Synthesis and Characterization of New Long-Wavelength-Absorbing Oxonol Dyes from the 2,2-Difluoro-1,3,2-dioxaborine Type

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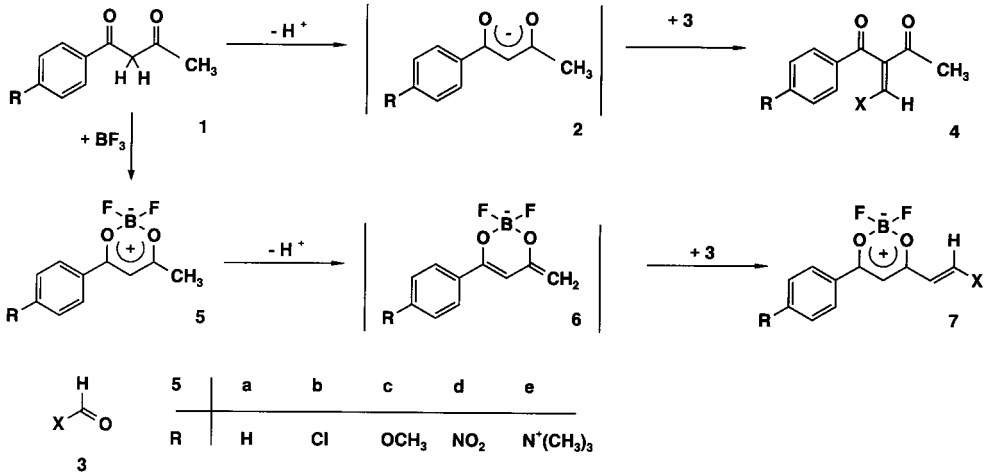
Dedicated to the memory of Professor Rudolf Gompper

Abstract: By starting from methyl- and methylene-substituted 2,2-difluoro-1,3,2-dioxaborines **5**, **20**, and **21** and different types of reactive formyl derivatives (**14**–**17**) a series of anionic, cationic, and betainic methine dyes has been prepared. These dioxaborine dyes **22**–**28** represent a new type of oxonol dye that exhibits intense long-wavelength absorptions in the near-infrared region. The positions of these absorption bands are recorded between 730 and 1050 nm and are strongly influenced by the length of the conjugated system, by the substitution pattern at their pendant aryl groups, and by the different bridging groups attached to their chromophoric systems.

Keywords: betaines · boron · dyes · fluorescence spectroscopy · infrared spectroscopy

Introduction

As observed with other enolizable 1,3-dicarbonyl compounds, aroylacetones of the general structure **1** can be condensed with boronic acid or its derivatives to give 1,3-diketoboronates.[1] For example, with boron trifluoride the 2,2-difluoro-substituted diketoboronates **5** (2,2-difluoro-1,3,2-dioxaborines[b]) are formed. In contrast to compounds **1**, which react with simple formyl derivatives **3** to yield the condensation products **4**,[2] the dioxaborines **5** react with the same formyl derivatives **3** to yield compounds of the general structure **7** (Scheme 1).[3] Whereas for the reaction of the formyl compound **3** with the aroylacetones **1** the intermediate carbanions **2** have been assumed,[4] for the reaction of **3** with the 1,3,2-dioxaborines **5** the anionic species **6** appear to be the intermediates. Hence, in contrast to the parent carbonyl compound **1**, their boron-containing derivatives **5** possess a reactive methyl group that is strongly activated (after its deprotonation) for an electrophilic attack of a suitable reagent (Scheme 1).



Scheme 1.

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[b] Although the name 2,2-difluoro-1,3,2-dioxaborine was introduced by Reynolds et al.,[3] it is not correct in respect to the IUPAC rules. Owing to the betainic valence formulae given here, the correct name of the boron-containing heterocycle is *2,2-difluoro-1,3,2-oxaoxoniaboratine*. However, for simplicity the former name is used in this paper.

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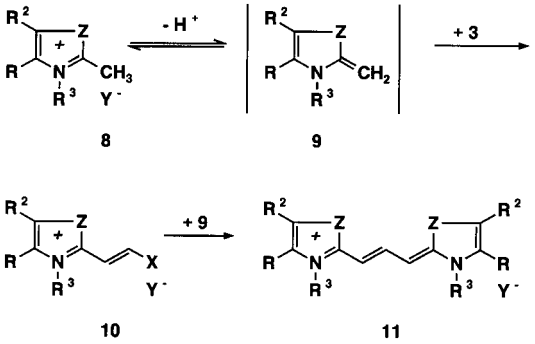
Evidently, the reaction of methyl-substituted 1,3,2-dioxaborines **5** with the formyl compounds **3** has some parallels to the reaction of methyl-substituted quaternary heterocyclic compounds **8** that react, via intermediate methylene bases **9**, with the formyl compounds **3** to yield condensation products of the general structure **10** (Scheme 2: Y = counterion, Z = heteroatom).[5]

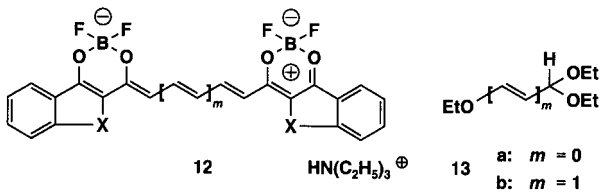


Scheme 2.

When the moiety X in compounds **10** is a nucleofugal group, such as halogen, OR, SR, or NR_2, the compounds are usually able to react with a second equivalent of **8** (via **9**) to yield cationic methines of the general structure **11**.[6] (Scheme 2)

Owing to the similarity in the reactivity of **5** and **8** towards the electrophilic reagents **3**, reaction of the condensation products **7** with their precursors **5** (via **6**) should also be possible. The products that are formed in this case are, however, species which are composed of an *anionic* chromophore and a *cationic* counterion. Therefore, these compounds have to be attributed to the oxonol type of methine dyes.[5, 7] As a consequence, their isolation strongly depends, inter alia, on the proper choice of the cationic counterion.

Usually, the protonated forms of the auxiliary base used in this condensation reaction can act as the counterion. For example, when 4-methyl-substituted naphtho[1,2-d]- or thionaphtho[3,2-d]-1,3,2-dioxaborines were condensed with trialkylorthoformates **13a** or ethoxyacroleine diethylacetals **13b** in presence of triethylamine, anionic methine dyes of the general structure **12** with X = CH=CH or S and the hydrotriethylammonium ion as the counterion are formed.[8] The

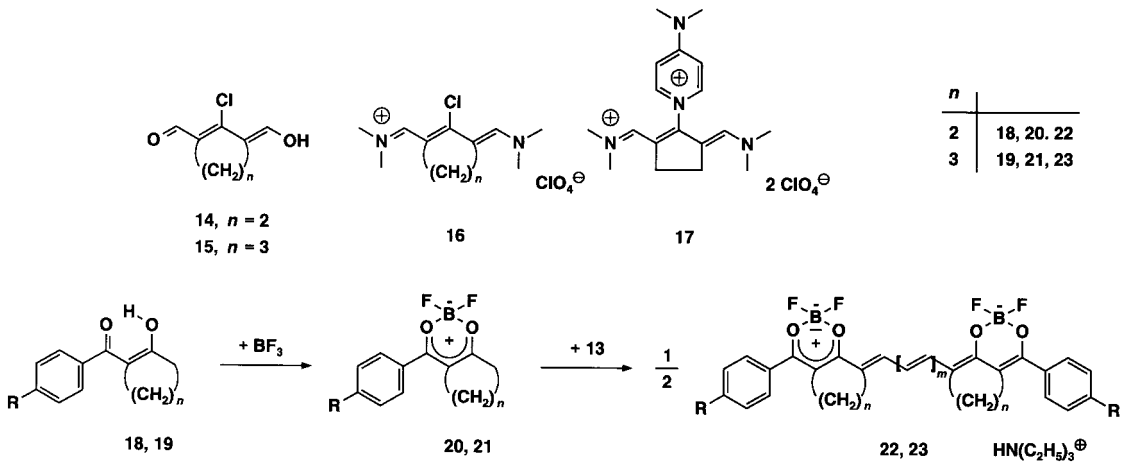


dyes **12** exhibit long-wavelength absorptions; their maxima shift by about 100 nm on increasing the number of vinyl groups. Hence, the 1,3,2-dioxaborines **12** represent an interesting class of long-wavelength-absorbing methine dyes that attain absorptions in the near-infrared region with a relatively low number of methine groups. Because the 1,3,2-dioxaborine-based methine dyes do not easily crystallize, only a few crystalline compounds of this structural type have been prepared.

Results and Discussion

To overcome this difficulty and to synthesize a series of better crystallizing, long-wavelength-absorbing methines with pendant 2,2-difluoro-1,3,2-dioxaborine groups, we have developed three different strategies. The first involves the synthesis of methine dyes with a more rigid molecular framework, especially within the methine chains, by starting from bridged 1,3,2-dioxaborine reactants and by using bridged methine precursors. Whereas bridged methine precursors, for example, the formyl compounds **14** and **15** or the iminium perchlorate **16**, are easily available from cycloalkanones by a Vilsmeier–Arnold reaction,[9] bridged 1,3,2-dioxaborines, for example, compounds **20** and **21**, are available by reaction of the BF_3/acetic acid complex with 2-aroyl-cycloalkenols **18** and **19**. These starting materials were prepared from the literature procedures[10] by acylating 1-morpholinocycloalkenes with appropriate aroyl chlorides and subsequent hydrolysis of the aroylated enamines primarily formed (Scheme 3).

Thus, by heating the bridged 1,3,2-dioxaborine derivatives **20** and **21** with triethylorthoformate **13a** or ethoxyacrolein diethyl acetal **13b** in acetic anhydride in the presence of triethylamine, deeply colored solutions were formed from



Scheme 3.

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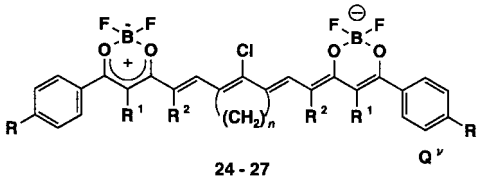
which the corresponding condensation products could be obtained as crystalline solids in few special cases. For example, by starting from the 4-nitro-substituted 1,3,2-dioxaborine derivative **20d** the corresponding nitro-substituted oxonol dyes **22** ($m=0$) and **23** ($m=1$) containing the hydrotriethylammonium ion as cation were obtained in satisfactory yield.

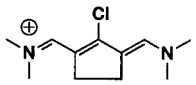
A better result was obtained, however, when the same bridged 1,3,2-dioxaborine derivatives **20** and **21** were heated with the bridged formyl compounds **14** or **15**. Crystalline condensation products of the general structure **24** or **25** were obtained when the chloro- or nitro-substituted 1,3,2-dioxaborine derivatives **20b** and **20d**, respectively, and the bridged formyl compounds **14** and **15** are used. Crystalline condensation products of the same structural type **24** and **25** were obtained also when the bridged formyl compounds **14** and **15** were condensed with the unbridged 1,3,2-dioxaborine derivatives **5b** and **5d** (see Table 1).

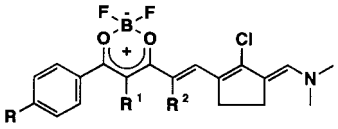
A more complicated result was obtained if instead of the formyl derivatives **14** and **15** the bridged iminium salt **16** as methine precursor was used. Depending on the 1,3,2-dioxaborine reactants used and the conditions applied, monocondensation products as well as bis-condensation products of the starting 1,3,2-dioxaborine derivative were obtained. Thus, by starting from **16** and the methoxy-substituted 1,3,2-dioxaborines **5c**, **20c**, and **21c** the corresponding monocondensation products **28** with $R=CH_3O$ could be isolated as crystalline solids under the same conditions described above.

Although the products **28** are stable under the mentioned preparation conditions, they can be transformed into their corresponding symmetrically substituted methine dyes **24** by applying more drastic conditions, for example, by refluxing with the corresponding 1,3,2-dioxaborines **20** in acetic anhydride in the presence of triethylamine for five hours. However, the methines **24** with $R^1/R^2=(CH_2)_n$ so formed do not crystallize from the reaction mixture after cooling. Therefore, their formation could be detected only spectroscopically. For example, their solutions exhibit intense long-wavelength absorptions at about 1000 nm.



24 - 27

	n	Q^{ν}
24	2	$HN(C_2H_5)_3^{\oplus}$
25	3	$HN(C_2H_5)_3^{\oplus}$
26	2	
27	2	$ClO_4^{\ominus}$



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By starting from the iminium salt **16** and the chloro- and nitro-substituted 1,3,2-dioxaborines **5b** and **5d**, respectively, under the same conditions used as before, instead of mono-

Table 1. Preparative data for the methine dyes **22**–**29**.

	R	R^1	R^2	n	Reactants	Yield [%]	M.p. [°C]	Formula	(M_w)	N:calcd	N: found
22	NO_2	–	–	2	**20d, 13a**	56	280 (decomp)	$C_{31}H_{33}B_2F_4N_3O_8$	(706.5)	5.95	6.09
23	NO_2	–	–	2	**20d, 13b**	23	198 (decomp)	$C_{33}H_{35}B_2F_4N_3O_8I$	(735.5)	5.74	5.33
24a	Cl	H	H	2	**5b, 14**	7	238 (decomp)	$C_{33}H_{25}B_2F_4NO_4Cl_3$	(703.5)	1.99	1.92
24b	NO_2	H	H	2	**5d, 14**	12	263 (decomp)	$C_{33}H_{25}B_2F_4N_3O_8Cl$	(724.6)	5.80	5.37
24c	Cl	$(CH_2)_2$		2	**20b, 14**	62	240 (decomp)	$C_{37}H_{29}B_2F_4NO_4Cl_3$	(755.6)	1.85	1.68
24d	NO_2	$(CH_2)_2$		2	**20d, 14**	81	235 (decomp)	$C_{37}H_{29}B_2F_4N_3O_8Cl$	(776.7)	5.41	5.74
25a	Cl	H	H	3	**5b, 15**	10	215–218	$C_{34}H_{27}B_2F_4NO_4Cl_3$	(717.5)	1.95	1.76
25b	NO_2	H	H	3	**5d, 15**	17	232 (decomp)	$C_{34}H_{27}B_2F_4N_3O_8Cl$	(738.7)	5.69	5.36
25c	Cl	$(CH_2)_2$		3	**20b, 15**	46	255 (decomp)	$C_{38}H_{31}B_2F_4NO_4Cl_3$	(769.6)	1.82	1.44
25d	NO_2	$(CH_2)_2$		3	**20d, 15**	75	>360	$C_{38}H_{31}B_2F_4N_3O_8Cl$	(790.7)	5.32	4.83
26a	Cl	H	H	2	**5b, 16**	26	220 (decomp)	$C_{38}H_{36}B_2F_4N_2O_4Cl_4$	(824.1)	3.40	3.27
26b	NO_2	H	H	2	**5d, 16**	81	240 (decomp)	$C_{38}H_{36}B_2F_4N_4O_8Cl_2$	(845.2)	6.63	6.11
27	$N(CH_3)_3$	H	H	2	**5e, 16**	73	215 (decomp)	$C_{33}H_{36}B_2F_4N_2O_8Cl_2$	(757.2)	3.70	3.26
28a	OCH_3	H	H	–	**5c, 16**	25	280 (decomp)	$C_{20}H_{21}BF_2ClNO_3$	(407.6)	3.44	3.37
28b	OCH_3	$(CH_2)_2$		–	**20c, 16**	88	>360	$C_{22}H_{23}BF_2ClNO_3$	(433.7)	3.23	3.19
28c	OCH_3	$(CH_2)_3$		–	**21c, 16**	56	227–229	$C_{23}H_{25}BF_2ClNO_3$	(447.7)	3.13	3.03
29a	H	H	H	–	**5a, 17**	50	300 (decomp)	$C_{34}H_{30}B_2F_4N_2O_4$	(628.3)	4.46	4.32
29b	Cl	H	H	–	**5b, 17**	65	280 (decomp)	$C_{34}H_{28}B_2F_4N_2O_4Cl_2$	(697.1)	4.02	3.89
29c	OCH_3	H	H	–	**5c, 17**	65	330 (decomp)	$C_{36}H_{34}B_2F_4N_2O_6$	(688.3)	4.07	4.11
29d	NO_2	H	H	–	**5d, 17**	45	360	$C_{34}H_{28}B_2F_4N_4O_8$	(718.3)	7.80	7.67
29e	H	$(CH_2)_2$		–	**20a, 17**	63	290 (decomp)	$C_{38}H_{34}B_2F_4N_2O_4$	(680.3)	4.12	4.01
29f	Cl	$(CH_2)_2$		–	**20b, 17**	55	312–314	$C_{38}H_{32}B_2F_4N_2O_4Cl_2$	(749.2)	3.74	3.35
29g	OCH_3	$(CH_2)_2$		–	**20c, 17**	78	265–268	$C_{40}H_{38}B_2F_4N_2O_6$	(740.4)	3.78	3.89
29h	NO_2	$(CH_2)_2$		–	**20d, 17**	76	>360	$C_{38}H_{32}B_2F_4N_4O_8$	(770.3)	7.27	7.78
29i	Cl	$(CH_2)_3$		–	**21b, 17**	35	220 (decomp)	$C_{40}H_{36}B_2F_4N_2O_4Cl_2$	(777.4)	3.60	3.62
29j	OCH_3	$(CH_2)_3$		–	**21c, 17**	27	189 (decomp)	$C_{42}H_{42}B_2F_4N_2O_6$	(768.4)	3.65	3.34
29k	NO_2	$(CH_2)_3$		–	**21d, 17**	25	275 (decomp)	$C_{40}H_{36}B_2F_4N_4O_8$	(798.4)	7.02	6.91

condensation products **28**, the corresponding bis-condensation products were formed. They precipitate from the hot reaction mixture immediately. However, the products do not contain, as expected, the hydrotriethylammonium ion as cationic moiety, but as seen in the structural formula for **26**, the bridged iminium ion generated from the corresponding starting material **16** acts as the cationic counterion.

Evidence for this statement comes not only from the elemental analytic data of the products **26** (see Table 1), but also from their spectroscopic data (see Table 2). For example, compound **26b** exhibits two absorption maxima at about 480 and 940 nm in its VIS/NIR spectrum. With reference to the spectral data of compound **16**, the maximum in the visible region can be attributed to its cationic moiety, whereas the

Table 2. Spectral properties of the methine dyes **22**–**29** prepared; VIS/NIR data measured in DMF, ^{1}H NMR data measured in [D$_6$]DMSO.

	R	R^1	R^2	n	λ_{max} [nm] (log ε)	^{1}H NMR, δ-values (assignement), J [Hz]
22	NO_2	–	–	2	734 (4.92)	1.16 (t, 9H; CH_3), 2.88 (m, 4H; CH_2), 2.93 (m, 4H; CH_2), 3.09 (q, 6H; CH_2), 7.76 (s, 1H; CH). 7.88 (d, ^3J = 8.8 Hz, 4H; CH) , 8.15 (d, ^3J = 8.8 Hz, 4H; CH), 8.82 (1H; NH)
23	NO_2	–	–	2	830 (5.13)	1.16 (t, 9H; CH_3), 2.70 (m, 4H; CH_2), 2.92 (m, 4H; CH_2), 3.08 (q, 6H; CH_2), 6.03 (t, ^3J = 13.2 Hz, 1H; CH), 7.59 (d, ^3J = 13.3 Hz, 2H; CH), 7.59 (d, ^3J = 8.6 Hz, 4H; CH), 8.21 (d, ^3J = 8.6 Hz, 4H; CH), 8.83 (s, 1H; NH)
24a	Cl	H	H	2	892 (5.28)	1.16 (t, 3H; CH_3), 2.76 (m, 4H; CH_2), 3.1 (q, 6H; CH_2), 5.88 (d, ^3J = 13.7 Hz, 2H; CH), 6.71 (s, 2H; CH), 7.54 (d, ^3J = 8.5 Hz, 4H), 7.91 (d, ^3J = 8.5 Hz, 4H; CH), 8.10 (d, ^3J = 13.4 Hz, 2H; CH), 8.8 (s, 1H; NH)
24b	NO_2	H	H	2	941 (5.19)	1.16 (t, 9H; CH_3), 2.78 (m, 4H; CH_2), 3.1 (q, 6H; CH_2), 5.88 (d, ^3J = 13.5 Hz, 2H; CH), 6.92 (s, 2H; CH), 7.71 (d, ^3J = 13.5 Hz, 2H; CH), 8.13 (d, ^3J = 8.8 Hz, 4H; CH)), 8.29 (d, ^3J = 8.9 Hz, 4H; CH), 8.8 (s, 1H; NH)
24c	Cl	$(CH_2)_2$		2	981 (5.04)	1.16 (t, 9H; CH_3), 2.63 (m, 4H; CH_2), 2.80 (m, 4H; CH_2), 2.83 (m, 4H; CH_2), 3.1 (q, 6H; CH_2), 7.25 (d, ^3J = 8.9 Hz, 4H; CH), 7.28 (s, 2H; CH), 7.49 (d, ^3J = 8.5 Hz, 4H; CH), 8.8 (s, 1H; NH)
24d	NO_2	$(CH_2)_2$		2	1041 (4.99)	1.16 (t, 9H; CH_3), 2.69 (m, 4H; CH_2), 2.82 (m, 4H; CH_2), 2.84 (m, 4H; CH_2), 3.1 (q, 6H; CH_2), 7.35 (s, 2H; CH), 7.57 (d, ^3J = 9.0 Hz, 4H; CH), 7.85 (d, ^3J = 9.0 Hz, 4H; CH), 8.8 (s, 1H; NH), 8.8 (s, 1H; NH)
25a	Cl	H	H	3	866 (5.22)	1.16 (t, 9H; CH_3), 1.78 (m, 2H; CH_2), 2.53 (m, 4H; CH_2), 3.1 (q, 6H; CH_2), 5.96 (d, ^3J = 13.6 Hz, 2H; CH), 6.72 (s, 2H; CH), 7.56 (d, ^3J = 8.5 Hz, 4H; CH), 7.93 (d, ^3J = 8.5 Hz, 4H; CH), 8.13 (d, ^3J = 13.4 Hz, 2H; CH), 8.8 (s, 1H; NH)
25b	NO_2	H	H	3	941 (5.19)	1.16 (t, 9H; CH_3), 1.79 (m, 2H; CH_2), 2.57 (m, 4H; CH_2), 3.1 (q, 6H; CH_2), 6.07 (d, ^3J = 13.6 Hz, 2H; CH), 6.87 (s, 2H; CH), 8,12 (d, ^3J = 8.8 Hz, 4H; CH), 8.18 (d, ^3J = 13.4 Hz, 2H; CH), 8.26 (d, ^3J = 8.9 Hz, 4H; CH), 8.8 (s, 1H; NH)
25c	Cl	$(CH_2)_2$		3	948 (4.92)	1.16 (t, 9H; CH_3), 1.73 (m, 2H; CH_2), 2.75 (m, 4H; CH_2), 2.88 (m, 8H; CH_2), 3.1 (q, 6H; CH_2), 7.43 (d, ^3J = 6.9 Hz, 4H; CH), 7.65 (s, 2H; CH), 7.74 (d, ^3J = 7.2 Hz, 4H; CH), 8.8 (s, 1H; NH)
25d	NO_2	$(CH_2)_2$		3	1000 (4.98)	1.16 (t, 9H; CH_3), 1.74 (m, 2H; CH_2), 2.77 (m, 4H; CH_2), 2.90 (m, 8H; CH_2), 3.1 (q, 6H; CH_2), 7.63 (d, ^3J = 8.5 Hz, 4H; CH), 7.79 (d, ^3J = 8.3 Hz, 4H; CH), 7.84(s, 2H; CH), 8.8 (s, 1H; NH)
26a	Cl	H	H	2	892, 477[a]	2.76 (m, 4H; CH_2), 3.09 (m, 4H; CH_2), 3.31 (s, 12H; $N(CH_3)_2$), 5.88 (d, ^3J = 13.7 Hz, 2H; CH), 6.71 (s, 2H; CH), 7.54 (d, ^3J = 8.5 Hz, 4H; CH), 7.65 (s, 2H; CH), 7.91 (d, ^3J = 8.5 Hz, 4H; CH), 8.10 (d, ^3J = 13.4 Hz, 2H; CH)
26b	NO_2	H	H	2	941, 477[a]	2.78 (m, 4H; CH_2), 3.1 (q, 4H; CH_2), 3.31 (s, 12H; $N(CH_3)_2$), 5.88 (d, ^3J = 13.5 Hz, 2H; CH), 6.92 (s, 2H; CH), 7.64 (s, 2H; CH), 7.71 (d, ^3J = 13.5 Hz, 2H; CH), 8.13 (d, ^3J = 8.8 Hz, 4H; CH), 8.29 (d, ^3J = 8.9 Hz, 4H; CH), 8.8 (s, 1H; NH)
27	$N(CH_3)_3$	H	H	2	894 (5.13)	2.79 (m, 4H; CH_2), 3.64 (s, 18H; $N^+(CH_3)_3$), 5.84 (d, ^3J = 13.6 Hz, 2H; CH), 6.87 (s, 2H; CH), 7.69 (d, ^3J = 13.5 Hz, 2H; CH), 8.06 (d, ^3J = 9.2 Hz, 4H; CH), 8.13 (d, ^3J = 9.2 Hz, 4H; CH)
28a	OCH_3	H	H	–	674 (5.10)	2.72 (m, 4H; CH_2), 3.26 (s, 6H; $N(CH_3)_2$), 3.86 (s, 3H; OCH_3), 5.78 (d, ^3J = 13.9 Hz, 1H; CH), 6.67 (s, 1H; CH), 7.06 (d, ^3J = 8.8 Hz, 2H; CH), 7.31 (s, 1H; CH), 7.84 (d, ^3J = 13.9 Hz, 1H; CH), 7.95 (d, ^3J = 8.9 HZ, 2H; CH)
28b	OCH_3	$(CH_2)_2$		–	708 (5.07)	2.94 (m, 4H; CH_2), 3.08 (m, 4H; CH_2), 3.26 (s, 6H; $N(CH_3)_2$), 3.85 (s, 3H; OCH_3), 7.16 (d, ^3J = 8.9 Hz, 2H; CH), 7.35 (s, 1H; CH), 7.98 (d, ^3J = 8.9 Hz, 2H; CH), 8.13 (s, 1H; CH)
28c	OCH_3	$(CH_2)_3$		–	686 (5.01)	1.61 (m, 2H; CH_2), 2.56 (m, 2H; CH_2), 2.76 (m, 2H; CH_2), 3.07 (m, 4H; CH_2), 3.24 (s, 6H; $N(CH_3)_2$), 3.83 (s, 3H; OCH_3), 7.03 (d, ^3J = 8.7 Hz, 2H; CH), 7.32 (s, 1H; CH), 7.63 (d, ^3J = 8.7 Hz, 2H; CH), 8.04 (s, 1H; CH)
29a	H	H	H	–	893 (5.28)	2.98 (m, 4H; CH_2), 3.34 (s, 6H; $N(CH_3)_2$), 5.88 (d, ^3J = 13.3 Hz, 2H; CH), 6.67 (s, 2H; CH), 6.96 (d, ^3J = 13.3 Hz, 2H; CH), 7.24 (d, ^3J = 7.4 Hz, 2H; Py-H), 7.47 (m, 2H), 7.72 (m, 4H), 7.90 (d, ^3J = 7.6 Hz, 4H; CH), 8.28 (d, ^3J = 7.4 Hz, 2H; Py-H)
29b	Cl	H	H	–	903 (5.19)	2.89 (m, 4H; CH_2), 3.34 (s, 6H; $N(CH_3)_2$), 5.88 (d, ^3J = 13.3 Hz, 2H; CH), 6.70 (s, 2H; CH), 6.97 (d, ^3J = 13.3 Hz, 2H; CH), 7.24 (d, ^3J = 7.3 Hz, 2H; Py-H) 7.54 (d, ^3J = 8.4 Hz, 4H; CH), 7.91 (d, ^3J = 7.9 Hz, 4H; CH), 8.26 (d, ^3J = 7.3 Hz, 2H; Py-H)

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Table 2. (Continued)

	R	R^1	R^2	n	λ_{max} [nm] (log ε)	^{1}H NMR, δ-values (assignement), J [Hz]
29c	OCH_3	H	H	–	898 (5.28)	2.86 (m, 4H; CH_2), 3.33 (s, 6H; $N(CH_3)_2$), 4.04 (s, 6H; OCH_3), 5.80 (d, ^3J = 13.2 Hz, 2H; CH), 6.54 (s, 2H; CH), 6.89 (d, ^3J = 13.2 Hz, 2H; CH), 7.02 (d, ^3J = 8.7 Hz, 4H; CH), 7.22 (d, ^3J = 7.3 Hz, 2H; Py-H), 7.86 (d, 4H; J = 8.6), 8.26 (d, ^3J = 7.3 Hz, 2H; Py-H)
29d	NO_2	H	H	–	961 (5.16)	2.93 (m, 4H; CH_2), 3.33 (s, 6H; $N(CH_3)_2$), 6.02 (d, ^3J = 14.0 Hz, 2H; CH), 6.81 (s, 2H; CH), 7.05 (d, ^3J = 14.0 Hz, 2H; CH), 7.26 (d, ^3J = 7.5 Hz, 2H; Py-H) 8.31 (d, ^3J = 8.4 Hz, 4H; CH), 8.30 (d, ^3J = 8.5 Hz, 4H; CH), 8.34 (d, ^3J = 7.5 Hz, 2H; Py-H)
29e	H	$(CH_2)_2$		–	986	2.96 (m, 4H; CH_2), 3.05 (m, 8H; CH_2), 3.35 (s, 6H; $N(CH_3)_2$), 6.52 (s, 2H; CH), 7.24 (d, ^3J = 7.4 Hz, 2H; Py-H), 7.49 (m, 6H; CH), 7.81 (d, ^3J = 7.9 Hz, 4H; CH) 8.23 (d, ^3J = 7.4 Hz, 2H; Py-H)
29f	Cl	$(CH_2)_2$		–	998	2.94 (m, 4H; CH_2), 3.10 (m, 8H; CH_2), 3.35 (s, 6H; $N(CH_3)_2$), 6.53 (s, 2H; CH), 7.25 (d, ^3J = 7.5 Hz, 2H; Py-H), 7.54 (d, ^3J = 8.6 Hz, 4H; CH), 7.81 (d, ^3J = 8.6 Hz, 4H; CH), 8.23 (d, ^3J = 7.5 Hz, 2H; Py-H)
29g	OCH_3	$(CH_2)_2$		–	992	2.90 (m, 4H; CH_2), 2.95 (m, 8H; CH_2), 3.33 (s, 6H; $N(CH_3)_2$), 3.83 (s, = 6H; OCH_3), 6.45 (s, 2H; CH), 7.04 (d, ^3J = 9.0 Hz, 4H; CH), 7.22 (d, ^3J = 7.3 Hz, 2H; Py-H), 7.79 (d, ^3J = 8.4 Hz, 4H; CH), 8.19 (d, ^3J = 7.3 Hz, 2H; Py-H)
29h	NO_2	$(CH_2)_2$		–	1052	2.85 (m, 8H; CH_2), 2.92 (m, 4H; CH_2), 3.34 (s, 6H; $N(CH_3)_2$), 6.49 (s, 2H; CH), 7.23 (d, ^3J = 8.0 Hz, 2H; Py-H), 8.03 (d, ^3J = 9.0 Hz, 4H; CH), 8.17 (d, ^3J = 8.8 Hz, 4H; CH), 8.30 (d, ^3J = 8.0 Hz, 2H; Py-H)
29i	Cl	$(CH_2)_3$		–	928 (4.92)	1.58 (m, 4H; CH_2), 2.45 (m, 4H; CH_2), 2.76 (m, 4H; CH_2), 3.17 (m, 4H; CH_2), 3.32 (s, 6H; $N(CH_3)_2$), 6.99 (s, 2H; CH), 7.25 (d, ^3J = 8.0 Hz, 2H; Py-H), 7.49 (d, ^3J = 8.7 Hz, 4H; CH), 7.57 (d, ^3J = 8.7 Hz, 4H; CH), 8.26 (d, ^3J = 8.0 Hz, 2H; Py-H)
29j	OCH_3	$(CH_2)_3$		–	929 (4.98)	1.57 (m, 4H; CH_2), 2.45 (m, 4H; CH_2), 2.77 (m, 4H; CH_2), 3.18 (m, 4H; CH_2), 3.33 (s, 6H; $N(CH_3)_2$), 3.81 (s, 6H; OCH_3), 7.0 (s, 2H; CH), 7.01 (d, ^3J = 8.8 Hz, 4H; CH), 7.25 (d, ^3J = 8.1 Hz, 2H; Py-H), 7.56 (d, ^3J = 8.4 Hz, 4H; CH), 8.28(d, ^3J = 8.1 Hz, 2H; Py-H)
29k	NO_2	$(CH_2)_3$		–	965 (4.82)	1.62 (m, 4H; CH_2), 2.47 (m, 4H; CH_2), 2.80 (m, 4H; CH_2), 3.21 (m, 4H; CH_2), 3.34 (s, 6H; $N(CH_3)_2$), 7.06 (s, 2H; CH), 7.29 (d, ^3J = 7.8 Hz, 2H; Py-H), 7.83 (d, ^3J = 8.7 Hz, 4H; CH), 8.27 (d, ^3J = 9.0 Hz, 4H; CH), 8.31 (d, ^3J = 7.8 Hz, 2H; Py-H)

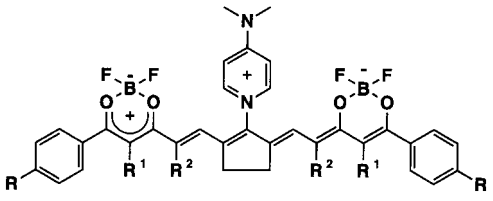
[a] Owing to the insolubility of the compound, its absorption data were estimated qualitatively only.

second maximum in the near infrared region can be attributed to the anionic 1,3,2-dioxaborine chromophore unambiguously.

A second strategy for preparing crystalline 1,3,2-dioxaborine methines involves the use of 1,3,2-dioxaborine reactants containing suitable cationic groups, for example, at their pendant aryl groups. The cationic 1,3,2-dioxaborine derivative **5e** is an example of such a compound. This salt can be prepared, as recorded elsewhere,[11] by reaction of 4-acetylphenyltrimethylammonium perchlorate with acetic anhydride in presence of boron trifluoride. It condenses with compound **16** under the same conditions mentioned above to give a deeply colored crystalline methine dye **27**. This dye is composed of a cationic 1,3,2-dioxaborine moiety and a perchlorate anion and could be obtained, as seen from Table 1, in satisfactory yield.

Finally, a third route to prepare crystalline methine dyes from the 1,3,2-dioxaborine precursors **5** or **20** and **21** has been developed. It involves the use of methine precursors with suitable cationic moieties attached to their molecular framework. The dicationic compound **17** was used as methine precursor for this strategy. This diperchlorate **17**, which has been applied as methine precursor by other authors, can be easily prepared by reaction of the iminium salt **16** with 4-dimethylaminopyridine.[12]

By heating of compound **17** with one of the neutral 1,3,2-dioxaborine reactants **5**, **20**, or **21** in acetic anhydride in presence of triethylamine, deeply colored methines **29** were formed. As a result of their zwitterionic nature, these salts **29** exhibit a high tendency to crystallize and can, therefore, easily be isolated in most satisfactory yields (see Table 1) from the reaction mixture.



29

The structures of all the crystalline methine dyes described here were confirmed by their analytical and spectroscopic data unambiguously. Some of the spectroscopic data are depicted in the Table 2. Thus, in the ^{1}H NMR spectra of the methine compounds **22**–**29** characteristic proton signals were detected. They could be attributed, according to their intensities and coupling parameters, unambiguously to the corresponding CH_n fragments (n = 1, 2, or 3) in these compounds.

All the 1,3,2-dioxaborine methine dyes prepared are deeply colored compounds that exhibit intense long-wavelength absorption bands. Their positions depend, in a characteristic manner, on the length of their methine chain, on their

substitution pattern, and on the size of their bridging groups (see Table 2).

Thus, the trimethine dye **22** ($m=0$) absorbs at about 730 nm and the pentamethine dye **23** ($m=1$) at 830 nm. For the heptamethine dyes **24b**, **25b**, and **29d**, bearing the same nitrophenyl substituent as in **22** and **23** and no bridging group at their 1,3,2-dioxaborine moieties, longest wavelength absorption maxima at about 940 nm were recorded. Hence, a vinylene shift of about 100 nm is observed on going from a trimethine to a pentamethine to a heptamethine system indicating a pronounced polymethinic character of these novel boron-containing oxonol dyes.

Concerning the aryl substituents, a significant influence on the position of the long-wavelength absorptions is also observed. Thus, extremely long-wavelength absorption maxima were found for all nitro-substituted dyes. They absorb, as exemplified in the series **29**, at wavelengths nearly 70 nm longer than their H-substituted parent compounds.

A significant influence on the position of the longest wavelength absorptions of the boron-containing methine dyes is also observed for the bridging groups attached at the central methine chains. Whereas trimethylene bridged dyes absorb nearly at the same wavelength than their unbridged analogues (compare, for example, the absorption data of the dyes **28a**, **29c**, or **29d** with the one of their trimethylene bridged analogues **28c**, **29j**, or **29k**, respectively), dimethylene bridged dyes, for example, the compounds **28b**, **29g**, or **29h**, absorb at considerably longer wavelength than their unbridged analogues **28a**, **29c**, or **29d**, respectively (see Figure 1). Both electronic and steric effects should be taken into consideration when accounting for these observations.

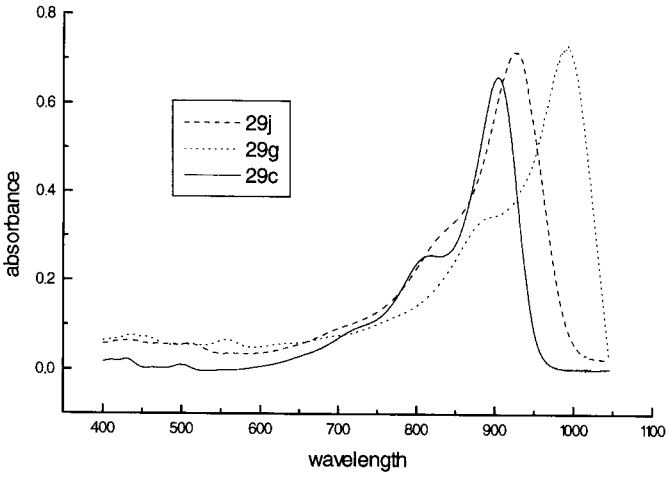


Figure 1. Absorption spectra of some betainic methine dyes **29**; wavelength given in nm.

Most of the methine dyes prepared exhibit a pronounced fluorescence in the NIR region. The wavelengths and intensities of this fluorescence are also influenced by the structural pattern of the corresponding methine dyes. Details on this subject will be recorded and discussed in a subsequent paper more in detail.

Experimental Section

Melting points were determined by means of a Boetius heating-table microscope and are uncorrected. The visible and near-infrared spectra were recorded with a Carl–Zeiss Spectrometer M40 and a Shimadzu spectrometer UV3101, respectively, and the NMR spectra with a Varian 300 MHz spectrometer Gemini 300. The elemental analytical data were estimated by means of a LECO analyzer CHNS 932. (Owing to the formation of boron carbide during the combustion of the compounds the estimated C and H values are incorrect to some extent and, therefore, were not documented).

Preparation of the alkylene-bridged 2,2-difluoro-1,3,2-dioxaborines 20 and 21 (general procedure): A solution of an aroyl chloride (1.0 mol) in benzene (100 mL) was added over a period of 1 h at 45 °C under stirring to a mixture of a *N*-(cyloalkenyl)morpholine (1.1 mol), triethylamine (111 g, 1.0 mol), and benzene (400 mL). After stirring overnight the mixture was neutralized by addition of aqueous hydrochloric acid and was subsequently refluxed for 15 min. After cooling the organic layer was separated, washed with water (3×100 mL), dried with Na_2SO_4, and evaporated under reduced pressure after filtration. The oily residue was mixed with a equivalent of BF_3/acetic acid adduct and refluxed for 1 h. After cooling the solid formed was isolated by filtration and recrystallized. The following alkylene-bridged 2,2-difluoro-1,3,2-dioxaborines **20** and **21** were prepared.

2,2-Difluoro-4-phenyl-5,6,7-trihydrocyclopenta[1,2-b]-1,3,2-dioxaborine (20a): Compound **20a** was prepared from benzoyl chloride (1 mol, 14.1 g) and *N*-(1-cyclopentenyl)morpholine (1.1 mol, 168.3 g). Yield: 141.6 g (60%); m.p. 165–168 °C (acetic acid); ^{1}H NMR ($CDCl_3$): $\delta=2.13$ (m, 2H; CH_2), 2.79 (t, 2H; CH_2), 3.03 (t, 2H; CH_2), 7.50 (t, $^3J=7.3$, 7.6 Hz, 2H; CH), 7.62 (t, $^3J=7.3$ Hz, 1H; CH), 8.00 (d, $^3J=7.6$ Hz, 2H; CH); $C_{12}H_{11}BF_2O_2$ (236.0): calcd C 61.06, H, 4.70; found C 61.82, H, 4.58.

2,2-Difluoro-4-(4-chlorophenyl)-5,6,7-trihydrocyclopenta[1,2-b]-1,3,2-dioxaborine (20b): Compound **20b** was prepared from 4-chlorobenzoyl chloride (1 mol, 17.5 g) and *N*-(1-cyclopentenyl)morpholine (1.1 mol, 168.3 g). Yield: 170.4 g (270.5%); m.p. 195–197 °C (acetic acid); ^{1}H NMR ($CDCl_3$): $\delta=2.15$ (m, 2H; CH_2), 2.82 (t, 2H; CH_2), 3.02 (t, 2H; CH_2), 7.48 (d, $^3J=8.6$ Hz, 2H; CH), 7.93 (d, $^3J=8.6$ Hz, 2H; CH); $C_{12}H_{10}BF_2O_2Cl$ (270.5): calcd C 53.29, H 3.73, Cl 13.11; found: C 53.89, H 3.80, Cl 13.25.

2,2-Difluoro-4-(4-methoxyphenyl)-5,6,7-trihydrocyclopenta[1,2-b]-1,3,2-dioxaborine (20c): Compound **20c** was prepared from 4-methoxybenzoyl chloride (1 mol, 17.1 g) and *N*-(1-cyclopentenyl)morpholine (1.1 mol, 168.3 g). Yield: 207.5 g (78%); m.p. 212–214 °C (acetic acid); ^{1}H NMR ($CDCl_3$): $\delta=2.12$ (m, 2H; CH_2), 2.77 (t, 2H; CH_2), 3.02 (t, 2H; CH_2), 3.88 (s, 3H; OCH_3), 6.97 (d, $^3J=9.0$ Hz, 2H; CH), 8.05 (d, $^3J=9.0$ Hz, 2H; CH); $C_{13}H_{13}BF_2O_3$ (266.0): calcd C 58.69, H 4.92; found C 59.28, H 4.78.

2,2-Difluoro-4-(4-nitrophenyl)-5,6,7-trihydrocyclopenta[1,2-b]-1,3,2-dioxaborine (20d): Compound **20d** was prepared from 4-nitrobenzoyl chloride (1 mol, 18.5 g) and *N*-(1-cyclopentenyl)morpholine (1.1 mol, 168.3 g). Yield: 233.2 g (83%); m.p. 157–158 °C (acetic acid); ^{1}H NMR (CD_3NO_2): $\delta=2.20$ (m, 2H; CH_2), 2.91 (t, 2H; CH_2), 3.10 (t, 2H; CH_2), 8.22 (d, $^3J=8.8$ Hz, 2H; CH), 8.36 (d, $^3J=8.8$ Hz, 2H; CH); $C_{12}H_{10}BF_2NO_4$ (281.0): calcd C 51.28, H 3.56, NO_2 4.99; found C 51.17, H 3.42, NO_2 4.90.

2,2-Difluoro-4-phenyl-5,6,7,8-tetrahydrocyclohexa-[1,2-b]-1,3,2-dioxaborine (21a): Compound **21a** was prepared from benzoyl chloride (1 mol, 14.1 g) and *N*-(1-cyclohexenyl)morpholine (1.1 mol, 183.7 g): Yield: 112.5 g (45%); m.p. 113–115 °C (ethyl acetate); ^{1}H NMR ($CDCl_3$): $\delta=1.67$ (m, 2H; CH_2) 1.82 (m, 2H; CH_2), 2.58 (t, 2H; CH_2), 2.65 (t, 2H; CH_2), 7.46 (t, $^3J=7.2$, 7.4 Hz, 2H; CH), 7.56 (t, $^3J=7.2$ Hz, 1H; CH), 7.72 (d, $^3J=7.4$ Hz, 2H; CH); $C_{13}H_{13}BF_2O_2$ (250.0): calcd C 62.44, H 5.24; found C 62.72, H, 5.11.

2,2-Difluoro-4-(4-chloro-phenyl)-5,6,7,8-tetrahydrocyclohexa-[1,2-b]-1,3,2-dioxaborine (21b): Compound **21b** was prepared from 4-chlorobenzoyl chloride (1 mol, 17.5 g) and *N*-(1-cyclohexenyl)morpholine (1.1 mol, 183.7 g). Yield: 122.3 g (43%); m.p. 165–169 °C (ethyl acetate); ^{1}H NMR ([D$_6$]DMSO): $\delta=1.61$ (m, 2H; CH_2) 1.76 (m, 2H; CH_2), 2.51 (t, 2H; CH_2), 2.74 (t, 2H; CH_2), 7.63 (t, $^3J=8.6$ Hz, 2H; CH), 7.81 (d, $^3J=8.6$ Hz, 2H; CH); $C_{13}H_{12}BF_2O_2Cl$ (284.5): calcd C 54.88, H 4.25, Cl 12.46; found C 55.21, H 4.11, Cl 12.65.

2,2-Difluoro-4-(4-methoxyphenyl)-5,6,7,8-tetrahydrocyclohexa-[1,2-b]-1,3,2-dioxaborine (21c): Compound **21c** was prepared from 4-methoxybenzoyl chloride (1 mol, 17.1 g) and *N*-(1-cyclohexenyl)morpholine (1.1 mol,

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183.7 g). Yield: 207.2 g (74%); m.p. 190–193 °C (acetic acid); ^{1}H NMR ($CDCl_3$): $\delta = 1.68$ (m, 2H; CH_2) 1.82 (m, 2H; CH_2), 2.62 (t, 2H; CH_2), 2.65 (t, 2H; CH_2), 3.87 (s, 3H; OCH_3), 6.95 (t, $^3J = 9.0$ Hz, 2H; CH), 7.82 (d, $^3J = 9.0$ Hz, 2H; CH); $C_{14}H_{15}BF_2O_3$ (280.1): calcd C 60.03, H 5.41; found C 60.45, H 5.40.

2,2-Difluoro-4-(4-nitrophenyl)-5,6,7,8-tetrahydrocyclohexa-[1,2-b]-1,3,2-dioxaborine (21d): Compound **21d** was prepared from 4-nitrobenzoyl chloride (1 mol, 18.5 g) and *N*-(1-cyclohexenyl)morpholine (1.1 mol, 183.7 g). Yield: 128.9 g (44%); m.p. 136–138 (ethyl acetate); ^{1}H NMR ($CDCl_3$): $\delta = 1.73$ (m, 2H; CH_2) 1.85 (m, 2H; CH_2), 2.52 (t, 2H; CH_2), 2.73 (t, 2H; CH_2), 7.87 (d, $^3J = 8.8$ Hz, 2H; CH), 8.30 (t, $^3J = 8.8$ Hz, 2H; CH); $C_{13}H_{12}BF_2NO_4$ (293.1): calcd C 52.92, H 4.10, NO_2 4.75; found C 53.13, H 4.45, NO_2 4.70.

Preparation of the dimethylene-bridged methine dyes 22 and 23 (general procedure): A mixture of **20d** (2.93 g, 10 mmol), triethylorthoformate (**13a**, 2.13 g, 10 mmol) or 3-ethoxyacrolein diethylacetal (**13b**, 1.80 g, 10 mmol), and triethylamine (2.00 g, 20 mmol) in acetic anhydride (5 mL) and acetonitrile (50 mL) was heated at 60 °C for 30 min. After standing overnight the product had precipitated and was isolated by filtration. The preparative data of the compounds **22** and **23** so prepared are depicted in Table 1.

Preparation of the alkylene-bridged heptamethines 24 and 25 (general procedure): A mixture of compounds **5** or **20** (20 mmol), a bridged formyl compound **14** or **15** (10 mmol), and acetic anhydride (5 mL) in acetonitrile (80 mL) was heated at 60 °C for 10 min. After addition of triethylamine (40 mmol, 4 g) the resulting mixture was refluxed for 10 min and then cooled at room temperature. After standing overnight, the crystalline solid formed was isolated by filtration, washed with cooled acetonitrile, and recrystallized from acetonitrile. The preparative data of the compounds prepared by this procedure are depicted in Table 1.

Preparation of the alkylene-bridged heptamethines 26, 27, and 28 (general procedure): Compounds **5** or **20** (10 mmol) and the bridged iminium perchlorate **16** (10 mmol for preparing the dyes **26** and **28** and 5 mmol for preparing the dyes **27**) was added to a mixture of acetic anhydride (5 mL) and acetonitrile (80 mL). After heating the mixture at 60 °C for 10 min, triethylamine (20 mmol, 2 g) was added, and the resulting mixture was refluxed for further 10 min, cooled at room temperature, and kept overnight. The crystalline solid formed was isolated by filtration, washed with cooled acetonitrile, and recrystallized from acetonitrile. The preparative data of the compounds so prepared are depicted in Table 1.

Preparation of the betainic 2,2-difluoro-1,3,2-dioxaborine dyes 29 (general procedure): Compounds **5** or **20** (20 mmol) and the iminium diperchlorate **17** (10 mmol, 5 g) was added to a mixture of acetic anhydride (5 mL), acetonitrile (100 mL), and triethylamine (20 mmol, 2.0 g). After refluxing for 10 min, this mixture was cooled to room temperature. The solid formed was isolated by filtration and washed, subsequently, with water, acetic anhydride, ethyl acetate, and ether. For purification the products were recrystallized from dimethylformamide (compound **19a** and **19c**) or nitromethane. The preparative data of the compounds so prepared are depicted in Table 1.

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