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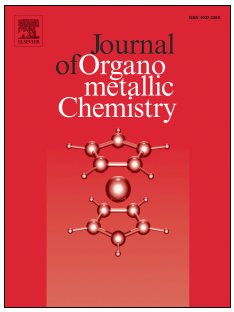

Synthesis, NMR, X-ray and UV/Vis characterization and preliminary luminescence study of some boron β-iminoenolates having 6-aminocoumarin moiety

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Boron β-iminoenolates having coumarin-6-yl moiety on the nitrogen atom and BF_2 or BPh_2 fragment fluoresce both in solid state and in frozen 2-methyltetrahydrofuran at 77 K. No fluorescence was observed in solution. The fluorescence starts to appear in aggregation state after admixing their THF solutions with water.

Synthesis, NMR, X-ray and UV/Vis characterization and preliminary luminescence study of some boron β-iminoenolates having 6-aminocoumarin moiety

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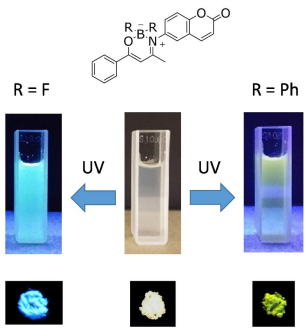

Abstract: Six coumarin-based polarized ethylenes (enaminoketones, enaminoester and enaminoamide) were prepared using the condensation of the parent β-dicarbonyl compounds with 6-aminocoumarin. Reaction of the polarized ethylenes with an appropriate source of trivalent boron gave corresponding boron β-iminoenolates having either BF_2 or BPh_2 fragment. The prepared iminoenolates were characterized by means of multinuclear magnetic resonance in solution, single-crystal X-ray diffraction and UV/Vis spectroscopy. A preliminary luminescence study of the iminoenolates as well as their parent enamines was done. The compounds exhibited fluorescence in a solid state as well as in a frozen 2-methyltetrahydrofuran at 77 K. Exploratory tests showed promising AIE/AIEE properties of the tested compounds. On the other hand, no fluorescence in a solution state (with one exception) was observed.

Keywords: Enaminone, boron, fluorescence, iminoenolate, NMR, X-ray.

1. Introduction

Luminescent organic molecules have received a great attention due to their applicability as materials for organic light-emitting diodes (OLEDs) [1, 2], organic field-effect transistors (OFETs) [3], fluorescent probes [4, 5] and many others. During the years a number of noteworthy luminophores

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have been introduced: e.g. coumarin and its derivatives (for recent review see e.g. ref. [6]), polyaromatics [7], porphyrins [8–11], xanthenes [12], boranils [13,14] etc. One way how to affect the luminescent properties of an organic molecule can be an incorporation of a BR_2 fragment into a suitable bidentate ligand [1, 15]. Recently some interesting fluorescent boron difluoride complexes of coumarins have been synthetized and characterized [16, 17]. BODIPY are another example of well-known BF_2-containing molecules having excellent fluorescence properties [4, 18–26]. Despite of their advantages, BODIPY also suffer from some drawbacks which limit them in use, especially weak luminescence in a solid state [15]. Searching for novel luminophores is then an important goal for chemists. Difluoroboron complexes of β-enaminones **I** (Fig. 1) which belong among the family of β-iminoenolate boron complexes [27] have recently attracted attention as a promising class of fluorophores and number of them have been synthetized and characterized [28–38]. Xia et al. [32] described excellent solution-state fluorescence for some heterocyclic β-iminoenolates. Shankarling et al. [38] described synthesis, spectral and electrochemical characterization of some boron difluoride complexes of benzoindoline-based β-enaminones. These compounds exhibit fluorescence both in a solution and in a solid state, which is not too usual. Generally compounds **I** possess a weak fluorescence in solution, but strong in solid state [29, 33] which is typical for substances having AIE or AIEE (aggregation-induced emission/aggregation-induced emission enhancement) properties [33]. Substances with these properties can have a range of potential applications e.g. as OLED, sensors or agents for photodynamic therapy [39]. To the best of our knowledge, the fluorescence properties of diarylboron chelates of β-enaminones **I** are less examined, in comparison with their difluoro analogues. Balaban et al. [40] described synthesis and spectral characterization of some dialkyl and diphenyl boron chelates of enaminoketones. Ramos-Ortíz [41] prepared and characterized some enaminone-based boronates with NLO properties. Catechol-based enaminone complexes of boron have been prepared and characterized by Atwood et al. [42] Kunick et al. [31] described synthesis and structure of some boron complexes of 4-anilinomethylene-1-benzazepine-2,5-diones. During the past several years we have published synthesis, NMR and X-ray characterization, basic fluorescence and DSC study and some interesting chemical behaviour for number of 2,2-diphenyl-1,3,2-oxazaborines derived from enaminones and related compounds [28, 43–45].

Inspired by the above-mentioned, we decided to combine the enaminone-based oxazaborines (both BF_2 and BPh_2) with another important fluorophore: coumarin. The resulting compounds could be potential fluorophores having AIE or AIEE properties. In the present work we describe the synthesis, NMR and X-ray characterization and preliminary fluorescence study of some novel coumarin-based oxazaborines with general formula **II** (Fig. 1).

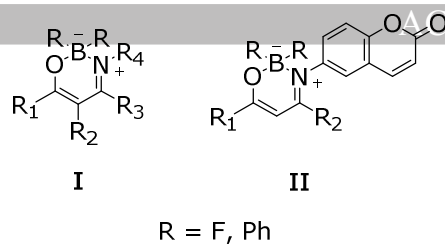


Fig. 1. General formula of boron iminoenolates (left) and subjects studied here (right).

2. Materials and methods

2.1. General

NMR Spectra were measured using NMR spectrometers Bruker AVANCE III operating at 400.13 MHz (^{1}H), 376.50 MHz (^{19}F), 127.38 MHz (^{11}B) and 100.12 MHz (^{13}C) and Bruker Ascend™ operating at 500.13 MHz (^{1}H), 470.66 MHz (^{19}F), 160.48 (^{11}B) and 125.12 MHz (^{13}C). Proton spectra in $CDCl_3$ were calibrated on an internal TMS (δ = 0.00 ppm) and in DMSO-d6 on the middle signal of the solvent multiplet (δ = 2.50 ppm). Carbon spectra were measured with broadband proton decoupling in an ordinary way or using APT pulse sequence. Calibration of the carbon spectra was done on the middle of the solvent multiplet (δ = 77.23 ppm in $CDCl_3$ and 39.51 in DMSO-d6). Fluorine-19 NMR spectra were measured without proton decoupling using α,α,α-trifluorotoluene as the secondary external standard (δ = -63.9 ppm against $CFCl_3$ as the primary standard) [46]. Boron-11 NMR were measured in 5 mm quartz NMR tubes (Norell) using $B(OMe)_3$ as an external standard (δ = 18.1 ppm) [47]. All the pulse sequences were taken from the Bruker pulse sequence library. Elemental analyses were performed on a Flash EA 2000 CHNS automatic analyser (Thermo Fisher Scientific). HRMS were measured on a MALDI LTQ Orbitrap XL (Thermo Fisher Scientific) with 2,5-dihydroxybenzoic acid (DHB) as the matrix. Melting points were measured on a Kofler hot-stage microscope Boetius PHMK 80/2644 and were not corrected.

The absorption spectra were measured on a UV/Vis Perkin-Elmer Lambda 35 spectrophotometer at room temperature. The emission spectra were measured on a Perkin-Elmer LS55 Spectrofluorimeter equipped with a commercial low temperature accessory and a special commercial cuvette. The fluorescence spectra in solid phase were recorded from the surface of the pressed powder in the special cuvette. The spectra were corrected for the characteristics of the emission monochromator and for the photomultiplier response and by excitation at the wavelengths of the absorption maxima.

The X-ray data for colorless crystals of **6b** and light yellow crystals of **7a** were obtained at 150 K using an Oxford Cryostream low-temperature device on a Nonius Kappa CCD diffractometer with Mo K_α radiation (λ = 0.71073 Å), a graphite monochromator, and the ϕ and χ scan mode. Data reductions were performed with DENZO-SMN [48]. The absorption was corrected by integration methods [49]. Structures were solved by direct methods (Sir92) [50] and refined by full matrix least-square based on

F^2 (SHELXL97) [51]. Hydrogen atoms were mostly localized on a Fourier difference electron density map, however, to ensure uniformity of treatment of crystal, all hydrogen atoms were recalculated into idealized positions (riding model) and assigned temperature factors $H_{iso}(H) = 1.2\ U_{eq}$ (pivot atom) or of $1.5U_{eq}$ (methyl). Hydrogen atoms in methyl moieties and in aromatic rings were placed with C–H distances of 0.96 and 0.93 Å resp.

$R_{int} = \sum | F_o^2 - F_{o,mean}^2 | / \sum F_o^2$, GOF = $[\sum(w(F_o^2 - F_c^2)^2)/(N_{diffrs} - N_{params})]^{½}$ for all data, $R(F) = \sum | \, | F_o | - | F_c | \, | / \sum | F_o |$ for observed data, $wR(F^2) = [\sum(w(F_o^2 - F_c^2)^2)/(\sum w(F_o^2)^2)]^{½}$ for all data.

2.2. Material

All the solvents and reagents were used commercial without further treatments. The procedures for synthesis of 6-nitrocoumarin (**2**) and 6-aminocoumarin (**3**) and their characterization data are in Supporting Information. β-Dicarbonyl compounds **4** were used commercial without further treatments. Diphenylborinic acid was prepared according to the literature procedure (see Supporting Information).

*2.2.1. General procedure for the synthesis of **5a–c***

The mixture of 6-aminocoumarin (**3**) (0.6 g, 3.7 mmol), β-diketone **4** (3.7 mmol) and *p*-toluenesulfonic acid (6 mg, 0.03 mmol) in toluene (20 mL) was refluxed for 10–48 h. Water formed during the reaction was removed in the form of azeotrope until only clear toluene distilled. The volatile components were then evaporated under reduced pressure. Products **5a–c** (white or yellow solids) were purified either by recrystallization or firstly isolated by column chromatography and then recrystallized. The following compounds were prepared in this manner:

*6-{[(2Z)-4-Oxopent-2-en-2-yl]amino}-2H-chromen-2-one (**5a**).* From pentane-1,3-dione (**4a**). Reflux for 10 h; recrystallization from methanol. Yield: 0.36 g (40 %) of pale yellow solid. M.p.: 132–133 °C. ^{1}H NMR ($CDCl_3$/400 MHz): δ_H 2.01 (3H, s), 2.12 (3H, s), 5.25 (1H, s), 6.47 (1H, d, J = 9.5 Hz), 7.25–7.33 (3H, m), 7.72 (1H, d, J = 9.5 Hz), 12.49 (1H, br s) ppm; ^{13}C NMR ($CDCl_3$/101 MHz): δ_C 19.8, 29.3, 98.3, 117.5, 117.6, 119.2, 123.3, 128.6, 135.3, 142.9, 151.6, 159.8, 160.4, 196.8. Anal. Calc. for $C_{19}H_{15}NO_3$: C, 69.12; H, 5.39; N, 5.76. Found: C, 68.91; H, 5.34; N, 5.66.

*6-{[(2Z)-4-Oxo-4-phenylbut-2-en-2-yl]amino}-2H-chromen-2-one (**5b**).* From 1-phenylbutane-1,3-dione (**4b**). Reflux for 20 h; can be recrystallized from ethanol. Yield: 5.23 g (75 %) of light yellow solid. M.p.: 157–158.5 °C. ^{1}H NMR ($CDCl_3$/400 MHz): δ_H 2.15 (3H, s), 5.95 (1H, s), 6.48 (1H, d, J = 9.6 Hz), 7.30 (1H, m), 7.34–7.36 (2H, m), 7.43–7.51 (3H, m), 7.68 (1H, d, J = 9.6 Hz), 7.91–7.93 (2H, m), 13.13 (1H, br s) ppm; ^{13}C NMR ($CDCl_3$ /100 MHz,): δ_C 20.6, 95.0, 117.9, 118.0, 119.5, 123.6, 127.3, 128.6, 128.8, 131.4, 135.4, 139.8, 142.9, 152.0, 160.5, 161.9, 189.4 ppm. Anal. Calc. for $C_{19}H_{15}NO_3$: C, 74.74; H, 4.95; N, 4.59. Found: C, 74.56; H, 4.97; N, 4.80.

*6-{[(3Z)-5-Oxohept-3-en-3-yl]amino}-2H-chromen-2-one (**5c**).* From heptane-3,5-dione (**4c**). Reflux for 48 h; flash chromatography (silica gel, $CHCl_3$/EtOAc, 3:2); recrystallization from methanol. Yield: 0.88 g (52 %) of light yellow solid. M.p.: 73.5–74.5 °C. ^{1}H NMR ($CDCl_3$/400 MHz): δ_H 1.08 (3H, t, *J* = 7.5 Hz), 1.15 (3H, t, *J* = 7.5 Hz), 2.32 (2H, q, *J* = 7.5 Hz), 2.41 (2H, q, *J* = 7.5 Hz), 5.28 (1H, s), 6.47 (1H, d, *J* = 9.5 Hz), 7.28 – 7.34 (3H, m), 7.68 (1H, d, *J* = 9.5 Hz), 12.50 (1H, br s) ppm; ^{13}C NMR ($CDCl_3$/100 MHz,): δ_C 9.9, 12.5, 25.2, 35.5, 95.2, 117.6, 117.8, 119.3, 123.9, 129.2, 135.4, 143.0, 151.8, 160.5, 165.5, 201.0 ppm. Anal. Calc. for $C_{16}H_{17}NO_3$: C, 70.83; H, 6.32; N, 5.16. Found: C, 70.61; H, 6.11; N, 5.09.

*2.2.2. Synthesis of enaminoamide **5d** and enaminoester **5e***

(**Method A**) A 50 mL flask was charged with 6-aminocoumarin (**3**) (1.1 g, 6.83 mmol), ethyl acetoacetate (**4d**) (10.5 g, 80.7 mmol) and catalytic amount of acetic acid (0.03 mL). The reaction mixture was heated gently in order to dissolve 6-aminocoumarin (**3**). The clear solution was then stirred for 3.5 days at room temperature. Precipitated product **5e** was filtered off and washed with ethanol.

(**Method B**) A 250 mL flask fitted with a condenser was charged with 6-aminocoumarin (**3**) (3.68 g, 0.02 mol), ethyl acetoacetate (**4d**) (3 g, 0.02 mol), acetic acid (0.08 mL) and toluene (150 mL). The reaction mixture was heated to boiling for 14 h. The water formed during the reaction was distilled off as water-toluene azeotrope. After the reaction was finished, enaminoamide **5d** precipitated upon cooling and was removed by suction. Enaminoester **5e** was isolated from the filtrate by evaporation and recrystallization of the residue from ethanol.

*(2Z)-N-(2-Oxo-2H-chromen-6-yl)-3-[(2-oxo-2H-chromen-6-yl)amino]but-2-enamide (**5d**).* (**Method B**) The precipitate was washed with DCM and hot ethanol. Yield: 2.78 g (36 %) of yellow-brown solid; m.p.: 238–239 °C. ^{1}H NMR (DMSO-d_6/400 MHz): δ_H 2.07 (3H, s), 4.90 (1H, s), 6.46 (1H, d, *J* = 9.5 Hz), 6.53 (1H, d, *J* = 9.5 Hz), 7.34 (1H, d, *J* = 9.0 Hz), 7.36–7.38 (1H, m), 7.41–7.44 (1H, m), 7.55 (1H, d, *J* = 2.8 Hz), 7.64 (1H, dd, *J* = 9.0 Hz, 2.5 Hz), 8.02–8.06 (2H, m), 8.10 (1H, d, *J* = 2.5 Hz), 9.79 (1H, br s), 11.23 (1H, br s) ppm; ^{13}C NMR (DMSO-d_6/100 MHz,): δ_C 20.1, 90.1, 116.4, 116.5, 116.8, 117.0, 117.05, 118.7, 119.2, 121.8, 123.0, 127.2, 135.9, 136.4, 143.9, 144.5, 148.7, 150.1, 155.8, 159.9, 160.1, 168.3 ppm. Anal. Calc. for $C_{22}H_{16}N_2O_5$: C, 68.04; H, 4.15; N, 7.21. Found: C, 67.92; H, 4.23; N, 7.38.

*Ethyl (2Z)-3-[(2-oxo-2H-chromen-6-yl)amino]but-2-enoate (**5e**).* Pale yellow solid. (**Method A**) Yield: 0.72 g (39 %); m.p.: 117–118 °C. (**Method B**) Yield: 0.86 g (16 %); mp 112.5–113.5 °C. Spectral data from both the methods were consistent. ^{1}H NMR ($CDCl_3$/400 MHz): δ_H 1.30 (3H, t, *J* = 7.0 Hz), 1.99 (3H, s), 4.16 (2H, q, *J* = 7.0 Hz), 4.75 (1H, s), 6.46 (1H, d, *J* = 9.5 Hz), 7.20 (1H, d, *J* = 2.3 Hz), 7.25 – 7.32 (2H, m), 7.66 (1H, d, *J* = 9.5 Hz), 10.40 (1H, br s) ppm; ^{13}C NMR ($CDCl_3$/100 MHz,): δ_C 14.7, 20.4, 59.2, 87.3, 117.7, 117.8, 119.4, 123.2, 128.7, 136.1, 143.0, 151.5,

158.5, 160.7, 170.6 ppm. Anal. Calc. for $C_{15}H_{15}NO_4$: C, 65.92; H, 5.53; N, 5.13. Found: C, 65.68; H, 5.46; N, 4.91.

*2.2.3. General procedure for the synthesis of 2,2-difluoro-1,3,2λ⁴-oxazaborines **6***

The procedure was adopted from ref. [52] The enaminone **5** (1.5 mmol) was dissolved or suspended in dry DCM (10 mL) and triethylamine (3 mL, 3 mmol) was added afterwards. The reaction mixture was stirred at room temperature for 20 min. Consequently, $BF_3 \cdot Et_2O$ (0.56 mL, 4.5 mmol) was added, the mixture was refluxed for 3 h and then stirred at laboratory temperature for another 12–96 h. The crude product was obtained by evaporation of the solvent or by filtration of the precipitate. The following compounds were prepared using this procedure:

*2,2-Difluoro-4,6-dimethyl-3-(2-oxo-2H-chromen-6-yl)-1,3,2λ⁴-oxazaborine (**6a**).* Prepared from **5a**, reaction time 16 h, recrystallization from ethanol. Yield: 0.28 g (65 %) of yellow solid, m.p.: 217–219 °C. ^{1}H NMR ($CDCl_3$/400 MHz): δ_H 1.99 (3H, s), 2.23 (3H, s), 5.60 (1H, s), 6.50 (1H, d, *J* = 9.5 Hz), 7.34–7.37 (1H, m), 7.40–7.42 (2H, m), 7.70 (1H, d, *J* = 9.5 Hz) ppm; ^{13}C NMR ($CDCl_3$/100 MHz,): δ_C 21.6, 23.3, 99.2, 118.0, 118.2, 119.6, 125.5, 130.0, 136.0, 142.9, 153.6, 160.3, 172.0, 178.5 ppm. HRMS (MALDI, *m/z*) Calcd. for $C_{14}H_{13}BF_2NO_3$ $[M+H]^+$ 292.09511; Found 292.09531; Calcd. for $C_{14}H_{12}BFNO_3$ $[M–F]^+$ 272.08888; Found 272.08907; Calcd. for $C_{14}H_{12}BF_2NNaO_3$ $[M+Na]^+$ 314.07705; Found 314.07735; Calcd. for $C_{14}H_{12}BF_2KNO_3$ $[M+K]^+$ 330.05099; Found 330.05134.

*2,2-Difluoro-4-methyl-6-phenyl-3-(2-oxo-2H-chromen-6-yl)-1,3,2λ⁴-oxazaborine (**6b**).* Prepared from **5b**, reaction time 24 h, purification by extraction with boiling ethanol. Yield: 1.61 g (83 %) of light yellow solid, m.p.: 214–216.5 °C. ^{1}H NMR ($CDCl_3$/400 MHz): δ_H 2.13 (3H, s), 6.27 (1H, s), 6.50 (1H, d, *J* = 9.5 Hz), 7.41–7.42 (2H, m), 7.47–7.51 (3H, m), 7.55–7.60 (1H, m), 7.72 (1H, d, *J* = 9.8 Hz), 7.99–8.01 (2H, m) ppm; ^{13}C NMR ($CDCl_3$/100 MHz,): δ_C 22.2, 95.9, 118.0, 118.2, 119.6, 125.5, 127.8, 129.0, 129.9, 133.1, 136.2, 142.9, 153.6, 160.3, 172.0, 172.3 ppm. Anal. Calc. for $C_{19}H_{14}BF_2NO_3$: C, 64.62; H, 4.00; N, 3.97 %. Found: C, 64.35; H, 3.94; N, 3.85.

Crystallographic data for **6b**: $C_{19}H_{14}BF_2NO_3$, M = 353.12, triclinic, *P* -1, *a* = 6.6760(2), *b* = 6.9680(3), *c* = 17.9561(8) Å, α = 88.422(3), β = 79.445(3), γ = 76.136(3) °, Z = 2, V = 797.12(6) Å^3, D_c = 1.471 g.cm^{-3}, μ = 0.114 mm^{-1}, T_{min}/T_{max} = 0.980/0.991; -7 ≤ h ≤ 8, -9 ≤ k ≤ 8, -23 ≤ l ≤ 22; 10245 reflections measured (θ_{max} = 27.30 °), 3515 independent (R_{int} = 0.0415), 2685 with $I > 2\sigma(I)$, 235 parameters, *S* = 1.112, *R1*(obs. data) = 0.0498, *wR2*(all data) = 0.1040; max., min. residual electron density = 0.311, -0.276 eÅ^{-3}.

*4,6-Diethyl-2,2-difluoro-3-(2-oxo-2H-chromen-6-yl)-1,3,2λ⁴-oxazaborine (**6c**).* Prepared from **5c**, reaction time 12 h, purification by flash chromatography (silica gel, DCM) and subsequent recrystallization from ethanol. Yield: 0.51 g (85 %) of white solid, m.p.: 133–135 °C. ^{1}H NMR ($CDCl_3$/400 MHz): δ_H 1.12 (3H, t, *J* = 7.6 Hz), 1.26 (3H, t, *J* = 7.6 Hz), 2.24 (2H, q, *J* = 7.6 Hz), 2.49

(2H, q, *J* = 7.6 Hz), 5.62 (1H, s), 6.49 (1H, d, *J* = 9.6 Hz), 7.34–7.42 (3H, m), 7.70 (1H, d, *J* = 9.6 Hz) ppm. ^{13}C NMR ($CDCl_3$/100 MHz,): δ_C 10.6, 12.1, 27.3, 30.1, 95.5, 118.0, 118.1, 119.5, 125.7, 130.2, 135.7, 142.9, 153.6, 160.3, 176.8, 183.1 ppm. HRMS (MALDI, *m/z*) Calcd. for $C_{16}H_{17}BF_2NO_3$ $[M+H]^+$ 320.12641; Found 320.12669; Calcd. for $C_{16}H_{16}BFNO_3$ $[M–F]^+$ 300.12018; Found 300.12040; Calcd. for $C_{16}H_{16}BF_2NNaO_3$ $[M+Na]^+$ 342.10835; Found 342.10865; Calcd. for $C_{16}H_{16}BF_2KNO_3$ $[M+K]^+$ 358.08229; Found 358.08261.

*2,2-Difluoro-4-methyl-3-(2-oxo-2H-chromen-6-yl)-6-[(2-oxo-2H-chromen-6-yl)amino]-1,3,2 λ^4-oxazaborine (**6d**).* Prepared from **5d**, reaction time 96 h, precipitated product washed with ether. Yield: 0.95 g (85 %) of yellow solid, m.p.: 253.5–255 °C. ^{1}H NMR (DMSO-d_6/400 MHz): δ_H 1.89 (3H, s), 5.19 (1H, br s), 6.52–6.55 (2H, m), 7.40–7.44 (2H, m), 7.48 (1H, d, *J* = 9.0 Hz), 7.58–7.62 (2H, m), 7.68 (1H, d, *J* = 2.5 Hz), 8.08–8.12 (2H, m), 10.78 (1H, br s) ppm; ^{13}C NMR (DMSO-d_6/125 MHz,): δ_C 21.1, 82.2 (br), 116.6, 116.8, 117.0, 117.4, 119.0, 119.2, 120.2 (br), 125.4 (br), 126.8, 131.2, 133.0, 136.8, 143.9, 144.0, 150.6 (br), 152.2, 159.9, 163.8 (br), 167.3 (br) ppm. HRMS (MALDI, *m/z*) Calcd. for $C_{22}H_{15}BFN_2O_5$ $[M–F]^+$ 417.10526; Found 417.10564.

*2.2.4. General procedure for the synthesis of 2,2-diphenyl-1,3,2λ^4-oxazaborines **7***

Method A: A flask fitted with a calcium chloride drying tube was charged with enaminone **5a–c** (2 mmol) in anhydrous DCM (20 mL). Afterwards triphenylborane (0.61 g, 2.5 mmol) was added gradually under stream of argon. The reaction mixture was stirred for 2–7 days at laboratory temperature, then the solvent was removed in vacuo. The crude product was isolated by column chromatography of the residue followed by further purification.

Method B: the procedure is the same as in the Method A, but diphenylborinic acid (0.91 g, 5 mmol) was added instead of triphenylborane.

The following compounds were prepared using the above-mentioned methodologies:

*4,6-Dimethyl-3-(2-oxo-2H-chromen-6-yl)-2,2-diphenyl-1,3,2 λ^4-oxazaborine (**7a**).* Prepared from **5a** using **Method A**, reaction time 7 days; column chromatography (silica gel, DCM); product precipitated upon extracting the residue from the chromatography with boiling ethanol. Yield: 0.58 g (69 %) of white solid, m.p.: 163.5–164.5 °C. ^{1}H NMR ($CDCl_3$/400 MHz): δ_H 1.98 (3H, s), 2.09 (3H, s), 5.45 (1H, s), 6.34 (1H, d, *J* = 9.5 Hz), 6.85 (1H, d, *J* = 2.3 Hz), 6.93 (1H, dd, *J* = 8.8 Hz, 2.5 Hz), 7.05 (1H, d, *J* = 8.5 Hz), 7.15 (6H, br s), 7.25–7.31 (4H, m), 7.40 (1H, d, *J* = 9.5 Hz) ppm; ^{13}C NMR ($CDCl_3$/100 MHz,): δ_C 22.3, 23.7, 100.3, 117.2, 117.4, 118.7, 125.9, 126.5, 127.0, 130.5, 133.6, 139.4, 142.9, 152.4, 160.5, 169.4, 179.7 ppm. Anal. Calc. for $C_{26}H_{22}BNO_3$: C, 76.68; H, 5.44; N, 3.44. Found: C, 76.52; H, 5.48; N, 3.72.

Crystallographic data for **7a**: $C_{26}H_{22}BNO_3$, M = 407.26, monoclinic, *P* 21/*c*, *a* = 12.1011(9), *b* = 11.6340(7), *c* = 15.8901(8) Å, β = 108.900(5) °, Z = 4, V = 2116.5(2) Å^3, D_c = 1.278 g.cm^{-3}, μ = 0.082

mm^{-1}, T_{min}/T_{max} = 0.981/0.989; -15 ≤ h ≤ 15, -13 ≤ k ≤ 15, -19 ≤ l ≤ 20; 23028 reflections measured (θ_{max} = 27.50 °), 4805 independent (R_{int} = 0.0553), 3315 with $I > 2\sigma(I)$, 280 parameters, S = 1.129, *R1*(obs. data) = 0.0620, *wR2*(all data) = 0.1237; max., min. residual electron density = 0.332, -0.345 eÅ^{-3}.

*4-Methyl-3-(2-oxo-2H-chromen-6-yl)-2,2,6-triphenyl-1,3,2λ^4-oxazaborine (**7b**).* Prepared from **5b** using **Method B**, reaction time 5 days; column chromatography (silica gel, DCM); DCM was added to the residue from the chromatography and the solution was extracted with saturated aqueous solution of $NaHCO_3$. Organic layer was dried over Na_2SO_4 and evaporated; the product precipitated from the residue upon extraction with boiling cyclohexane. Yield: 1.64 g (70 %) of yellow solid, m.p.: 118–119 °C. ^{1}H NMR ($CDCl_3$/400 MHz): δ_H 2.13 (3H, s), 6.16 (1H, s), 6.35 (1H, d, *J* = 9.6 Hz), 6.93 (1H, d, *J* = 2.5 Hz), 7.01 (1H, dd, *J* = 8.8 Hz, 2.5 Hz), 7.08 (1H, d, *J* = 8.8 Hz), 7.13–7.17 (6H, m), 7.34–7.44 (7H, m), 7.47–7.51 (1H, m), 7.92–7.94 (2H, m) ppm; ^{13}C NMR ($CDCl_3$/100 MHz,): δ_C 27.1, 97.3, 117.3, 117.5, 118.7, 125.8, 126.5, 127.0, 127.8, 128.8, 130.5, 132.3, 133.7, 134.3, 139.6, 142.9, 152.4, 160.5, 170.0, 172.9 ppm. Anal. Calc. for $C_{31}H_{24}BNO_3$: C, 79.33; H, 5.15; N, 2.98. Found: C, 79.61; H, 5.42; N, 2.72.

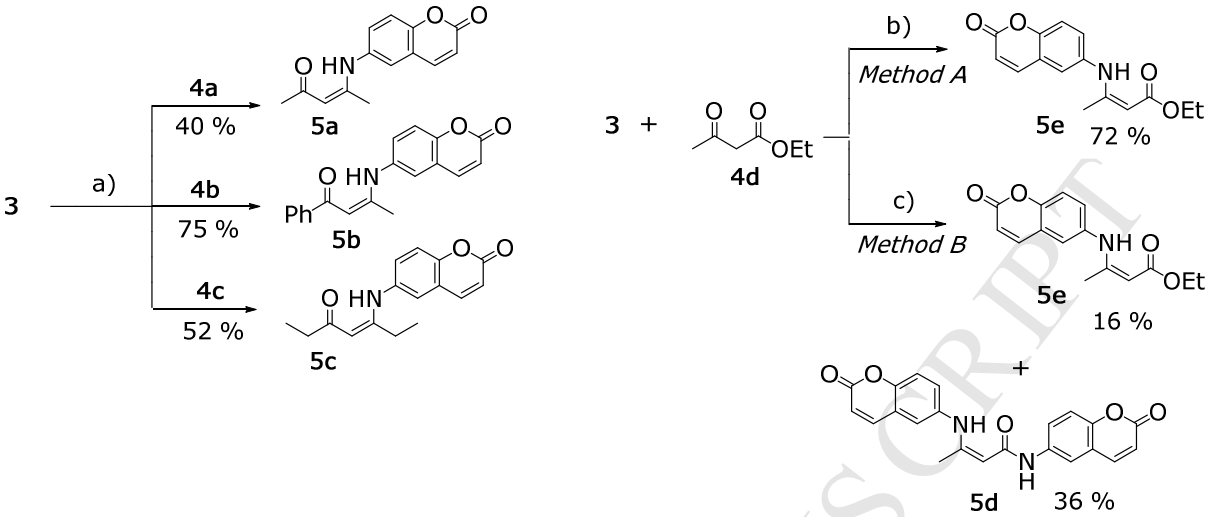
*4,6-Diethyl-3-(2-oxo-2H-chromen-6-yl)-2,2-diphenyl-1,3,2λ^4-oxazaborine (**7c**).* Prepared from **5c** using **Method A**, reaction time 6 days; column chromatography (silica gel, DCM); product precipitated after standing overnight with cyclohexane; recrystallization from methanol. Yield: 0.45 g (56 %) of white solid, m.p.: 134–134.5 °C. **Method B** gave 14% yield after 2 days using column chromatography (silica gel, DCM) and recrystallization from methanol. ^{1}H NMR ($CDCl_3$/400 MHz): δ_H 1.11 (3H, t, *J* = 7.5 Hz), 1.16 (3H, t, *J* = 7.5 Hz), 2.26 (2H, q, *J* = 7.6 Hz), 2.34 (2H, q, *J* = 7.5 Hz), 5.48 (1H, s), 6.34 (1H, d, *J* = 9.6 Hz), 6.86 (1H, d, *J* = 2.4 Hz), 6.93 (1H, dd, *J* = 8.8 Hz, 2.4 Hz), 7.03 (1H, d, *J* = 8.8 Hz), 7.11–7.18 (6H, m), 7.24–7.31 (4H, m), 7.41 (1H, d, *J* = 9.6 Hz) ppm; ^{13}C NMR ($CDCl_3$/100 MHz,): δ_C 10.7, 12.5, 28.0, 30.4, 96.7, 117.1, 117.4, 118.6, 126.0, 126.4, 127.0, 130.7, 133.6, 139.1, 142.9, 152.3, 160.5, 174.2, 184.1 ppm. Anal. Calc. for $C_{28}H_{26}BNO_3$: C, 77.25; H, 6.02; N, 3.22. Found: C, 76.97; H, 5.98; N, 3.10.

3. Results and discussion

3.1. Synthesis

Starting β-enaminones **5** were prepared employing the condensation of 6-aminocoumarin **3** (prepared from coumarin **1** via nitration and subsequent reduction of the formed 6-nitrocoumarin **2**) with appropriate β-dicarbonyl compounds **4a–d** according to the Scheme 1. Enaminoketones **5a–c** were prepared using the standard methodology under acid catalysis with azeotropic removal of the reaction water. The regioselective reaction in the case of benzoylacetone (synthesis of **5b**) can be ascribed by the well-known difference in the reactivity of acyl and benzoyl groups. Ethyl acetoacetate (**4d**) can react either on its ester or ketone carbonyl group to provide in principle three products: enaminoester, oxoamide and enaminoamide. Upon changing the reaction conditions we were able to affect the

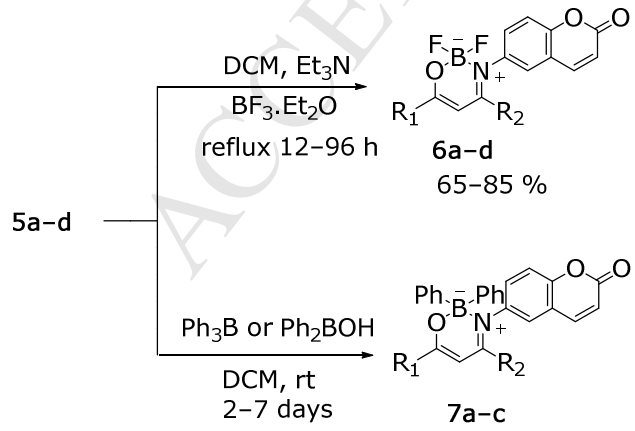
composition of the reaction mixture. When performing the reaction in large excess of **4d**, only the enaminoester **5e** was isolated (Method A). On the other hand, using the similar conditions as in the cases of the preparation of **5a–c** (Method B), the enaminoamide **5d** was the major product (Scheme 1).



Reaction conditions: a) toluene, PTSA, azeotropic removal of water; b) cat. AcOH, rt; c) AcOH, toluene, azeotropic removal of water.

Scheme 1. The synthesis of the starting enaminones.

The classic synthesis of boron β-iminoenolates is the reaction of β-enaminones with the appropriate compounds of trivalent boron. 2,2-Difluoro-1,3,2-oxazaborines **6a–d** were prepared by the reaction of enaminones **5a–c** and enaminoamide **5d** with boron trifluoride ethyl etherate in refluxing dichloromethane under basic conditions (Scheme 2). Similarly, their 2,2-diphenyl analogues **7a–c** were obtained upon treatment enaminones **5a–c** with triphenylborane or triphenylborinic acid at laboratory temperature (Scheme 2). Only a mixture of products was obtained in the reaction of enaminoester **5e** with both $BF_3 \cdot Et_2O$ and Ph_2BOH or Ph_3B.



6a: $R_1 = R_2$ =Me
6b: R_1 = Ph, R_2 = Me
6c: $R_1 = R_2$ = Et
6d: R_1 = NH-coumarin-6-yl, R_2 = Me

7a: $R_1 = R_2$ =Me
7b: R_1 = Ph, R_2 = Me
7c: $R_1 = R_2$ = Et

Scheme 2. The synthesis of target 1,3,2-oxazaborines **6** and **7**.

3.2. The absorption spectra

The absorption spectra of all the studied compounds in 1,4-dioxane (DO) are composed of one broad band with a maximum in the region 308–380 nm and either of another one with a maximum (**5d** and **6b**, **d**) or of a shoulder (**5**, **6a**, **c**) in the region 250–290 nm. The spectra of the compounds **7** possess another broad band at 271 nm. From the chemical structure of the studied compounds and their absorption spectra, it is evident that alkyl size (R_1, R_2) has practically no (compounds **6a**, **c** and **7a**, **c**) or only a small effect (compounds **5a**, **c**) on the position of the absorption maximum in dioxane. The replacement of the alkyl R_1 by the phenyl group (compounds **5b**, **6b**, **7b**) causes a considerable bathochromic shift (Fig. 2, Fig. 3 left, Table 1). The transition from compounds **5** to **6** results in a slight hypsochromic shift (1–12 nm). The substitution of the fluorine atoms by phenyl groups (**6**→**7**) results in a bathochromic shift of 31–36 nm (Fig. 2, right and Fig. 3, left). Compound **5e** exhibits a bathochromic shift of 14 nm compared to **5a** and a hypsochromic shift of 33 nm in comparison with **5b** (Table 1); a quite analogous relation exists between **6a**,**b** and **6d** (Fig. 2 right). The compounds **5d** and **6d** may consist from two, more or less conjugated, aminocoumarin chromophores (Fig. 3 right).

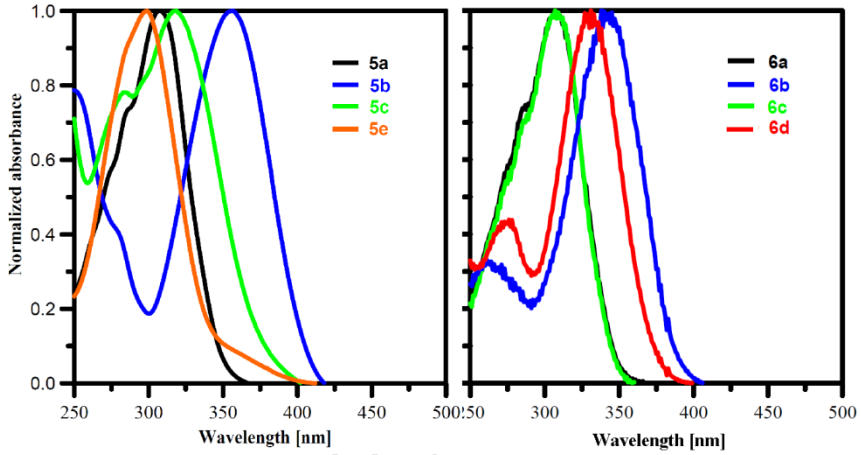


Fig. 2. The absorption spectra of **5a–c,e** (left) and **6a–d** (right) in 1,4-dioxane.

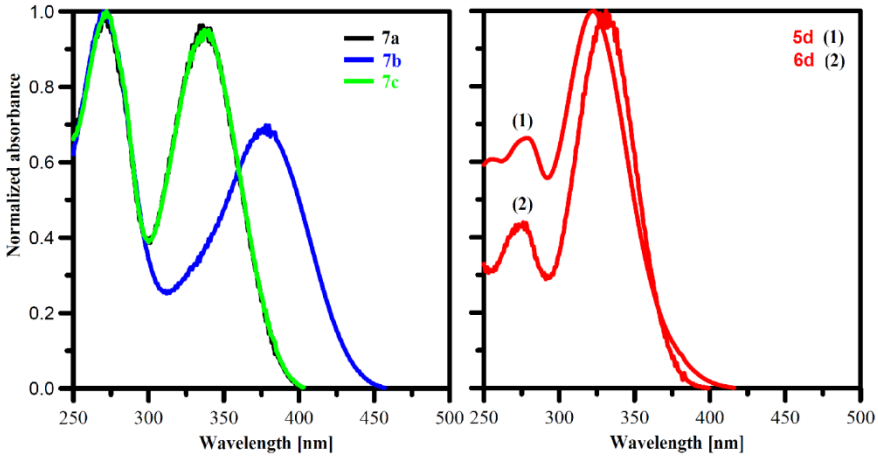


Fig. 3. The absorption spectra of **7a–c** (left) and **5d** and **6d** in 1,4-dioxane

Table 1

Optical properties of the prepared compounds

Comp.	$\lambda_{A(max)}$ [nm]			$\lambda_{F(max)}/\lambda_{Ph(max)}$ (77 K) [nm]	λ_F(powder) [nm]
	DO	ε [10^3 mol^{-1} dm^3 cm^{-1}]	2-MTHF	2-MTHF	
5a	308	25.24	308	433/462,500,537	446
5b	355	30.87	355	429	420,463,480
5c	317	21.47	319	435/489,514	435
5d	322	69.18	317	455/535	517
5e	298	38.53	299	441	-
6a	307	22.87	307	426/462,497	399
6b	343	22.86	343	450*	402
6c	308	26.74	307	428/463,498,542	427
6d	331	33.66	334	421/479,511	481*
7a	334/272	11.17/17.74	338	457	553
7b	377/272	15.34/33.24	377	502	527*
7c	339/277	10.87/14.89	338	450*	484*

* denotes a very weak emission

3.3. The luminescence spectra

With the exception of compound **5d** (λ_F = 470 nm in dioxane), the studied compounds do not fluoresce in a solution at room temperature. However, in 2-methyltetrahydrofuran (2-MTHF) at 77 K all the investigated compounds exhibit more or less strong fluorescence. Furthermore, a dual luminescence for some compounds of the series **5** and **6** was detected. The used spectrophotometer LS55 makes possible to separate a luminescence with a lifetime shorter than 10^{-6} s (i.e. fluorescence) from a luminescence with a lifetime longer than 10^{-3} s (i.e. phosphorescence). The broadband with the maximum in the region at 450 nm recorded in the fluorescence mode corresponds to the fluorescence from the first singlet ππ* state (for example Fig. 4~~, left and Fig. 5, left~~). By the recording in the phosphorescence mode, a bathochromaticlly shifted luminescence exhibiting a vibronic structure was detected (Fig. 4 ~~left~~ and Fig. 5 right). The phosphorescence spectra of some compounds **5** and **6**, excepting **6d**, show very similar phosphorescence spectra (Fig. 5, right). On the contrary the structure of **6d** consists of two coumarin units and, probably, therefore, its phosphorescence spectrum is bathochromically shifted. Very similar absorption and fluorescence band shapes, maxima and

character of phosphorescence spectra of compounds **5** and **6** give evidence that chromophoric system is formed by coumarin moiety.

The compounds of type **7** show only a broad fluorescence band in 2-MTHF at 77 K (Fig. 5, ~~right~~ left). The longest absorption band in this series in DO at room temperature, in comparison with the compounds **5** and **6**, is bathochromically shifted by about 30–36 nm. This could indicate a reordering of the singlet ππ* and triplet nπ* states; it means that for the series of the compounds **7,** the triplet nπ* has a higher ~~excitation~~ energy than the singlet ππ* and does not apply in the deactivation cascade; compared to compounds **6**, less probable intersystem crossing for compounds 7 caused by absence of fluorine atoms may be considered, too. All the studied compounds in a powder-state show more or less intense broadband luminescence (Figs. 6, 7) with a maximum in the region 400–480 nm (**5, 6**) and at 553 and 527 nm (**7a, b**). Significantly, the compounds **5a**, **6a**, and **7a** exhibit medium to strong fluorescence emission, while the compound **6d** exhibit the lowest fluorescence intensity of this series (Figs.6, 7). The compounds **5c**,**d**, and **6b,c** show a relatively high fluorescence, however the compounds **5b**, **6d**, **7b** show very weak fluorescence (Fig. 6, 7). The compound **5e** does not exhibit any fluorescence in a solid state.

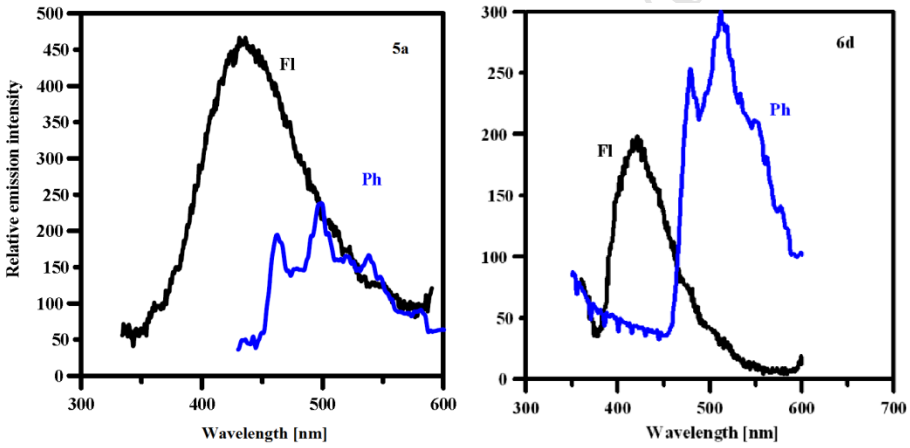


Fig. 4. The fluorescence and phosphorescence spectra of **5a** (left) and **6d** (right) in 2-MTHF at 77 K

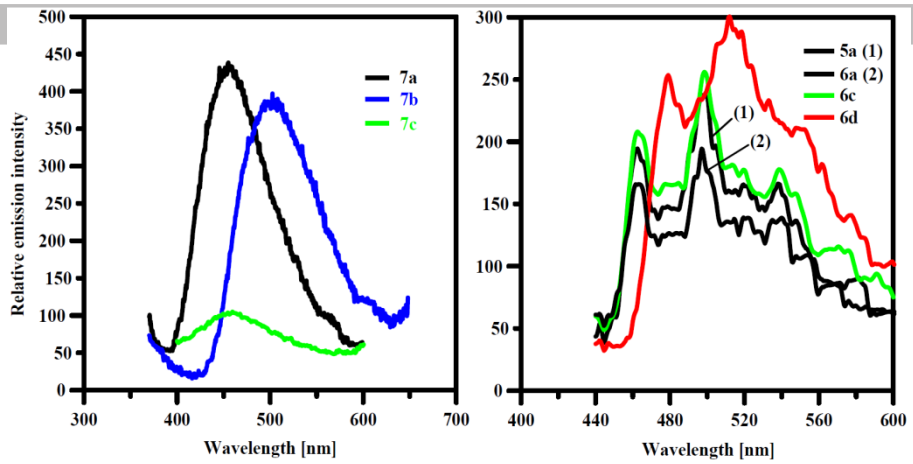


Fig. 5: The fluorescence spectra of **7a-c** (left) and phosphorescence spectra of **5a** and **6a, c, d** (right) in 2-MTHF at 77 K

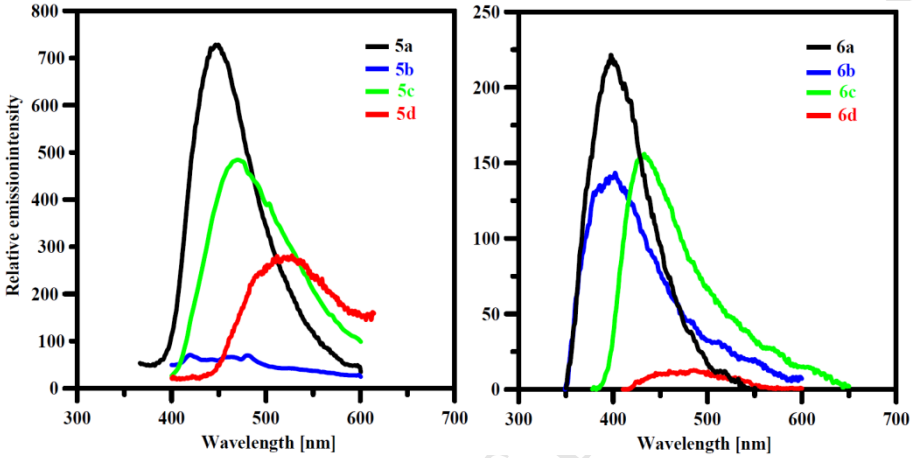


Fig. 6: The fluorescence spectra of **5a–d** (left) and **6a–d** (right) in solid state

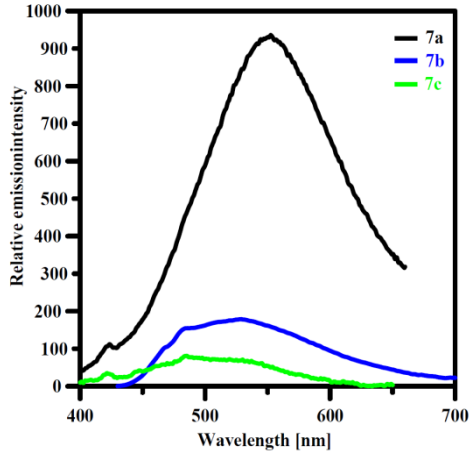


Fig. 7: The fluorescence spectra of **7a-c** in solid state

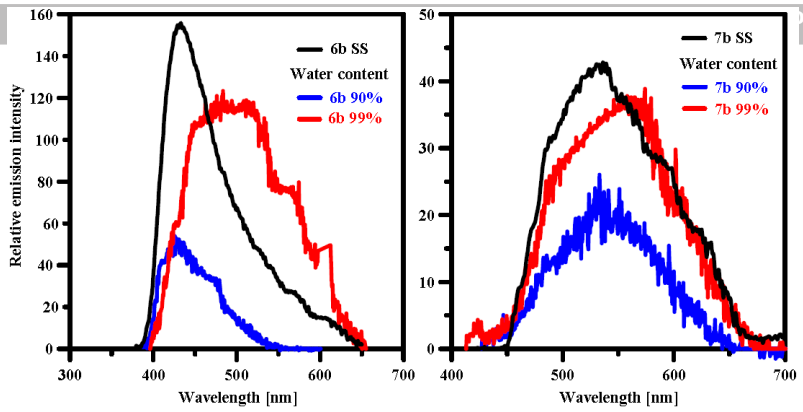


Fig. 8. The fluorescence spectra of **6b** (left) and **7b** (right) in a solid (SS) and in an aggregated state (THF/water solution)

The finding that some boron iminoenolates have appeared to be promising substrates for receiving AIE/AIEE (aggregation-induced emission/aggregation-induced emission enhancement) properties [36] encouraged us to perform an introductory study for selected representatives **6b** and **7b**. These compounds do not exhibit fluorescence in THF, however, after the admixing of their THF solutions with water (fw 90 %), a white turbidity and simultaneously a fluorescence start to appear (Figs. 8, 9).

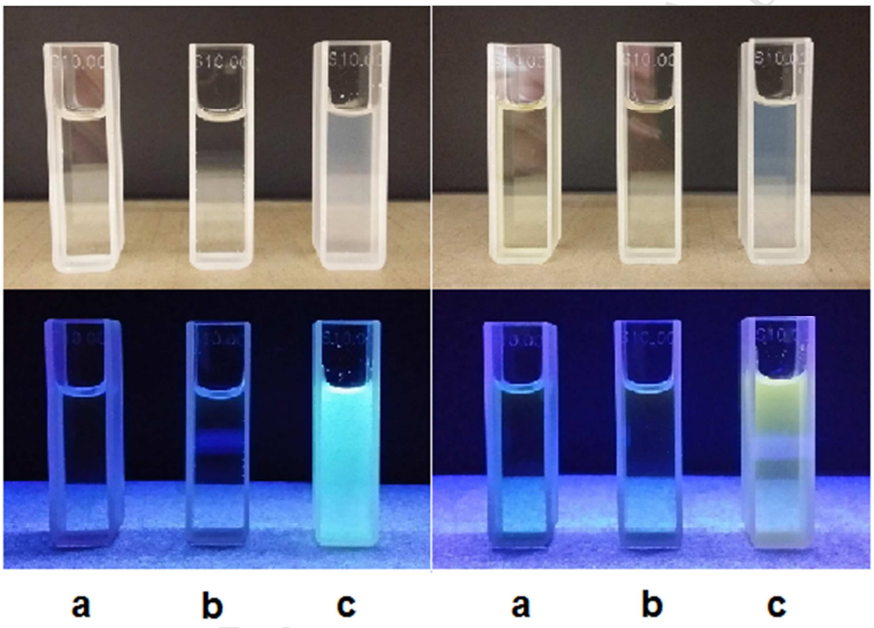


Fig. 9. 10^{-4}M solutions of compounds **6b** (left) and **7b** (right) without (top) and under UV (λ = 360 nm) light (bottom): (**a** – THF, **b** – 50 % (v/v) water/THF, **c** – 99 % (v/v) water/THF).

The fluorescence intensity becomes stronger when used THF/water mixture with fw of 99 %. For compound **7b**, no significant changes were observed in the shape and position of spectra in the aggregated state when compared with the solid state spectrum, but a bathochromic shift of the fluorescence maxima, primarily in fw of 99 % was detected for compound **6b**.

These changes in fluorescence properties in dependence on water content are documented by the photographs (Fig. 9). All the above-mentioned results indicate that compounds **6b** and **7b** are AIE/AIEE active molecules.

3.4. NMR Study

It should be noted that difluoroboron iminoenolates are studied by means of ^{19}F NMR relatively often. The interpretations of these data are, however, sometimes questionable. A signal consisting of four 1:1:1:1 lines is sometimes interpreted as two 1:1 doublets meaning two non-equivalent fluorines split by boron. Similarly, the presence of two 1:1 lines is occasionally explained as one 1:1 doublet meaning two equivalent fluorines split by boron. Due to the spin number of boron-11 (I = 3/2), one boron atom splits each neighbouring fluorine into four 1:1:1:1 lines [via $^{1}J(^{11}B–^{19}F)$] although distortion of the signals due to the relaxation phenomena or absence of the splitting due to a broadening of the signals is possible. In the case of the non-equivalence of the fluorines, an additional splitting into doublets can be observed (due to the geminal $^{19}F–^{19}F$ coupling). Thus the above-mentioned presence of four 1:1:1:1 lines could be most commonly interpreted as two equivalent fluorines split by boron-11 coupling (assuming that all the line distances are equal). Two 1:1 lines can be understood as two non-equivalent fluorines where splitting is not observed owing to the broadening of the signals (due to either dynamics of a molecule or the quadrupolar effect of boron or some other reasons). The whole situation can be more complicated if an observable isotopic shift is present and the splitting of the fluorines by boron-10 (I = 3) into seven lines appears in the spectrum. Basic facts about boron NMR were published e.g. several decades ago in ref. [54] Representative spectra for both the asymmetric and symmetric case are shown in ref. [29]

Fluorine-19 NMR spectra of compounds **6a,b** in $CDCl_3$ consist of two broad signals of identical intensity revealing the presence of two non-equivalent fluorine atoms (see Supporting Info, Figs. S35, 37). That indicates the lack of symmetry caused by a non-planarity of the molecules. In principle (according to the above-mentioned paragraph) the fluorine signals should be split into doublets via geminal coupling with neighbouring fluorine. Each line of the doublet should be split into another 1:1:1:1 multiplet via one-bond coupling with ^{11}B (under the assumption of neglecting the $^{10}B–^{19}F$ coupling). The absence of the splitting can be attributed to a molecular dynamics causing considerable broadening of the signals. This assumption was supported by the fact that in other solvents (acetone, acetonitrile) only one broad signal appeared. The dynamics of **6b** was studied by means of ^{19}F VT-NMR study in CD_3CN (Figs. 10, S46). At the laboratory temperature (293 K) the spectrum consists of a broad singlet. Upon gradual cooling-down the sample, the appearance of the spectrum changes. At 283 K it reaches the coalescence point below which the fluorine atoms are further non-equivalent. At 263 K the spectrum can be described as a broad AB system where only geminal coupling between neighbouring fluorines is observable. Upon cooling-down the sample to 238 K, each fluorine signal is split into eight lines. This can be interpreted by the manifestation of both $^{19}F–^{19}F$ (with $^{2}J(^{19}F,^{19}F)$

about 95 Hz) and $^{19}F–^{11}B$ coupling (with $^{1}J(^{19}F,^{11}B)$ about 14 Hz). The shoulders at the left edge of the signals are probably due to the ^{10}B isotopomer. On the other hand, heating the sample results in the sharpening the signal which is at 333 K sufficient for $^{19}F–^{11}B$ coupling to be observed (splitting into approximately 1:1:1:1 multiplet with $^{1}J(^{19}F,^{11}B)$ about 14 Hz). For the analysis of the splittings see Figures 11 and S47. At the temperature interval 238–333 K the molecule of **6b** thus changes from asymmetrical case to symmetrical (Figure 10). Nice examples of both asymmetric and symmetric boron iminoenolates described Gardinier et al. [29] Here the dynamic behaviour was not observed, each molecule represented either the symmetric or the asymmetric case.

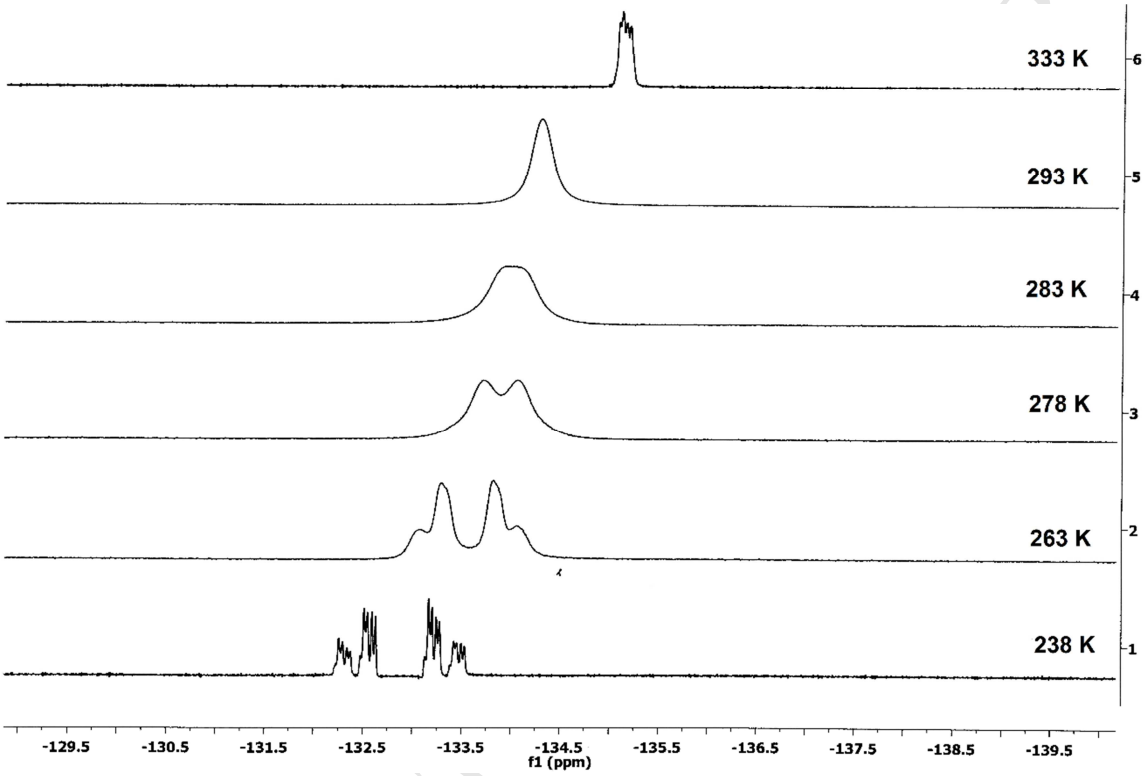


Fig. 10. ^{19}F VT-NMR study of the compound **6b** in acetonitrile-d3.

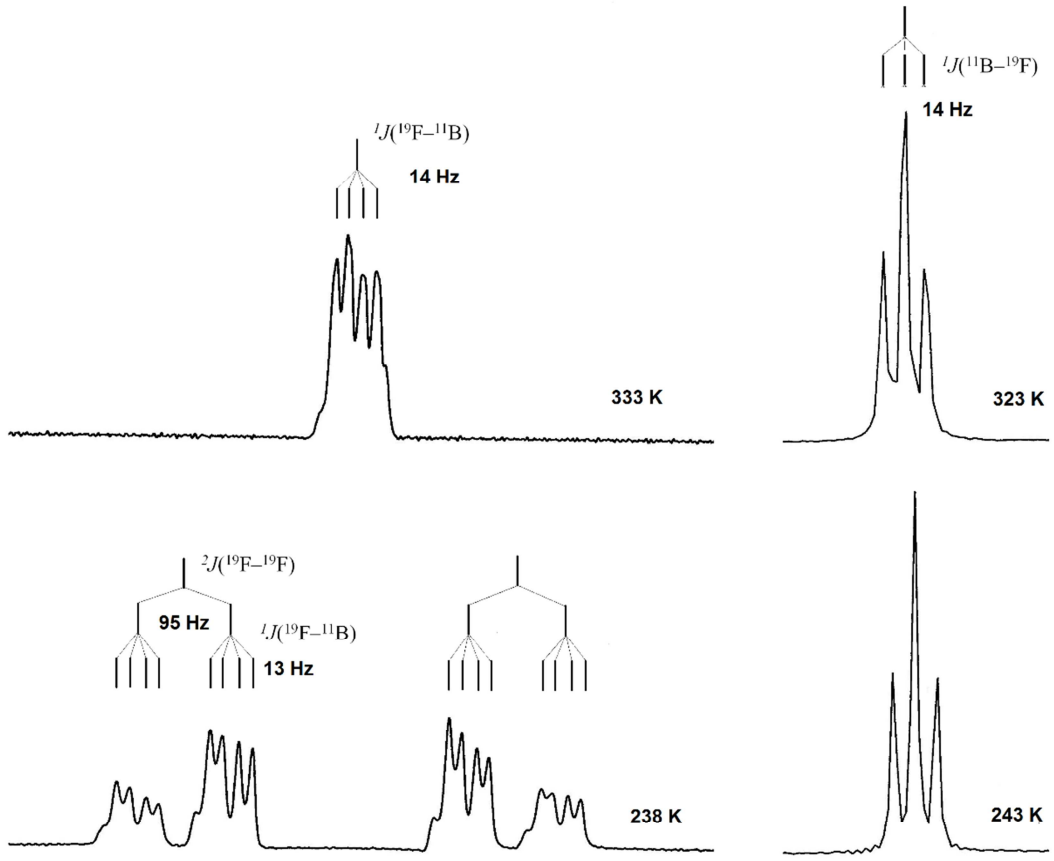


Fig. 11. Left part: analysis of ^{19}F NMR spectrum of **6b** in CD_3CN at various temperatures. Right part: ^{11}B NMR spectrum of **6b** in CD_3CN at various temperatures.

Unlike **6a,b** the spectrum of **6c** in $CDCl_3$ (Fig. S39) consists of two broad doublets with *J* ca 95 Hz. This can be accounted for the geminal coupling between two non-equivalent fluorines. Due to the broadening of the signals the considerably smaller boron-fluorine coupling is not observable under the conditions of the measurement.

The values of the fluorine chemical shifts (Table 2) lie in the range common for these compounds [29, 39, 55–57] (approx. -130 – -140 ppm). Slightly lower values (about -122 – -124 ppm) described Xia et al. [32] for difluoroboron chelates of some heterocyclic enaminoketones. No significant isotopic shifts due to ^{10}B were observed.

Boron signal in ^{11}B NMR spectra of compounds **6a–c** in $CDCl_3$ is split into triplet with $^{1}J(^{11}B,^{19}F)$ about 14 Hz. The appearance of the signal is unaffected by temperature. The equivalence of both the boron-fluorine coupling constants is probably due to only a slight difference between chemical environments of both the fluorines which is reflected also by a small difference in their chemical shifts ($\Delta\delta$ ~ 1 ppm at 238 K in CD_3CN). This is also supported by the fact that $^{1}J(^{11}B,^{19}F)$ for **6a–c** are comparable with those described in [29] for symmetric cases (about 15 Hz). Compared to $B(OMe)_3$ the signals of compounds **6** are upfielded which is typical for four-coordinate boron compounds [54,

58]. Values of the chemical shifts range around zero, similarly to the values described for other difluoroboron iminoenolates [13, 29, 33, 56] and trifluoroborane adducts with four-coordinated nitrogen [59].

Table 2

^{11}B and ^{19}F NMR parameters of compounds **6** and **7**

	^{11}B	^{19}F
6a	0.36, t, $^{1}J(^{11}B, ^{19}F)$ = 15.2 Hz	-134.0, -135.6 (2 × br s)
6b	0.68, t, $^{1}J(^{11}B, ^{19}F)$ = 14.6 Hz	-134.5, -136.3 (2 × br s)
6c	0.42, t, $^{1}J(^{11}B, ^{19}F)$ = 15.3 Hz	-134.0 (d, 95.8 Hz), -135.8 (d, 93.3 Hz)
6d	0.49, br s	-136.0, br s
7a	5.29, br s	
7b	5.53, br s	
7c	4.89, br s	

Measured in $CDCl_3$ with exception of 6d (in DMSO-d6).

Compound **6d** is insoluble in $CDCl_3$. Both its ^{19}F NMR and ^{11}B NMR spectra in DMSO-d6 at laboratory temperature consist of one broad singlet (see Figs. S41,42).

In general, ^{11}B NMR signals of BPh_2 fragment are shifted more downfield from those of BF_2 fragment [54]. Values in the range δ = 1.4–5.8 ppm can be extracted for similar O–B–N heterocycles from the literature [13, 28, 43–45, 56]. Boron-11 NMR spectra of compounds **7** consist of a broad signal with chemical shifts at the downfield edge of the range (δ = 4.9–5.5 ppm). This can be caused e.g. by rather greater steric compulsion around the boron atom (two phenyl groups and coumarinyl fragment) resulting in a decreased π-bonding to the adjacent phenyl rings, and therefore lowered shielding of the central boron atom. It is supported by the fact that for similar O–B–N heterocycles, a change of the substituent on the nitrogen atom from hydrogen to methyl led to a significant increasing in ^{11}B shift (δ from 1.8–2.5 to 3.7–4.4 ppm) [43, 44]. For ^{11}B and ^{19}F NMR data of compounds **6** and **7** see Table 2.

A comparison of ^{13}C NMR spectra of the parent compounds **5** with the corresponding **6** and **7** reveals a significant upfield shift for C3 carbon atom (numbering according to the ORTEPs) in the boron heterocycles (Δδ 15.2–18.3). This suggests that more contributing resonance form of the oxazaborines is the enol-imino than keto-enamino (Fig. 12, left). In the cases of compounds **6a**,**b** and **7a** the signals of carbon C2 (and in some instances also C13 and/or C14) are split (see Figure S34 in the Supporting Info). A possible explanation lies in a long-range coupling of the carbons with boron-11. To the best of our knowledge, such observations are relative rare (due to the quadrupole character of boron and resulting broadening the lines), for other examples see refs. [60, 61] The atypical shape of the multiplets could be explained according to ref. [60] On the other hand, the splitting of the ipso carbons (C15, C21) [which should be split into 1:1:1:1 quartet via $^{1}J(^{11}B–^{13}C)$] has never been observed. Generally, the signals of the carbons were very broad and missed from the spectra (only in the case of

7b a very broad signal with δ ~ 147 ppm was found after applying the exponential window function with large line-broadening factor).

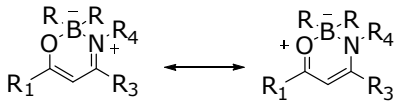


Fig. 12. Possible resonance forms of oxazaborines.

In the proton spectra of **6** and **7**, the most striking change is the significant downfield shift of the olefinic proton H2 in comparison with compounds **5**. Compounds **6** possess Δδ = 0.32–0.35 ppm, the shift for compounds **7** is lower (Δδ = 0.2 ppm). This behaviour is typical for this kind of compounds (see e.g. refs. [32, 55] It is probably related to the vicinity of the positively charged nitrogen.

3.5. Crystallography

Structures of **6b** (Fig. 13) and **7a** (Fig. 14) are composed of the difluoro or diphenylboron fragment and anisobidentately bound ketiminate ligand. A boat-like conformation of the central ligand core is found for **7a** with the deviation of 0.179(2)Å for C2 and 0.621(2)Å for B1 atoms from the plane defined by the N1, C1, C3 and O1 atoms. On the other hand, only the deviation of the boron atom of 0.307(2)Å from the plane defined by all five core atoms of the ligand forming thus an envelope conformation is found for **6b.** The reason is a lower steric hindrance or electron density on the boron atom in **6b**. Another difference between both the compounds, caused probably by a deformation of the central iminoenolate skeleton, is a tilting of the coumarin ring in **7a** producing a lack of C(=O)O stacking. On the other hand, this stacking can be found in **6b**.

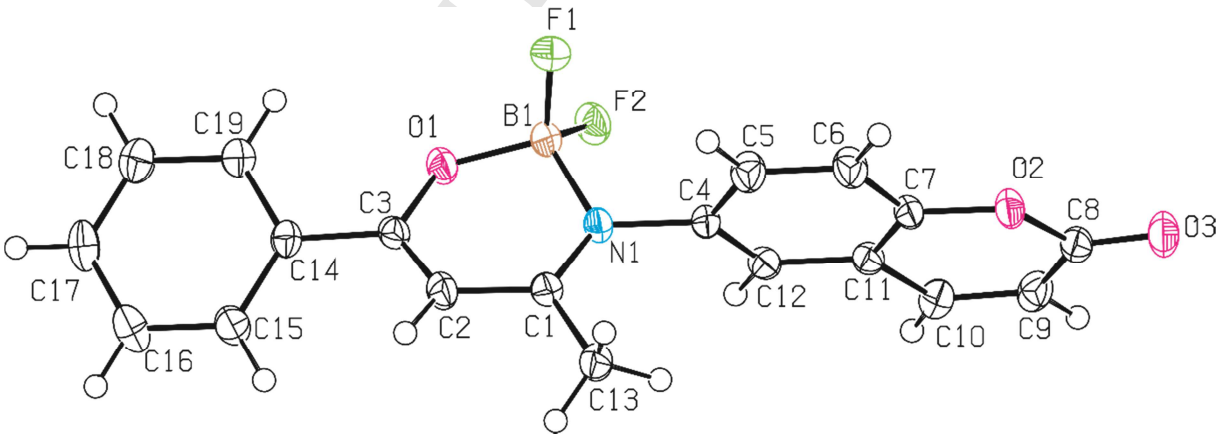


Fig. 13. The molecular structure (ORTEP 50% probability level) of **6b**. Selected interatomic distances [Å] and angles [°]: O1–B1 1.466(2), B1–N1 1.559(3), N1–C1 1.323(2), C1–C2 1.413(3), C2–C3 1.358(3), O1–C3 1.325(2), N1–C4 1.449(2), O2–C7 1.377(2), O2–C8 1.377(2), O3–C8 1.207(2); F1–B1–F2 109.89(16), C3–O1–B1 122.48(15), O1–B1–N1 109.50(15), C1–N1–B1 121.26(15), C7–O2–C8 121.94(15), O2–C8–O3 116.40(19).

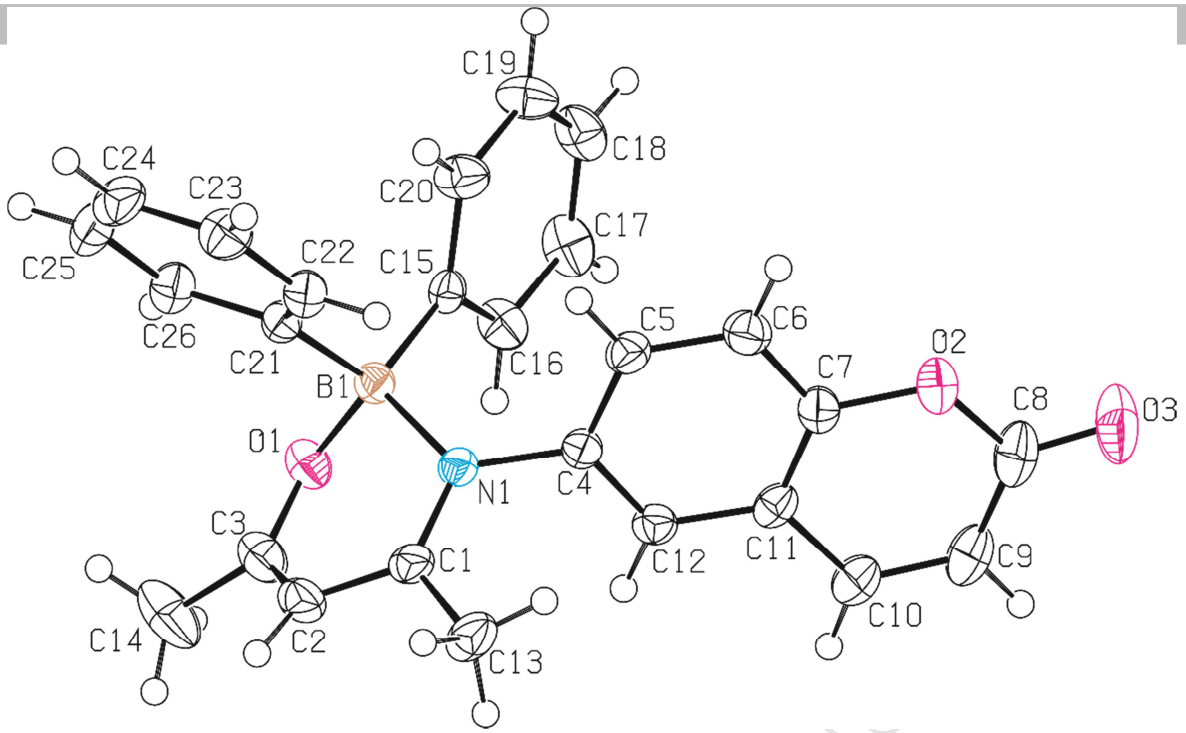


Fig. 14. The molecular structure (ORTEP 50% probability level) of **7a**. Selected interatomic distances [Å] and angles [°]: O1–B1 1.519(3), B1–N1 1.594(3), N1–C1 1.325(3), C1–C2 1.415(3), C2–C3 1.359(4), O1–C3 1.313(3), N1–C4 1.438(3), O2–C7 1.387(3), O2–C8 1.382(3), O3–C8 1.208(3); C15–B1–C21 113.72(18), C3–O1–B1 116.38(17), O1–B1–N1 104.14(16), C1–N1–B1 117.05(18), C7–O2–C8 121.6(2), O2–C8–O3 116.5(3).

Upon comparison of the relevant bond lengths of compounds **6b** and **7a** with those obtained for keto-enamine arrangement [62] and with standard values [63] following facts can be retrieved:

A considerable shortening the C2–C3 and C1–N1 bonds as well as lengthening the C1–C2 and C3–O1 bonds.

The C2–C3 and C3–O1 bond lengths are close to those reported for C=C–O of enols (1.362 Å and 1.333 Å resp.).

The O–B bond length is significantly shorter than the N–B one.

With a respect to the above-mentioned as well as other angles and distances characteristic for boron iminoenolate complexes, it can be stated that the π-electron density/a multiple bond character is localized mainly between C1–N1 and C2–C3 atoms of the ligand respectively which means greater contribution of enol-imino form against keto-enamino. Both the structures are similar to already reported structures of boron diphenyl [43] or difluoro [29, 32, 34, 55, 64–66] iminoenolate complexes. The conclusions are thus analogous to those made on the basis of ^{1}H and ^{13}C NMR in solution (*vide supra*).

4. Conclusions

The aim of the work was to combine two known luminophores: coumarin and boron iminoenolate and investigate whether the combination would led to fluorescent molecules. Seven novel boron β-iminoenolates, substituted with fluoride or phenyl group on the boron atom and coumarin-6-yl fragment on the nitrogen, were prepared upon reacting the corresponding enamines with compounds of trivalent boron (boron trifluoride diethyl etherate, triphenyl borane or diphenylborinic acid). The compounds prepared were characterized by means of ^{11}B, ^{19}F, ^{13}C and ^{1}H NMR spectroscopy in solution, single-crystal X-ray diffraction and UV/Vis spectroscopy. ^{19}F VT-NMR study of the selected substrate in the range 238–333 K revealed chemical exchange between the fluorines with the coalescence point about 283 K. The preliminary fluorescence study revealed that all the studied compounds (both the starting β-enaminones and the corresponding boron iminoenolates) show more or less intense broad band luminescence in powder state with a maximum depending on the substitution on the boron atom. With the exception of compound **5d**, the studied compounds do not fluoresce in solution at room temperature. On the other hand, all the investigated compounds exhibit more or less strong fluorescence in a frozen 2-methyltetrahydrofuran at 77 K. Tests performed for compounds **6b** and **7b** also revealed that these compounds are AIE/AIEE active. From the above mentioned it follows that coumarin-6-yl-containing boron iminoenolates proved to be interesting luminophores. For understanding the relations structure – photophysical characteristics – UV/Vis spectra of the studied compounds, a detailed investigation of the luminescence characteristics including quantum yields and a quantum chemical study of the characteristics of the excited states is now in progress in our laboratory.

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Appendix A. Supplementary material

CCDC 1050226 and 1050227 contain the supplementary crystallographic data for **6b** and **7a**, respectively. Copies of this information may be obtained free of charge from the Cambridge Crystallographic Data Centre via The Director, CCDC, 12 Union Road, Cambridge CB2 1EY, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http:// www.ccdc.cam.ac.uk).

Additional experimental procedures as well as copies of NMR spectra are presented in the Supporting Information file.

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