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Polymethine dyes derived from boron complexes of acetylhydroxycoumarins

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Abstract

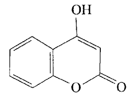
Novel dyes were obtained by condensation of boron derivatives of 3-acetyl-4-hydroxy- or 7-hydroxy-8-acylcoumarin with triethyl orthoformate or Fischer's aldehyde. The reaction of the former boron complexes with DMF followed by condensation of the resultant hemicyanine with dimethylquinolinium iodides furnished non-symmetric polymethine dyes with a quinoline as the terminal heterocyclic unit.

Keywords: 3-Acetyl-4-hydroxycoumarin; 8-Acyl-7-hydroxycoumarins; Difluoro[1,3-propanedionato-*O,O'*]boron derivatives; Polymethine dyes; NMR

1. Introduction

Recently we have studied tautomeric transformations of 4-hydroxycoumarin and its 3-substituted analogs [1–3]. In particular, by using photoelectron spectroscopy we have shown that 4-hydroxycoumarin exists in the gas phase as a mixture of enol **1** and diketone **2** [4].

On the other hand, six tautomeric structures **3**–**8** can be suggested for 3-acetyl-4-hydroxycoumarin. Nevertheless, the results of photoelectron studies and quantum mechanical calculations indicate only two forms **3** and **4** present in a gas phase. These two tautomers are involved in the formation of highly stable boron chelates in the solution as well. These results have been reported by us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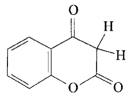
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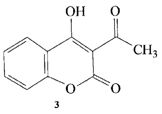
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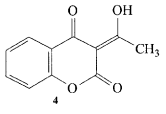
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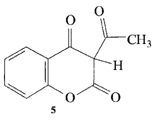
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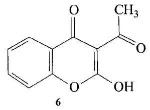
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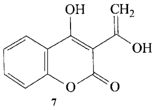
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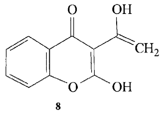
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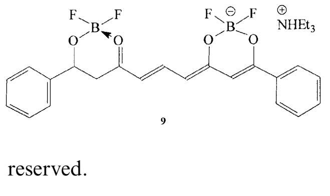
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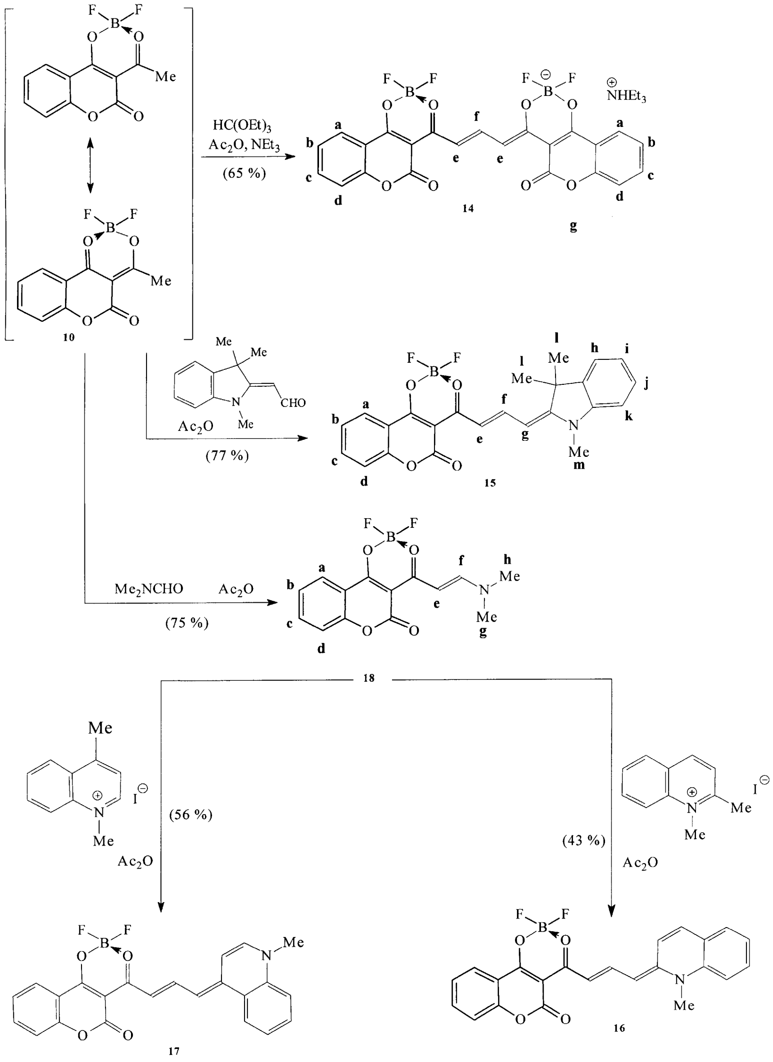
recently. Similar boron complexes have been obtained from 8-acetyl-7-hydroxycoumarin [5]

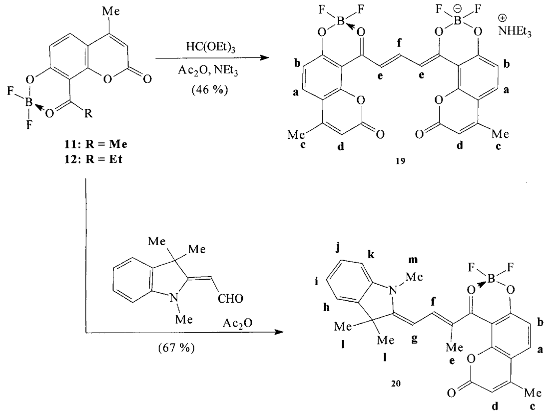
It is known that incorporation of the boron atom greatly increases reactivity of the methyl group of the acetyl substituent in ortho-hydroxyacetophenones, benzoylacetones, and acetylnaphthols [6–8]. The methyl group in such complexes undergoes a facile condensation with carbonyl compounds or equivalents including aldehydes [6], formamides [7], acetals, orthoesters, and anils [8]. Depending on the structure of the condensation reagent the boron complexes can be transformed into symmetric dyes or non-symmetric dyes that contain two different end units at the polymethine chain. For example, dye **9** has been obtained by condensation of triethyl orthoformate with a boron chelate derived from benzoylacetone [7].

In general, these classes of dyes show intensive luminescence.

This report pertains to the synthesis of novel polymethine dyes that are derived from boron-

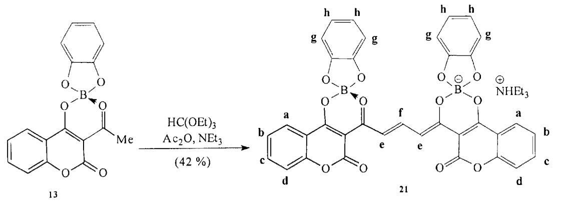


Scheme 1.



Scheme 2.

containing coumarins **10** (Scheme 1), **11** and **12** (Scheme 2), and **13** [Eq. (1)].



(1)

It was reasoned that the high stability of these boron coordination compounds, due to their quasi-aromatic structure [5], as illustrated for **10** in Scheme 1, would be retained in the dye products. The inherent luminescence of coumarins also played a role in the initiation of this work.

2. Results and discussion

The synthesis of several dyes starting with coumarin derivative **10** is shown in Scheme 1. Thus, condensation of **10** with triethyl orthoformate in acetic anhydride in the presence of triethylamine furnished symmetric dye **14** of high purity by direct crystallization from the reaction medium. A subsequent crystallization of **14** from glacial acetic acid did not increase the melting point. In a similar way, the reaction of **10** with Fischer's aldehyde in acetic anhydride gave a non-symmetric dye **15**. The quinoline derivatives **16** and **17** were obtained by condensation of **10** with *N,N*-dimethylformamide in acetic anhydride followed by the reaction of the resultant intermediate product **18** with the respective dimethylquinolinium iodide.

The synthesis of symmetric dye **19** by the reaction of the substrate **11** with triethyl orthoformate is presented in Scheme 2. The starting material **12** was also allowed to react with Fischer's aldehyde to give a non-symmetric dye **20**. Finally, a 1,2-phenylenedioxaboryl derivative **13** was condensed with triethyl orthoformate under standard conditions to give the expected dye **21** [Eq. (1)].

The reported yields are for analytically pure compounds, as shown by good results of elemental analysis. The pure dyes were characterized by spectral methods. In particular, the expected molecular ion peaks are observed in the EI mas spectra of several dyes, and in all cases the fragmentation patterns are fully consistent with the given structures. The ^{1}H NMR spectra of dyes **16** and **17** could not be recorded due to low solubility. On the other hand, for the remaining compounds the large values of the coupling constants between protons of the trimethine chain ($J > 12$ Hz) are indicative of all-trans configurations. The simplicity of the ^{1}H NMR spectra for symmetric dyes is also consistent with symmetrical electron density distribution along the chromophore composed of terminal heterocyclic units and the polymethine linker. This conclusion is also in agreement with a single boron resonance at δ 0.48 in the ^{11}B NMR spectrum of **14**.

Diheterocyclic dyes **14–17**, **19**, and **21** show electronic absorption in the region of 569–650 nm with a high extinction coefficient ranging from 96 000 M^{-1} cm^{-1} for **21** to 145 000 M^{-1} cm^{-1} for **14**, which is comparable to the absorption characteristics of analogous cyanines and suggests similarity in the frontier orbitals of the two classes of chromophores. The hypochromically shifted absorption of **20** ($\lambda_{max} = 431$ nm, $\varepsilon = 62\,000$ $M^{-1}cm^{-1}$) is undoubtably due to the steric hindrance caused by the presence of the methyl group at the polymethine chain. Specifically, this steric crowding causes deviation of the chromophore system from planarity which, in turn, raises the HOMO-LUMO energy gap. The electronic spectra of selected dyes are illustrated in Fig. 1. Included

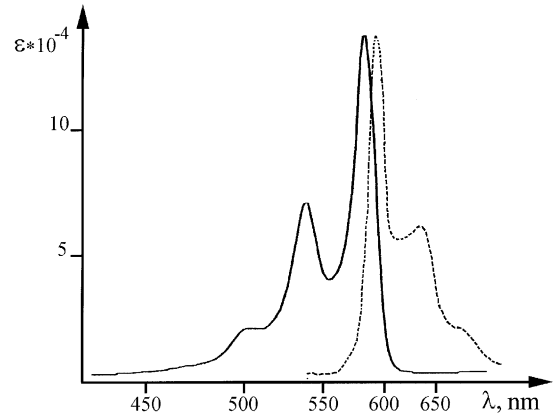


Fig. 1. The electronic absorption spectrum and spectrum of fluorescence of compound **14**.

in Fig. 1 is compound **14** the absorption spectrum of which is characterized by a remarkably narrow band with a high extinction coefficient. The vibrational structure of the spectrum of **14** is characteristic for polymethine dyes. Interestingly, dye **14** shows substantial fluorescence in chloroform with maximum at 595 nm and a Stokes' shift of 14 nm. The vibrational structure is retained in the fluorescence spectrum . In opposite, 3-acetyl-4-hydroxycoumarin **3** and its boron complex **10** has no fluorescence at all.

It has been reported [7] that the presence of phenyl substituents in difluoro[1,3-propanedionato-*O,O′*]boron-containing dyes, such as in **9**, results in a batochromic shift of the absorption in comparison to the parent dye without the phenyl groups. Compound **14** can be regarded as a close analog of **9** in which the phenyl group and the propanedionatoboron unit are additionally connected by a lactone function to form a planar heterocyclic system. This feature is responsible for a batochromic shift of 19 nm in the spectrum of **14** relative to **9** with a concomitant increase in the absorption intensity ($\Delta\varepsilon = 17\,000$ M^{-1} cm^{-1}).

Finally, we wish to comment on the chemical stability of the dyes. Thus, all difluoroboron derivatives were found to be remarkably stable when stored in the solid state in the presence of air or in solution. For example, no any changes were observed for solid samples of **14** and **19** stored under normal laboratory conditions for several months, and for their solutions in water or aqueous mineral acids heated under reflux for 1 h. On the other hand, the phenylenedioxaboryl derivative **21** is much less stable. In aqueous solution at pH 7 under reflux conditions the decomposition is complete after a few minutes.

3. Note on the nomenclature

The boron coordination compounds presented in this report are highly conjugated dyes for which an unambiguous IUPAC nomenclature has not been developed [9]. Therefore, the full names proposed below are each for a single resonance structure selected in such a way that it provides a well-defined backbone of the molecule with clearly defined substituents according to the existing IUPAC recommendations [9]. In particular, the bis-boron dyes **14** and **21** are named as substituted derivatives of anionic 1,3,2(4*H*)-dioxaboratabenzo[*c*]coumarin (Rule D-7.6). This heterocyclic system is derived from benzo[*c*]coumarin (Rule B-3) by using replacement nomenclature (Rule B-4).

4. Experimental

The ^{1}H NMR spectra (200 MHz) were recorded on a Bruker WP-200-SY spectrometer in DMSO-d_6 or CDCl$_3$ with TMS as an internal reference. The ^{11}B NMR spectra 250 MHz were recorded on a Bruker WM-250 instrument in DMSO-d_6 with boron trifluoride etherate as an internal reference. The electronic absorption spectra were taken in CHCl$_3$ on a Specord UV–vis spectrophotometer. The mass spectra were recorded on a MAT-112 spectrometer operating at 80 eV. Mp's (Pyrex capillary) are not corrected. Boron coordination compounds **10–13** were obtained by the reaction of the corresponding acylhydroxycoumarine with boron trifluoride etherate, as described previously [5].

*4.1. Dyes **14, 19, 21***

A solution of a boron chelate **10**, **11** or **13** (2 mmol) in acetic anhydride (5 mL) was treated with triethyl orthoformate (0.15 g, 1 mmol) and triethylamine (0.28 g, 2 mmol). The mixture was heated to 60 °C for 30 min and then cooled and allowed to stand for 4 h. The resultant precipitate was filtered, washed with hexane, and crystallized from glacial acetic acid.

*4.1.1. Triethylammonium 2,2-difluoro-4-[($O^{4''}$-B)-4′-[(difluoroboryl)oxy]-4′-(4″-oxo-3″,4″-dihydrocoumarin-3″-ylidene)-2′-buten-1′-ylidene]dioxaboratabenzo[c]coumarin (**14**)*

Yield 65%; mp 285–286 °C; ^{1}H NMR (DMSO-d_6): δ 1.14 (t, 9H, 3CH$_3$–), 3.15 (q, 6H, 3-CH$_2$–), 7.50 (m, 6H, 2H^c, 2H^d, 2H^e), 7.81 (t, 2H, 2H^b), 8.05 (d, 2H, 2H^a), 8.87 (t, 1H, H^f); ^{11}B NMR (DMSO-d_6) δ 0.48; VIS (CHCl$_3$): λ_{max} 581 nm (ε 145 000). Anal. calcd. for $C_{29}H_{27}B_2F_4NO_8$: C, 58.62; H, 4.42; N, 2.28. Found: C, 58.57; H, 4.46; N, 2.24.

*4.1.2. Triethylammonium 3,3-difluoro-7-methyl-1-[($O^{7''}$-B)-4′-[(difluoroboryl)oxy]-4′-(4″-methyl-7″-oxo-7″,8″-dihydrocoumarin-8″-ylidene)-2′-buten-1′ylidene]-2,4,3(1H)-dioxaboratabenzo[h]-coumarin (**19**)*

Yield 46%; mp 310–311 °C; ^{1}H NMR (DMSO-d_6) : δ 1.15 (t, 9H, 3CH$_3$–), 2.21 (s, 6H, 2CH$_3^c$–), 3.00 (q, 6H, 3-CH$_2$–), 6.29 (s, 2H, 2H^d), 6.97 (d, 2H, J = 9 Hz, 2H^b), 7.43 (d, 2H, 2H^e), 7.92 (2H, ä, J = 9 Hz, 2H^a), 9.05 (t, 1H, H^f); VIS (CHCl$_3$): λ_{max} 567 nm 130 000 (ε). Anal. calcd. for $C_{31}H_{31}B_2F_4NO_8$: C, 57.89; H, 4.86; N, 2.18. Found: C, 57.92; H, 4.80; N, 2.15.

*4.1.3. Triethylammonium 2,2-(ortho-phenylenedioxy-4-[($O^{4''}$-B)-4′-(4″-oxo-3″,4″-dihydrocoumarin-3″-ylidene)-4′-[(ortho-phenylenedioxyboryl)oxy]-2′-buten-1′-ylidene]-1,3,2(4H)-dioxaboratabenzo[c]coumarin (**21**)*

Yield 42%; mp 318–319 °C; ^{1}H NMR (DMSO-d_6): δ 1.14 (t, 9H, 3CH$_3$–), 3.15 (q, 6H, 3-CH$_2$–), 6.60 (m, 8H, 4H^g, 4H^h), 7.40 (m, 6H, 2H^c, 2H^d, 2H^e), 7.77 (t, 2H, 2H^b), 7.95 (d, 2H, 2H^a), 8.67 (t, 1H, H^f); VIS (CHCl$_3$): λ_{max} 596 nm 96 000 (ε). Anal. calcd. for $C_{42}H_{39}B_2NO_{12}$: C, 65.40; H, 5.10; N, 1.82. Found: C, 65.38; H, 5.14; N, 1.83.

*4.1.4. (O^1-B)-1-[4′-[(Difluoroboryl)oxy]-coumarin-3′-yl]-3-(dimethylamino)prop-2-en-1-one (**18**)*

A solution of **10** (0.5 g, 2 mmol) in acetic anhydride (5 ml) was treated dropwise with *N,N*-dimethylformamide (0.15 ml, 2 mmol). The mixture was heated to 90 °C for 30 min, then cooled and treated dropwise with ethanol (2.5 ml, caution: exothermic). After cooling the resultant light-yellow precipitate was filtered off and crystallized from ethyl acetate. Yield 0.46 g (75%); mp 298–300 °C; ^{1}H NMR (CDCl$_3$): δ 3.25, 3.43 (s, s, 3H, 3H, H^g, H^h), 7.03 (d, 1H, J = 15.8 Hz, H^f), 7.30 (m, 2H, H^c, H^d), 7.68 (t, 1H, H^b), 8.14 (d, 1H, H^a), 8.48 (d, 1H, J = 15.8 Hz, H^e); vis (CHCl$_3$): λ_{max} 392 nm 36 700 (ε). Anal. calcd. for $C_{14}H_{12}BF_2NO_4$: C, 54.76; H, 3.94; N, 4.56. Found: C, 54.69; H, 3.95; N, 4.50.

*4.2. Dyes **15** and **20***

A solution of **10** or **12** (2.5 mmol) in acetic anhydride (6 ml) was treated with a solution of Fischer's aldehyde in acetic anhydride (3 ml). The mixture was heated to 90 °C for 30 min, cooled and allowed to stand for 24 h. The resultant precipitate was filtered off, washed with glacial acetic acid, and dried under a reduced pressure.

*4.2.1. 2-[($O^{4''}$-B)-4′[(difluoroboryl)oxy]-4′-(4″-oxo-3″,4″-dihydrocoumarin-3″-ylidene)-2′-buten-1′-ylidene]-1,3,3-trimethylindoline (**15**)*

Yield 77%; mp 328–330 °C; ^{1}H NMR (CDCl$_3$): δ 1.76 (s, 6H, 2CH$_3^l$–), 3.86 (s, 3H, CH$_3^m$–), 6.62 (d, 1H, H^g), 7.33–7.50 (m, 6H, H^c, H^e, H^h, H^i, H^j, H^k), 7.66 (d, 1H, H^d), 7.75 (t, 1H, H^b), 8.08 (d, 1H, H^a), 8.84 (t, 1H, H^f); vis (CHCl$_3$): λ_{max} 569 nm 98 200 (ε). Anal. calcd. for $C_{24}H_{20}BF_2NO_4$: C, 66.23; H, 4.63; N, 3.22. Found: C, 66.47; H, 4.61; N, 3.18.

*4.2.2. 2-[($O^{7''}$-B)-4′[(difluoroboryl)oxy]-3′-methyl-4′-(4″-methyl-7″-oxo-7″,8″-dihydrocoumarin-8″-ylidene)-2′-buten-1′-ylidene]-1,3,3-trimethylindoline (**20**)*

Yield 67%; mp 215–216 °C; ^{1}H NMR (CDCl$_3$): δ 2.06 (s, 6H, 2CH$_3^l$–),2.20 (s, 3H, CH$_3^e$–), 2.47 (d, 3H, J = 1.2 Hz, CH$_3^c$–) 3.21 (s, 3H, CH$_3^m$–), 5.47 (d, 1H, J = 12.7 Hz, H^g), 6.23 (d, 1H, J = 1.2 Hz, H^d), 6.70 (d, 1H, H^k), 6.92 (t, 1H, H^i), 7.00 (d, 1H, H^h), 7.17 (t, 1H, H^j), 7.20 (d, 1H, J = 8.66 Hz, H^b), 7.35 (d, 1H, J = 12.7 Hz, H^f), 7.65 (d, 1H, J = 8.66 Hz, H^a); vis ($CHCl_3$): λ_{max} 431 nm 62 000 (ε). Anal. calcd. for $C_{26}H_{24}BF_2NO_4$: C, 67.41; H, 5.22; N, 3.02. Found: C, 67.38; H, 5.17; N, 3.09.

4.3. Dyes **16** and **17**

A solution of **18** (0.4 g, 1.3 mmol) in acetic anhydride (5 ml) was treated with a solution of 1,2- or 1,4-dimethylquinolinium iodide (0.37 g, 1.3 mmol) in acetic anhydride (5 ml) and triethylamine (0.3 ml). The mixture was heated to 90 °C for 30 min, and then cooled and allowed to stand for 24 h. The resultant precipitate of **16** or **17** was filtered off, washed with acetic acid, and dried under a reduced pressure.

*4.3.1. 2-[(O$^{4''}$-B)-4′[(difluoroboryl)oxy]-4′-(4″-oxo-3″,4″-dihydrocoumarin-3″-ylidene)-2′-buten-1′-ylidene]-1-methyl-1,2-dihydroquinoline (**16**)*

Yield 43%; mp > 350 °C (decomp); vis ($CHCl_3$): λ_{max} 596 nm 138 000 (ε). Anal. calcd. for $C_{23}H_{16}BF_2NO_4$: C, 65.90; H, 3.85; N, 3.34. Found: C, 65.84; H, 3.89; N, 3.29.

*4.3.2. 4-[(O$^{4''}$-B)-4′[(difluoroboryl)oxy]-4′-(4″-oxo-3″,4″-dihydrocoumarin-3″-ylidene)-2′-buten-1′-ylidene]-1-methyl-1,4-dihydroquinoline (**17**)*

Yield 56%; mp > 350 °C (decomp); vis ($CHCl_3$): λ_{max} 650 nm 121 000 (ε). Anal. calcd. for $C_{23}H_{16}BF_2NO_4$: C, 65.90; H, 3.85; N, 3.34. Found: C, 65.87; H, 3.91; N, 3.37.

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