

Synthesis of Reactive Condensation Products of Acetylacetone and Their Transformation into Deeply Coloured Methine Dyes ¹⁾

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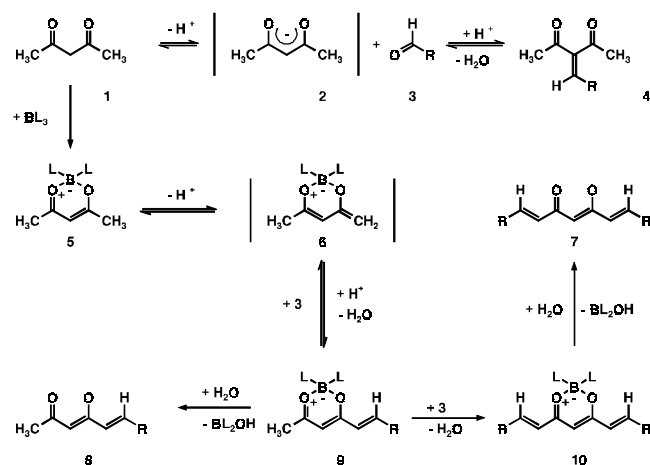
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Abstract. Starting from acetylacetone **1**, boric acid and a diol, or a 2-aminothiazole **16** and perchloric acid several dimethyl-substituted 1,3,2-dioxaborines **5** and thiazolo[3,2-*a*]pyrimidinium salts **17**, resp., have been prepared and transformed by reaction with 4-*N,N*-dimethylamino-benzaldehyde

3a or 3-methyl-2-methylmercapto-benzthiazolium perchlorate **13** into deeply colored polymethine dyes **11**, **12**, **14**, **15**, and **18–21**, and **23–24** their spectroscopic data were recorded.

Similarly to other enolizable 1,3-dicarbonyl compounds, acetylacetone **1** can react with simple formyl compounds **3** or their heteroanalogues to yield condensation products of the general structure **4** [1]. The reaction runs, obviously, on the intermediate carbanionic species **2** which is generated from the starting compound **1** by an appropriate auxiliary base.

In contrast, the 1,3,2-dioxaborines **5** which are easily available from **1** by reaction with suitable boron acid derivatives BL₃, such as boron trifluoride (L = F) or with a mixture of boric acid and a diol [2], can react with the formyl reagents **3** alternatively at their exocyclic methyl group giving rise to the formation of the condensation products of the general structure **9**. The condensation reactions run in this case, however, on the intermediate carbanionic species **6** formed by deprotonation of the exocyclic methyl group.



Scheme 1 Different reactivity of free and complexed 2,4-pentanedione towards formyl compounds **3**

nation of the exocyclic methyl groups by an auxiliary base.

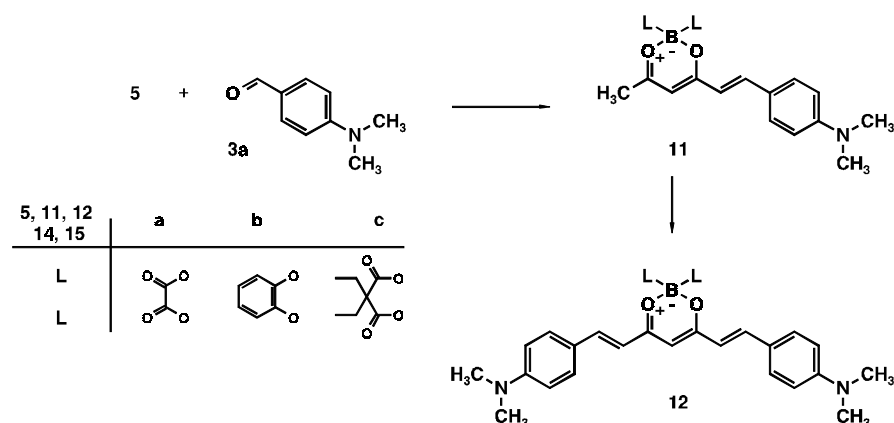
Frequently, the condensation with the formyl compound **3** can run a second time on the other methyl group of the 1,3,2-dioxaborine educt. Then, bis-condensation products of the structure **10** are formed [3].

As carbonyl compounds condensed with 4,6-dimethyl-1,3,2-dioxaborines **5** aromatic aldehydes (R = Aryl) have been used in the literature hitherto [4]. In the most cases reported, the condensation products primarily formed were not isolated, but transformed by hydrolysis into their corresponding boron-free acetylacetone derivatives **7** or **8**. Some of them, especially the bis-condensation products **7** received some interest as synthetic analogous of the natural dye curcumine [5]. Owing to an extended conjugated π -system, they exhibit, in contrast to the condensation products **4** with a cross-conjugated π -system, intense absorptions in the visible spectral region which are strongly influenced by the substituents in the aryl moieties.

By avoiding the hydrolytic splitting, the isolation of the 1,3,2-dioxaborine derivatives **9** and **10** is possible, however [6]. Thus, by starting with 4-dimethylamino-benzaldehyde (**3a**) a series of bis-condensation products of the general structure **12** could be prepared. Under special conditions, namely by a short-time heating of the 4,6-dimethyl-1,3,2-dioxaborines **5** with a stoichiometric amount of the aldehyde **3a**, mono-condensation products **11**, as exemplified with the 4,6-dimethyl-1,3,2-dioxaborine educt **5a**, could be obtained. As best solvent for the condensation reactions, acetic anhydride rendered. After cooling of the reaction mixture, the condensation products **11** and **12** formed crystallized and could be isolated by filtration.

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Scheme 2 Condensation reaction of the 1,3,2-dioxaborines **5** with 4-dimethylaminobenzaldehyde **3a**

Table 1 Spectroscopic data of the methine dyes prepared

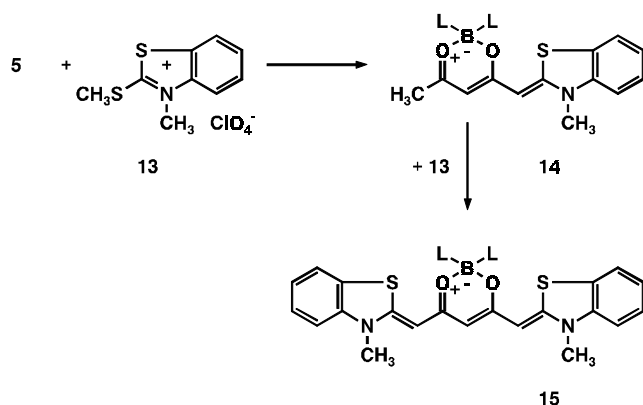
Nr	R ¹ (L ₂) a)	R ²	λ_{max} (log ϵ) [in DMF]	¹ H NMR δ /ppm, [in DMSO-d ₆]
11a	ox	–	530 (4.65) ^{b)}	2.28 (s, 3H, CH ₃), 3.13 (s, 6H, NCH ₃), 5.95 (s, 1H, CH), 6.38 (d, 1H, CH), 6.69 (d, 2H, CH), 7.54 (d, 2H, CH), 8.07 (d, 1H, CH)
12a	ox	–	662 (5.07)	3.08 (s, 12H, NCH ₃), 6.41 (s, 1H, CH), 6.78 (m, 6H, CH), 7.68 (d, 4H, CH), 7.89 (d, 2H, CH)
12c	mal	–	625 (4.97)	0.91 (t, 6H, CH ₃), 1.90 (q, 4H, CH ₂), 3.07 (s, 12H, NCH ₃), 6.40 (s, 1H, CH), 6.77 (m, 6H, CH), 7.61 (d, 4H, CH), 7.72 (d, 2H, CH)
14a	ox	–	427 (4.79)	2.09 (s, 3H, CH ₃), 3.93 (s, 3H, NCH ₃), 5.89 (s, 1H, CH), 6.23 (s, 1H, CH), 7.44 (t, 1H, CH), 7.60 (t, 1H, CH), 7.83 (d, 1H, CH), 8.10 (d, 1H, CH)
14b	cat	–	428 (4.89)	2.04 (s, 3H, CH ₃), 3.84 (s, 3H, NCH ₃), 5.81 (s, 1H, CH), 6.05 (s, 1H, CH), 6.59 (s, 5H, CH), 7.32 (t, 1H, CH), 7.52 (t, 1H, CH), 7.70 (d, 1H, CH), 7.96 (d, 1H, CH)
15a	ox	–	550 (5.44)	3.60 (s, 6H, NCH ₃), 5.74 (s, 1H, CH), 5.86 (s, 2H, CH), 7.20 (t, 2H, CH), 7.41 (t, 2H, CH), 7.50 (d, 2H, CH), 7.83 (d, 2H, CH)
15b	cat	–	544 (5.36)	3.60 (s, 6H, NCH ₃), 5.74 (s, 1H, CH), 5.76 (s, 2H, CH), 6.57 (m, 4H, CH), 7.11 (m, 2H, CH), 7.35 (m, 4H, CH), 7.69 (d, 2H, CH)
15c	mal	–	543 (4.61)	0.98 (t, 6H, CH ₃), 1.92 (q, 4H, CH ₂), 3.66 (s, 6H, NCH ₃), 5.70 (s, 1H, CH), 5.80 (s, 2H, CH), 7.18 (t, 2H, CH), 7.47 (m, 4H, CH), 7.64 (d, 2H, CH)
18b	benzo	–	545 (4.87)	3.08 (s, 6H, NCH ₃), 3.25 (s, 3H, CH ₃), 6.82 (d, 2H, CH), 7.15 (d, 1H, CH), 7.72 (d, 2H, CH), 7.80 (m, 2H, CH), 7.91 (s, 1H, CH), 8.27 (d, 1H, CH), 8.36 (m, 1H, CH), 8.57 (m, 1H, CH)
19a	H	H	574 (4.74)	3.05 (ss, 12H, NCH ₃), 6.79 (t, 4H, CH), 7.10 (d, 1H, CH), 7.46 (d, 1H, CH), 7.64 (d, 2H, CH), 7.79 (d, 2H, CH), 8.11 (d, 1H, CH), 8.16 (t, 2H, CH), 8.25 (s, 1H, CH), 9.00 (d, 1H, CH)
19b	benzo	–	603 (4.79)	3.07 (s, 12H, NCH ₃), 6.80 (m, 4H, CH), 7.16 (d, 1H, CH), 7.51 (d, 1H, CH), 7.68 (m, 6H, CH), 7.91 (d, 1H, CH), 8.09 (s, 1H, CH), 8.22 (d, 1H, CH), 8.32 (d, 2H, CH)
19c	naphtho	–	603 (4.85)	3.03 (s, 6H, NCH ₃), 3.08 (s, 6H, CH ₃), 6.74 (d, 2H, CH), 6.84 (d, 2H, CH), 7.13 (d, 1H, CH), 7.55 (m, 3H, CH), 7.73 (d, 2H, CH), 7.82 (m, 3H, CH), 8.11 (s, 1H, CH), 8.18 (m, 5H, CH)
20b	benzo	–	474 (5.04)	2.98 (s, 3H, NCH ₃), 3.87 (s, 3H, CH ₃), 6.41 (s, 1H, CH), 7.07 (s, 1H, CH), 7.37 (t, 1H, CH), 7.54 (m, 3H, CH), 7.70 (d, 1H, CH), 8.01 (d, 1H, CH), 8.11 (d, 1H, CH), 8.25 (m, 5H, CH)
21a	H	H	522 (5.02)	3.65 (s, 6H, NCH ₃), 5.80 (s, 1H, CH), 6.22 (s, 1H, CH), 6.76 (s, 1H, CH), 7.12 (m, 2H, CH), 7.29 (m, 4H, CH), 7.65 (d, 1H, CH), 7.74 (m, 2H, CH), 8.50 (d, 1H, CH)
21b	benzo	–	549 (4.95)	3.73 (s, 3H, NCH ₃), 3.84 (s, 3H, NCH ₃), 6.21 (s, 1H, CH), 6.49 (s, 1H, CH), 7.22 (m, 3H, CH), 7.44 (m, 3H, CH), 7.58 (m, 3H, CH), 7.77 (d, 1H, CH), 7.95 (d, 1H, CH), 8.12 (d, 1H, CH), 8.54 (d, 1H, CH)
21c	naphtho	–	549 (4.82)	3.76 (s, 3H, NCH ₃), 3.85 (s, 3H, NCH ₃), 6.28 (s, 1H, CH), 6.53 (s, 1H, CH), 7.25 (m, 3H, CH), 7.36 (m, 2H, CH), 7.48 (m, 3H, CH), 7.62 (d, 1H, CH), 7.73 (m, 3H, CH), 7.96 (d, 1H, CH), 8.10 (m, 3H, CH), 8.67 (d, 1H, CH)
23a	H	H	625 (5.98)	3.07 (s, 6H, CH ₃), 6.39 (d, 2H, CH), 7.78 (s, 2H, CH), 7.93 (d, 2H, CH), 8.33 (d, 2H, CH), 8.58 (t, 1H, CH)
23b	benzo	–	643 (5.01)	2.97 (s, 6H, CH ₃), 6.06 (d, 2H, CH), 7.10 (m, 2H, CH), 8.08 (m, 2H, CH), 8.21 (d, 2H, CH), 8.60 (m, 1H, CH)
23c	naphtho	–	662 (5.23)	3.02 (s, 6H, CH ₃), 6.00 (d, 2H, CH), 7.02 (m, 2H, CH), 7.60 (m, 5H, CH), 8.02 (d, 2H, CH), 8.10 (m, 3H, CH), 8.28 (d, 2H, CH), 8.50 (m, 1H, CH)
24b	benzo	–	757 (5.42)	2.95 (s, 6H, CH ₃), 6.04 (d, 2H, CH), 6.43 (t, 1H, CH), 7.08 (d, 2H, CH), 7.58 (m, 4H, CH), 7.93 (t, 2H, CH), 8.07 (m, 2H, CH), 8.19 (d, 2H, CH)

a) ox: oxalato, mal: diethylmalonato, cat: catecholato; b) in acetone

The condensation products **11** and **12** are deeply coloured compounds. Their structure was confirmed by elemental analysis and NMR spectroscopic measurements (see Table 1).

As characteristic feature of the products **12** their strong fluorescence is to be mentioned [7]. Its intensity is influenced significantly by the substitution pattern at the boron group and is rather strong for the oxalato-substituted derivative **12a**. Details on this studies will be published, however, in a forthcoming paper.

In analogy to 4-dimethylaminobenzaldehyde (**3a**) 3-methyl-2-methylmercapto-benzthiazolium perchlorate (**13**) is also able to condense with the methyl groups of the 4,6-dimethyl-1,3,2-dioxaborines **5**. In this case mono- or bis-condensation products of the structure **14** or **15**, resp., were also available. Whereas the mono-condensation products **14** are orange coloured compounds which were obtained by condensing the educts **5** and **13** in a stoichiometric ratio, the bis-condensation products **15** are deeply red coloured compounds which were obtained by condensing the educts **5** and **13** in a 1:2 ratio.

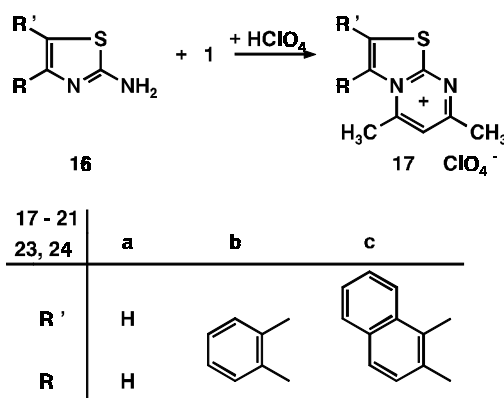


Scheme 3 Condensation reaction of the 1,3,2-dioxaborines **5** with 3-methyl-2-methylmercaptobenzthiazolium perchlorate **13**

The structure of the products **14** and **15** follows from their elemental analysis as well as from their NMR spectral data (see Table 1).

In analogy with the boron compounds BL_3 , acetylacetone **1** is able to condense, similarly to other 2-amino-azoles [8], with 2-amino-thiazoles **16** in presence of a strong mineralic acid, such as perchloric acid, to yield the 5,7-dimethyl-thiazolo[3,2-*a*]pyrimidinium perchlorates (**17**) [9]. Similar to other quarternary heterocyclic compounds, the methyl groups in these compounds should be reactive towards electrophilic reagents also. Due to the unsymmetrical structure of the thiazolo[3,2-*a*]pyrimidinium perchlorates **17**, the reactivity of both these groups has to be different, however.

To check this postulate we have condensed the dimethyl derivatives of three different substituted thiazo-



Scheme 4 Preparation route for the dimethyl-substituted thiazolo[3,2-*a*]pyrimidinium perchlorates **17**

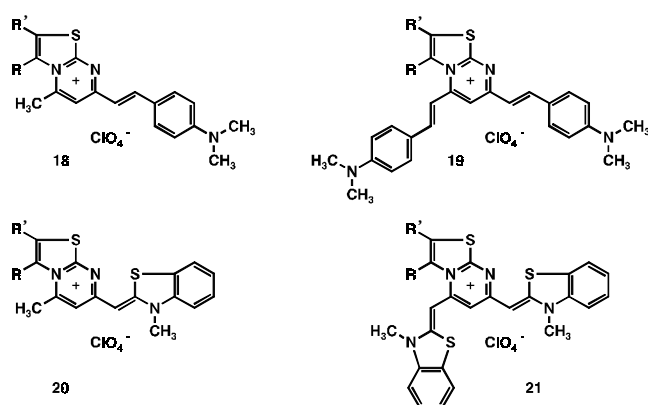
lo[3,2-*a*]pyrimidinium perchlorates **17a–c** with the electrophiles 4-dimethylaminobenzaldehyde (**3a**) and 1-methyl-2-methylmercapto-benzthiazolium perchlorate (**13**).

Thus, if the bis-methylsubstituted thiazolo[3,2-*a*]pyrimidinium perchlorates **17a–c** were allowed to react with **3a** in presence of acetic anhydride mono- or bis-condensation products of the structure **18** or **19**, resp., were obtained. Whereas the mono-condensation products **18** could be obtained by condensing the educts **17** with a stoichiometric amount of **3a**, the bis-condensation products were obtained by using an excess of **3a**.

A similar result was obtained by condensing the thiazolo[3,2-*a*]pyrimidinium perchlorates **17a–c** with 1-methyl-2-methylmercapto-benzthiazolium perchlorate (**13**) under the same conditions, but in presence of triethylamine. Also in this case mono- or bis-condensation products of the structure **20** and **21**, depending on the ratio of the components used, were obtained.

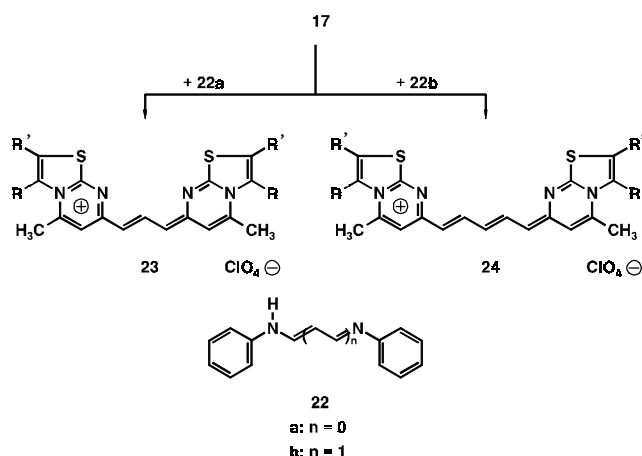
The structure of the products **18–21** was confirmed by means of elemental analysis and NMR spectroscopic measurements (see Table 1). Thus, the mono-condensation products exhibit, as exemplified with the compounds **18a** and **20a**, in their 1H NMR spectra characteristic signals at about 2.00 ppm and 3.00 ppm. Whereas the high-field signals can be attributed to the *N*-bound methyl groups the low-field signals at about 3.00 ppm can be attributed to the methyl group at the thiazolo[3,2-*a*]pyrimidinium moieties. From NOESY experiments which were performed with the mono-condensation products **18a** and **20a** follow unambiguously, that in these products the methyl-groups at C(7) of the thiazolo[3,2-*a*]pyrimidinium moiety have been reacted with the electrophilic reagents **3a** or **13**.

A special result was obtained by condensing the thiazolo[3,2-*a*]pyrimidinium perchlorates **17a–c** with bifunctional reagents, such as with *N,N'*-diphenyl-formamidine (**22a**) or with its vinylogous, the 3-anilinoacroleine anil (**22b**), in acetic anhydride in presence of



Scheme 5 Mono and Bis-4-dimethylaminostyryl thiazolo[3,2-*a*]pyrimidinium perchlorates **18**–**21**

triethylamine. Under this condition the trimethincyanines **23** and the pentamethinecyanines **24** were obtained. Owing to the different reactivity of both the methyl groups in the thiazolo[3,2-*a*]pyrimidinium perchlorate educts **17** only their methyl group at C(7) reacts with the reagents used.



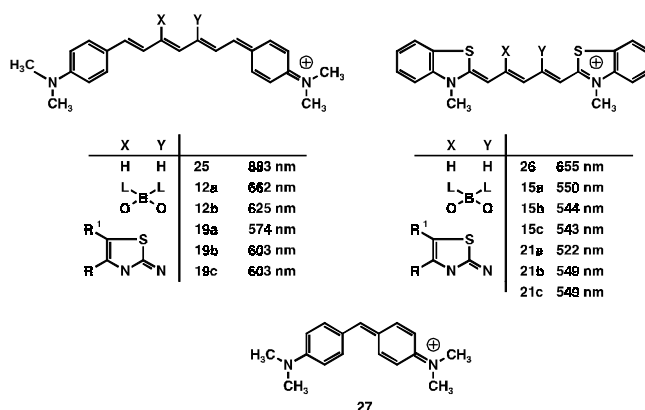
Scheme 6 Trimethines **23** and pentamethines **24** derived from the thiazolo[3,2-*a*]pyrimidinium perchlorates **17**

As a characteristic feature of the condensation products **18**–**21** as well as of the products **23** and **24** their deep colour has to be mentioned. It was originated by intense absorption bands their maxima are found in the visible spectral range and their positions depend on the substitution pattern of the compounds studied (see Table 1).

It is obvious to compare the absorption data of some of the compounds prepared with the ones of compounds structural related to them. Thus, the methine dye **25** which can be considered as the parent compound of the dyes **12** and **19** absorbs with 883 nm at considerably longer wavelength than their heterocyclic modified analogues [10]. The same is to observe with the dye **26**

which can be considered as the parent compound of the dyes **15** and **21**. It also absorbs with 655 nm at significantly longer wavelength than its heterocyclic modified analogues **15** and **21** [11]. These spectral effects can be understood in respect to simple rules given by Dewar [12]. Thus, the heterocyclic 1,3,2-dioxaborine and thi-azolo[3,2-*a*]pyrimidine fragments which modify the methine chain in the parent compounds **25** and **26** are linked with their donor moieties *O* or *N* at odd positions of the corresponding methine chain. Hence, a hypsochromic shift of the longest wavelength absorption is, in agreement with the Dewar's rule, caused.

A mentionable fact is to reveal by comparing the absorption wavelength of the dyes **18** and **23** with the absorption wavelength of the well-known methine dye **27** [13]. As symmetrically substituted methine dye analogues of the unsymmetrical substituted methine dye **18b** both these dyes **23b** and **27** absorb with 643 nm and 610 nm [11], resp., at considerably longer wavelength than the compound **18b** which absorbs at 546 nm.



Scheme 7 Comparison of the UV/VIS spectral data of some chain-substituted methines

This absorption is found more than 80 nm at shorter wavelength than the arithmetic mean value (626,5 nm) of the absorption maxima of both the other compounds **23b** and **27**. Such negative deviation of the absorption wavelength of an unsymmetrical substituted methine dye in respect to the arithmetic mean value of the absorption maxima of the appropriate symmetrically substituted methine dye analogues is, as demonstrated with a huge number of examples [14], typically for nearly all unsymmetrical substituted methine dyes [15]. The magnitude of this negative deviation is controlled by the electronic properties of the corresponding fragments building the corresponding symmetrically and unsymmetrical substituted dyes. The larger the difference in the electronic properties of two fragments the larger the negative deviation is to observe [16].

Experimental

Melting points were determined by means of heating table microscope (Boëtius). The NMR spectra were recorded with a Varian 300 MHz spectrometer Gemini 300 or with a JEOL 200 MHz spectrometer JNM FX 200. The elemental analytical data were determined by means of a LECO analyzer CHNS 932. The 1,3,2-dioxaborines **5a** and **5b** used as educts were prepared accordingly to the literature [2].

4,6-Dimethyl-2,2-(diethylmalonato)-1,3,2-dioxaborine (**5c**)

A mixture of acetylacetone (**1**, 0.1 mol, 10.0 g), diethylmalonic acid (0.1 mol, 16.0 g), boric acid (0.1 mol, 6.2 g), and 1,2-dichloroethane (100 mL) was refluxed at a Dean-Stark condenser until all water (ca. 6 mL) was separated. Then, the mixture was concentrated *in vacuo* and the product precipitated after cooling was isolated by filtration; yield 20.0 g (75%); *m.p.* 103–108 °C. – ¹H NMR (CDCl₃): δ/ppm = 0.93 (t, 6H, CH₃), 2.00 (q, 4H, CH₂), 2.31 (s, 6H, CH₃), 6.02 (s, 1H, CH).

4-(4-Dimethylaminostyryl)-6-methyl-2,2-oxalato-1,3,2-dioxaborine (**11a**)

A mixture of 4,6-dimethyl-2,2-oxalyl-1,3,2-dioxaborine (**5a**, 5 mmol, 1.0 g) and 4-dimethylaminobenzaldehyde (**3a**, 4 mmol, 0.6 g) in acetic anhydride (15 mL) was heated at 80 °C for 15 min. After standing at room temperature for 2 h the product formed was isolated by filtration, washed with acetic acid and ethanol, and dried; yield 16 %; *m.p.* 257–259 °C.

C₁₆H₁₆BN₂O₆ Calcd.: C 58.39 H 4.90 N 4.26
(329.1) Found: C 58.96 H 5.22 N 4.08.

Preparation of 4,6-Bis-(4-dimethylaminostryl)-1,3,2-dioxaborines **12a–c** (General Procedure)

A mixture of a 4,6-dimethyl-1,3,2-dioxaborine **5** (2.5 mmol) and 4-(*N,N*-dimethylamino)-benzaldehyde (**3a**) (40 mmol) in acetic acid (20 mL) was heated under stirring for 2 h. At standing overnight at room temperature, the products formed were isolated by filtration and recrystallized from DMF or acetic acid. The following products were so obtained:

4,6-bis-(4-dimethylaminostryl)-2,2-oxalato-1,3,2-dioxaborines (**12a**) in a yield of 61%; *m.p.* 259–261 °C.

C₂₅H₂₅BN₂O₆ Calcd.: C 65.21 H 5.43 N 6.09
(459.8) Found: C 65.64 H 5.49 N 5.66.

2,2-Catecholato-4,6-bis-(4-dimethylaminostyryl)-1,3,2-dioxaborine (**12b**) in a yield of 67%; *m.p.* 321–324 °C.

C₂₉H₂₉BN₂O₄ Calcd.: C 72.60 H 6.05 N 5.85
(478.8) Found: C 71.85 H 6.30 N 5.87.

2,2-(Diethylmalonato)-4,6-bis-(4-dimethylaminostryl)-1,3,2-dioxaborine (**12c**) in a yield of 47%; *m.p.* 321–324 °C.

C₃₀H₃₀BN₂O₆ Calcd.: C 67.93 H 6.65 N 5.28
(530.4) Found: C 67.69 H 6.96 N 4.96.

6-Methyl-4-(*N*-methyl-1,3-benzthiazolyliidenemethylene)-1,3,2-dioxaborines **14** (General Procedure)

A mixture of a 4,6-dimethyl-1,3,2-dioxaborine **5** (5 mmol) and 3-methyl-2-methylmercapto-benzthiazolium perchlorate

(**13a**) (5 mmol, 1.7 g) in DMF (20 mL) was heated to 40–50 °C and was added with triethylamine (0.5 mL). After stirring at room temperature for 2 h, the products formed were obtained by filtration, washed with DMF (5 mL) and subsequently, with ethanol (10 mL), and recrystallized from acetonitrile or DMF.

The following products were so obtained:

6-Methyl-4-(*N*-methyl-1,3-benzthiazolyliidenemethylene)-2,2-oxalato-1,3,2-dioxaborine (**14a**) in a yield of 34%; *m.p.* > 360 °C.

C₁₅H₁₂BN₂O₆S Calcd.: C 52.18 H 3.48 N 4.06 S 9.28
(345.1) Found: C 50.98 H 4.07 N 4.16 S 9.27.

2,2-Catecholato-6-methyl-4-(*N*-methyl-1,3-benzthiazolyliidenemethylene)-1,3,2-dioxaborine (**14b**) in a yield of 34%; *m.p.* > 360 °C.

C₁₉H₁₅BN₂O₄S Calcd.: C 62.47 H 4.38 N 3.83 S 8.77
(365.2) Found: C 61.45 H 4.83 N 3.98 S 8.62.

Preparation of 4,6-Bis-(*N*-methyl-1,3-benzthiazolyliidenemethylene)-1,3,2-dioxaborines **15a–c** (General Procedure)

To a boiling mixture of a 4,6-dimethyl-1,3,2-dioxaborine **5** (2 mmol) and 3-methyl-2-methylmercapto-benzthiazolium perchlorate (**13a**, 6 mmol, 1.8 g) in DMF (10 mL) triethylamine (1.0 mL) was added. After refluxing for 10 min, the products formed were obtained from the cold reaction mixture by filtration, washed with DMF (5 mL) and, subsequently, washed with ethanol (10 mL), and recrystallized from acetonitrile or DMF.

The following products were so obtained:

4,6-Bis-(*N*-methyl-1,3-benzthiazolyliidenemethylene)-2,2-oxalato-1,3,2-dioxaborine (**15a**) in a yield of 36%; *m.p.* > 360 °C.

C₂₃H₁₇BN₂O₆S₂ Calcd.: C 56.10 H 3.46 N 5.69 S 13.01
(492.3) Found: C 55.92 H 3.71 N 5.67 S 13.00.

2,2-Catecholato-4,6-bis-(*N*-methyl-1,3-benzthiazolyliidenemethylene)-1,3,2-dioxaborine (**15b**) in a yield of 11%; *m.p.* > 360 °C.

C₂₇H₂₁BN₂O₆S₂ Calcd.: C 61.54 H 4.79 N 7.17 S 10.94
(512.4) Found: C 61.24 H 5.40 N 6.82 S 10.86.

2,2-Diethylmalonato-4,6-bis-(*N*-methyl-1,3-benzthiazolyliidenemethylene)-1,3,2-dioxaborine (**15c**) in a yield of 43%; *m.p.* > 360 °C.

C₂₈H₃₃BN₂O₆S₂ Calcd.: C 59.89 H 4.81 N 4.99 S 11.41
(568.5) Found: C 58.45 H 4.76 N 4.82 S 11.55.

Preparation of the Dimethyl-substituted Thiazolo[3,2-*a*]pyrimidinium Perchlorates **17a–c** (General Procedure)

A mixture of acetylacetone (**1**, 0.4 mol, 40 g), perchloric acid (0.12 mol), and a 2-amino-thiazole **16** (0.12 mol) in ethanol (16 mL) was refluxed under stirring for 6 h. After standing overnight, the products formed were isolated by filtration, washed with acetone (50 mL) and diethyl ether (50 mL), and recrystallized from methanol.

The following products were so obtained:

5,7-Dimethyl[1,3]thiazolo[3,2-*a*]pyrimidin-4-ium perchlorate (**17a**) in a yield of 76% from 2-amino-thiazole; *m.p.* 224–225 °C (218–219 °C, ref. [9]). – ¹H NMR (in DMSO-*d*₆),

δ /ppm = 2.76 (s, 3H, CH₃), 2.91 (s, 3H, CH₃), 7.94 (s, 1H, CH), 8.47 (d, 1H, CH), 8.74 (d, 1H, CH).

2,4-Dimethylpyrimido[2,1-d][1,3]benzthiazol-5-ium perchlorate (17b) in a yield of 70% from 2-amino-benzthiazole; *m.p.* 247–249 °C (238–239 °C, ref. [9]). – ¹H NMR (in DMSO-d₆), δ /ppm = 2.82 (s, 3H, CH₃), 3.30 (s, 3H, CH₃), 7.80 (s, 1H, CH), 7.89 (m, 2H, CH), 8.27 (m, 1H, CH), 8.64 (m, 1H, CH).

8,10-Dimethylnaphtho[2',1':4,5][1,3]thiazolo[3,2-a]pyrimidin-7-ium perchlorate (17c) in a yield of 93% from 2-amino-naphtho[2,1-d]thiazole; *m.p.* 260 °C (260 °C, ref. [9]). – ¹H NMR (in DMSO-d₆), δ /ppm = 2.86 (s, 3H, CH₃), 3.43 (s, 3H, CH₃), 7.93 (t, 2H, CH), 8.13 (s, 1H, CH), 8.34 (m, 3H, CH), 8.79 (d, 1H, CH).

2-(4-Dimethylaminostyryl)-4-methylpyrimido[2,1-d][1,3]benzthiazol-5-ium perchlorate (18b)

A mixture of 4,6-dimethyl-pyrimido[2,1-d][1,3]benzthiazol-5-ium perchlorate (**17b**, 1 mmol, 0.32 g) and 4-dimethylaminobenzaldehyde (**3a**, 1 mmol, 0.15 g) in acetic anhydride (3 mL) was heated at 50 °C for 5 min. After cooling at room temperature the product precipitated was isolated by filtration, washed with methanol, and dried; yield 22%; *m.p.* 274–277 °C.

C₂₁H₂₀ClN₃O₄S Calcd.: C 56.56 H 4.52 N 9.43 S 7.18 (445.9) Found: C 55.95 H 4.75 N 8.94 S 6.92.

Preparation of the Bis-(4-dimethylaminostyryl)-substituted Thiazolo[3,2-a]pyrimidinium Perchlorates 19a–c (General Procedure)

To a boiling mixture of a dimethyl-substituted thiazolo[3,2-a]pyrimidinium perchlorates **17** (5 mmol) and 4-dimethylaminobenzaldehyde (**3a**, 40 mmol, 6.0 g) in acetic acid (20 mL) triethylamine (0.5 mL) was added. After boiling for 20 min the reaction mixture was cooled at room temperature and the products formed were isolated by filtration, washed with DMF (5 mL) and ethanol (10 mL), and recrystallized from acetonitrile or DMF.

The following products were so obtained:

5,7-[Bis-(4-dimethylamino-styryl)][1,3]thiazolo[3,2-a]pyrimidin-4-ium perchlorate (19a) in a yield of 57%; *m.p.* 257–260 °C.

C₂₆H₂₇ClN₄O₄S Calcd.: C 58.09 H 5.67 N 11.67 S 5.34 (527.1) Found: C 57.99 H 5.78 N 11.33 S 5.38.

2,4-[Bis-(4-dimethylamino-styryl)]-pyrimido[2,1-d][1,3]benzthiazol-5-ium perchlorate (19b) in a yield of 69%; *m.p.* 248–254 °C.

C₃₀H₂₉ClN₄O₄S Calcd.: C 60.96 H 5.54 N 9.71 S 4.93 (577.1) Found: C 60.43 H 5.55 N 9.35 S 5.07.

8,10-[Bis-(4-dimethylamino-styryl)]-naphtho[2',1':4,5][1,3]thiazolo[3,2-a]pyrimidin-7-ium perchlorate (19c) in a yield of 64%; *m.p.* 300 °C (dec.).

C₃₄H₃₁ClN₄O₄S Calcd.: C 63.47 H 5.43 N 8.94 S 5.11 (627.1) Found: C 63.76 H 5.31 N 8.78 S 5.01.

2-(3-Methyl-2-benzthiazolylidenemethylene)-4-methylpyrimido[2,1-d][1,3]benzthiazol-5-ium perchlorate (20b); yield 75%; *m.p.* > 360 °C.

C₂₀H₁₆ClNO₄S₂ Calcd.: C 52.00 H 3.47 N 9.10 S 13.87 (461.9) Found: C 51.99 H 3.86 N 10.04 S 13.14.

Preparation of the Bis-(3-methyl-2-benzthiazolylidenemethylene)-substituted Thiazolo[3,2-a]pyrimidinium Perchlorates 21 (General Procedure)

A mixture of a dimethyl-substituted thiazolo[3,2-a]pyrimidinium perchlorates **17** (2 mmol) and 3-methyl-2-methylmercapto-benzthiazolium perchlorate (**13a**, 6 mmol, 1.7 g) in DMF (10 mL) was heated at boiling, added with triethylamine (1.0 mL), and refluxed for 10 min. After standing overnight the product separated was isolated by filtration and washed with ethanol (10 mL).

The following products were so obtained:

5,7-Bis-[2-(3-methyl-2-benzthiazolylidenemethylene)][1,3]thiazolo[3,2-a]pyrimidin-4-ium perchlorate (21a) in a yield of 43%; *m.p.* 260 °C (dec.).

C₂₄H₁₉ClN₄O₄S₃ Calcd.: C 51.57 H 3.40 N 10.03 S 17.18 (559.1) Found: C 50.54 H 4.14 N 10.57 S 16.59.

2,4-Bis-[2-(3-methyl-2-benzthiazolylidenemethylene)]-pyrimido[2,1-d][1,3]benzthiazol-5-ium perchlorate (21b) in a yield of 35%; *m.p.* > 260 °C.

C₂₈H₂₁ClN₄O₄S₃ Calcd.: C 55.22 H 3.45 N 9.20 S 15.78 (609.1) Found: C 55.05 H 3.80 N 9.27 S 15.69.

8,10-Bis-[2-(3-methyl-2-benzthiazolylidenemethylene)]-naphtho[2',1':4,5][1,3]thiazolo[3,2-a]pyrimidin-7-ium perchlorate (21c) in a yield of 33%; *m.p.* > 300 °C (dec.).

C₃₂H₂₃ClN₄O₄S₃ Calcd.: C 58.31 H 3.49 N 8.50 S 14.58 (659.2) Found: C 58.06 H 3.99 N 8.69 S 14.29.

Preparation of Thiazolo[3,2-a]pyrimidinium substituted trimethinium Perchlorates 23a–c

A mixture of a dimethyl-substituted thiazolo[3,2-a]pyrimidinium perchlorates **17** (2 mmol), pyridine (5 mL), *N,N'*-diphenyl-formamidine (**22a**) (1 mmol, 0.572 g), and acetic anhydride (1 mL) was refluxed for 5 min. After cooling the reaction mixture, the products formed were isolated by filtration, washed with acetone (5 mL), and recrystallized from DMF. The following products were so obtained:

5-Methyl-7-[3-(5-methyl-7H-[1,3]thiazolo[3,2-a]pyrimidin-7-ylidene)-1-propenyl][1,3]thiazolo[3,2-a]pyrimidin-7-ium perchlorate (23a) in a yield of 17%; *m.p.* 267–269 °C.

C₁₇H₁₅ClN₄O₄S₂ Calcd.: C 46.52 H 3.42 N 12.17 S 14.60 (438.9) Found: C 46.59 H 3.40 N 13.11 S 14.69.

2-Methyl-4-[3-(2-methyl-4H-pyrimidino[2,1-d][1,3]benzthiazol-5-ylidene)-1-propenyl]-pyrimidino[2,1-d][1,3]benzthiazol-5-ium perchlorate (23b); yield 24%; *m.p.* 321–323 °C.

C₂₅H₁₉ClN₄O₄S₂ Calcd.: C 55.71 H 3.53 N 10.40 S 11.88 (539.0) Found: C 55.10 H 4.12 N 10.24 S 11.19.

8-Methyl-10-[3-(8-methyl-10H-naphtho[2',1':4,5][1,3]thiazolo[3,2-a]pyrimidin-7-ylidene)-1-propenyl]-naphtho[2',1':4,5][1,3]thiazolo[3,2-a]pyrimidin-7-ium perchlorate (23c) yield 14%; *m.p.* > 360 °C.

C₃₃H₂₃ClN₄O₄S₂ Calcd.: C 62.02 H 3.60 N 8.77 S 10.22 (639.1) Found: C 62.09 H 4.05 N 8.73 S 10.01.

2-Methyl-4-[5-(2-methyl-4H-pyrimidino[2,1-d][1,3]benzthiazol-5-ylidene)-1-pentadienyl]-pyrimidino[2,1-d][1,3]benzthiazol-5-ium perchlorate (24b)

A mixture of 2,4-dimethylpyrimido[2,1-d][1,3]benzthiazol-5-ium perchlorate (**17b**, 2 mmol, 0.63 g), 3-anilino-acroleine-

anil (**22b**, 1 mmol, 0.32 g), acetic anhydride (6 mL), triethylamine (0.4 mL), and acetonitrile (6 mL) was heated at 40 °C under stirring for 30 min. After standing overnight, the product formed was isolated from the reaction mixture by filtration and washed with hot acetonitrile (3 × 15 mL); yield 28 %, *m.p.* 280 °C (dec.).

$C_{27}H_{21}ClN_4O_4S$ Calcd.: C 57.40 H 3.72 N 9.92 S 11.34 (565.1) Found: C 57.11 H 4.46 N 9.38 S 10.92.

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