

# Syntheses, structures, luminescence and electrochemistry of benzene- and biphenyl-centered bis- and tris-1,3,2-diazaboroles and -1,3,2-diazaborolidines

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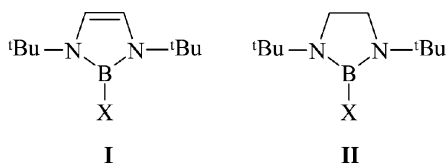
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Reaction of 1,4-bis(dibromoboryl)benzene (**1a**) with 2 equiv. of the diazabutadiene  ${}^t\text{BuN}=\text{CH}-\text{CH}=\text{N}{}^t\text{Bu}$  and subsequent reduction of the obtained bis(1,3,2-diazaborolium)salt **2a** with sodium amalgam afforded the 1,4-bis(1,3,2-diazaborolyl)benzene **3a**. Similarly, 1,3-bis(dibromoboryl)benzene (**1b**), 1,3,5-tris(dibromoboryl)benzene (**1c**) and 4,4'-bis(dibromoboryl)biphenyl (**1d**) were converted into compounds **3b**, **3c** and **3d** which contain two or three diazaborolyl substituents at the arene core. Treatment of precursors **1a,b,d** with two equiv. or **1c** with three equiv. of *N,N'*-di-*tert*-butylethane-1,2-diamine in the presence of an excess of  $\text{NEt}_3$  gave rise to the diazaborolidine derivatives **4a–4d**. Reaction of 1,3-bis(diiodoboryl)benzene **1e** with two equivalents of *N,N'*-dimethylethane-1,2-diamine in the presence of  $\text{NEt}_3$  furnished the corresponding 1,3-bis(diazaborolidinyl)benzene **4e**. The novel compounds were characterized by elemental analyses and spectroscopy ( ${}^1\text{H}$ ,  ${}^{13}\text{C}$ ,  ${}^{11}\text{B}$  NMR, MS). The molecular structures of **3c**, **4a** and **4e** were elucidated by X-ray-diffraction analyses. In addition to this, the oxidative cyclovoltammograms and blue emission spectra of these novel compounds were discussed. Here, the electronic communication between boron heterocycles on the different spacer-units and the luminescence of the oligo-diazaborolylarenes were of interest.

## Introduction

The recent development of a high-yield synthesis of boron-functionalized 2,3-dihydro-1*H*-1,3,2-diazaboroles (**I**) has had new impact upon the chemistry of such compounds.<sup>1–3</sup>

More recently we focussed our interest on electron-transfer processes of 2,3-dihydro-1*H*-1,3,2-diazaboroles and of the corresponding 1,3,2-diazaborolidines **II**. It was shown that these systems were irreversibly oxidized under cyclovoltammetric conditions. In contrast to this, their reduction could not be achieved in the range from 0 to  $-3$  V. In their He(i) UV-photoelectron spectra the investigated diazaboroles **I** and diazaborolidines **II** exhibit first ionization potentials ranging from 7.1 to 7.7 eV.<sup>4</sup>

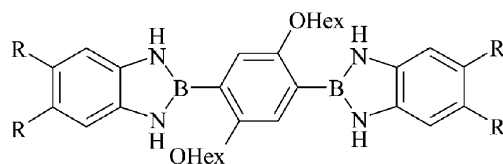


X = Br, H,  $\text{CH}_3$ , SMe, CN

Then we focussed our interest on a conceivable electronic communication between two diazaborolyl- or diazaborolidinyl-substituents at a ferrocene scaffold. The cyclovoltammograms of ferrocenyl-functionalized diazaboroles and diazaborolidines were dominated by the quasi-reversible oxidation of the Fe center.<sup>5</sup> A particular wave at more anodic voltages that might be due to the oxidation of one or both heterocycles was not observed.

Recently aromatic systems such as benzene were employed as a linchpin connecting up to six boryl groups<sup>6</sup> and up to three

boron clusters.<sup>7</sup> With this in mind, we were interested in the preparation of polynuclear, electron-delocalized systems, that are not only important for academic reasons, but may also have practical use as precursors for emissive organic materials, *e.g.* organic light emitting diodes. In this context a paper by Maruyama and Kawanishi on violet-blue emissions of aromatic diazaboroles of types **III** and **IV** seems particularly promising.<sup>8</sup>



**III**: R = H; **IV**: 2 R =  $-\text{CH}=\text{CH}-\text{CH}=\text{CH}-$

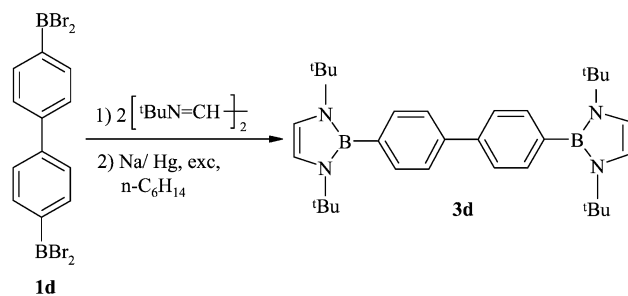
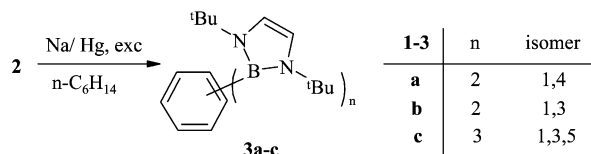
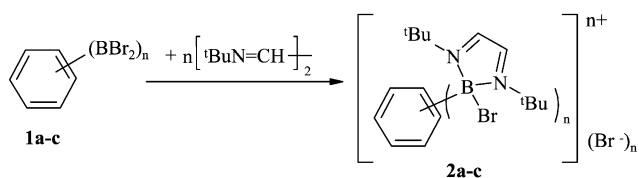
The intention of this work is the synthesis of bis- and tris-borolyl-functionalized benzene- and biphenyl-moieties and the investigation of their structural, electrochemical and optical properties.

## Results and discussion

The multiply 1,3,2-diazaborol-functionalized arenes **3a–3d** required in this study were conveniently synthesized *via* the cyclocondensation of the corresponding multiply dibromoborylated arenes **1a–1d**<sup>9</sup> with  ${}^t\text{BuN}=\text{CH}-\text{CH}=\text{N}{}^t\text{Bu}$ <sup>10</sup> and the subsequent reduction of the borolium salts **2a–2d** with an excess of sodium amalgam in hexane (Scheme 1).

Like in previous cases these borolium salts are analytically not uniform and contain different counter ions.<sup>2,5</sup> This prevents reliable elemental analyses but is not relevant for the subsequent reduction to the boroles in good yield. Due to the insolubility

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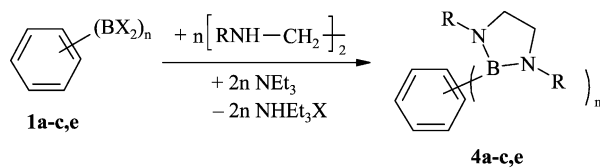
Scheme 1

of salts **2a–2d** in polar organic solvents (e.g.  $\text{CD}_2\text{Cl}_2$ ,  $\text{CD}_3\text{CN}$ ,  $d_6$ -acetone) no useful  $^1\text{H}$ , or  $^{13}\text{C}$  NMR spectra were obtained.

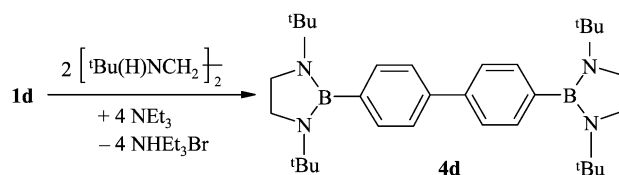
Products **3a–3d** were isolated as colorless microcrystalline solids in 69–73%.

The related saturated systems, the multiply 1,3,2-diazaborolidine-functionalized arenes **4a–4d** result from the reaction of **1a–1d** with the required equivalents of *N,N'*-di-*tert*-butylethane-1,2-diamine in the presence of  $\text{NEt}_3$  in boiling hexane (**4a,b**) or in toluene at  $80^\circ\text{C}$  (**4c,d**). Analogously compound **4e** was prepared from 1,3-bis(dibromoboryl)benzene **1e**,<sup>11</sup> two equivalents of *N,N'*-diethylethane-1,2-diamine and four equivalents of  $\text{NEt}_3$  in boiling hexane. 1,3,2-Diazaborolidines **4a–4e** were obtained as colorless microcrystalline air and moisture sensitive solids in 66–93% yield (Scheme 2).

Inspection of the  $^{11}\text{B}\{^1\text{H}\}$  NMR spectra of the novel 1,3,2-diazaboroles **3a–3d** ( $\delta^{11}\text{B} = 25.8\text{--}25.9$ ) and 1,3,2-diazaborolidines **4a–4e** ( $\delta^{11}\text{B} = 31.1\text{--}32.2$ ) show the expected shielding ( $\Delta\delta^{11}\text{B} = 5.3\text{--}6.1$ ) in going from the saturated heterocycles to the  $6\pi$ -heteroarenes. These data compare well with the chemical shift of the 2-phenyl-substituted diazaborole  $^1\text{BuNCH}=\text{CHN}(^1\text{Bu})\text{BPh}$  ( $\delta^{11}\text{B} = 26.4$ )<sup>12</sup> and those of the pair  $\text{MeN}-\text{CH}\equiv\text{CHN}(\text{Me})\text{BPh}$  ( $\delta^{11}\text{B} = 25.6$ ) and  $\text{MeNCH}_2\text{CH}_2\text{N}(\text{Me})\text{BPh}$  ( $\delta^{11}\text{B} = 32.2$ )<sup>13</sup> underlining the fact that the substitution pattern of the arene spacer has no influence on the chemical shift of the boron nuclei. In the  $^1\text{H}$  NMR spectra of the diazaboroles **3a–3d** the protons at the  $\text{C}=\text{C}$  double bond of the heterocycle were observed as singlets at  $\delta = 6.36\text{--}6.49$ , the corresponding carbon atoms in the  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum appeared as singlets at  $\delta = 112.8\text{--}113.0$ . In  $^1\text{BuNCH}\equiv\text{CHN}(^1\text{Bu})\text{BPh}$ , the corresponding singlets were registered at  $\delta^1\text{H} = 6.36$  and  $\delta^{13}\text{C} = 112.9$ . In the diazaborolidines **4a–4d** the NMR active nuclei of the  $\text{CH}_2\text{CH}_2$ -unit give rise to singlets at  $\delta^1\text{H} = 3.19\text{--}3.21$  and  $\delta^{13}\text{C} = 45.2\text{--}45.8$ . The donor/acceptor qualities of the boron containing substituents towards the central arene units are reflected to some extent in the  $^1\text{H}$  NMR- and  $^{13}\text{C}\{^1\text{H}\}$ -absorptions on the latter. It is obvious to compare the



4	n	isomer	R	X
a	2	1,4	<sup>t</sup> Bu	Br
b	2	1,3	<sup>t</sup> Bu	Br
c	3	1,3,5	<sup>t</sup> Bu	Br
e	2	1,3	Me	I



Scheme 2

data with corresponding resonances in precursors **1a–1d**. Note: For the assignments of  $^1\text{H}$  and  $^{13}\text{C}$  NMR resonances, a numbering scheme following the standard IUPAC nomenclature is employed, which is different from the atom labeling in the crystal structure analyses. In the  $^1\text{H}$  NMR spectra of the compounds **3a** and **4a** singlets at  $\delta = 7.57$  and  $7.45$  are attributed to the protons at C-2, C-3, C-5 and C-6. The corresponding signal in **1a** is markedly deshielded ( $\delta = 7.86$ ), indicating a considerably higher electron transfer from the boron containing substituents in **3a** and **4b** when compared to the dibromoboryl unit. In keeping with this the resonance for the atoms C-2, C-3, C-5 and C-6 in **3a** ( $\delta = 133.2$ ) and **4a** ( $\delta = 131.6$ ) are observed at higher field than in the  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of **1a** ( $\delta = 136.5$ ). This effect is even more pronounced in the series **1c**, **3c** and **4c**. In **1c** the protons in the positions 2,4,6 are responsible for a singlet at  $\delta = 9.03$  in the  $^1\text{H}$  NMR spectrum, this signal appears in **3c** at  $\delta = 7.37$  and **4c** at  $\delta = 7.45$ . The  $^{13}\text{C}\{^1\text{H}\}$  NMR spectra of **1c**, **3c** and **4c** show singlets at  $\delta = 151.4$ ,  $138.2$  and  $134.4$  ppm. Consistently the 4,4'-dibromoborylbiphenyl derivatives **1d**, **3d** and **4d** the protons in 3,3',5,5' positions experience chemical shifts of  $\delta = 8.11$ ,  $7.59$  and  $7.54$  whereas those in positions 2,2',6,6' are observed at  $7.23$ ,  $7.59$  and  $7.45$ . The  $^{13}\text{C}$  nuclei in the  $^{13}\text{C}\{^1\text{H}\}$  NMR spectra of **1d**, **3d** and **4d** are observed at  $\delta = 127.1$ ,  $125.8$  and  $126.0$  (C-2,2',6,6'),  $\delta = 138.6$ ,  $134.9$  and  $133.1$  (C-3,3',5,5') and  $\delta = 146.2$ ,  $139.9$  and  $139.9$  (C-1,1').

In line with literature reports the boron-bound *ipso*-aryl-C-atoms were not observed due to the coupling of the  $^{13}\text{C}$  nucleus with the quadrupole of the  $^{11}\text{B}$  nucleus.<sup>5,9,14</sup>

#### UV-Vis-, luminescence and electrochemical data

The bis(borolyl) systems **3a,b**, the bis(borolidinyl) derivatives **4a,b** and the bis(bromoboryl) species **1a,b** with a phenyl ring between each heterocyclic unit do not show luminescence. The UV-Vis maxima of these compounds range from  $245\text{ nm}$  to  $252\text{ nm}$ , whereas the UV-Vis absorption of **3c**, is shifted bathochromically to  $287\text{ nm}$  and exhibits a moderate blue luminescence at  $381\text{ nm}$

**Table 1** Photophysical data of **3c**, **1d**, **3d**, and **4d**

Compound	Solvent	Absorption ( $\lambda_{\text{max}}$ /nm)	Emission <sup>a</sup> ( $\lambda_{\text{max}}$ /nm)	Stokes shift ( $\lambda$ /nm)
<b>3c</b>	Hexane and thf	287	381	94
<b>1d</b>	Hexane	282	338	56
<b>1d</b>	thf	282	372	92
<b>3d</b>	Hexane	276	326	50
<b>3d</b>	thf	274	393	119
<b>4d</b>	Hexane	278	324	46
<b>4d</b>	thf	277	347	70

<sup>a</sup> [c] =  $1 \times 10^{-5}$  to  $1 \times 10^{-6}$  M l<sup>-1</sup>.

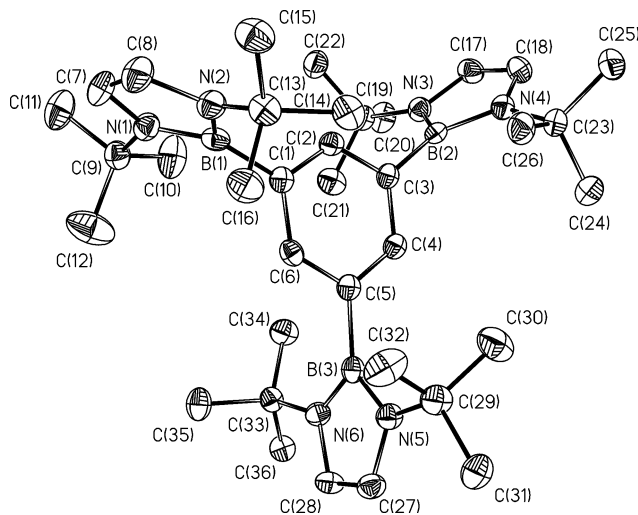
(Table 1). The position of the absorption band is independent of the solvent, but in ethereal solvents **3c** decomposes. The corresponding saturated tris(diazaborolidinyl)arene **4c** exhibits an absorption maximum at  $\lambda = 258$  nm and shows no luminescence in hexane, thf or dichloromethane. The optical behavior of the biphenyl-derivatives is much more pronounced. Compounds **1d**, **3d** and **4d**, display absorption peaks around 280 nm and a blue luminescence (Table 1). When the solvent is changed from hexane to thf, the emission band shifts to a longer wavelength, whereby this tendency is most evident for **3d** ( $\Delta\lambda = 67$  nm). The Stokes shifts range from 56 nm (**1d**) to 119 nm (**3d**) in thf. Generally this shift is less pronounced in hexane (Table 1). Such a solvatochromism can be rationalized by the stabilization of a polar excited state by the polar solvent.

Cyclic voltammograms for all compounds in this study except the dibromoboryl-precursors and compound **4c**, were recorded. It was expected that the cyclic voltammograms provide information on an electronical communication between the two boron-containing units. For this reason, compounds **3a**, **4a**, **3b**, **4b** were studied. All cyclic voltammograms show clear, irreversible oxidation signals; reductive experiments have not been successful. Generally, the unsaturated diazaboroles are about 250–300 mV easier to oxidize than the corresponding saturated rings. All potentials, detected by square wave techniques, are given in Table 2, where ferrocene/ferrocinium is used for standardization. The values for the first oxidation potentials vary from 168 mV for the phenylborole **3b** to 245 mV for **3d**. For the diazaborolidines, the potentials range from 329 mV for **4e** to 488 mV for the biphenyl-system **4d**. The oxidation potential of **4e** with methyl-groups at the nitrogen atoms, is significant lower (329 mV) than the potential of the corresponding borolidine **4b** with *tert*-butyl groups (458 mV). It was not possible to determine the potential of the tri-substituted diazaborolidinyl-arene **4c**, as this compound is not sufficiently soluble in dichloromethane or acetonitrile. If the borole- or borolidine-units are bridged by benzene, only one signal can be observed in the cyclic voltammograms and square wave voltammograms. This changes upon exchanging the benzene unit for the biphenyl system. **3d** and **4d** clearly

feature two signals (Table 2) with a difference of about 800 mV. The strong luminescence and electrochemical behavior may be taken as evidence for interaction and  $\pi$ -conjugation between the heterocycles. Unfortunately it was not possible to support this idea by X-ray-data.

### X-Ray crystallography

Compound **3c** (Fig. 1) adopts a paddle wheel structure, where the diazaborolyl-substituents B(1) to N(2), B(2) to N(4), B(3) to N(3) enclose dihedral angles of 89.9°, 104.1° and 87.1° with respect to the central arene unit. The boron–carbon distances B(1)–C(1) [1.578(2) Å], B(2)–C(3) [1.584(2) Å] and B(3)–C(5) [1.580(2) Å] are comparable to the B–C bond length in the borolyimidazolium cation **5** [1.580(11) Å].<sup>2d</sup> Atomic distances and valence angles within the diazaborol substituents are in good agreement with the corresponding data for cation **5**. Within the three rings the respective bonding parameters are identical with the threefold standard deviation and therefore average values are discussed. Thus the average B–N bond length [1.442(2) Å] indicates multiple bonding.

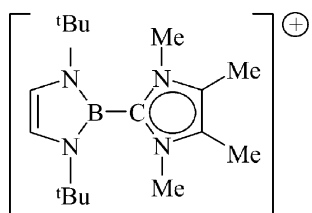


**Fig. 1** Molecular structure of **3c** in the crystal. Selected bond lengths [Å] and angles [°]: B(1)–N(1) 1.443(3), B(1)–N(2) 1.442(2), N(1)–C(7) 1.408(2), N(2)–C(8) 1.401(2), C(7)–C(8) 1.332(3), B(1)–C(1) 1.578(2), B(2)–N(3) 1.442(3), B(2)–N(4) 1.444(2), N(3)–C(17) 1.405(2), N(4)–C(18) 1.404(2), C(17)–C(18) 1.334(3), B(2)–C(3) 1.584(2), B(3)–N(5) 1.443(2), B(3)–N(6) 1.439(2), N(5)–C(27) 1.399(2), N(6)–C(28) 1.402(2), C(27)–C(28) 1.340 (3), B(3)–C(5) 1.580(2); N(1)–B(1)–N(2) 105.6(2), B(1)–N(1)–C(7) 106.9(2), B(1)–N(2)–C(8) 107.3(2), N(1)–C(7)–C(8) 110.2(2), N(2)–C(8)–C(7) 110.0(2), N(3)–B(2)–N(4) 105.8(1), B(2)–N(3)–C(17) 107.1(2), N(3)–C(17)–C(18) 109.9(2), B(2)–N(4)–C(18) 106.8(2), N(4)–C(18)–C(17) 110.4(2), N(5)–B(3)–N(6) 105.5(1), B(3)–N(5)–C(27) 107.4(2), B(3)–N(6)–C(28) 107.2(2), N(5)–C(27)–C(28) 109.7(2), N(6)–C(28)–C(27) 110.1(2).

**Table 2** First half-wave oxidation potential ( $E_{1/2}^{\text{oxid}}$ ) of **3a–3d** and **4a–4e** vs ferrocene/ferrocinium

Compound	<b>3a</b>	<b>3b</b>	<b>3c</b>	<b>3d</b>	<b>4a</b>	<b>4b</b>	<b>4c</b>	<b>4d</b>	<b>4e</b>
Oxidation potential <sup>a</sup> /mV	180	168	198	245, 1066	468	458	—	488, 1278	329

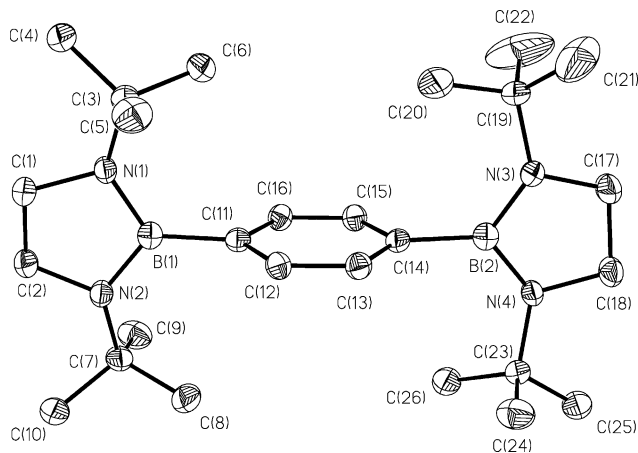
<sup>a</sup> The determinations were performed in a 0.1 M solution of TBAPF in CH<sub>2</sub>Cl<sub>2</sub> with concentrations of analyte of ca.  $1 \times 10^{-4}$  M at RT.



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In a series of diazaboroles the boron–nitrogen bond lengths range from 1.407(3) to 1.450(2) Å. The atomic distances C=C [av. 1.335(3) Å] and the N–C(sp<sup>2</sup>) bond lengths [av. 1.403(2) Å] also indicate multiple bonding. For the exocyclic N(sp<sup>2</sup>)–C(sp<sup>3</sup>) bonds average bond lengths of 1.486(2) Å are measured. The average endocyclic angles in **3c** N–B–N [105.6(1)°], B–N–C [107.1(2)°] and N–C–C [110.0(2)°] resemble those in **5** [105.9(4)°, 107.1(6)° and 110.5(3)°]. Due to steric congestion the exocyclic angles B–N–C(sp<sup>3</sup>) [av. 131.3(1)°] are significantly widened as compared to angles C(sp<sup>3</sup>)–N–C(sp<sup>2</sup>) [av. 120.9(1)°].

In the solid state compound **4a** (Fig. 2) is not planar. Instead the best planes through atoms N(1)–B(1)–N(2)–C(1)–C(2) (mean deviation = 0.0914 Å) and N(3)–B(2)–N(4)–C(17)–C(18) (mean deviation 0.0896 Å) are oriented nearly perpendicularly with regard to the central arene moiety (dihedral angles 89.5°, 93.5°).

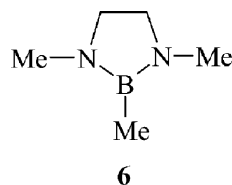


**Fig. 2** Molecular structure of **4a** in the crystal. Selected bond lengths [Å] and angles [°]: B(1)–N(1) 1.435(2), B(1)–N(2) 1.433(2), B(1)–C(11) 1.574(2), N(1)–C(1) 1.470(2), N(2)–C(2) 1.469(2), C(1)–C(2) 1.521(2), B(2)–N(3) 1.429(2), B(2)–N(4) 1.440(2), B(2)–C(14) 1.579(2), N(3)–C(17) 1.465(2), N(4)–C(18) 1.467(2), C(17)–C(18) 1.511(2); N(2)–B(1)–N(1) 109.1(1), B(1)–N(1)–C(1) 107.9(1), B(1)–N(2)–C(2) 108.1(1), N(1)–C(1)–C(2) 104.5(1), C(1)–C(2)–N(2) 104.6(1), N(3)–B(2)–N(4) 108.6(1), B(2)–N(3)–C(17) 108.4(1), B(2)–N(4)–C(18) 108.0(1), N(3)–C(17)–C(18) 104.7(1), C(17)–C(18)–N(4) 104.6(1).

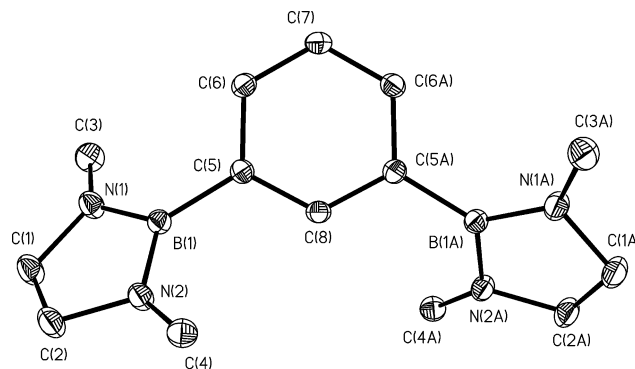
Again the structural parameters within both rings do not differ significantly and average values are discussed. The B–N bond lengths [1.429(2)–1.440(2) Å, av. 1.434(2) Å] are slightly shorter (although not significantly) than those in the unsaturated rings of **3c**. The endocyclic N–C bond lengths **4a** [1.465(2)–1.470(2) Å, av. 1.468(2) Å] are longer than in the tris(diazaboroly)benzene **3c** [av. 1.403(2) Å]. The endocyclic carbon–carbon bond lengths [1.511(2) and 1.521(2) Å] are in the range of single bonds for **4a**. The angles N–B–N in **4a** [108.6(1) and 109.1(1)°] are markedly

obtuse in comparison to those in the unsaturated rings in **3c** [av. 105.6(1)°]. The endocyclic angles B–N–C [av. 108.1(1)°], however, are close to those in **3c** [av. 107.1(2)°]. The data resemble those previously determined in diazaborolidine **6** (B–N 1.423(2) Å, C–N<sub>endo</sub> 1.461(1) av. Å, C–C 1.535(2) Å, N–B–N 107.8(1)°, B–N–C 110.1(1)°).<sup>15</sup>

In compound **4e** (Fig. 3) atoms C(7) and C(8) are located on a twofold axis. The heterocycles are not completely planar (sum of angles 536.7°; mean deviation from best plane 0.0686 Å) and enclose angles of 45.5° with the central arene unit. Bonding parameters within the diazaborolidine ring [av. B–N 1.422(1) Å av. C–N 1.464(1) Å and C–C 1.537(1) Å, N–B–N 108.5(1)°, B–N–C av. 109.3(1)°, N–C–C 104.2°] resemble those in **4a** and **6**.



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**Fig. 3** Molecular structure of **4e** in the crystal. "A" letters in the atom labels indicate atoms at equivalent position ( $-x, y, 1/2 - z$ ). Selected bond lengths [Å] and angles [°]: B(1)–N(1) 1.420(1), B(1)–N(2) 1.425(1), N(1)–C(1) 1.463(1), N(2)–C(2) 1.465(1), C(1)–C(2) 1.537(1), B(1)–C(5) 1.567(1); N(1)–B(1)–N(2) 108.5(1), B(1)–N(1)–C(1) 109.9(1), B(1)–N(2)–C(2) 109.5(1), N(1)–C(1)–C(2) 104.3(1), N(2)–C(2)–C(1) 104.5(1).

## Conclusions

We have extended methodologies for the synthesis of 1,3,2-diazaboroles to the construction of bis- and tris-(1,3,2-diazaboroly)benzenes and -biphenyls. Moreover the corresponding 1,3,2-diazaborolidine functionalized arenes have been prepared by established routes. X-Ray structure analyses show that the heterocycles are twisted out of the plane of the arene core in the crystal, thus preventing significant electronic communication by  $\pi$ -electron delocalization. In keeping with this, with the exception of 4,4'-bis-1,3,2-diazaborolybiphenyl, only one oxidative wave was observed by cyclic voltammetry. In the case of the biphenyl derivative, however, two discrete and well separated irreversible waves are in agreement with an electronic communication between both substituents *via* the  $\pi$ -system of the spacer. Interestingly, this compound, like 4,4'-bis(dibromoboryl)biphenyl, is strongly luminescent and emits blue light. This observation challenges us

to look for other spacer systems *e.g.* oligothiophenes, which are essential building units in light emitting materials. Work in this direction is underway and first results will be published in due course.

## Experimental

### General procedures

All manipulations were performed under an atmosphere of dry argon using standard Schlenk techniques. All solvents were dried by standard methods and freshly distilled prior use. The compounds 1,4-bis(dibromoboryl)benzene,<sup>9</sup> 1,3-bis(dibromoboryl)benzene,<sup>9</sup> 1,3-bis(diiodoboryl)benzene,<sup>11</sup> 1,3,5-tris(dibromoboryl)benzene,<sup>9</sup> 4,4'-bis(dibromoboryl)-biphenyl<sup>9</sup> and 'BuN=CH–CH=N'Bu<sup>10</sup> were prepared according to literature methods. MeN(H)CH<sub>2</sub>CH<sub>2</sub>N(H)Me and 'BuN(H)CH<sub>2</sub>CH<sub>2</sub>N(H)'Bu were purchased from commercial sources. NMR spectra were recorded in C<sub>6</sub>D<sub>6</sub> at room temperature on a Bruker AM Avance DRX 500 (<sup>1</sup>H, <sup>11</sup>B, <sup>13</sup>C) spectrometer using SiMe<sub>4</sub> and BF<sub>3</sub>·OEt<sub>2</sub> as external standards. Mass spectra were taken with a VG Autospec sector field mass spectrometer (Micromass). The UV-Vis spectra were recorded on a Perkin Elmer UV Win Lab spectrometer and the emission spectra on a Perkin Elmer Luminescence Spectrometer. The electrochemical experiments were performed with a PAR Model 270A instrument and the relevant software (Model 270). A system of microelectrodes with a three-electrode array was used. A platinum wire (1.5 cm length, 0.5 mm diameter) that was wound around the counter electrode served as working electrode. A silver wire (1.5 cm length, 1.0 mm diameter) served as a pseudo-reference electrode. All experiments were conducted in a glass device, which was flame-dried prior to use and filled with dry argon. The cyclic voltammograms were recorded with scan rates of 5–700 mV s<sup>-1</sup>. All published potentials were confirmed by square-wave voltammetry (frequency: 5 Hz). The oxidation potentials were referenced *versus* the ferrocene/ferrocinium couple (*E*<sub>ox</sub> = 0 eV).

### Preparations

**General procedure for bis- and tris-(diazaborolyl)arenes 3a–3d.** Solutions of 1 mmol of **1a**, **1b** or **1d** and 2 mmol of glyoxal-bis(*tert*-butyl)imine each in 50 mL of hexane were added dropwise and simultaneously within 1.5 h into a flask of hexane (50 mL). Similarly, solutions of **1c** (1 mmol) and glyoxal-bis(*tert*-butyl)imine (3 mmol), each in 50 mL of hexane, were combined. Borolium salts **2a–2d** separated as orange-yellow precipitates, which were filtered off and washed with hexane (3 × 20 mL). Slurries of the salts in 150 mL hexane were combined with an excess of 1% sodium amalgam and the mixture was vigorously stirred for 12 h at room temperature. The supernatant yellow solutions were decanted, filtered and concentrated until the onset of crystallization. Storage of the concentrates at –30 °C for 12 h afforded analytically pure **3a**, **3b** and **3d** as colorless needles. Compound **3c** was recrystallized twice from toluene to yield colorless crystals.

**3a.** 69% yield, found: C, 71.76; H, 10.50; N, 12.68; C<sub>26</sub>H<sub>44</sub>B<sub>2</sub>N<sub>4</sub> requires C, 71.91; H, 10.21; N, 12.90%. <sup>1</sup>H NMR: δ 1.26 [s, 36 H, 'Bu], 6.45 [s, 4 H, NCH], 7.57 [s, 4 H, aryl]. <sup>13</sup>C{<sup>1</sup>H} NMR: δ 32.6 [s, C(CH<sub>3</sub>)<sub>3</sub>], 53.3 [s, C(CH<sub>3</sub>)<sub>3</sub>], 113.0 [s, NCH], 133.2 [s, CH-aryl]. <sup>11</sup>B{<sup>1</sup>H} NMR: δ 25.9 (s). MS/EI (70 eV): *m/z* = 434 [M<sup>+</sup>, 100%].

**3b.** 83% yield, found: C, 71.61; H, 10.33; N, 13.21; C<sub>26</sub>H<sub>44</sub>B<sub>2</sub>N<sub>4</sub> requires C, 71.91; H, 10.21; N, 12.90%. <sup>1</sup>H NMR: δ 1.26 [s, 36 H, 'Bu], 6.47 [s, 4 H, NCH], 7.48 [t, 1 H, <sup>3</sup>J<sub>H,H</sub> = 7.4 Hz, aryl], 7.82 [d, <sup>3</sup>J<sub>H,H</sub> = 7.4 Hz, 2 H, aryl], 8.10 [s, 1 H, aryl]. <sup>13</sup>C{<sup>1</sup>H} NMR: δ 32.8 [s, C(CH<sub>3</sub>)<sub>3</sub>], 52.9 [s, C(CH<sub>3</sub>)<sub>3</sub>], 112.7 [s, NCH], 127.9 [s, C-5], 132.8 [s, C-4,-6], 138.0 [s, C-2]. <sup>11</sup>B{<sup>1</sup>H} NMR: δ 25.8 (s). MS/EI (70 eV): *m/z* = 434 [M<sup>+</sup>, 100%], 419 [M<sup>+</sup> – CH<sub>3</sub>, 100%].

**3c.** 73% yield, C<sub>36</sub>H<sub>63</sub>B<sub>3</sub>N<sub>6</sub> requires C, 70.59, H, 10.37, N, 13.72%. The great sensitivity towards temperature, air and moisture precluded reliable elemental analyses. <sup>1</sup>H NMR: δ 1.30 [s, 54 H, 'Bu], 6.49 [s, 6 H, NCH], 7.73 [s, 3 H, aryl]. <sup>13</sup>C{<sup>1</sup>H} NMR: δ 33.0 [s, C(CH<sub>3</sub>)<sub>3</sub>], 53.3 [s, C(CH<sub>3</sub>)<sub>3</sub>], 112.8 [s, NCH], 138.2 [s, CH-aryl]. <sup>11</sup>B{<sup>1</sup>H} NMR: δ 25.8 (s). MS/EI (70 eV): *m/z* = 612 [M<sup>+</sup>, 100%].

**3d.** 69% yield, found: C, 75.08; H, 9.41; N, 11.06; C<sub>32</sub>H<sub>48</sub>B<sub>2</sub>N<sub>4</sub> requires C, 75.30; H, 9.48; N, 10.98%. <sup>1</sup>H NMR: δ 1.26 [s, 36 H, 'Bu], 6.48 [s, 4 H, NCH], 7.49 [m, 4 H, aryl], 7.54 [m, 4 H, aryl]. <sup>13</sup>C{<sup>1</sup>H} NMR: δ 32.6 [s, C(CH<sub>3</sub>)<sub>3</sub>], 53.3 [s, C(CH<sub>3</sub>)<sub>3</sub>], 112.9 [s, NCH], 125.8 [s, C-2,2',-6,6'], 134.9 [s, C-3,3',-5,5'], 139.9 [s, C-1,1']. <sup>11</sup>B{<sup>1</sup>H} NMR: δ 25.9 (s). MS/EI (70 eV): *m/z* = 510 [M<sup>+</sup>, 100%].

### General procedure for bis- and tris-(diazaborolidinyl)arenes 4a–4d.

Solutions of 1 mmol of the bis(dibromoboryl)arenes **1a** and **1b** in 50 mL of hexane or **1d** in 50 mL of toluene were added dropwise to a chilled solution (0 °C) of triethylamine (4 mmol) in 100 mL hexane (for **1a,b**) or toluene (**1d**) whereby colorless solids precipitated. Subsequently the mixtures were warmed to 20 °C before 2 mmol of neat 1,2-bis(*tert*-butylamino)ethane were added. Analogously the solution of 1 mmol of **1c** in 50 mL of toluene was combined with 6 mmol of NEt<sub>3</sub> and 3 mmol of 'Bu(H)NCH<sub>2</sub>CH<sub>2</sub>N(H)'Bu. The resulting mixtures were heated under reflux for 3 h, cooled down to room temperature and filtered. The filtrates were concentrated until the onset of crystallization, and then stored at –30 °C for 12 h to afford **4a–4d** as colorless needles. Products **4c** and **4d** were recrystallized twice from toluene.

**4a.** 66% yield, found: C, 71.24; H, 11.04; N, 12.78; C<sub>26</sub>H<sub>44</sub>B<sub>2</sub>N<sub>4</sub> requires C, 71.25; H, 11.12; N, 12.78%. <sup>1</sup>H NMR: δ 1.09 [s, 36 H, 'Bu], 3.19 [s, 8 H, NCH<sub>2</sub>], 7.45 [s, 4 H, aryl]. <sup>13</sup>C{<sup>1</sup>H} NMR: δ 31.0 [s, C(CH<sub>3</sub>)<sub>3</sub>], 45.2 [s, NCH<sub>2</sub>], 51.9 [s, C(CH<sub>3</sub>)<sub>3</sub>], 131.6 [s, CH-aryl]. <sup>11</sup>B{<sup>1</sup>H} NMR: δ 31.8 (s). MS/EI (70 eV): *m/z* = 438 [M<sup>+</sup>, 5%], 432 [M<sup>+</sup> – CH<sub>3</sub>, 100%].

**4b.** 78% yield, found: C, 71.29; H, 11.16; N, 12.53; C<sub>32</sub>H<sub>48</sub>B<sub>2</sub>N<sub>4</sub> requires C, 71.25; H, 11.12; N, 12.78%. <sup>1</sup>H NMR: δ 1.09 [s, 36 H, 'Bu], 3.20 [s, 8 H, NCH<sub>2</sub>], 7.17 [t, <sup>3</sup>J<sub>H,H</sub> = 7.1 Hz, 1 H, aryl], 7.33 [d, <sup>3</sup>J<sub>H,H</sub> = 7.1 Hz, 2 H, aryl], 7.57 [s, 1 H, aryl]. <sup>13</sup>C{<sup>1</sup>H} NMR: δ 31.2 [s, C(CH<sub>3</sub>)<sub>3</sub>], 45.2 [s, NCH<sub>2</sub>], 51.9 [s, C(CH<sub>3</sub>)<sub>3</sub>], 126.5 [s, C-5], 130.9 [s, C-4,-6], 138.0 [s, C-2]. <sup>11</sup>B{<sup>1</sup>H} NMR: δ 32.2 (s). MS/EI (70 eV): *m/z* = 438 [M<sup>+</sup>, 10%], 432 [M<sup>+</sup> – CH<sub>3</sub>, 100%].

**82%** yield, found: C, 69.85; H, 11.27; N, 13.50; C<sub>38</sub>H<sub>68</sub>B<sub>3</sub>N<sub>6</sub> requires C, 69.92; H, 11.25; N, 13.58%. <sup>1</sup>H NMR: δ 1.14 [s, 54 H, 'Bu], 3.21 [s, 12 H, NCH<sub>2</sub>], 7.45 [s, 3 H, aryl]. <sup>13</sup>C{<sup>1</sup>H} NMR: δ 30.3 [s, C(CH<sub>3</sub>)<sub>3</sub>], 45.3 [s, NCH<sub>2</sub>], 51.9 [s, C(CH<sub>3</sub>)<sub>3</sub>], 134.4 [s, C-2,-4,-6]. <sup>11</sup>B{<sup>1</sup>H} NMR: δ 31.1 (s). MS/EI (70 eV): *m/z* = 618 [M<sup>+</sup>, 11%], 603 [M<sup>+</sup> – CH<sub>3</sub>, 100%].

**4d.** 92% yield, found: C, 74.50; H, 10.33; N, 10.88; C<sub>32</sub>H<sub>48</sub>B<sub>2</sub>N<sub>4</sub> requires C, 74.72; H, 10.19; N, 10.89%. <sup>1</sup>H NMR: δ 1.08 [s, 36 H, 'Bu], 3.21 [s, 8 H, NCH<sub>2</sub>], 7.45 [d, <sup>3</sup>J<sub>H,H</sub> = 7.9 Hz, 4 H, aryl], 7.54 [d, <sup>3</sup>J<sub>H,H</sub> = 7.9 Hz, 4 H, aryl]. <sup>13</sup>C{<sup>1</sup>H} NMR: δ 31.0 [s, C(CH<sub>3</sub>)<sub>3</sub>],

**Table 3** Crystallographic data for compounds **3c**, **4a**, and **4e**

Compound	<b>3c</b>	<b>4a</b>	<b>4e</b>
Empirical formula	C <sub>36</sub> H <sub>63</sub> B <sub>3</sub> N <sub>6</sub>	C <sub>26</sub> H <sub>48</sub> B <sub>2</sub> N <sub>4</sub>	C <sub>14</sub> H <sub>24</sub> B <sub>2</sub> N <sub>4</sub>
Color	Colorless	Colorless	Colorless
Size/mm	0.22 × 0.12 × 0.10	0.30 × 0.30 × 0.10	0.30 × 0.30 × 0.20
<i>M</i>	612.35	438.30	269.99
Space group	<i>P</i> 2 <sub>1</sub> / <i>n</i>	<i>P</i> 2 <sub>1</sub> / <i>c</i>	<i>C</i> 2/ <i>c</i>
Crystal system	Monoclinic	Monoclinic	Monoclinic
<i>a</i> /Å	10.7200(3)	10.5590(3)	15.3070(3)
<i>b</i> /Å	16.2980(5)	26.7150(10)	6.9600(2)
<i>c</i> /Å	21.5920(5)	10.7350(4)	14.7780(3)
$\beta$ /°	93.2260(16)	114.7080(19)	101.0520(15)
<i>V</i> /Å <sup>3</sup>	3766.46(18)	2750.94(16)	1545.20(6)
<i>Z</i>	4	4	4
<i>d</i> <sub>calcd</sub> /g cm <sup>-3</sup>	1.080	1.058	1.161
<i>F</i> (000)	1344	968	584
$\mu$ /mm <sup>-1</sup>	0.063	0.061	0.069
$\theta$	3.03 to 27.51	3.05 to 27.49	3.23 to 30.00
<i>T</i> /K	95	100	100
Refl. measured	60255	29214	17028
Unique refl.	8615	6275	2239
<i>R</i> (int)	0.118	0.061	0.032
No. refl. ( <i>I</i> ) > 2 $\sigma$ ( <i>I</i> )	4782	3775	1962
Refined parameters	424	301	95
<i>R</i> ( <i>I</i> > 2 $\sigma$ ( <i>I</i> ))	<i>R</i> 1 = 0.0534; <i>wR</i> 2 = 0.1060	<i>R</i> 1 = 0.0531; <i>wR</i> 2 = 0.1249	<i>R</i> 1 = 0.0392; <i>wR</i> 2 = 0.1048
<i>R</i> indices (all data)	<i>R</i> 1 = 0.1212; <i>wR</i> 2 = 0.1256	<i>R</i> 1 = 0.1036; <i>wR</i> 2 = 0.1437	<i>R</i> 1 = 0.0452; <i>wR</i> 2 = 0.1086
$\Delta\rho$ max, min/Å <sup>-3</sup>	0.189, -0.198	0.252, -0.208	0.346, -0.160

45.2 [s, NCH<sub>2</sub>], 51.9 [s, C(CH<sub>3</sub>)<sub>3</sub>], 126.0 [s, C-2,2',-6,6'], 133.1 [s, C-3,3',-5,5'], 139.6 [s, C-1,1']. <sup>11</sup>B{<sup>1</sup>H} NMR:  $\delta$  32.0 (s). MS/EI (70 eV): *m/z* = 514 [M<sup>+</sup>, 9%], 499 [M<sup>+</sup> - CH<sub>3</sub>, 100%].

**1,3-{MeN(CH<sub>2</sub>CH<sub>2</sub>N(Me)B)}<sub>2</sub>C<sub>6</sub>H<sub>4</sub> (**4e**).** As described before a cold hexane solution (100 mL, 0 °C) of 4 mmol triethylamine was combined with 30 mL of a hexane solution of 1 mmol of 1,3-bis(diiodoboryl)benzene (**1e**). After 30 min the mixture was warmed up to 20 °C and then treated with 2 mmol neat *N,N'*-dimethylethylene-1,2-diamine. It was heated to 80 °C for 3 h, filtered and the filtrate was evaporated to dryness. A colorless oil was distilled at 1 × 10<sup>-5</sup> bar to give 91% of pure **4e** as a colorless oil (boiling range 110–120 °C). Crystals of the product were grown from a 1 : 1 hexane–pentane mixture at -30 °C.

**4e.** 91% yield, found: C, 61.89; H, 8.67; N, 20.27; C<sub>14</sub>H<sub>24</sub>B<sub>2</sub>N<sub>4</sub> requires C, 62.28; H, 8.96; N, 20.75%, <sup>1</sup>H NMR:  $\delta$  2.65 [s, 6 H, CH<sub>3</sub>], 3.07 [s, 4 H, NCH<sub>2</sub>], 7.43 [t, <sup>3</sup>*J*<sub>H,H</sub> = 7.6 Hz, 1 H, aryl], 7.61 [d, <sup>3</sup>*J*<sub>H,H</sub> = 7.6 Hz, 2 H, aryl], 7.89 [s, 1 H, aryl]. <sup>13</sup>C{<sup>1</sup>H} NMR:  $\delta$  34.4 [s, NCH<sub>3</sub>], 51.9 [s, NCH<sub>2</sub>], 129.9 [s, C-5], 133.5 [s, C-4,-6], 138.8 [s, C-2]. <sup>11</sup>B{<sup>1</sup>H} NMR:  $\delta$  32.0 (s). MS/EI (70 eV): *m/z* = 438 [M<sup>+</sup>, 10%], 432 [M<sup>+</sup> - CH<sub>3</sub>, 100%].

### X-Ray crystallography

X-Ray quality crystals of **3c**, **4a** and **4e** were grown from hexane solutions at -30 °C. Details of the crystal structure analyses are summarized in Table 3.

CCDC reference numbers 287003–287005.

For crystallographic data in CIF or other electronic format see DOI: 10.1039/b514920g

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