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Polymethine dyes derived from the boron difluoride complex of 3-acetyl-5,7-di(pyrrolidin-1-yl)-4-hydroxycoumarin

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ABSTRACT

A boron difluoride complex of 3-acetyl-5,7-di(pyrrolidin-1-yl)-4-hydroxycoumarin was synthesized and converted into polymethine dyes which included an anionic, symmetric cyanine and several merocyanine compounds. The spectral luminescent behaviour of the dyes was studied. As the electron-withdrawing ability of the 2,2-difluoro-1,3,2-dioxaborine ring was significantly reduced by the two pyrrolidino groups on the latter nucleus, the newly synthesized dyes exhibited changes in spectral parameters and much increased resistance to hydrolysis.

1. Introduction

The polymethine dyes derived from the dioxaborine nucleus are noted for their deep colour and intense luminescence. Since they were first reported in 1984, there has been a continued interest in their outstanding optical properties [1]. Much recent attention has been paid to nonlinear optical characteristics of such dyes, in particular, their second- and third-order hyperpolarizabilities [2,3], as well as the effective two-photon absorption cross-section [4–6]. Annelation of the coumarin nucleus to the dioxaborine ring (see structure A, Fig. 1) resulted in enhanced absorption and fluorescence of the corresponding dyes [7]. On the other hand, such compounds are known to be hydrolytically unstable. To prevent hydrolytic cleavage of the dioxaborine ring, we previously proposed to introduce a dialkylamino group into the coumarin moiety (as in structure B, Fig. 1) [8]. As also shown, this structural modification not only makes the dyes more resistant to hydrolysis but also gives rise to significant spectral effects. In particular, absorption and fluorescence intensities increase to a large extent, so that some of the dyes concerned have molar absorptivity of 320 000 l mol^{-1} cm^{-1} and quantum yield of 0.85. It might be expected that introduction of the second dialkylamino group into the coumarin nucleus of the dyes should substantially affect their spectral and other physicochemical parameters. In this context, the present work addresses the synthesis and spectral investigation of the dyes derived from the type C nuclei.

2. Experimental

Electronic absorption spectra were recorded on a Shimadzu UV-3100 spectrophotometer in acetonitrile and chloroform. ^{1}H (300 MHz, 25 °C, $Si(CH_3)_4$ as internal standard) and ^{19}F NMR (282 MHz, $CFCl_3$ as internal standard) spectra were obtained with a Varian VXR-300 instrument. LC/MS spectra were recorded using a liquid chromatography/mass spectrometric system consisting of an Agilent 1100 Series high-performance liquid chromatograph equipped with a diode-matrix and an Agilent LC/MSD SL mass-selective detector. Fluorescence spectra were recorded on a Hitachi MPF-4 fluorescence spectrophotometer. Relative fluorescence quantum yields (φ) were determined relative to Rhodamine 6G ($\varphi = 0.95$, EtOH) [9] and indodicarbocyanine iodide ($\varphi = 0.25$, EtOH) [10].

The crystals of styryl **11** were grown from a concentrated acetonitrile solution. X-ray diffraction data were collected on a Bruker Smart Apex II diffractometer using graphite-monochromated Mo κ_α radiation. The structure was solved by direct methods and refined by the full-matrix least-squares technique against F^2 of all data using the SHELXTL PLUS software [11] (Table 1).

Hydrolysis rate constant determination. To a dye solution in aqueous acetonitrile (9:1) with an optical density of 1, DBU (0.1 ml) was added so that the dye:DBU ratio was 1:10 000. On stirring the solution, absorption spectra were recorded at regular time

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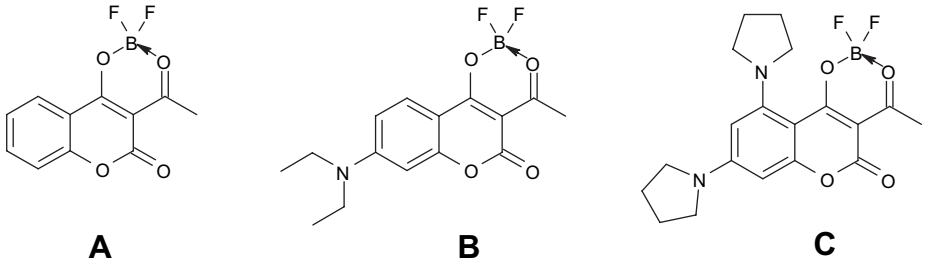
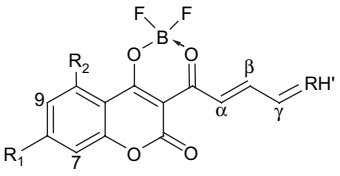


Fig. 1.

intervals. The kinetic curve was obtained by plotting optical density (at the absorption maximum) versus time. A quasi-first-order dependence on the dye concentration was assumed for the hydrolysis rate and the corresponding rate constant was calculated as a slope of the linear-fitted kinetic plot. As found, $k = 2.60 \times 10^{-5}\ s^{-1}$; $\epsilon = 1.93\%$; $r = 0.9983$ for dye **7** and $k = 1.69 \times 10^{-3}\ s^{-1}$; $\epsilon = 0.46\%$; $r = 0.9998$ for dye **13**.



2.1. Complex of 5,7-di(pyrrolidin-1-yl)-4-hydroxy-benzo[d]pyrano-2-one with 2,4,6-trichlorophenol (**2**)

A mixture of phenol **1** [12] (11.6 g, 50 mmol) and di-(2,4,6-trichlorophenyl) malonate (23.2 g, 50 mmol) in toluene (70 ml) was refluxed for 2 h. The mixture was cooled, the product was filtered off and washed with toluene. Yield 26 g (75%). M.p. 142–144 °C. ^{1}H NMR ($CDCl_3$): δ 2.00 (m, 8H, CH_2), 3.34 (m, 8H, CH_2), 5.01 (s, 1H, 3-H), 6.31 (s, 1H, 8-H), 6.70 (s, 1H, 6-H), 7.56 (s, 4H, 3′-H, 5′-H) 10.50 (s, 2H, OH), 17.11 (s, 1H, OH). Anal. calcd for $C_{29}H_{26}N_2Cl_6O_5$: C, 50.07; H, 3.75; N, 4.02; Cl, 30.6. Found: C, 49.31; H, 4.19; N, 4.27; Cl, 29.39.

2.2. 3-Acetyl-5,7-di(pyrrolidin-1-yl)-4-hydroxy-2H-chromen-2-one (**3**)

A mixture of complex **2** (18 g, 25.9 mmol), acetic anhydride (18 ml), and pyridine (36 ml) was refluxed for 2 h. The mixture was cooled, the product was filtered off and washed with *i*-PrOH. Yield 6.39 g (73%). M.p. 182–183 °C. ^{1}H NMR ($CDCl_3$): δ 1.99 (m, 4H, CH_2), 2.07 (m, 4H, CH_2), 2.70 (s, 3H, CH_3), 3.41 (m, 8H, NCH_2), 5.67 (s, 1H, 7-H), 5.93 (s, 1H, 9-H). λ_{max} 396 nm ($CHCl_3$). Anal. calcd for $C_{19}H_{22}N_2O_4$: C, 66.65; H, 6.48; N, 8.18. Found: C, 66.67; H, 6.48; N, 8.13.

2.3. 2,2-Difluoro-8,10-di(pyrrolidin-1-yl)-4-methyl-5-oxo-2H, 5H-benzo[d]pyrano[4,3-d]-1,3,2-dioxaborine hydrotetrafluoroborate (**4**)

A mixture of **3** (1.71 g, 5 mmol) and BF_3-etherate (12 ml) was refluxed for 2–3 min. An excess of BF_3-etherate was removed under vacuum. Yield 2.34 g (98%). M.p. 190–193 °C (decomp.). ^{1}H NMR (CD_3CN): δ 2.08 (m, 4H, CH_2), 2.29 (m, 4H, CH_2), 2.81 (s, 3H, CH_3), 3.57 (m, 4H, NCH_2), 3.89 (m, 4H, NCH_2), 6.49 (s, 1H, 7-H), 6.71 (s, 1H, 9-H). ^{19}F NMR (CD_3CN): δ −151.35 (s, 4F, BF_4), −141.75 (s, 2F, BF_2). λ_{max} 404 nm (MeCN). Anal. calcd for $C_{19}H_{22}B_2F_6N_2O_4$: C, 47.77; H, 4.6; N, 5.87. Found: C, 47.65; H, 4.44; N, 5.98.

2.4. 2,2-Difluoro-8,10-di(pyrrolidin-1-yl)-4-methyl-5-oxo-2H, 5H-benzo[d]pyrano[4,3-d]-1,3,2-dioxaborine (**5**)

Triethylamine (1.17 g, 11.6 mmol) was added with stirring to the reaction mixture containing salt **4** (2 g, 4.18 mmol) in CH_2Cl_2. This solution was washed twice with water, dried, and evaporated. Crude **5** was crystallized from EtOAc. Yield 1.34 g (82%). M.p. 200–202 °C. ^{1}H NMR ($CDCl_3$): δ 1.98 (m, 4H, CH_2), 2.08 (m, 4H, CH_2), 2.75 (s, 3H, CH_3), 3.44 (m, 8H, NCH_2), 5.45 (s, 1H, 7-H), 5.92 (s, 1H, 9-H). λ_{max} 406 nm (MeCN). Anal. calcd for $C_{19}H_{21}BF_4N_2O_4$: C, 58.49; H, 5.42; N, 7.18. Found: C, 58.41; H, 5.36; N, 5.46.

2.5. 2,2-Difluoro-8,10-di(pyrrolidin-1-yl)-5-oxo-4-[2-(phenylamino)vinyl]-2H,5H-benzo[d]pyrano[4,3-d]-1,3,2-dioxaborine (**6**)

A mixture of **5** (0.7 g, 1.8 mmol) and ethyl isoformanilide (0.7 g, 4.7 mmol) was fused at 130 °C for 1 h. The melt was cooled and

Table 1
Crystal data and structural refinements for styryl **11**

Empirical formula	$C_{58}H_{63}B_2F_4N_7O_8$	D_c (Mg m^{-3})	1.357
Formula weight	1083.77	μ (Mo Kα) (mm^{-1})	0.100
Crystal system	Triclinic	F(000)	1140
Space group	P-1	Data collected/unique	14 949/6726
a (Å)	12.8845(2)	Limiting indices	$-13 \le h \le 13$
b (Å)	13.2137(2)		$-14 \le k \le 14$
c (Å)	18.0156(3)		$-19 \le l \le 19$
α (°)	81.5180(10)	Parameter	714
β (°)	69.9350(10)	Max/min transmission	0.9931/0.9707
γ (°)	66.9930(10)	$R1$, $wR2$ ($I > 2\sigma(I)$)	$R1 = 0.0446$, $wR2 = 0.1091$
V (Å^3)	2651.54(7)	$R1$, $wR2$ (all data)	$R1 = 0.0752$, $wR2 = 0.1273$
Crystal size (mm)	0.30 × 0.25 × 0.07	Goodness of fit on F^2	1.024
Z	2	Δ (e Å^{-3}) (max, min)	0.248/−0.179

triturated with chloroform. The resulting solid was collected by filtration and washed with chloroform. Yield 0.73 g (82%). M.p. 282–284 °C. ^{1}H NMR (DMSO-d_6): δ 1.89 (m, 4H, CH_2), 1.98 (m, 4H, CH_2), 3.31 (m, 8H, NCH_2), 5.65 (s, 1H, 7-H), 5.96 (s, 1H, 9-H), 7.39 (m, 6H, α-H, Ph), 8.63 (t, $^3J_{H,H} = 13.2$ Hz, 1H, β-H), 11.50 (d, $^3J_{H,H} = 14.2$ Hz, 1H, NH). λ_{max} 490 nm (MeCN). Anal. calcd for $C_{21}H_{23}BF_2N_2O_4$: C, 60.60; H, 5.57; N, 6.73. Found: C, 60.54; H, 5.65; N, 6.65.

2.6. Diisopropylethylammonium 2,2-difluoro-4-[3-(2,2-difluoro-8,10-di(pyrrolidin-1-yl)-5-oxo-2H,5H-benzo[d]pyrano[4,3-d]-1,3,2-dioxaborin-4-yl)-2-propen-1-ylidene]-8,10-di(pyrrolidin-1-yl)-5-oxo-2H,4H,5H-benzo[d]pyrano[4,3-d]-1,3,2-dioxaborinate (**7**)

A mixture of complex **5** (200 mg, 0.51 mmol), hemicyanine **7** (253 mg, 0.51 mmol), and diisopropylethylamine (4 ml) in acetic anhydride (5 ml) was stirred at room temperature for 24 h. The product was filtered off and washed with acetic anhydride and diethyl ether. Yield 250 mg (53%). M.p. 259–261 °C (MeCN). ^{1}H NMR (DMSO-d_6): δ 1.42 (m, 15H, CH_3), 2.03 (m, 8H, CH_2), 2.13 (m, 8H, CH_2), 3.17 (m, 2H, NCH_2), 3.34 (m, 16H, NCH_2), 3.77 (m, 2H, NCH), 5.82 (s, 2H, 7-H), 6.09 (s, 2H, 9-H), 7.36 (d, $^3J_{H,H} = 13.5$ Hz, 2H, α-H), 8.34 (br s, 1H, N^+H), 8.70 (t, $^3J_{H,H} = 13.5$ Hz, 1H, β-H). Anal. calcd for $C_{47}H_{59}O_8N_5B_2F_4$: C, 61.37; H, 6.42; N, 7.62. Found: C, 61.25; H, 6.38; N, 7.63.

2.7. 2,2-Difluoro-8,10-di(pyrrolidin-1-yl)-5-oxo-4-[3-(1,3,3-trimethylindolin-2-ylidene)-1-propenyl]-2H,5H-benzo[d]pyrano[4,3-d]-1,3,2-dioxaborine (**8**)

A mixture of complex **5** (230 mg, 0.59 mmol) and (1,3,3-trimethyl-1,3-dihydroindol-2-ylidene)acetaldehyde (142 mg, 0.71 mmol) in acetic anhydride (3–5 ml) was refluxed for 5 min. The mixture was cooled and allowed to stand for 12 h to crystallize. The product was filtered off, washed with acetic acid and diethyl ether. Yield 280 mg (83%). M.p. 220–223 °C. ^{1}H NMR ($CDCl_3$): δ 1.68 (s, 6H, CH_3), 1.96 (m, 4H, CH_2), 2.06 (m, 4H, CH_2), 3.39 (m, 11H, NCH_2, NCH_3), 5.53 (s, 1H, 7-H), 5.91 (s, 1H, 9-H), 5.92 (d, $^3J_{H,H} = 8.4$ Hz, 1H, 7′-H), 6.90 (d, $^3J_{H,H} = 12.9$ Hz, 1H, α-H), 7.10 (t, $^3J_{H,H} = 7.5$ Hz, 1H, 5′-H), 7.29 (m, 2H, 4′-H, 6′-H), 7.58 (d, $^3J_{H,H} = 13.5$ Hz, 1H, γ-H), 8.60 (t, $^3J_{H,H} = 13.4$ Hz, 1H, β-H). Anal. calcd for $C_{32}H_{34}BF_2N_3O_4$: C, 67.02; H, 5.98; N, 7.33. Found: C, 66.94; H, 5.90; N, 7.35.

2.8. 2,2-Difluoro-8,10-di(pyrrolidin-1-yl)-4-[3-(3-methylbenzo[d]thiazol-2(3H)-ylidene)-1-propenyl]-5-oxo-2H,5H-benzo[d]pyrano[4,3-d]-1,3,2-dioxaborine (**9**)

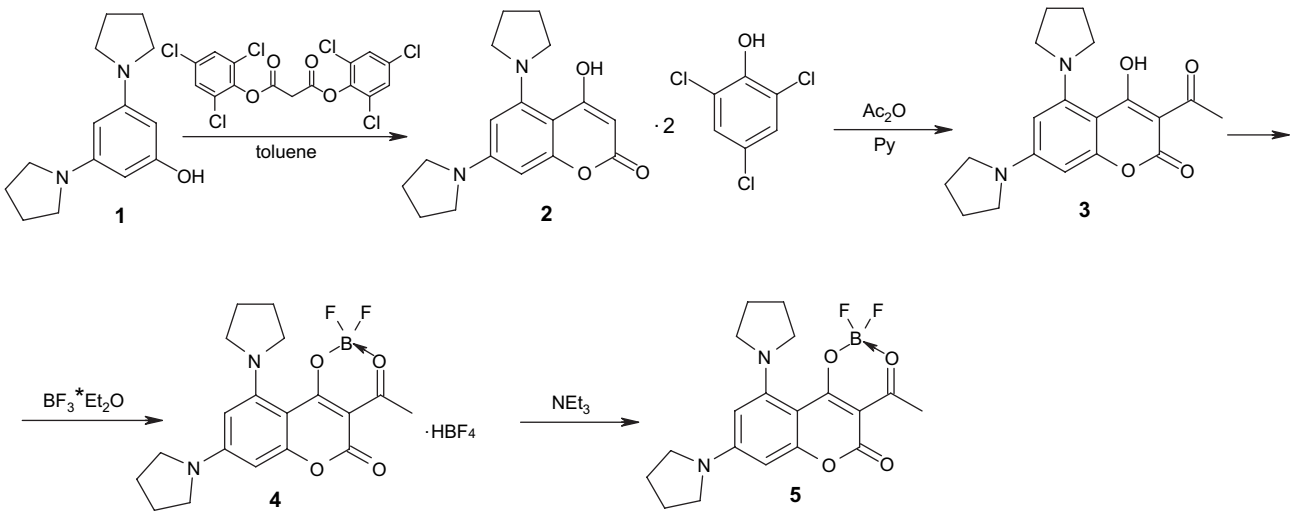
A mixture of complex **5** (196 mg, 0.5 mmol), 2-(anilidovinyl)-3-methylbenzothiazolium *p*-toluenesulfonate (220 mg, 0.5 mmol), and diisopropylethylamine (140 mg, 0.1 mmol) in pyridine (3–5 ml) was refluxed for 3 min. The mixture was cooled and allowed to stand for 12 h to crystallize. The product was filtered off and washed with acetic acid and diethyl ether. Yield 84 mg (30%). M.p. >300 °C (MeCN). ^{1}H NMR (DMSO-d_6): δ 1.88 (m, 4H, CH_2), 1.98 (m, 4H, CH_2), 3.32 (m, 8H, NCH_2), 3.84 (s, 3H, NCH_3), 5.65 (s, 1H, 7-H), 5.93 (s, 1H, 9-H), 6.57 (d, $^3J_{H,H} = 13.5$ Hz, 1H, α-H), 7.42 (m, 3H, γ-H, 5′-H, 6′-H), 7.70 (d, $^3J_{H,H} = 7.8$ Hz, 1H, 4′-H), 7.96 (d, $^3J_{H,H} = 7.8$ Hz, 1H, 7′-H), 8.15 (t, $^3J_{H,H} = 13.0$ Hz, 1H, β-H). Anal. calcd for $C_{29}H_{28}BF_2N_3O_4S$: C, 61.82; H, 5.01; N, 7.46. Found: C, 61.96; H, 5.12; N, 7.52.

2.9. 2,2-Difluoro-8,10-di(pyrrolidin-1-yl)-4-[3-(1-methylquinolin-2(1H)-ylidene)-1-propenyl]-5-oxo-2H,5H-benzo[d]pyrano[4,3-d]-1,3,2-dioxaborine (**10**)

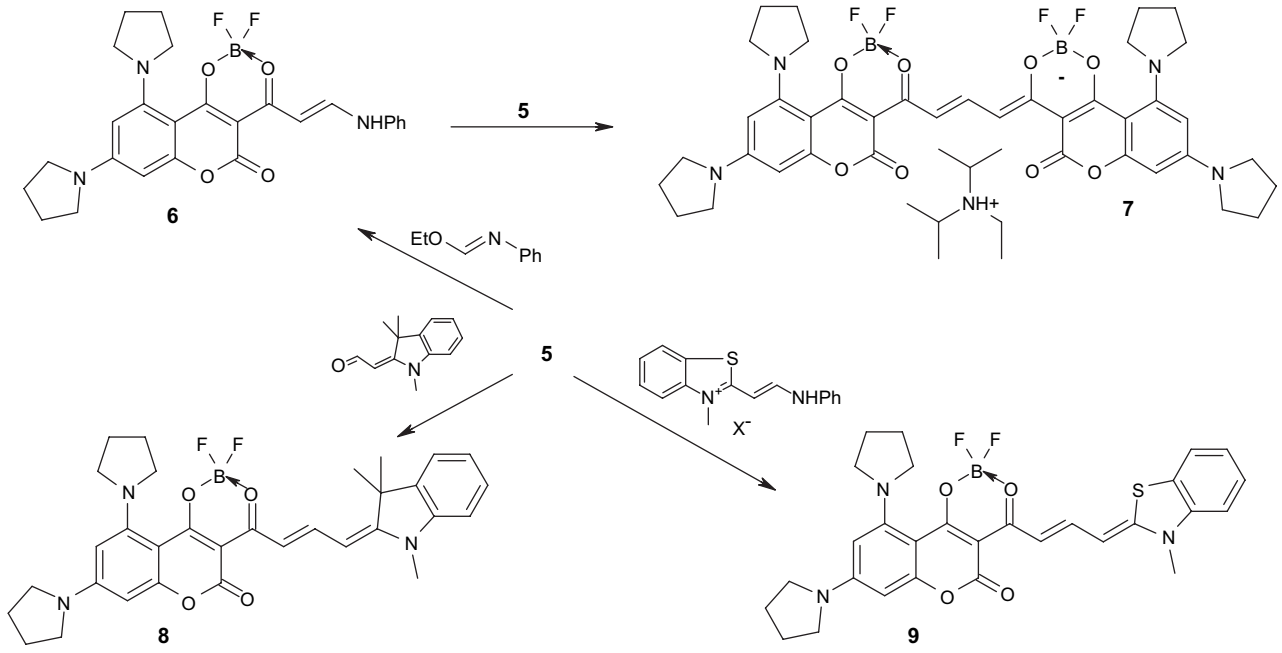
A mixture of complex **4** (240 mg, 0.5 mmol), 2-(anilinovinyl)-1-methylquinolinium *p*-toluenesulfonate (220 mg, 0.5 mmol) and triethylamine (150 mg, 1.49 mmol) in acetic anhydride (4 ml) was stirred at room temperature for 5 h. The product was filtered off and washed with acetic acid and diethyl ether. Yield 180 mg (65%). M.p. >300 °C (MeCN). ^{1}H NMR (DMSO-d_6): δ 1.88 (m, 4H, CH_2), 1.96 (m, 4H, CH_2), 3.32 (m, 8H, NCH_2), 4.01 (s, 3H, NCH_3), 5.67 (s, 1H, 7-H), 5.92 (s, 1H, 9-H), 6.54 (d, $^3J_{H,H} = 13.0$ Hz, 1H, α-H), 7.33 (d, $^3J_{H,H} = 12.6$ Hz, 1H, γ-H), 7.54 (t, $^3J_{H,H} = 7.0$ Hz, 1H, 6′-H), 7.81 (t, $^3J_{H,H} = 7.0$ Hz, 1H, 7′-H), 7.93 (d, $^3J_{H,H} = 7.7$ Hz, 1H, 8′-H), 8.00 (d, $^3J_{H,H} = 8.7$ Hz, 1H, 5′-H), 8.03 (d, $^3J_{H,H} = 9.4$ Hz, 1H, 3′-H), 8.10 (d, $^3J_{H,H} = 9.4$ Hz, 1H, 4′-H), 8.49 (t, $^3J_{H,H} = 13.0$ Hz, 1H, β-H). Anal. calcd for $C_{31}H_{30}BF_2N_3O_4$: C, 66.80; H, 5.42; N, 7.54. Found: C, 66.97; H, 5.49; N, 7.60.

2.10. 2,2-Difluoro-4-(4-(dimethylamino)styryl)-8,10-di(pyrrolidin-1-yl)-5-oxo-2H,5H-benzo[d]pyrano[4,3-d]-1,3,2-dioxaborine (**11**)

A mixture of complex **4** (478 mg, 1 mmol) and 4-dimethylaminobenzaldehyde (163 mg, 1.1 mmol) in acetic anhydride (2 ml) was refluxed for 1–2 min. The solution was cooled and triethylamine was added (230 mg, 2.28 mmol). After standing for 1 h, the



Scheme 1.



Scheme 2.

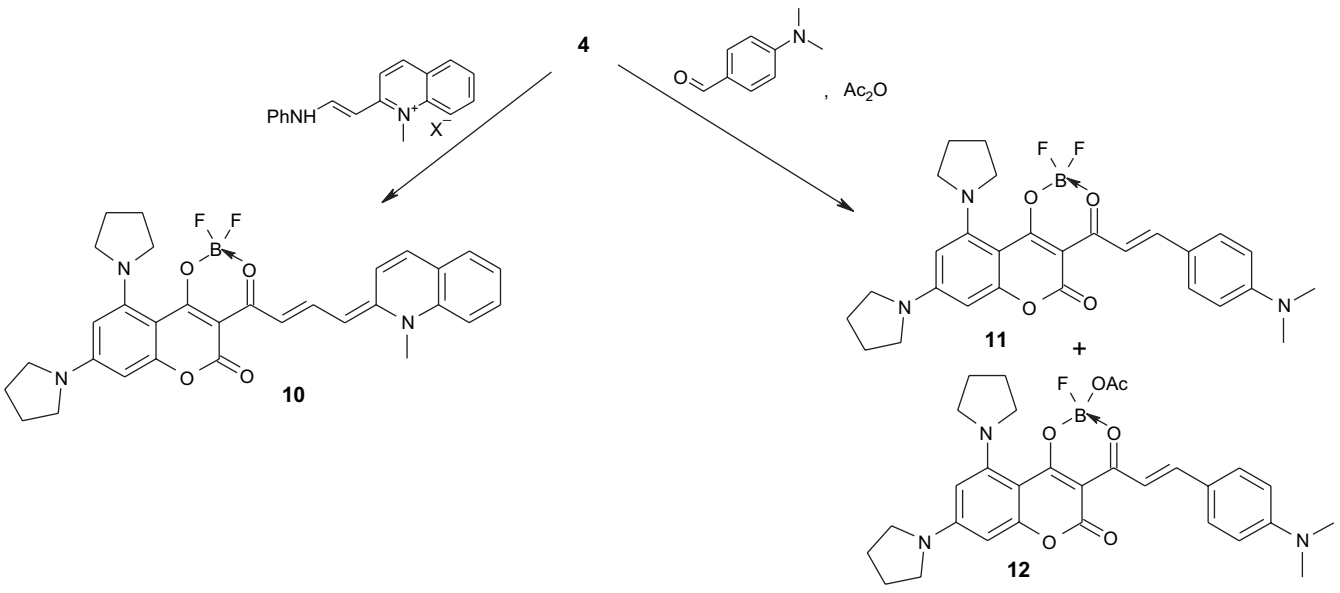
resulting solution was chromatographed on silica gel with CH_2Cl_2. The first coloured fraction was obtained and evaporated to give **11**. Yield 100 mg (19%). M.p. 269–271 °C. ^{1}H NMR ($CDCl_3$): 1.98 (m, 4H, CH_2), 2.07 (m, 4H, CH_2), 3.11 (s, 6H, NCH_3), 3.44 (m, 8H, NCH_2), 5.49 (s, 1H, 7-H), 5.93 (s, 1H, 9-H), 6.70 (d, $^3J_{H,H} = 9$ Hz, 2H, 3′-H, 5′-H), 7.67 (d, $^3J_{H,H} = 9$ Hz, 2H, 2′-H, 6′-H), 8.22 (s, 2H, α-H, β-H). ^{19}F NMR ($CDCl_3$): −142.6 (BF_2). APSI MS: $M^+ + 1 = 522$. Anal. calcd for $C_{28}H_{30}BF_2N_3O_4$: C, 64.50; H, 5.80; N, 8.06. Found: C, 64.45; H, 5.79; N, 8.10.

*2.11. 2-Acetoxy-4-(4-(dimethylamino)styryl)-8,10-di(pyrrolidin-1-yl)-2-fluoro-5-oxo-2H,5H-benzo[d]pyrano[4,3-d]-1,3,2-dioxaborine (**12**)*

After washing dye **11**, 1% methanol was added to the eluent and the second fraction, crude styryl **12** (345 mg), was collected and finally purified by chromatography using CH_2Cl_2 with 1% MeOH as the eluent. Yield 150 mg (27%). M.p. 182–185 °C. ^{1}H NMR ($CDCl_3$): 1.93 (m, 4H, CH_2), 2.04 (m, 7H, CH_2, Ac), 3.08 (s, 6H, NCH_3), 3.39 (m, 8H, NCH_2), 5.45 (s, 1H, 7-H), 5.89 (s, 1H, 9-H), 6.67 (d, $^3J_{H,H} = 8.4$ Hz, 2H, 3′-H, 5′-H), 7.62 (d, $^3J_{H,H} = 8.4$ Hz, 2H, 2′-H, 6′-H), 8.11 (d, $^3J_{H,H} = 15.5$ Hz, 1H, α-H), 8.25 (d, $^3J_{H,H} = 15.5$ Hz, 1H, β-H). ^{19}F NMR ($CDCl_3$): 19.68 (BFOAc). APSI MS: $[M\text{-}59(OAc)]^+ = 502$. Anal. calcd for $C_{30}H_{33}BFN_3O_6$: C, 64.18; H, 5.92; N, 7.48. Found: C, 64.98; H, 5.83; N, 7.40.

3. Results and discussion

Starting coumarin **2** was synthesized similarly to compound B (Fig. 1) [13]. It was, however, found that the cyclization reaction yields not a free coumarin molecule but its complex with two molecules of 2,4,6-trichlorophenol (see Scheme 1). The



Scheme 3.

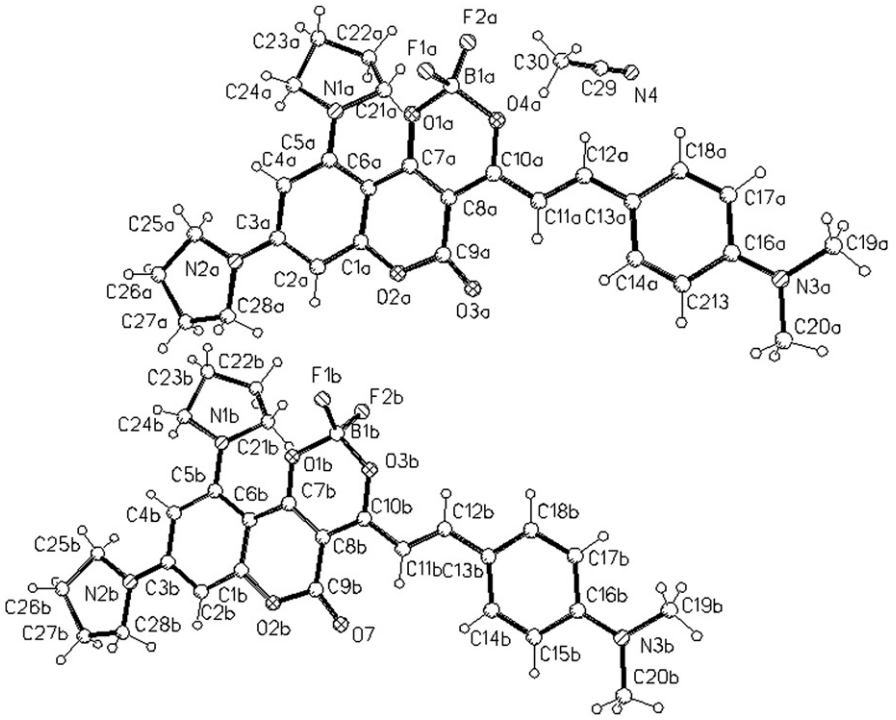


Fig. 2. Perspective view and labeling scheme for molecule **11** (according to the data of X-ray diffraction analysis).

composition of this stable complex remains unchanged on recrystallization. Isolation of free coumarin **2** proved unnecessary because it was conveniently acylated with acetic anhydride in pyridine to give derivative **3**. The latter behaved differently from its unsubstituted (structure A, Fig. 1) and 8-diethylamino-substituted (structure B, Fig. 1) analogues in the preparation of the boron complex. Compound **3** was initially reacted with boron trifluoride etherate to produce salt **4** which afforded, when treated with base, complex **5** (this complex could not be obtained by a one-step reaction).

Introduction of the second electron-donating dialkylamino group leads to the reduced electron-withdrawing ability of the dioxaborine ring. At the same time, the acidity of the methyl group at position 4 decreases, as evidenced by an upfield shift of its ^{1}H NMR signals (2.75 ppm, $CDCl_3$) relative to the corresponding proton resonances in the complex containing a single 8-dialkylamino group (2.84 ppm, $CDCl_3$). Another manifestation of this effect is the reduced reactivity of the 4-methyl group in condensation reactions. As an example, free complex **5** is inert to 4-dialkylaminobenzaldehyde but forms dye **8** with more reactive (1,3,3-trimethyl-1,3-dihydroindol-2-ylidene)-acetaldehyde (see Scheme 2). To conduct the reaction with 4-dialkylaminobenzaldehyde, we started from salt **4** as shown in Scheme 3. In compound **4**, one dialkylamino group is protonated by tetrafluoroboric acid. As a result, this substituent switches from the electron-donating to electron-withdrawing electronic nature, which, in turn makes the 4-methyl group more reactive. Thus, salt **4** reacts readily with 4-dialkylaminobenzaldehyde in acetic anhydride to provide a dye mixture. Two dyes with the same absorption maxima were separated by chromatography and characterized as the styryls **11** and **12**. The latter is formed through the substitution of one fluorine atom by an acetate group, as the reaction is performed in acetic anhydride. The acetate group gives rise to a characteristic signal in the ^{1}H NMR spectrum and also causes the ^{19}F resonance of styryl **11** (−142 ppm) to largely shift from that of styryl **12** (20 ppm). The mass spectrum of styryl **12** lacks the molecular ion but shows the peak [M-59] thus suggesting an easy elimination of the acetate group. In the ^{1}H NMR spectrum of styryl **11**, the signals from two protons of the polymethine chain appear as a singlet rather than two doublets.

The crystals of styryl **11** were grown from an acetonitrile solution and X-ray diffraction analysis clearly demonstrated the *trans* configuration of the vinylene moiety (the *trans* geometry could not be determined by NMR spectroscopy since the vinylene signals are accidentally equivalent and resonate at 8.22 ppm) (see Fig. 2).

As also shown, the crystal lattice incorporates the molecules of dye **11** and acetonitrile in the 2:1 ratio. The unit cell contains three molecules, namely, two nonequivalent dye molecules and a solvent molecule. Due to steric hindrances caused by the dioxaborine ring, the 10-pyrrolidino group is much more twisted out of the plane of the coumarin nucleus (the torsion angles C(6A)–C(5A)–N(1A)–C(21A) and C(6B)–C(5B)–N(1B)–C(21B) are 33.1(4)° and 38.3(4)°, respectively, for two molecules of styryl **11**) than the same group at position 8 (the corresponding torsion angles C(4A)–C(3A)–N(2A)–C(25A) and C(4B)–C(3B)–N(2B)–C(25B) are −0.4(4)° and 3.0(4)°). In both dye molecules **11**, the N–C(sp^2) bond of the pyrrolidino substituent at position 8 is shorter than that at position 10 (compare the respective distances C(3A)–N(2A) of 1.344(3) Å and C(3B)–N(2B) of 1.363(3) Å for the former bond with C(5A)–N(1A) of 1.365(3) Å and C(5B)–N(1B) of 1.378(3) Å for the latter).

Table 2
Spectral properties of dyes **7**–**12**

Dye	$\lambda_{abs(CHCl_3)}$ (nm)	$\lambda_{abs(MeCN)}$, (nm) ($\varepsilon \times 10^{-5}$, l mol^{-1} cm^{-1})	$\lambda_{fl(CHCl_3)}$, (nm) (φ)	$\lambda_{fl(MeCN)}$, (nm) (φ)
7	646	633 (3.00)	669 (0.25)	661 (0.29)
8	585	588 (1.81)	608 (0.55)	607 (0.1)
9	601	599 (1.88)	620 (0.49)	611 (0.16)
10	632	620 (1.95)	662 (0.05)	663 (0.07)
11	568	571 (0.95)	608 (0.22)	638 (<0.005)
12	569	570 (0.74)	609 (0.14)	638 (<0.005)

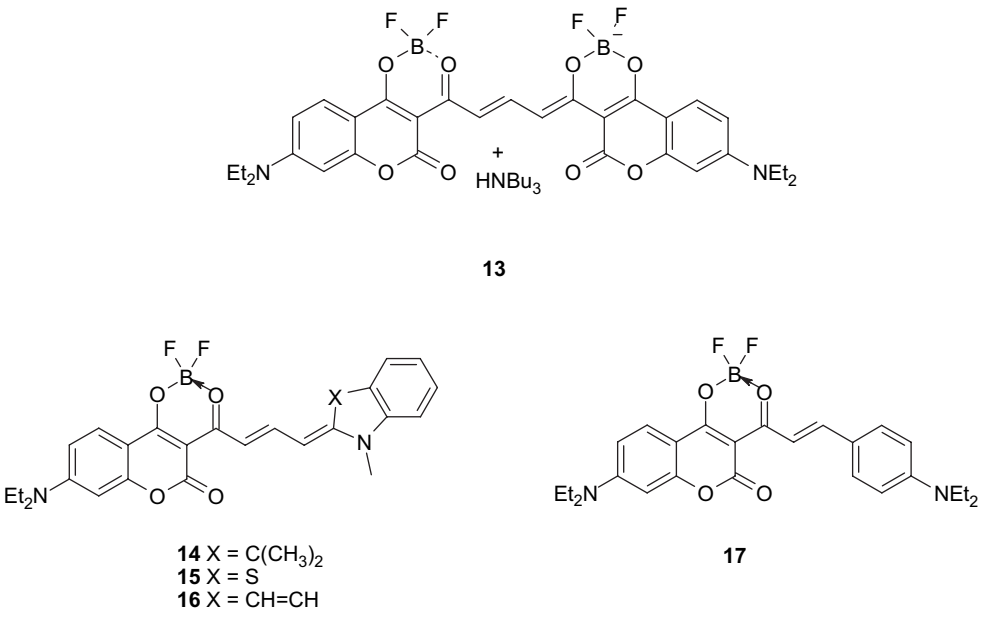


Fig. 3.

Accordingly, the conjugation of the pyrrolidine nitrogen atom with the coumarin nucleus is stronger at position 8 than at position 10. As far as the dioxaborine ring is concerned, the C–O^1 bond (with the lengths C(7A)–O(1A) of 1.309(3) Å and C(7B)–O(1B) of 1.304(3) Å) has a more pronounced double character than the C–O^3 bond (with the lengths C(10A)–O(4A) of 1.312(3) Å and C(10B)–O(3B) of 1.321 (3) Å). The dioxaborine moiety is not planar: the torsion angles C(8A)–C(7A)–O(1A)–B(1A) and C(8B)–C(7B)–O(1B)–B(1B) in two dye molecules are −4.1(4)° and 14.2(4)°, respectively.

Though X-ray diffraction analysis was not performed for styryl **12** (suitable crystals could not be obtained), it was possible to observe the stepwise substitution of fluorine atoms by acetate groups when boiling styryl **11** in acetic anhydride. Thin-layer chromatography of the reaction mixture allows one to monitor gradual substitution of the first fluorine atom and to detect, after an hour of boiling, formation of a new dye in which two fluorine atoms are apparently substituted by acetate groups. A similar substitution of fluorine atoms by carboxyl groups was described by Rohde [14].

Heating complex **5** with ethyl isoformanilide affords hemicyanine **6** which, when stirred with **5** at room temperature in the mixture of acetic anhydride and diisopropylethylamine for 24 h, produces symmetric dye **7** (see Scheme 2). Due to the reduced electron-withdrawing ability of the dioxaborine ring, it is necessary to use a large excess of the amine when preparing the symmetric dye. With one or even several equivalents of the amine, the reaction practically does not occur. Dyes **9** and **10** are more conveniently obtained from the corresponding benzothiazole and quinoline hemicyanines.

Comparing the data of Table 2 with the previously reported spectroscopic evidence [8], it is clear that fused dioxaborine dyes containing two dialkylamino groups on the coumarin moiety somewhat differ in spectral properties from their mono-substituted analogues (Fig. 3). Symmetric dye **7**, if compared to 8-diethylamino-substituted dye **13** [8], exhibits a 18 nm bathochromic shift of the absorption maximum and an increase in absorption intensity from 252 000 l mol^{-1} cm^{-1} to 300 000 l mol^{-1} cm^{-1}, the latter value approaching the known upper limit for such short-chained cyanines. At the same time, the fluorescence quantum yield is reduced and appears almost insensitive to the nature of the solvent, as against dye **13** [8].

Absorption maxima of merocyanines **8**–**10** are 4–17 nm shifted to longer wavelengths from those of analogous dyes **14**–**16** bearing the 8-diethylamino group (see Fig. 4). Molar extinction coefficients of dyes **8**–**10** somewhat increase with the rising electron-donating

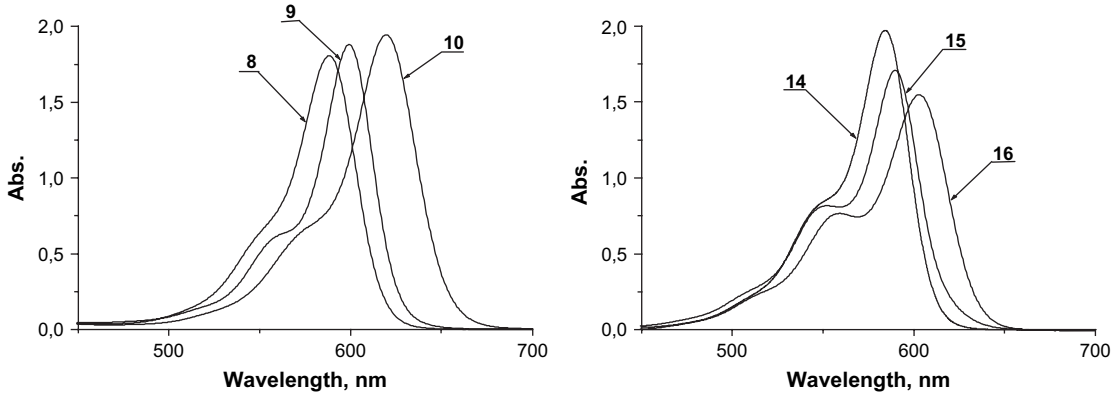


Fig. 4. Absorption spectra of merocyanines **8**–**10** and **14**–**16** in acetonitrile ($C = 1 \times 10^{-5}$ mol l^{-1}).

ability of the second heterocyclic end nucleus (contrary to what was observed for their 8-diethylamino-substituted analogues **14**–**16**). Vice versa, as far as styryl **11** and its 8-diethylamino analogue **17** (both containing the weakly-electron-donating 4-dialkylaminophenyl end group) are concerned, the latter dye absorbs at a longer wavelength and more intensely ($\lambda_{max}(CH_3CN) = 590$ nm, $\epsilon = 125\,000\ l\ mol^{-1}\ cm^{-1}$ [8]). This spectral peculiarity arises from the lower electron-withdrawing ability of the dioxaborine ring in mono-dialkylamino (structure B, Fig. 1) than in bis-dialkylamino-substituted (structure C, Fig. 1) dyes. Solvatochromic and solvatofluorochromic effects observed for dyes **7**–**12** in going from chloroform to acetonitrile solutions (see Table 2) are comparable to those for dyes **13**–**17** [8].

The lability towards alkaline conditions is a general weakness of dioxaborine dyes [14]. The introduction of the second dialkylamino group into the coumarin moiety of the compounds leads to much higher resistance to bases. For instance, dye **13** has a decoloration rate constant of $1.69 \times 10^{-3}\ s^{-1}$ and a half-life period of 410 s, whereas the corresponding values for dye **7** are $2.60 \times 10^{-5}\ s^{-1}$ and 26 663 s. Much higher stability of dipyrrolidino-substituted than of diethylamino-substituted dyes may be attributable to the following factors. First, the electron-withdrawing ability of the dioxaborine ring is significantly decreased when passing from one to two *tert*-amino substituents on the coumarin nucleus, the pyrrolidino group being, in addition, more basic than the diethylamino group. Second, the bulky pyrrolidino group at position 10 sterically hinders nucleophilic attack on the dioxaborine ring.

4. Conclusions

Two dialkylamino groups on the coumarin nucleus fused to the 2,2-difluoro-1,3,2-dioxaborine ring notably reduce the electron-withdrawing ability of the dioxaborine moiety. As a result, certain changes in spectral luminescent properties are observed in going from diethylamino-substituted to dipyrrolidino-substituted dyes. This modification of the dye structure also leads to drastically increased resistance to hydrolysis.

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