cm^{-1})	λ_{em}(MeCN), nm (φ)	$t_{0.5}$, s	k, s^{-1}
7b		568 (0.79)	590 (<0.005)	50	$1.40 \cdot 10^{-2}$
8b		584 (1.95)	607 (0.125)	300	$2.33 \cdot 10^{-3}$
8d		678 (2.31)	701 (0.52)	42	$1.64 \cdot 10^{-2}$
9b		593 (1.83)	621 (0.05)	340	$2.04 \cdot 10^{-3}$
10b		588 (1.81)	607 (0.1)	7330	$9.46 \cdot 10^{-5}$
11b		583 (1.85)	605 (0.18)	2240	$3.09 \cdot 10^{-4}$
12b		562 (1.25)[a]	[b]	890	$7.80 \cdot 10^{-4}$
13b		567 (1.32)	[b]	700	$9.87 \cdot 10^{-4}$
14b		576 (1.21)	[b]	330	$2.12 \cdot 10^{-3}$

Table 2 (*continued*)

Dye	Structure	λ_{abs}(MeCN), nm ($\varepsilon\cdot10^{-5}$, $M^{-1}\ cm^{-1}$)	λ_{em}(MeCN), nm (φ)	$t_{0.5}$, s	k, s^{-1}
15b		554 (0.88)	566 (0.013)	113	$5.20\cdot10^{-3}$
16b		558 (1.29)	575 (0.021)	175	$3.96\cdot10^{-3}$
20		581 (1.34)	620 (0.28)	11890	$5.83\cdot10^{-5}$
8e		590 (1.71)	608 (0.105)	1050	$6.61\cdot10^{-4}$
8f		646 (1.26)	670 (0.05)	4310	$1.61\cdot10^{-4}$

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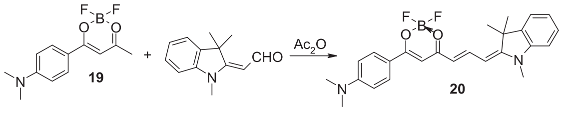
[a] In CH_2Cl_2.

[b] Emission spectra were not recorded.



Scheme 4. Synthesis of merocyanine 20.

3.1. Measuring of the hydrolytic stability constants

0.1 ml DBU 10 ml was added to the stirred aqueous-acetonitrile (9:1) dye solution with optical density ~1 (molar ratio Dye:DBU – 1:10000), and the series of the absorption spectra, depending on the reaction time, were recorded. The kinetic curve was plotted based on the changing of optical density of the absorption

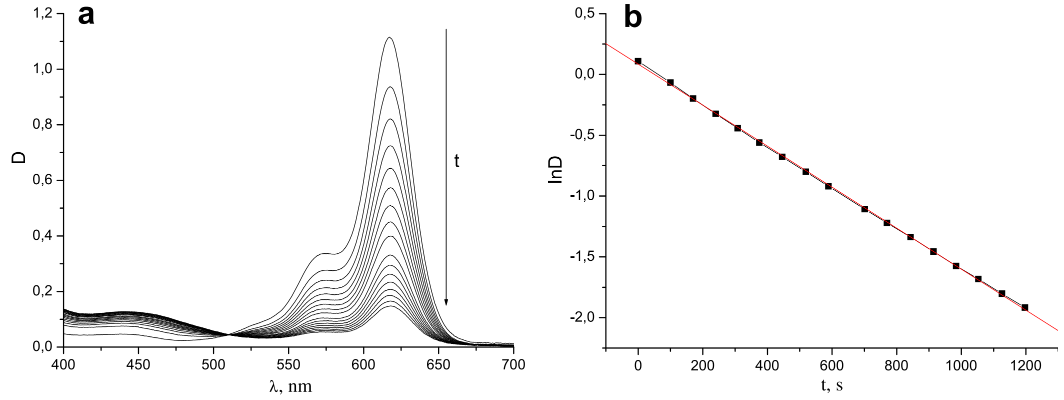
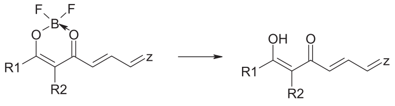
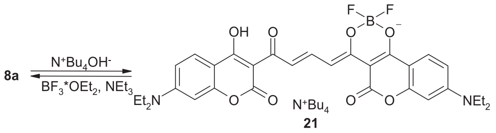


Fig. 2. a) absorption spectra of water-acetonitrile (1:9) solution of **8a** ($0.6\cdot10^{-5}$ M) with DBU ($1\cdot10^{4}$ eq.) depending on time; b) kinetic curve in the coordinates lnD-t.



Scheme 5. Hydrolysis of DOB-dyes.



Scheme 6. Partial hydrolysis of symmetrical anionic dye **8a**.

maximum (Fig. 2b). In all cases the rate of hydrolysis was first order with respect to the dye concentration.

Synthesis of dyes **7a**, **8a**, **8c**, **7b**, **8b**, **8d**, **8e** and **8f** was described in literature [11]; **10a** and **10b** [12]; **12a** and **12b** [4]; **13a** and **14a** [7]; **15a**, **15b**, **16a** and **16b** [13].

3.2. *2,2-Difluoro-4-methyl-5-oxo-(5H)-(2,3,4,6,7,8-hexahydroquinolyzine)[9,10,1-g,h]chromeno[4,3-d]-1,3,2-(2H)-dioxaborine (**2**)*

A mixture of coumarin **1** (1.3 g, 5 mmol) and BF_3-etherate (1.0 g, 7 mmol) in acetic anhydride (5 ml) was refluxed for 10 min. The mixture was cooled, the product was filtered off and washed with ether. Yield: 1.62 g (93%); m.p. 249–251 °C (dec.); ^{1}H NMR ($CDCl_3$): $\delta = 1.88$ (m, 4 H, CH_2), 2,76 (m, 4 H, CH_2), 2.81 (s, 3 H, CH_3), 3.44 (m, 4 H, NCH_2), 7.46 (s, 1 H, Ar-H); λ_{abs} 449 nm ($CHCl_3$); elemental analysis calcd (%) for $C_{17}H_{16}BF_2NO_4$: C 58.79, H 4.61, N 4.03; found: C 58.66, H 4.58, N 3.97.

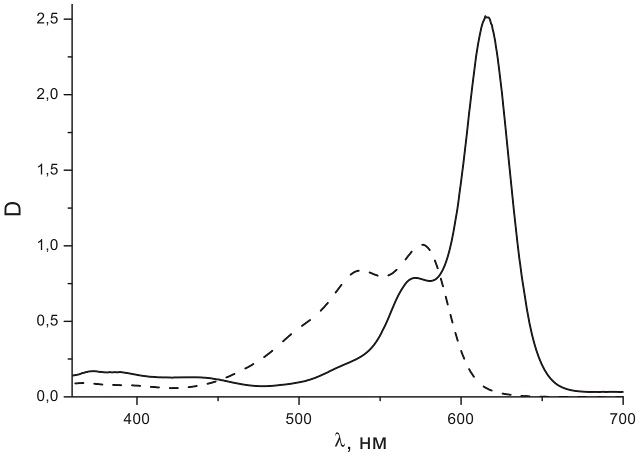


Fig. 4. Absorption spectra of dyes **8a** (—) and **21** (–) in acetonitrile ($1\cdot10^{-5}$ M).

3.3. *8-(Dimethylamino)-4-hydroxy-6-methyl-(6H)-pyrano[3,2-c] quinolino-2,5-dion (**4**)*

A mixture of quinolone **3** (3.75 g, 17 mmol) and di-(2,4,6-trichlorophenyl) malonate (8.0 g, 17 mmol) was heated at 190 °C for 15 min. The melt was triturated with acetone and compound **4** was filtered off. Yield: 3.7 g (75%); m.p. >300 °C; elemental analysis calcd (%) for $C_{15}H_{14}N_2O_4$: C 62.93, H 4.93, N 9.79; found: C 62.76, H 5.03, N 9.89.

3.4. *3-Acetyl-7-(dimethylamino)-4-hydroxy-1-methylquinolin-2 (1H)-on (**5**)*

A mixture of compound **4** (4.45 g, 16 mmol), sodium hydroxide (8.9 g, 223 mmol), water (12 ml) and ethylene glycol (77 ml) was refluxed for 1.5 h. The mixture was cooled and neutralized with

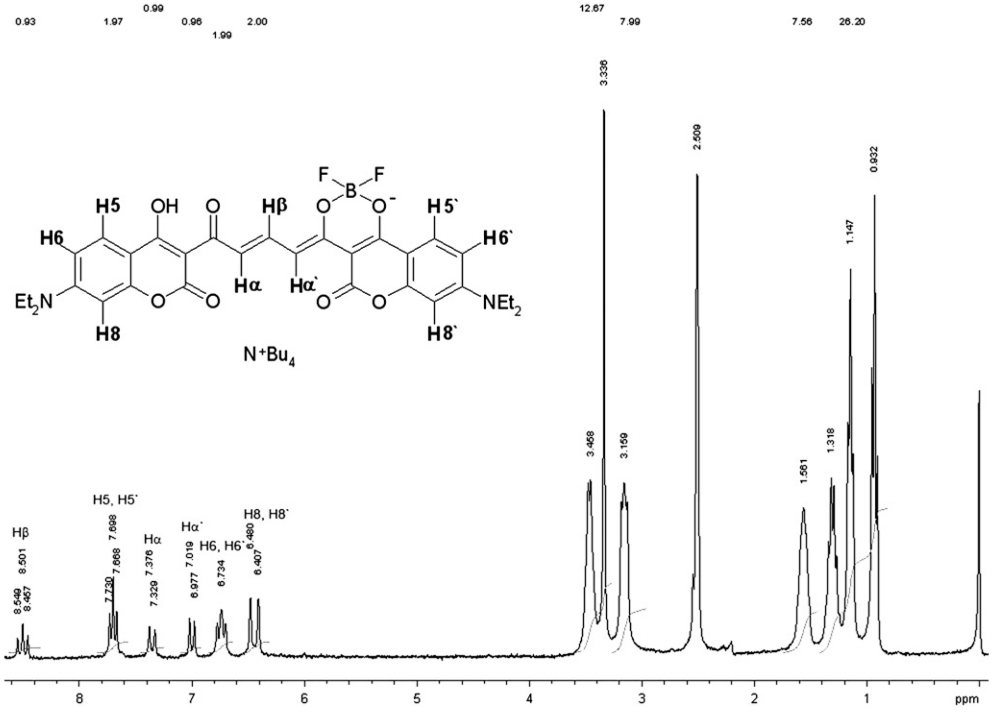
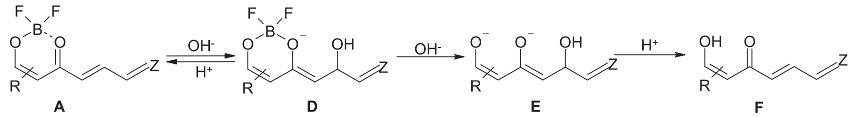


Fig. 3. ^{1}H NMR spectrum of dye **21** in DMSO-d_6.



Scheme 7. Proposed mechanism for DOB-dyes hydrolysis.

hydrochloric acid. The product was filtered off and washed with water. Yield: 2.2 g (53%); m.p. 244–245 °C (DMF); ^{1}H NMR (DMSO-d_6): $\delta = 2.66$ (s, 3 H, CH_3), 3.13 (s, 6 H, NCH_3), 3.50 (s, 3 H, NCH_3), 6.32 (s, 1 H, 8-H), 6.74 (d, $J = 9.3$ Hz,1 H, 6-H), 7.85 (d, $J = 9.3$ Hz, 1 H, 5-H), 16.93 (s, 1 H, OH); λ_{abs} 386 nm ($CHCl_3$); elemental analysis calcd (%) for $C_{14}H_{16}N_2O_3$: C 64.60, H 6.20, N 10.76; found: C 64.63, H 6.25, N 10.71.

3.5. 2,2-Difluoro-4,6-dimethyl-5-oxo-(5H)-8-dimethylaminoquinolino[4,3-d]-1,3,2-(2H)-dioxaborine (*6*)

A mixture of quinolone **5** (400 mg, 1.54 mmol), BF_3-etherate (280 mg, 1.97 mmol), acetic anhydride (370 mg, 3.6 mmol) in dry acetonitrile (3 ml) was refluxed for 15 min. The mixture was allowed to stand for 12 h and the product was filtered off. Yield: 430 mg (90%); m.p. 294–295 °C; ^{1}H NMR (DMSO-d_6): $\delta = 2.79$ (s, 3 H, CH_3), 3.21 (s, 6 H, NCH_3), 3.50 (s, 3 H, NCH_3), 6.30 (s, 1 H, 7-H), 6.83 (d, $J = 9.3$ Hz, 1 H, 9-H), 7.90 (d, $J = 9.3$ Hz, 1 H, 10-H); λ_{abs} 425 nm (MeCN); elemental analysis calcd (%) for $C_{14}H_{15}BF_4N_2O_3$: C 54.55, H 4.87, N 9.09; found: C 54.67, H 4.94, N 9.14.

3.6. Dyes 9a and 11a

A mixture of the corresponding dioxaborine (1 mmol), ethylisoformanilide (0.5 mmol) and triethylamine (1.5 mmol) in acetic anhydride (5 ml) was stirred at room temperature for 24 h. The product was filtered off.

3.7. Thiethylammonium 2,2-difluoro-4-[3-(2,2-difluoro-5-oxo-(5H)-(2,3,4,6,7,8-hexahydroquinolyzine)[9,10,1-g,h]chromeno[4,3-d]-1,3,2-(2H)-dioxaborin-4-ylidene)-1-propenyl]-5-oxo-(5H)-(2,3,4,6,7,8-hexahydroquinolyzine)[9,10,1-g,h]chromeno[4,3-d]-1,3,2-(2H)-dioxaborinate (*9a*)

Yield: 56%; m.p. >300 °C (MeCN); ^{1}H NMR (DMSO-d_6): $\delta = 1.19$ (т, $J = 7.3$ Hz, 9 H, CH_3), 1.89 (m, 8 H, CH_2), 2.74 (m, 8 H, CH_2), 3.11 (m, 6 H, NCH_2), 3.36 (m, 8 H, NCH_2), 7.28 (d, $J = 13.5$ Hz, 2 H, α-H), 7.37 (s, 2 H, 10-H), 8.64 (t, $J = 13.5$ Hz, 2 H, β-H), 8.88 (br.s, 1 H, N^+H); elemental analysis calcd (%) for $C_{41}H_{45}B_2F_4N_3O_8$: C 61.12, H 5.59, N 5.22; found: C 61.21, H 5.66, N 5.25.

3.8. Thiethylammonium 2,2-difluoro-4-[3-(2,2-difluoro-5-oxo-(5H)-6-methyl-8-(dimethylamino)-quinolino[4,3-d]-1,3,2-(2H)-dioxaborin-4-ylidene)-1-propenyl]-5-oxo-(5H)-6-methyl-8-dimethylamino-quinolino[4,3-d]-1,3,2-(2H)-dioxaborinate (*11a*)

Yield: 75%; m.p. >300 °C (MeCN–CH_2Cl_2); ^{1}H NMR (DMSO-d_6): $\delta = 1.17$ (m, 9 H, CH_3), 3.10 (m, 6 H, NCH_2), 3.14 (s, 6 H, NCH_3), 3.35 (s, 12 H, NCH_3), 6.34 (s, 2 H, 7-H), 6.77 (d, $J = 9.4$ Hz, 2 H, 9-H), 7.67 (d, $J = 13.8$ Hz, 2 H, α-H), 7.86 (d, $J = 9.4$ Hz, 2 H, 10-H), 8.72 (t, $J = 13.8$ Hz, 2 H, β-H), 8.84 (br.s, 1 H, N^+H); elemental analysis calcd (%) for $C_{35}H_{43}B_2F_4N_5O_6$: C 57.77, H 5.91, N 9.63; found: C 57.93, H 6.07, N 9.55.

3.9. Dyes 9b and 11b

A mixture of the corresponding dioxaborine (1 mmol), (1,3,3-trimethyl-1,3-dihydroindol-2-ylidene)acetaldehyde (Fisher' aldehyde) (1.05 mmol) in acetic anhydride was refluxed for 5 min. The mixture was allowed to stand for 12 h and the product was filtered off.

3.10. 2,2-Difluoro-4-[3-(1,3,3-trimethylindolin-2-ylidene)-1-propenyl]-5-oxo-(5H)-(2,3,4,6,7,8- hexahydroquinolyzine)[9,10,1-g,h]chromeno[4,3-d]-1,3,2-(2H)-dioxaborine (*9b*)

Yield: 94%; m.p. >300 °C; ^{1}H NMR (DMSO-d_6): $\delta = 1.61$ (s, 6 H, CH_3), 1.85 (m, 4 H, CH_2), 2.70 (m, 4 H, CH_2), 3.30 (m, 4 H, NCH_2), 3.61 (s, 3 H, NCH_3), 6.38 (d, $J = 14.4$ Hz, 1 H, α′-H), 7.24 (m, 1 H, 5′-H), 7.38 (m, 4 H, 10-H, 6′-H, 7′-H, α-H), 7.57 (d, $J = 7.5$ Hz, 1 H, 4′-H), 8.52 (t, $J = 13.5$ Hz, 1 H, β-H); elemental analysis calcd (%) for $C_{30}H_{29}BF_2N_2O_4$: C 67.92, H 5.47, N 5.28; found: C 67.95, H 5.45, N 5.31.

3.11. 2,2-Difluoro-4-[3-(1,3,3-trimethylindolin-2-ylidene)-1-propenyl]-5-oxo-(5H)-6-methyl-8-dimethylamino-quinolino[4,3-d]-1,3,2-(2H)-dioxaborine (*11b*)

Yield: 26%; m.p. >300 °C (DMF); ^{1}H NMR (DMSO-d_6): $\delta = 1.66$ (s, 6 H, CH_3), 3.16 (s, 6 H, NCH_3), 3.57 (s, 3 H, NCH_3), 3.62 (s, 3 H, NCH_3), 6.34 (m, 2 H, 7-H, α′-H), 6.79 (d, $J = 9.6$ Hz, 1 H, 9-H), 7.25 (t, $J = 6.9$ Hz, 1 H, 5′-H), 7.40 (m, 2 H, 6′-H, 7′-H), 7.61 (d, $J = 6.9$ Hz, 1 H, 4′-H), 7.80 (d, $J = 12.6$ Hz, 1 H, α-H), 7.88 (d, $J = 9.6$ Hz, 1 H, 10-H), 8.57 (t, $J = 13.8$ Hz, 1 H, β-H); elemental analysis calcd (%) for $C_{27}H_{28}BF_2N_3O_3$: C 66.00, H 5.74, N 8.55; found: C 65.96, H 5.76, N 8.55.

3.12. Dyes 13b, 14b

A mixture of the corresponding dioxaborine [24] (1mmol), (1,3,3-trimethyl-1,3-dihydroindol-2-ylidene)acetaldehyde (Fisher' aldehyde) (1 mmol) in acetic anhydride (1.2 ml) was heated at 100°C for 1 h and cooled to room temperature. The resulting solid was suspended in diethyl ether (25 ml), and the mixture was allowed to stand for 2 h. The precipitate was filtered off and washed with diethyl ether.

3.13. 2,2-Difluoro-4-[3-(1,3,3-trimethyl-(1H,3H)indol-2-ylidene)-propenyl]-5H-indeno-[2,1-e]-1,3,2(2H)-dioxaborine (*13b*)

Yield: 0.16 g (39 %); m.p. 213–214 °C (MeCN); ^{1}H NMR $CDCl_3$, TMS: $\delta = 1.68$ (s, 6H, 2 × CH_3), 3.39 (s, 3H, NCH_3), 3.61 (s, 2H, CH_2), 5.68 (d, $J = 13.6$ Hz, 1H, CH_γ), 5.97 (d, $J = 13.6$ Hz, 1H, CH_α), 6.91 (d, $J = 8$ Hz, 1H, H_{Ar}), 7.11 (t, $J = 7.6$ Hz, 1H, H_{Ar}), 7.26–7.35 (m, 4H, H_{Ar}), 7.43 (m, 1 H, H_{Ar}), 7.85(d, $J = 7.6$ Hz, 1H, H_{Ar}), 8.47 (t, $J = 13.6$ Hz, 1 H, CH_β); elemental analysis calcd (%) for $C_{24}H_{22}BF_2NO_2$: C 71.13, H 5.47, N 3.46; found C 71.02, H 5.50, N 3.42.

3.14. 2,2-Difluoro-4-[3-(1,3,3-trimethyl-(1H,3H)indol-2-ylidene)-propenyl]-5H,6H-naphtho-[2,1-e]- 1,3,2(2H)-dioxaborine (*14b*)

Yield: 0.22 g (52%); m.p. 187–188 °C (AcOH); ^{1}H NMR DMSO: $\delta = 1.64$ (s, 6H, CH_3), 2.66 (m, 2H, CH_2), 2.92 (m, 2H, CH_2), 3.56

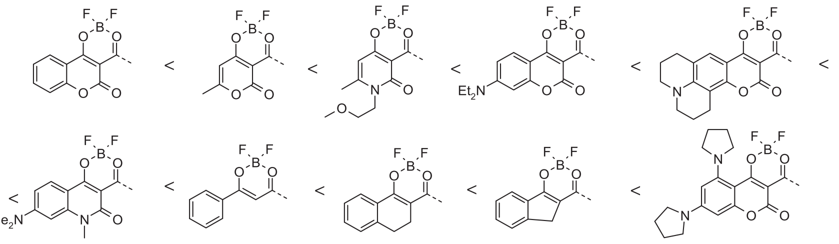


Fig. 5.

(s, 3H, NCH_3), 6.28 (d, $J = 13.0$ Hz, α-H), 7.23 (m, 1H, H_{Ar}), 7.39 (m, 4H, γ-H, H_{Ar}), 7.49 (m,2H, H_{Ar}), 7.58 (d, $J = 7.5$ Hz, H_{Ar}), 7.81 (d, $J = 7.5$ Hz, H_{Ar}), 8.42 (t, $J = 12.5$ Hz, β-H); elemental analysis calcd (%) for $C_{25}H_{24}BF_2NO_2$: C 71.62, H 5.77, N 3.34; found C 71.79, H 5.84, N 3.37.

*3.15. 2,2-Difluoro-4-[3-(1,3,3-trimethylindolin-2-ylidene)-1-propenyl]-6-(4-dimethylaminophenyl)-1,3,2-(2H)-dioxaborine (**20**)*

A mixture of compound **19** (50 mg, 0.2 mmol), (1,3,3-trimethyl-1,3-dihydroindol-2-ylidene)acetaldehyde (Fisher' aldehyde) (40 mg, 0.2 mmol) and triethylamine (40 mg, 0.4 mmol) in acetic anhydride was refluxed for 45 min. The mixture was cooled and allowed to stand for 12 h to crystallize. The product was filtered off, and washed with *i*-PrOH. Yield: 54 mg (63%); m.p. 263–265 °C; ^1H NMR (DMSO-d_6): $\delta = 1.60$ (s, 6 H, CH_3), 3.07 (s, 3 H, NCH_3), 3.41 (s, 6 H, NCH_3), 6.16 (m, 2 H, α-H, α′-H), 6.61 (s, 1 H, 5-H), 6.80 (d, $J = 6.6$ Hz, 2 H, 3′-H, 5′-H), 7.08–7.48 (m, 4 H, CH), 7.89 (d, $J = 6.6$ Hz, 2 H, 2′-H, 6′-H), 8.16 (m, 1 H, β-H); elemental analysis calcd (%) for $C_{25}H_{27}BF_2N_2O_2$: C 68.81, H 6.19, N 6.42; found: C 68.76, H 6.16, N 6.43.

3.16. Method of symmetrical dyes partial hydrolysis

A solution of the corresponding dye (1 mmol) and 25%-solution of tetrabutylammonium hydroxide in methanol (10 mmol) was allowed to stand at room temperature for 24 h. Acetic acid (10 mmol) was added to the mixture and the product was precipitated by the addition of water and filtered off.

*3.17. Tetrabutylammonium 2,2-difluoro-4-[4-(2-oxo-(2H)-4-hydroxy-7-(diethylamino)-chromen-3-il)-4-oxobut-2-en-1-ylidene]-5-oxo-(5H)-8-(diethylamino)-chromeno[4,3-d]-1,3,2-(2H)-dioxaborinate (**21**)*

From **8a**.Yield: 77%; m.p. 145–148 °C (EtOH); ^1H NMR (DMSO-d_6): $\delta = 0.93$ (m, 12 H, CH_3), 1.15 (m, 12 H, CH_3), 1.32 (m, 8 H, CH_2), 1.56 (m, 8 H, CH_2), 3.16 (m, 8 H, NCH_2), 3.46 (m, 8 H, NCH_2), 6.41 (s, 1 H), 6.47 (s, 1 H), 6.73 (m, 2 H), 7.00 (d, $J = 12.3$ Hz, 1 H), 7.37 (d, $J = 14.1$ Hz, 1 H), 7.69 (m, 2 H), 8.50 (m, 1 H), 15.50 (br.s, 1 H, OH); ^{19}F NMR (DMSO-d_6): −144.01 (BF_2); λ_{abs} 576 nm, ϵ $10.1 \cdot 10^4$ M^{-1} cm^{-1} (MeCN); λ_{em} 600 nm, φ 0.105 (MeCN); elemental analysis calcd (%) for $C_{47}H_{66}BF_2N_3O_8$: C 66.43, H 7.77, N 4.95; found: C 65.13, H 7.70, N 4.83.

3.18. Tetrabutylammonium 2,2-difluoro-4-[4-(2-oxo-(2H)-4-hydroxychromen-3-il)-4-охобут-2-en-1-ylidene]-5-oxo-(5H)-chromeno[4,3-d]-1,3,2-(2H)-dioxaborinate

From **7a**. Yield: 56%; m.p. 202–204 °C (EtOH); ^1H NMR ($CDCl_3$): $\delta = 0.98$ (m, 12 H, CH_3), 1.43 (m, 8 H, CH_2), 1.66 (m, 8 H, CH_2), 3.20 (m, 8 H, NCH_2), 7.22–7.36 (m, 5 H), 7.54–7.60 (m, 2 H), 7.65 (d, $J = 14.4$ Hz, 1 H), 8.03 (d, $J = 8.4$ Hz, 1 H), 8.10 (d, $J = 8.1$ Hz, 1 H), 8.84 (m, 1 H); λ_{abs} 551 nm (MeCN); elemental analysis calcd (%) for $C_{39}H_{48}BF_2NO_8$: C 66.20, H 6.84, N 1.98; found: C 65.93, H 6.79, N 1.90.

3.19. Tetrabutylammonium 2,2-difluoro-4-(4-oxo-6-hydroxy-6-phenylhexa-2,5-dien-1-ylidene)-5-phenyl-1,3,2-(2H)-dioxaborinate

From **12a**. Yield: 61 %; m.p. 135–138 °C (*i*-PrOH); ^1H NMR (DMSO-d_6): $\delta = 0.93$ (m, 12 H, CH_3), 1.30 (m, 8 H, CH_2), 1.55 (m, 8 H, CH_2), 3.15 (m, 8 H, NCH_2), 5.30 (d, $J = 10.5$ Hz, 1 H), 5.75 (d, $J = 13.8$ Hz, 1 H), 6.12 (s, 1 H), 6.33 (s, 1 H), 7.40–7.52 (m, 6 H), 7.77–8.03 (m, 5 H); ^{19}F NMR (DMSO-d_6): −142.50 (BF_2). λ_{abs} 525 nm (MeCN); elemental analysis calcd (%) for $C_{37}H_{52}BF_2NO_4$: C 71.26, H 8.40, N 2.25; found: C 71.03, H 8.34, N 2.31.

4. Conclusion

It was shown that the hydrolytic stability within the symmetrical DOB-dye series is increased as the electron-withdrawing properties of the DOB-fragment weaken (Fig. 5).

The DOB-based merocyanine dyes with the higher basicity of the second heterocyclic residue are characterized by the higher hydrolytic stability. Hydrolytic stability of DOB-dyes decreases by order of magnitude with lengthening of polymethine chain by each vinylen group. The mechanism of the DOB-dyes alkaline hydrolysis was suggested. The products of the partial hydrolysis of the symmetrical dioxaborine dyes were first obtained.

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