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# A new bicyclic oxazaborines with a bridged nitrogen atom, their thermic rearrangement and fluorescence properties

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ABSTRACT

Cyclic β-enaminones bearing secondary amino group react with 4-substituted benzenediazonium tetraphenylborates in dichloromethane to form substituted bicyclic [1,3,2λ$^4$]oxazaborines The oxazaborines rearrange, on heating to 200 °C in the absence of solvent or in DMF or DMSO, to isomeric 2*H*-[1,2,4,3λ$^4$] triazaborines. Previously prepared [1,3,2λ$^4$]oxazaborines derived from acyclic β-enaminones bearing secondary amino group either did not undergo the rearrangement or with a lot of difficulties and with negligible yield. The fluorescence behaviour of the prepared triazaborines was observed. These compounds fluoresce in 2-methyltetrahydrofurane and in solid state under low temperatures.



## 1. Introduction

During the last several years, unsaturated heterocyclic compounds containing a boron atom have invited interest either from the aspect of basic research or possible applications [1,2]. An introduction of the boron atom into an organic molecule substantially changes its electronic characteristics, which opens the way to the construction of optoelectronic materials for molecular electronics based on organic molecules. These materials could be used for organic light-emitting diodes (OLEDs). Complexes of diphenylboron compounds also belong among these compounds from the perspective of this aspect. The preparation of these compounds results from a reaction of *N*,*O*-chelating ligands with triphenylborane [3–6] or with diphenylborinic acid [7], *N*,*N*-chelating ligands with triphenylborane [8–13] or *N*,*C*-chelating ligands with diphenylboron chloride [14].

In our previous papers we described the synthesis and properties of heterocyclic compounds containing the $BPh_2$ group [15,16]. The reactions start from simple β-enaminones [15], β-enaminoamides [16] or β-enaminonitriles [17], unsubstituted in the α-position, and diazonium tetraphenylborates in dichloromethane. Depending on the structure of the starting "polarised ethylene" this reaction gave various products. β-Enaminones formed oxazaborines **I** ($R^1$ = Me, Ph), β-enaminoamides a mixture of oxazaborines **I** ($R^1$ = NHPh), diazaborinones **II**, or triazaborines **III** ($R^1$ = CONHPh), respectively, and β-enaminonitriles gave triazaborines **III** ($R^1$ = CN). If, in the case of the β-enaminonitriles [17], water was present in the reaction mixture, oxazaborine **I** ($R^1 = NH_2$) was also isolated (Scheme 1).

The aim of this work is the preparation of bicyclic compounds containing the $B(C_6H_5)_2$ group derived from cyclic enaminones **4** (Scheme 2) and investigation of their fluorescence properties.

## 2. Materials and methods

### 2.1. NMR spectroscopy

NMR spectra were measured at 295 K using a Bruker AVANCE 500 spectrometer equipped with a 5 mm broadband probe with a gradient of magnetic field in the direction of *z* axis operating at the frequencies 500.13 MHz ($^1$H), 125.77 MHz ($^{13}$C), 50.69 MHz ($^{15}$N) and a Bruker AVANCE III 400 operating at 400.13 MHz ($^1$H), 100.62 MHz ($^{13}$C), 128.38 MHz ($^{11}$B) and 40.55 MHz ($^{15}$N). The $^1$H

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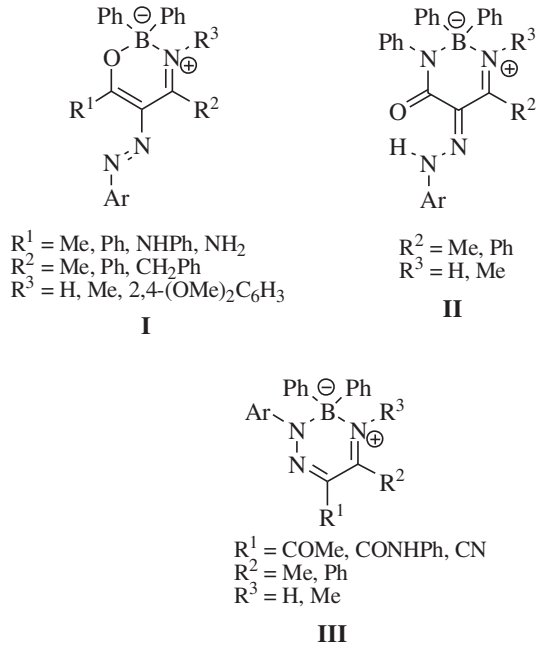
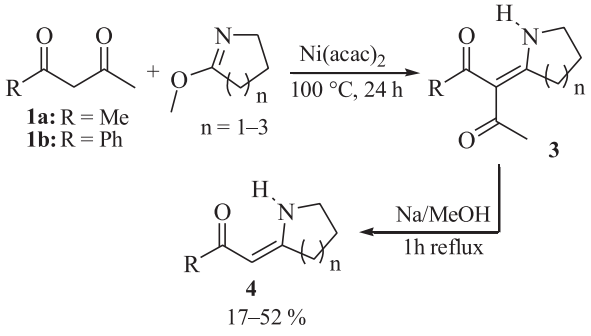



**Scheme 1.** Diphenylboron heterocycles prepared from β-enaminones, β-enaminoamides and β-enaminonitriles.

NMR spectra were calibrated in $CDCl_3$ on internal standard (hexamethyldisiloxane ($\delta$ 0.05) or tetramethylsilane ($\delta$ 0.00)) and the $^{13}C$ NMR spectra were calibrated on the central signal of the solvent multiplet ($\delta$ 76.9). The $^{13}C$ NMR spectra were measured in a standard way and by means of APT pulse sequence (spectral width 26.455 kHz, acquisition time 1.238 s, zero filling to 64 K and line broadening 1 Hz prior Fourier transformation). The $^{15}N$ NMR spectra were calibrated on external neat $^{15}N$ nitromethane placed in a coaxial capillary ($\delta$ 0.0). The $\delta$ ($^{15}N$) values were measured with the help of techniques with inversion detection (gradient selected 2D $^{1}H-^{15}N$ HMBC) processed in the magnitude mode. The gradient ratio was 70:30:50.1. Experiments were performed with the NH one-bond coupling 90 Hz, and NH long-range coupling 5 Hz, 2 K × 160 zero filled to 2 K × 1 K, sinebell squared in both dimensions. The $^{11}B$ NMR spectra were calibrated on external $B(OCH_3)_3$ placed in a coaxial capillary ($\delta$ 18.1). In order to suppress the signals of $^{11}B$ nuclei from a NMR tube glass, the measurements were carried out in Teflon sample tube liners (Aldrich) inserted into 5 mm tubes whose bottom part of about 25 mm length was cut off.

### 2.2. X-ray measurements

The crystal data for compounds **5a**–**c**, **5e**–**h**, **5j** and **6a**–**g**, **6i** were collected at room temperature using a Nonius Kappa CCD diffractometer with graphite monochromated Mo Kα radiation and corrected for Lorentz and polarization effects. The data sets were integrated with the Denzo-SMN package [18] and corrected for Lorentz, polarization and absorption effects (SORTAV [19]). The structures were solved by direct methods (SIR97 [20]) and refined using full-matrix least-squares. In all compounds all non-hydrogen atoms were refined anisotropically and hydrogens in part isotropically and in part included on calculated positions, riding on their carrier atoms.




**Scheme 2.** The reaction route from diketones to enaminones.

All the calculations were performed using SHELXL-97 [21] and PARST [22] implemented in WinGX [23] system of programs. The crystal data and refinement parameters are summarized in Tables S1 and S2. Selected structural parameters are given in Tables S3 and S4 (see Supplementary material).

Complete crystallographic data for the 16 structures in this paper have been deposited at the Cambridge Crystallographic Data Centre.

### 2.3. Spectroscopic studies

The used solvents, acetonitrile (MeCN), dibutyl ether (DBE), and 2-methyltetrahydrofuran (2-MeTHF), were of spectroscopic grade (Sigma–Aldrich). The absorption spectra were measured on Perkin Elmer Lambda 35 UV/VIS Spectrophotometer. The fluorescence spectra were measured using Hitachi Perkin Elmer LS 55 Spectrofluorimeter. The fluorescence spectra of the compounds were recorded by excitation at the wavelengths of the longest absorption maximum. Quantum yields of the fluorescence in the solid state were not determined.

### 2.4. Differential thermal analysis

The thermal properties were investigated by a differential thermal analysis (DSC) using calorimeter DSC 12E (Mettler Toledo). The temperature and enthalpy calibration was made with the help of pure In. Measurements were carried out in nitrogen atmosphere. Stability of nitrogen flow was controlled by mass flow controller FMA 5400/5500 (Omega). Empty aluminium pan was used as a standard. Sample (approx. 3 mg) in aluminium sample pan was studied in the range 30–220 °C. Different heating/cooling rates (1, 5, 15, 20 °C/min) were used.

### 2.5. Materials

Lactim-methylethers were synthesized according to the literature procedures [24] from lactams and dimethyl sulphate. Diazonium tetraphenylborates were prepared according to the literature [15]. In the case of 4-bromobenzenediazonium tetraphenylborate, the diazonium salt was washed only with ethanol and then it was dried under vacuum for 0.5 h at room temperature. CAUTION: diazonium tetraphenylborates in crystalline state can undergo explosive decomposition even at a very slight mechanical stimulation!!! Anhydrous dichloromethane was purchased from Fluka or distilled over $P_2O_5$ before used.

### 2.6. Synthesis

#### 2.6.1. Synthesis of 2- and 3-substituted diketones *3a*, *c*–*f* and *4b*

The title compounds were synthesized according to the literature [25]. A mixture of diketone **1a** or **1b** (234 mmol), corresponding lactim-methylethers (258 mmol) and a catalytic amount of nickel(II) acetylacetonate (0.59 g, 2.3 mmol) was heated at 100 °C for 24 h. Then the reaction mixture was cooled. The solid products were filtered and crystallized. (In the case of **3e** and **4b**, water (170 mL) was added and the reaction mixture was extracted

with dichloromethane (3 × 90 mL). The combined organic layers were dried over anhydrous sodium sulphate and concentrated under reduced pressure to afford the crude product. The crude product was purified chromatographically on silica gel.) The compounds prepared according to the procedure are summarised in Supplementary material.

*2.6.2. Synthesis of enaminones **4a, c–f***

The title compounds were synthesized according to the literature [26]. Sodium (7.38 g, 0.315 mol) was dissolved in methanol (168 mL). Diketone **3** (0.105 mol) was added and the reaction mixture was refluxed. After 1 h, the solvent was distilled off under vacuum and the crude product was purified by column chromatography on silica gel and crystallization or vacuum distillation. The compounds prepared according to the procedure are summarised in Supplementary material.

*2.6.3. General procedure for preparation of oxazaborines **5a–l***

To a cold (5 °C) solution of β-enaminones **4a–f** (5 mmol) in dry dichloromethane (15 mL) and toluene (25 mL, dried over sodium) freshly prepared corresponding benzenediazonium tetraphenylborate (5 mmol) was added. The reaction mixture was stirred 24 h at room temperature or 1 h at room temperature (after 1 h no diazonium salt was present in the reaction mixture, detection was performed by means of 4,5-dihydroxynaphthalene-2,7-disulfonate) and then 2 h at reflux. The reaction mixture was cooled to room temperature and solvents were evaporated *in vacuo*. The crude residue was chromatographed on silica gel with dichloromethane as the mobile phase to give compounds **5a–l**. The compounds prepared according to the procedure are summarised in Supplementary material.

*2.6.4. General procedure for the rearrangement of oxazaborines **5a–l***

*Method A*. Oxazaborines **5a**,**b**,**e**,**f**,**h**,**i**,**l** were heated at 200 °C for appropriate time. The reaction was monitored by TLC. The crude reaction mixture was chromatographed on silica gel with dichloromethane as the mobile phase to give compounds **6a**,**b**,**e**,**f**,**h**,**i**,**l**.

*Method B*. Oxazaborines **5** (2 mmol) were heated at reflux in DMF (10 mL) for appropriate time (see Table 2). The reaction was monitored by TLC. The solvent was evaporated *in vacuo* and the crude reaction mixture was chromatographed on silica gel with dichloromethane as the mobile phase to give compounds **6a–l**.

*Method C*. Oxazaborines **5** (2 mmol) were heated at reflux in DMSO (10 mL) for appropriate time (see Table 2). The reaction was monitored by TLC. The solvent was evaporated *in vacuo* and the crude reaction mixture was chromatographed on silica gel with dichloromethane as the mobile phase to give compounds **6a–l**.

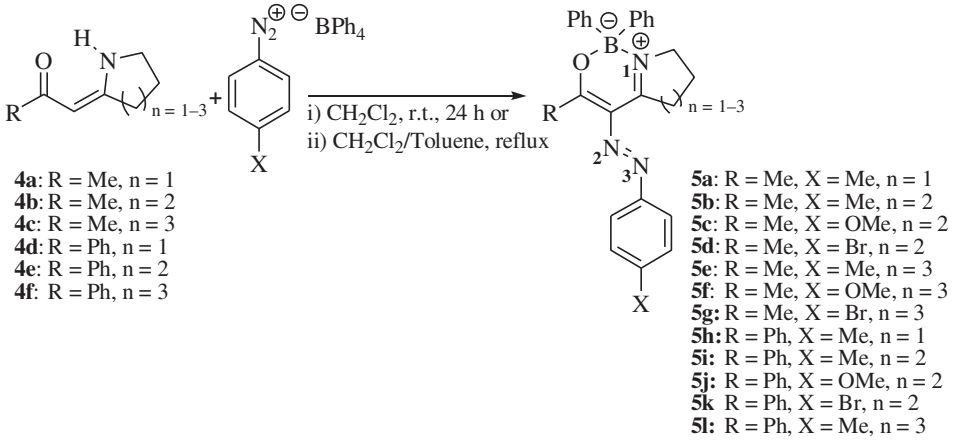
The compounds prepared according to the above-mentioned procedures are summarized in Supplementary material.

## 3. Results and discussion

The starting β-enaminones were prepared by two-step synthesis, starting from corresponding β-diketones **1** and lactim-methylethers (Scheme 2). β-Diketones **1a**,**b** react with the lactim-ethers in the presence of a catalytic amount of $Ni(acac)_2$ at 100 °C to form 2-, or 3-substituted diketones **3**, respectively [25]. The diketones undergo deacetylation by sodium methanolate in methanol (Ref. [26], for analogic reaction with ethanolate) to form enaminones **4**. In the case of the diketone **1a** and 6-methoxy-2,3,4,5-tetrahydropyridine, no product **3** was isolated but the deacetylated enaminone **4** directly.

The prepared enaminones **4a–f** were subjected to the reaction with substituted benzenediazonium tetraphenylborates (Scheme 3). The reaction proceeded in dry dichloromethane for approximately 1 day at room temperature or in dichloromethane/toluene for 1 h at room temperature and 2 h at reflux. Solvent was then evaporated *in vacuo* and the residue was subjected to column chromatography on silica gel. Twelve new condensed oxazaborines **5a–f** with bridged nitrogen atom in yields of 28–80% were obtained (Table 1). A suggestion of the mechanism of the oxazaborine formation is depicted in the literature [15].

As in the case of formerly studied oxazaborines **I** ($R^1$ = Me, Ph), we have also studied the behaviour of compound **5** upon heating to higher temperatures. Oxazaborines **I** underwent, at temperatures about 200 °C, a thermal rearrangement to triazaborines **III** ($R^1$ = COMe). The oxazaborines **I** with primary amino groups rearranged relatively easily, whereas oxazaborines **I** with secondary amino groups either did not undergo the rearrangement, or did so in negligible yields only. The newly prepared derivatives **5** were subjected to both melting at 200 °C and heating in DMF or DMSO under reflux. The products isolated were triazaborines **6** (Scheme 4, Table 2). The triazaborines **6a** and **6e** were formed (according to TLC) under solvent-free heating in very low, non-isolable yields only. Upon extending the time of heating, the starting unreacted oxazaborines **5a**,**b** were still detected in the melt, and the amount of unidentified decomposition products increased. In some cases, the primary products of azo coupling to enaminones **7** (Scheme 5) were identified in the reaction mixture together with the starting components and the products of the rearrangement. The primary




**Scheme 3.** The synthesis of oxazaborines.

**Table 1**
The yields of oxazaborines **5a**–**l**.

| Oxazaborine | Room temperature[a] Yield[c] [%] | Reflux in $CH_2Cl_2$/toluene[b] Yield[c] [%] |
|---|---|---|
| **5a** | 62 | 80 |
| **5b** | 49 | 48 |
| **5c** | [d] | 48 |
| **5d** | [d] | 77 |
| **5e** | 61 | 35 |
| **5f** | [d] | 52 |
| **5g** | [d] | 48 |
| **5h** | 37 | 44 |
| **5i** | 60 | 62 |
| **5j** | [d] | 44 |
| **5k** | [d] | 52 |
| **5l** | 28 | 52 |

[a] The reaction proceeded for 24 h.
[b] The reaction proceeded for 1 h at laboratory temperature and then for 2 h at reflux.
[c] After column chromatography and crystallization.
[d] Not performed.

**Table 2**
The yields of triazaborines **6a**–**l**.

| Triazaborine | Melting without solvent | | Heating in DMF | | Heating in DMSO | |
|---|---|---|---|---|---|---|
| | Time [h] | Yield[a] [%] | Time [h] | Yield[a] [%] | Time [h] | Yield[a] [%] |
| **6a** | 1 | 0 | 24 | 30 | 3.5 | 23 |
| **6b** | 1 | 20 | 5 | 34 | 2 | 35 |
| **6c** | – | – | 15 | 28 | 2 | 38 |
| **6d** | – | – | 14 | 43 | 1.5 | 45 |
| **6e** | 1 | 0 | 9 | 18 | 1 | 11 |
| **6f** | 5 | 6 | 20 | 6 | 1.5 | 11 |
| **6g** | – | – | 14 | 20 | 0.5 | 0 |
| **6h** | 3 | 16 | 24 | 56 | 2.5 | 40 |
| **6i** | 1 | 73 | 14 | 67 | 1.5 | 40 |
| **6j** | – | – | 11 | 27 | 2 | 37 |
| **6k** | – | – | 14 | 76 | 1 | 45 |
| **6l** | 1.5 | 48 | 19 | 10 | 1.5 | 15 |

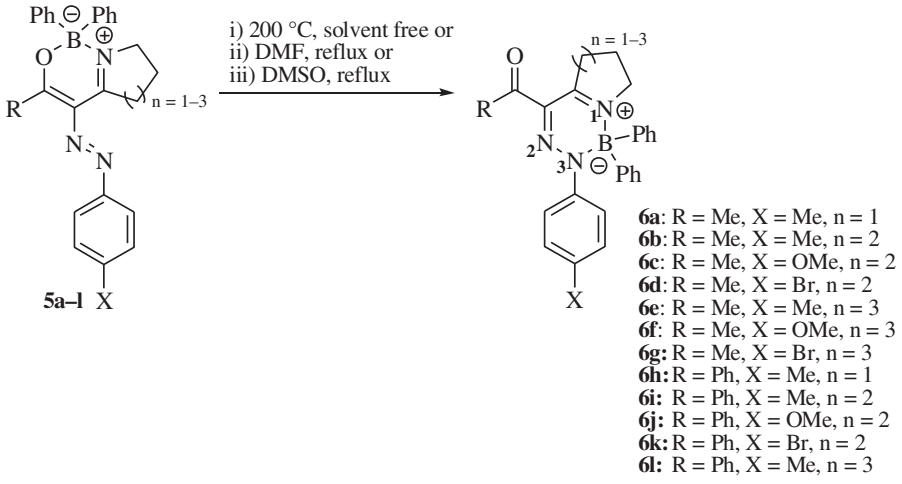
[a] After column chromatography and crystallization.

products were identified by means of TLC and $^1$H NMR. An enhancement of the yields of triazaborines **6a** and **6e** was achieved after performing the rearrangement in the solution. Higher yields of **6b**, **6f** and **6h** were obtained as well. On the other hand, solvent-free melting was better in the case of oxazaborine **5i**, and especially **5l**. In the case of oxazaborine **5b** the attempt to give rise to the rearrangement by means of microwave irradiation was also made, however no significant improvement of the yield of **6b**, compared to the conventional heating methods, was achieved. The course of the rearrangement was followed by TLC on Silufol (dichloromethane as the mobile phase).

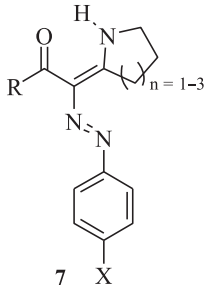
The rearrangement of oxazaborines **5** to triazaborines **6** is not reversible. Upon prolongation of the reaction time it is not possible to achieve the complete rearrangement to compound **6**, because the oxazaborines, at the relatively high temperatures of the rearrangement, decompose and decomposition products are formed, besides the triazaborines. On heating the pure triazaborines **6a** and **6d** to 200 °C for 1 h under inert conditions, not even traces of the corresponding oxazaborine were detected (by means of TLC) and no decomposition of the triazaborines took place; hence the triazaborines are stable at this temperature.

The rearrangement of the oxazaborines **5** to the triazaborines **6** proceeds probably via an intramolecular variant of the ANRORC mechanism. The dative covalent bond between oxygen and boron –O–B(Ph)$_2$– splits and a bond of the same kind $\rangle$N–B–(Ph)$_2$– between the nitrogen of the azo group and boron, is formed. There are not relevant data in the literature capable of explaining the direction and irreversibility of the rearrangement **5** → **6**. We tried to find out the heat of the rearrangement **5** → **6** by means of DSC. In the case of **5i**, where a significant amount of **6i** is formed under solvent-free heating, the endothermic peak of the melting overlaps with the peak of the rearrangement, hence it is not possible to evaluate the heat of the reaction. In the case of compound **5b**, with a lower melting point, only a small amount of the triazaborine **6b** is formed under solvent-free rearrangement; the major reaction is the decomposition of the oxazaborine, so that, even in this case, it is not possible to evaluate the heat of the reaction. The corresponding curves of the dependencies of the heat flow on temperature are shown in Fig. S1.

All the products prepared were characterized by means of multinuclear magnetic resonance and in many cases also by means of X-ray diffraction (see Supplementary material). The $^{11}$B chemical shifts are of some importance for identification of the compounds studied: in the case of oxazaborines **5** the values of $\delta$ ($^{11}$B) are positive, and for the compounds with a seven-membered annelated ring (**5e**, **5f**, **5g** and **5l**) these values are higher than 4 ppm. The triazaborines **6** have values of $\delta$ ($^{11}$B) lower than the oxazaborines **5**, but, similar to the case of the oxazaborines, those with annelated seven-membered rings have rather higher values of $\delta$ ($^{11}$B) compared to the ones with smaller annelated rings. The $^{15}$N chemical shift values of nitrogens N2 and N3 (Table 3) explicitly




**Scheme 4.** The rearrangement of oxazaborines to triazaborines.




**Scheme 5.** The structure of the primary products of azo coupling.

evidence the presence of an azo group and not a tautomeric hydrazo group. Quaternary nitrogen has $\delta$ ($^{15}$N) from −175 to −195 in both the oxazaborines and triazaborines (Table 4).

ORTEP [27] views for compounds **5a**, **5c**, **5e**–**h**, **5j** and **6b**–**g**, **6i** and crystal data for all compounds are shown in Supplementary material (Figs. S2–S15, Tables S1–S4). In structure **5b** (Fig. 1) the atom C6 was found disordered and refined over two positions with occupation factors of 0.62 and 0.38, respectively. In structure **5c** (Fig. S3) the phenyldiazenyl group was found disordered, with two opposite conformations, and refined with occupation factors of 0.55 and 0.45, respectively. In both compounds **5e** and **5f** (Figs. S4 and S5) the atom C6 was found disordered and refined over two positions with occupation factors of 0.69/0.31 and 0.62/0.38, respectively. In structure **6a** (Fig. 2) the C4 atom was found disordered and refined over two positions with occupation factors of 0.63 and 0.37, respectively. In structure **6i** (Fig. S15) the bonded atoms C4–C5 were found disordered and refined over two positions with occupation factors of 0.60 and 0.40, respectively.

All the boron heterocycles assume similar mixed boat-envelope conformation (B/E) as evidenced by the puckering parameters [28] in Tables S3 and S4. In compounds **5** the phenyldiazenyl moieties display different conformations with respect to the C2–N2 single bond, due to different steric demands of the substituents at the boron heterocycle.

We found out that the triazaborines prepared, in contrast to the oxazaborines, fluoresce, which substantiates the reason for the synthesis of these compounds.

The absorption spectra of **6a**–**d** and **6i**–**l** were measured in acetonitrile (MeCN), dibutyl ether (DBE) and 2-methyltetrahydrofuran (2-MeTHF) (Fig. 3 and Table 5). Dependent on the solvent polarity and the character of the substituent, the absorption maxima are between 410 and 440 nm. The data in Table 5 indicate that an enhancement of the solvent polarity causes a significant hypsochromic shift of the absorption maxima. Compounds **6a**–**d** show somewhat smaller shifts (~10 nm) than compounds **6i**–**l** (~15 nm).

All the chromophores studied did not exhibit any fluorescence in solutions at room temperature, but, except for compounds **6k** and **6l**, they fluoresce in 2-methyltetrahydrofuran in frozen state at 77 K (Fig. 4) and by recording the fluorescence from the powder solid phase of the compounds (Fig. 5). In comparison with the frozen state in the 2-methyltetrahydrofuran, the fluorescence maxima of all the chromophores in solid state are bathochromically shifted.

**Table 3**
The values of chemical shifts $^{15}$N and $^{11}$B for compounds **5a**–**l** (for the notation of nitrogens see Scheme 3).

| Oxazaborine | $\delta$ [ppm] | | | |
|---|---|---|---|---|
| | $^{15}$N1 | $^{15}$N2 | $^{15}$N3 | $^{11}$B |
| **5a** | −187.3 | 101.4 | 76.5 | 3.45 |
| **5b** | −195.4 | [a] | 85.6 | 3.15 |
| **5c** | −195.2 | [a] | 83.6 | 3.07 |
| **5d** | −193.4 | [a] | 78.8 | 3.27 |
| **5e** | −185.9 | [a] | 86.5 | 4.08 |
| **5f** | −185.7 | [a] | 84.9 | 4.06 |
| **5g** | −184.6 | [a] | 78.3 | 4.05 |
| **5h** | −182.2 | 106.1 | 83.3 | 3.67 |
| **5i** | −187.3 | 108.0 | 88.7 | 3.49 |
| **5j** | −188.7 | [a] | 89.7 | 3.52 |
| **5k** | −187.5 | [a] | 79.3 | 3.63 |
| **5l** | −174.4 | 106.2 | 89.3 | 4.32 |

[a] Not detected.

**Table 4**
The values of chemical shifts $^{15}$N and $^{11}$B for compounds **6a**–**l** (for the notation of nitrogens see Scheme 4).

| Triazaborine | $\delta$ [ppm] | | | |
|---|---|---|---|---|
| | $^{15}$N1 | $^{15}$N2 | $^{15}$N3 | $^{11}$B |
| **6a** | −178.8 | 23.3 | −157.1 | 0.18 |
| **6b** | [a] | [a] | [a] | −0.16 |
| **6c** | −190.1 | 22.2 | −163.0 | −0.24 |
| **6d** | −184.6 | 19.3 | −169.4 | −0.24 |
| **6e** | [b] | 24.8 | −159.3 | 0.53 |
| **6f** | −179.3 | 22.8 | −159.1 | 0.58 |
| **6g** | [b] | 19.8 | −165.6 | 0.56 |
| **6h** | −177.2 | 26.0 | −155.0 | 0.18 |
| **6i** | −186.9 | 23.0 | −162.6 | −0.11 |
| **6j** | [a] | [a] | [a] | −0.18 |
| **6k** | −183.1 | [b] | −168.6 | −0.05 |
| **6l** | −177.6 | 23.5 | −159.8 | 0.67 |

[a] Not measured.
[b] Not detected.

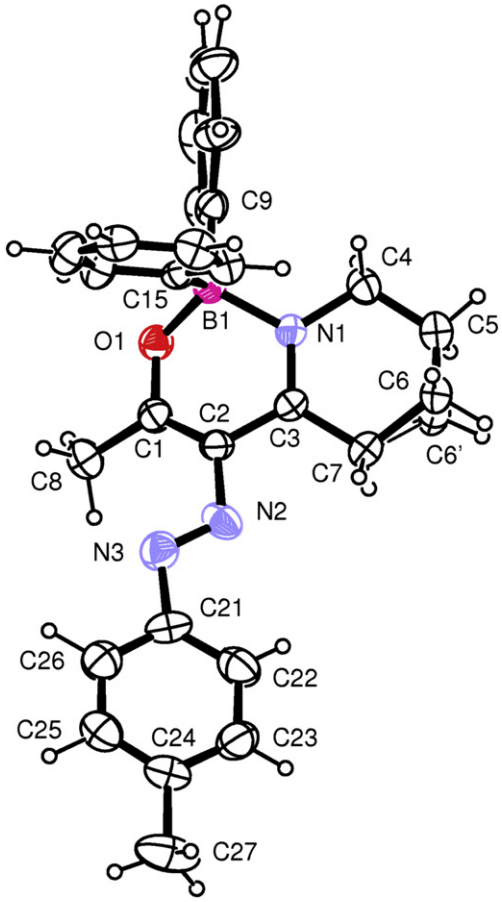



**Fig. 1.** ORTEP view of compound **5b** displaying the thermal ellipsoids at 30% probability. Both the disordered C6 and C6′ atoms are shown.

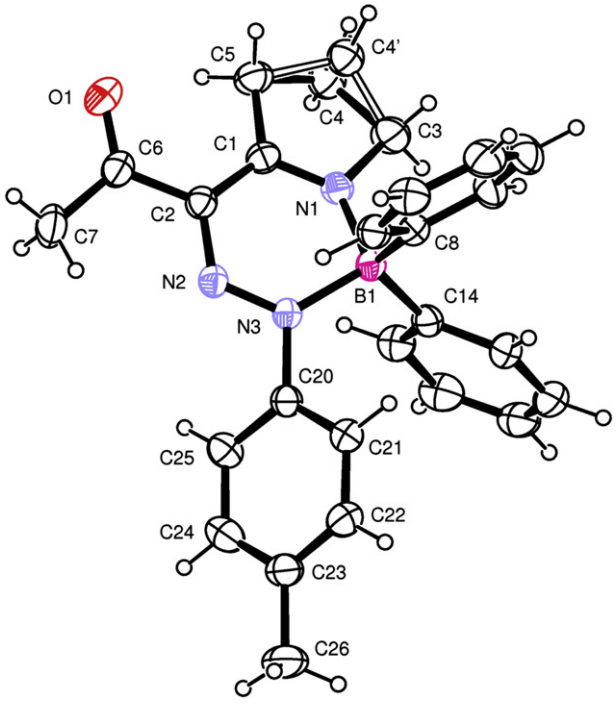



**Fig. 2.** ORTEP view of compound **6a** displaying the thermal ellipsoids at 30% probability. Both the disordered C4 and C4′ atoms are shown.

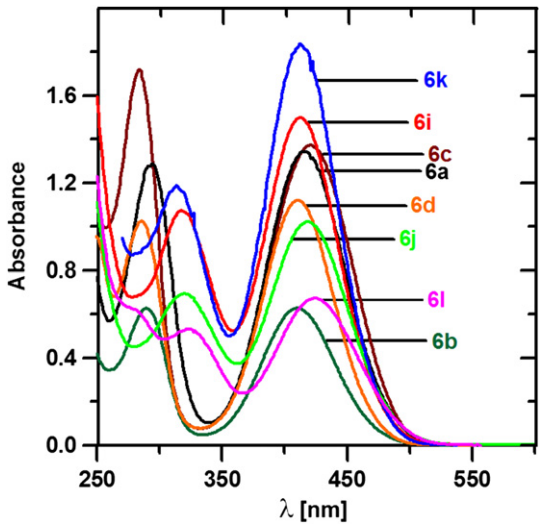



**Fig. 3.** Absorption spectra of triazaborines **6a**–**d** and **6i**–**l** in MeCN.

**Table 5**
The absorption ($\lambda^A$) maxima (nm) of prepared compounds in DBE, MeCN and in 2-MeTHF at room temperature (RT) and at 77 K (LT) and the fluorescence ($\lambda^F$) maxima (nm) in 2-MeTHF at 77 K (LT) and in solid state.

| Trizaborine | DBE | MeCN | 2-MeTHF | | Solid state |
|---|---|---|---|---|---|
| | $\lambda^A$ | $\lambda^A$ | $\lambda^A{}_{RT}$ | $\lambda^F{}_{LT}$ | $\lambda^F{}_{SS}$ |
| **6a** | 429 | 420 | 427 | 526 | 544 |
| **6b** | 419 | 410 | 418 | 511 | 549 |
| **6c** | 426 | 417 | 425 | 531 | 553 |
| **6d** | 421 | 410 | 418 | 505 | 541 |
| **6i** | 427 | 413 | 424 | 519 | 565 |
| **6j** | 434 | 418 | 431 | 530 | 588 |
| **6k** | 428 | 413 | 425 | – | 543 |
| **6l** | 440 | 424 | 436 | – | 592 |

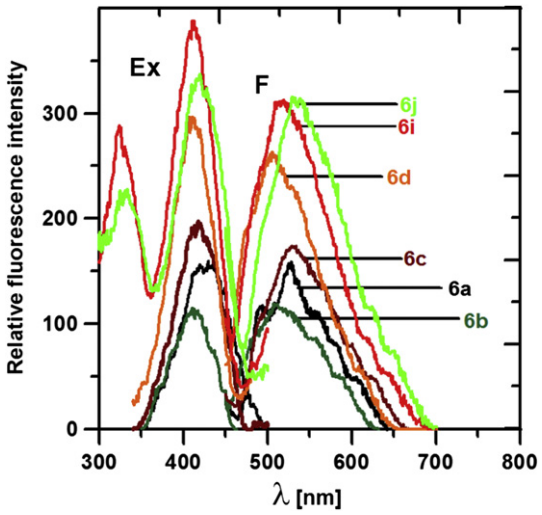



**Fig. 4.** Excitation (Ex) and fluorescence (F) spectra of triazaborines **6a**–**d** and **6i**–**l** measured in 2-MeTHF at 77 K.

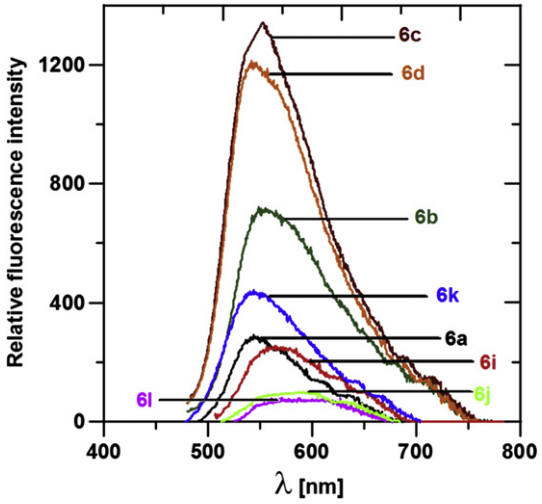



**Fig. 5.** Relative fluorescence intensity of triazaborines **6a**–**d** and **6i**–**l** in solid state.

## 4. Conclusions

A series of twelve bicyclic oxazaborines with bridged quaternary nitrogen atoms has been prepared by means of a reaction of substituted benzenediazonium tetraphenylborates with β-enaminones derived from cyclic secondary amines (pyrrolidine, piperidine, perhydroazepine). The reaction proceeds slowly in dry dichloromethane at room temperature and faster at the boiling point of the solvent mixture (dichloromethane/toluene). Upon heating to 200 °C under solvent-free conditions or in boiling DMF or DMSO, the oxazaborines rearrange to isomeric triazaborines through the B–O bond splitting and forming a new B–N bond with the nitrogen of the azo group. Complete rearrangement cannot be achieved due to the decomposition of the oxazaborines to unidentified products upon lengthening of the reaction time. The rearrangement of the oxazaborines to triazaborines was proved to be irreversible. The structure of the prepared oxazaborines and triazaborines was studied by means of $^{1}H$, $^{13}C$, $^{11}B$ and $^{15}N$ NMR and X-ray. Heterocyclic compounds containing the $BPh_2$ moiety, easily obtainable by the method described here, possess in their skeleton functional groups convenient for subsequent chemical

transformations and thus represent the intermediates for the preparation of other boron-containing heterocycles. Most of the compounds prepared exhibit fluorescence properties in powder and in 2-MeTHF in the frozen state.

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## Appendix A. Supplementary material

CCDC 831135–831150 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.cccdc.cam.ac.uk/data-request/cif.

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2011.11.004.

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