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Synthetic, Structural, Photophysical and Computational Studies on π-Conjugated 1,3,2-Benzodiazaboroles with Carbazole Building Blocks

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The reaction of the *N*-lithiated 3,6-di-*tert*-butyl-carbazole (**2**) with 2-bromo-1,3-diethyl-1,3,2-benzodiazaborole (**1a**) and 2-bromo-1,3-diphenyl-1,3,2-benzodiazaborole (**1b**) afforded the 2-*N*-carbazolyl-functionalized benzodiazaboroles **3a** and **3b** as colourless solids in 77 and 73% yield, respectively. Synthesis of 2[5′-*N*-carbazolyl-2′-thienyl]-1,3-diethyl-1,3,2-benzodiazaborole (**5a**) was effected by lithiation of *N*-(2-thienyl)carbazole (**4**) and subsequent reaction with equimolar amounts of **1a**, and **5a** was obtained in 68% yield. Similarly, 2[5′-*N*-carbazolyl-2′-thienyl]-1,3-diphenyl-1,3,2-benzodiazaborole (**5b**) was prepared from lithiated **4** and **1b** in 62% yield. Compounds **3a**,**b** and **5a**,**b** are characterized by elemental analyses, IR and NMR spectroscopy (^{1}H, ^{11}B, ^{13}C) and mass spectrometry. The molecular structures of **3a** and **5a** were elucidated by X-ray diffraction analysis. These borylated systems show intense blue luminescence. The spectroscopic results were reproduced by TD-DFT calculations at the [B3LYP/6-311G (d,p)] level of theory.

Introduction

Conjugated molecules and polymers containing three-coordinate boron have attracted considerable current interest because of their optical and electronic properties, which make them appropriate for use in functional materials.[1] Three-coordinate boron generally behaves as a π acceptor as a result of its vacant p_z orbital, which stabilizes the LUMO of an adjacent conjugated π-electron system and thus lowers the HOMO–LUMO gap of these molecules. The dimesitylboryl ($BMes_2$) moiety (Mes = 2,4,6-$Me_3C_6H_2$) is the most prominent substituent in which the unsaturated boron centre is stabilized by the steric effects of the *ortho*-methyl groups. Such materials exhibit sizeable second- and third-order nonlinear optic (NLO) coefficients[2,3] and large two-photon absorption (TPA) cross-sections[4] and can be used as efficient electron-transporting and/or emitting layers in organic light-emitting diodes (OLEDs)[5] or as sensors for fluoride ions.[6] Recently, a number of conjugated molecules with boryl side-groups that show very large Stokes shifts and high quantum yields have been synthesized.[7] At Bielefeld we have a long-standing interest in the chemistry of 1,3,2-diazaboroles.[8,9] We carried out studies on the syntheses and optical properties of extended π-conjugated systems with 1,3,2-diazaborolyl- and 1,3,2-benzodiazaborolyl ligands. We recently reported on the syntheses, photophysical properties and computational studies of benzene, diphenyl, 1,3,5-triphenylbenzene, thiophene and dithiophene cores that are functionalized by one, two or three 1,3,2-benzodiazaborole units.[10] This study was extended to 2-arylalkynyl-1,3,2-benzodiazaboroles, 2-(4′-X-$C_6H_4C{\equiv}C$)-1,3-Et_2-1,3,2-$N_2BC_6H_4$ (X = -H, -Me, -MeO, -MeS, Me_2N).[11] These borolylated systems show intense blue/violet luminescence with Stokes shifts up to 9500 cm^{-1} and quantum yields from 0.33 to 0.99. According to TD-DFT calculations, the HOMO–LUMO transitions in the UV/Vis spectra are assigned to π(diazaborolyl)–π*(thiophene/arene) transitions.[10,11] Herein we report the syntheses, photophysical properties and computational studies of 1,3,2-benzodiazaboroles with carbazole and 5′-carbazolyl-2′-thienyl substituents at the boron atom. The possibility of a push–pull interaction between the carbazole nitrogen atom and the borole was of particular interest.

Results and Discussion

Reaction of 2-bromo-1,3-diethyl-1,3,2-benzodiazaborole (**1a**)[12] with a slight excess of in situ generated *N*-lithiated 3,6-di-*tert*-butylcarbazole (**2**)[13] in *n*-pentane at room temperature led to the generation the 2-*N*-carbazolyl-1,3-diethylbenzodiazaborole (**3a**) as a colourless solid in 77% yield. Similarly, the analogous 2-*N*-carbazolyl-1,3-diphenyl-1,3,2-benzodiazaborole (**3b**) was synthesized as a colourless solid in 73% yield (Scheme 1).

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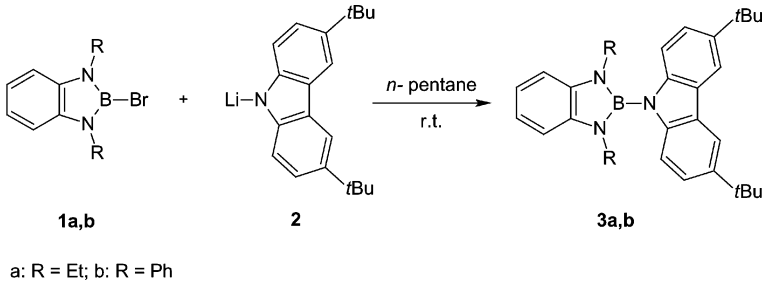
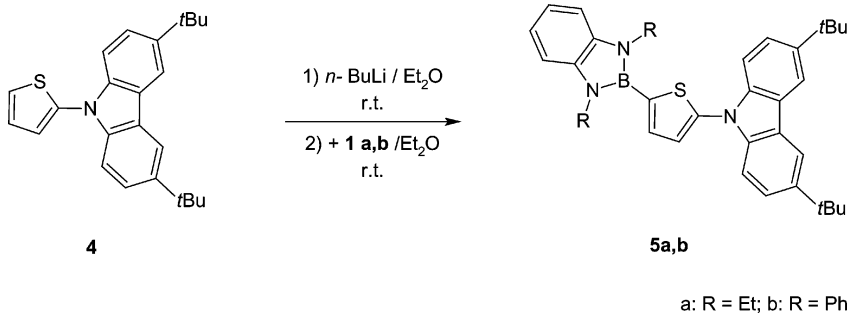


Scheme 1. Syntheses of benzodiazaboroles **3a**,**b**.



Scheme 2. Syntheses of 1,3,2-benzodiazaboroles **5a**,**b**.

In the next step the influence of a π-conducting spacer between the electron-accepting benzodiazaborole unit and the electron-donating carbazole system was investigated. Thiophene was selected as a bridging π spacer because in the UV/Vis and fluorescence spectra of known thienyldiazaboroles, significant bathochromic shifts were observed.[10] Moreover, the incorporation of thienyl fragments usually improves the thermostability of 1,3,2-diazaboroles. The synthesis of 2[5′-*N*-carbazolyl-2-thienyl]-1,3-diethylbenzodiazaborole (**5a**) (Scheme 2) was effected by lithiation of (2-thienyl)carbazole (**4**)[14] with *n*-butyllithium in ethyl ether at 20 °C and subsequent treatment of the reaction mixture with an equimolar amount of 2-bromo-1,3-diethyl-1,3,2-benzodiazaborole (**1a**).

Solid colourless **5a** was isolated from the reaction residue by *n*-hexane extraction and crystallization at 4 °C for 3 d (yield: 68%). Similarly, reaction between lithiated thienylcarbazole **4** and **1b** afforded **5b**, which crystallized from the *n*-pentane extracts of the reaction residue as an off-white solid in 60% yield. All the compounds synthesized here are air- and moisture sensitive. They can be stored at –5 °C under an argon atmosphere for several weeks without decomposition. In contrast to this, **5b** slowly decomposed at room temperature. Derivatives **3a**,**b** and **5a**,**b** are very soluble in the common aprotic organic solvents with the exception of alkanes (i.e. C_6H_6, $C_6H_5CH_3$, $CHCl_3$, CH_2Cl_2, thf, Et_2O). In the $^{11}B\{^1H\}$NMR spectra of the 1,3,2-benzodiazaboroles **3a** and **3b** ($CDCl_3$), singlets were observed at δ = 24.6 and 25.6 ppm, in agreement with the a singlet at δ = 23.1 ppm (C_6D_6) reported for **6**.[12]

The $^{11}B\{^1H\}$NMR resonance of compound **5a** (δ = 25.8 ppm) is slightly shifted relative to those of thiophene-functionalized 1,3,2-benzodiazaboroles **7** (δ = 26.2 ppm) and **8** (δ = 26.6 ppm).[10a] The $^{11}B\{^1H\}$NMR spectrum of **5b** is characterized by a singlet at δ = 21.3 ppm (Figure 1).

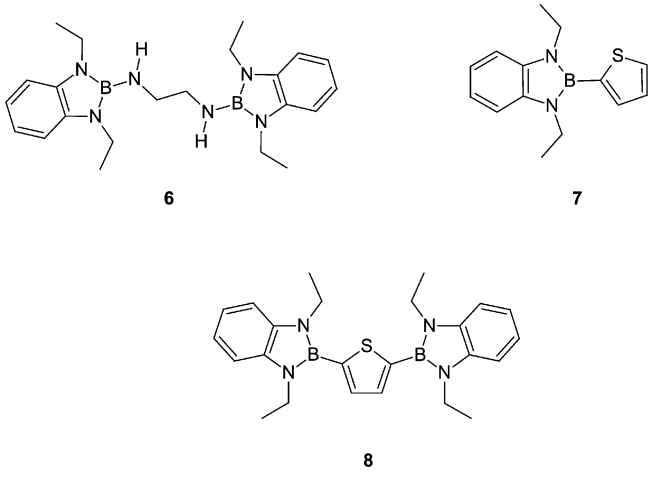


Figure 1. Compounds **6**–**8**.

X-ray Structural Analysis of 3a

Single crystals of **3a**, suitable for an X-ray structural study (Table 7), were grown from an *n*-pentane solution at –20 °C. They crystallize in space group $P2_1$ despite the fact that the structure is nearly centrosymmmetric, but the re-

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finement in the space group $P2_1/a$ leads to poor results. The asymmetric unit contains four independent molecules (**I**–**IV**), which differ significantly in the mutual orientation of the ring planes (Supporting Information). As bond lengths and bond angles are identical within the threefold standard deviation, only conformer **I** is discussed in more detail (Figure 2).

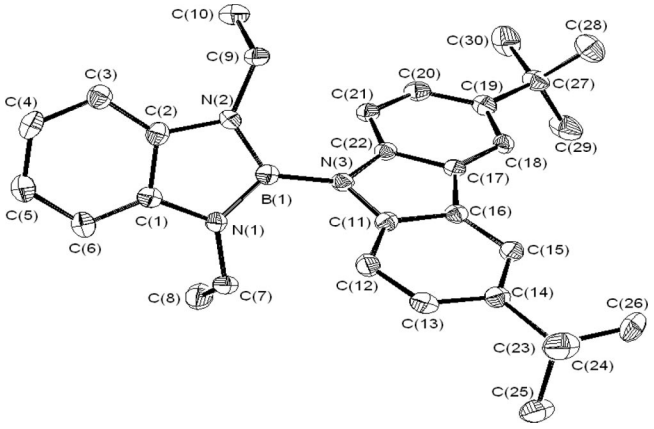

Figure 2. Molecular structure of **3a** (conformer **I**) in the crystal. Selected bond lengths [Å] and angles [°]: B(1)–N(1) 1.438(6), B(1)–N(2) 1.422(5), B(1)–N(3) 1.457(5), N(1)–C(1) 1.399(5), N(1)–C(7) 1.456(5), N(2)–C(2) 1.406(5), N(2)–C(9) 1.477(5), N(3)–C(11) 1.404(5), C(1)–C(2) 1.415(6), N(3)–C(22) 1.402(5), C(11)–C(16) 1.396(6), C(17)–C(22) 1.407(5), C(16)–C(17) 1.443(6). N(2)–B(1)–N(1) 107.2(3), N(2)–B(1)–N(3) 127.2(4), N(1)–B(1)–N(3) 125.5(4), C(1)–N(1)–B(1) 107.9(3), B(1)–N(1)–C(7) 129.8(3), C(2)–N(2)–B(1) 108.0(3), B(1)–N(2)–C(9) 130.4(3), N(1)–C(1)–C(2) 108.4(3), N(2)–C(2)–C(1) 108.4(3), B(1)–N(3)–C(11) 126.0(3), B(1)–N(3)–C(22) 127.4(3), N(3)–C(11)–C(16) 110.1(3), N(3)–C(22)–C(17) 110.0(3), C(11)–N(3)–C(22) 106.5(3), C(11)–C(16)–C(17) 107.0(3), C(16)–C(17)–C(22) 106.3(3).

The molecule is constructed of a planar 1,3,2-benzodiazaborole ring and a planar carbazole ring, which are connected by a B(1)–N(3) bond of 1.457(5) Å. In the remaining conformers B–N bond lengths of 1.472(6) (**II**), 1.471(5) (**III**) and 1.470(5) Å (**IV**) [av. 1.468(6) Å] are measured. For the average bond length in a sterically unhindered acyclic aminoborane, a value of 1.41 Å is given in the literature.[15a] A particularly short BN double bond was encountered in $(CF_3)_2B{=}N(iPr)_2$ [1.37(1) Å].[15b] Obviously in **3a** an optimal π conjugation within this unit is prevented by the nonplanar orientation of both ring fragments, which enclose dihedral angles of 55.9 (**I**), 75.5 (**II**), 57.2 (**III**) and 77.7° (**IV**) (av. 66.6°). The endocyclic B–N distances [B(1)–N(1) 1.438(6), B(1)–N(2) 1.422(5) Å] fall in the upper region of such values in monocyclic 1,3,2-diazaboroles [1.395(7)–1.450(2) Å][16] and are similar to such bond lengths in compound **9** [1.438(1), 1.440(1) Å].[12] The endocyclic bond lengths N(1)–C(1) [1.399(5) Å] and N(2)–C(2) [1.406(5) Å] also resemble those in **9** [1.398(1), 1.394(1) Å] and are typical for 1,3,2-diazaboroles. For the C–N distances in the carbazole part N(3)–C(11) and N(3)–C(22), comparable values [1.404(5) and 1.402(5) Å] are measured. The double bond length C(1)–C(2) [1.415(6) Å] is markedly elongated in comparison to monocyclic diazaboroles [1.315(11) to 1.362(8) Å] and compares well with that in **9** [1.412(1) Å]. The endocyclic bond angles in both ring systems are as expected (Figure 3).

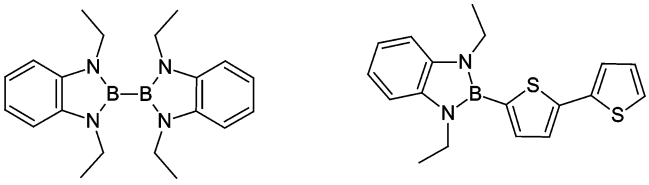

Figure 3. Compounds **9** and **10**.

X-ray Structural Analysis of 5a

Single crystals of **5a** suitable for an X-ray structural study (Table 7) were grown from a dichloromethane/methylcyclohexane mixture at 4 °C. The molecule is constructed of three planar rings (Figure 4), whereby the central thiophene ring is linked to the benzodiazaborole unit by a single bond B(1)–C(11) [1.557(2) Å] and to the carbazole system by a single bond N(3)–C(14) [1.405(2) Å]. The molecule markedly deviates from planarity as evident by the interplanar angles enclosed by the central thiophene ring and the diazaborole plane (34.7°) or the carbazole ring (41.4°).

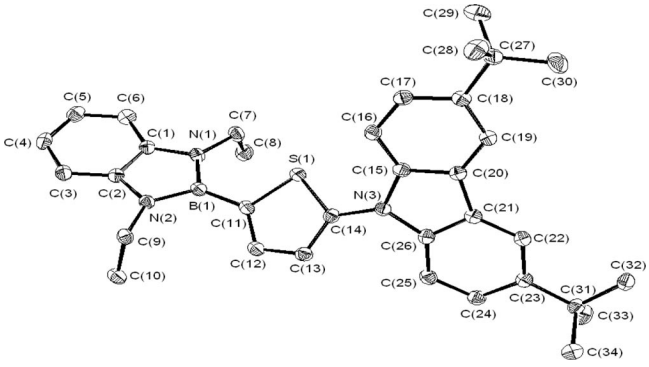

Figure 4. Molecular structure of **5a** in the crystal. Selected bond lengths [Å] and angles [°]:B(1)–N(1) 1.437(2), B(1)–N(2) 1.432(2), N(1)–C(1) 1.402(2), N(2)–C(2) 1.398(2), C(1)–C(2) 1.406(2), B(1)–C(11) 1.557(2), S(1)–C(11) 1.735(1), S(1)–C(14) 1.735(1), C(11)–C(12) 1.373(2), C(12)–C(13) 1.416(2), C(13)–C(14) 1.364(2), N(3)–C(14) 1.405(2), N(3)–C(15), 1.406(2), C(15)–C(20) 1.405(2), C(20)–C(21) 1.448(2), C(21)–C(26) 1.406(2), N(3)–C(26) 1.407(2), N(1)–C(7) 1.462(2), N(2)–C(9) 1.459(2); N(1)–B(1)–N(2) 106.7(1), B(1)–N(1)–C(1) 107.7(1), B(1)–N(1)–C(7) 131.5(1), B(1)–N(2)–C(9) 129.8(1), N(1)–C(1)–C(2) 108.8(1), N(2)–C(2)–C(1) 108.5(1), N(1)–B(1)–C(11) 127.8(1), N(2)–B(1)–C(11) 125.4(1), B(1)–C(11)–S(1) 120.5(1), B(1)–C(11)–C(12) 130.3(1), C(11)–S(1)–C(14) 92.8(1), S(1)–C(14)–C(13) 110.9(1), C(12)–C(13)–C(14) 112.2(1), S(1)–C(11)–C(12) 109.0(1), S(1)–C(14)–N(3) 120.5(1), C(13)–C(14)–N(3) 128.4(1), C(15)–N(3)–C(26) 108.2(1), C(14)–N(3)–C(15) 126.2(1), C(14)–N(3)–C(26) 125.2(1).

Bond lengths and bond angles within the benzodiazaborole part are as usual.[10–12] The bond lengths within the thiophene building block S(1)–C(11) [1.735(1) Å], S(1)–C(14) [1.735(1) Å], C(11)–C(12) [1.373(2) Å], C(12)–C(13) [1.416(2) Å] and C(13)–C(14) [1.364(2) Å] are close to those

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in the central thiophene ring in molecule **10** [1.736(3); 1.730(3); 1.379(4); 1.403(5); 1.375(4) Å][10a] (Figure 3).

As also observed in **10**, the exocyclic angles B(1)–C(11)–S(1) [120.5(1)°] and B(1)–C(11)–C(12) [130.3(1)°] differ significantly. Similar observations were made with angles S(1)–C(14)–N(3) [120.5(1)°] and C(13)–C(14)–N(4) [128.4(1)°].

UV/Vis and Luminescence Spectra

Table 1 lists selected photophysical data for compounds **3a**,**b** and **5a**,**b**, all of which exhibit intense blue luminescence under UV irradiation. For comparison, those of 2-*tert*-butyl-1,3-diethyl-1,3,2-benzodiazaborole (**2**-*t*BuBDB) and 3,6-di-*tert*-butylcarbazole (**2**-*H*) are also presented. The UV/Vis spectrum of **2**-*t*BuBDB displays an intense absorption band at 294 nm in cyclohexane as well as in thf solution. This band is assigned to the HOMO–LUMO transition. The fluorescence spectrum of a cyclohexane solution of this benzodiazaborole was registered at an excitation wavelength of 285 nm and shows an intense emission at 307 nm. A Stokes shift of 2400 cm^{-1} was deduced, which is in line with the absence of a significant charge transfer during the excitation. No solvatochromism was observed as absorption (λ_{max} = 287 nm) and emission spectra (λ_{max} = 309 nm) in thf gave identical values. The UV/Vis spectrum of a cyclohexane solution of 3,6-di-*tert*-butylcarbazole (**2**-*H*) is dominated by a strong absorption band at λ = 296 nm (ε = 18114 $L\,mol^{-1}\,cm^{-1}$) and a significantly weaker absorption band at λ = 337 nm (ε = 2672 $L\,mol^{-1}\,cm^{-1}$). The same situation is encountered in the more polar thf solution.[17] According to the theoretical calculations, the intense band at 296 nm may be assigned to a transition from the HOMO–1 into the LUMO of the molecule, whereas that at λ = 337 nm reflects the HOMO–LUMO transition (see also Table 3).

The fluorescence spectrum of a cyclohexane solution of the free carbazole displays a strong band at λ = 344 nm, regardless of the respective excitation wavelength (291 nm or 339 nm). Thus, the transition LUMO→HOMO gives rise to a Stokes shift, which clearly excludes transfer of charge within the molecule by UV light absorption. The situation is quite similar to that in 2-carbazolyl-1,3,2-benzodiazaborole **3a**. In the UV/Vis spectrum of a hexane solution, an intense band was observed at λ = 297 nm (ε = 16676 $L\,mol^{-1}\,cm^{-1}$) in addition to a weak band at λ = 340 nm (ε = 2643 $L\,mol^{-1}\,cm^{-1}$). In the luminescence spectrum, a strong band was found at λ = 345 nm (Stokes shift 500 cm^{-1}) (Figure 5). By considering the UV/Vis spectra of **2**-*t*BuBDB and carbazole **2**-*H*, it is obvious that absorption and emission occur in the carbazole part of **3a** without significant contributions from B/N-heterocycle and that a no-

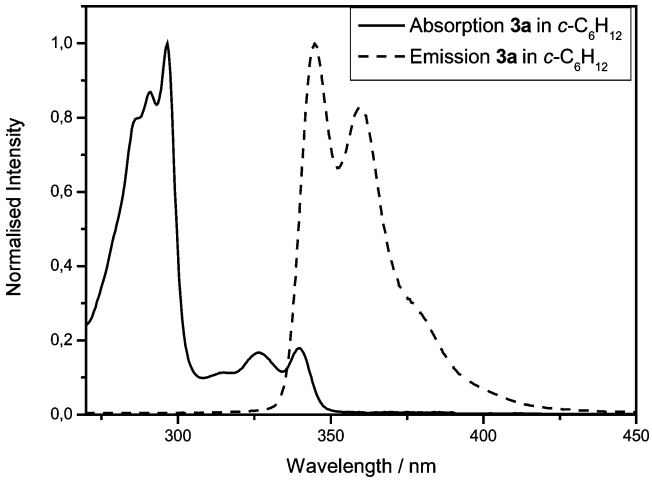

Figure 5. Absorption and emission spectra of **3a**.

Table 1. Selected photophysical data of compounds **2**-tBuBDB, **2**-*H*, **3a**,**b** and **5a**,**b**.

Compound	$\lambda_{max,abs.}$ [nm]	$\lambda_{max,abs.}$ [cm^{-1}]	ε [$L\,mol^{-1}\,cm^{-1}$]	$\lambda_{max,em.}$ [nm]	$\lambda_{max,em.}$ [cm^{-1}]	Stokes Shift [cm^{-1}]	Φ_f[c]
2-*t*BuBDB[a]	285	35100		307	34700	2400	
2-*t*BuBDB[b]	287	34800		309	34700	2400	
2-*H*[a]	296	33800	18114				
	337	29700	2672	344	29700	0	
2-*H*[b]	298	33600	14890				
	329	30400	2957	352	29400	1000	
3a[a]	297	33700	16676				
	340	29400	2643	345	28900	500	0.37
3a[b]	296	33800	23080				
	340	29400	4251	348	28700	700	0.09
3b[a]	296	33800	17336				
	335	29800	1532	342	29100	700	0.41
3b[b]	297	33700	15895				
	336	29800	3149	344	29000	800	0.33
5a[a]	296	33800	14488				
	321	31100	9509	371	25800	5300	0.14
5a[b]	296	33800	13661				
	323	31000	9509	389	25200	5800	0.15
5b[a]	296	33800	22628				
	328	30500	9931	386	25500	5000	0.13
5b[b]	296	33800	28555				
	330	30300	13194	388	25300	5000	0.15

[a] In *c*-C_6H_{12}. [b] In thf. [c] Against standard POPOP Φ = 0.93.

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table π conjugation between the two ring systems is absent. The excited state of molecule **3a** is not particularly polar, which is evidenced by similar absorption and emission wavenumbers in thf as well as by DFT calculations [B3LYP/6-311(d,p)] of the dipolar moments in the ground and the excited states (0.20 and 6.22 D). Other benzodiazaboroles in which the boron atom is directly attached to thienyl or aryl groups display Stokes shifts of 6200–9500 cm^{-1}. The UV spectrum of **3b** is similar with absorption bands at λ = 296 nm (ε = 17336 $L\,mol^{-1}\,cm^{-1}$) and 335 nm (ε = 1532 $L\,mol^{-1}\,cm^{-1}$). Emission occurs at 342 nm, which gives a Stokes shift of 700 cm^{-1}.

The UV/Vis spectrum of derivative **5a** in cyclohexane solution displays prominent bands at λ = 296 nm (ε = 14488 $L\,mol^{-1}\,cm^{-1}$) and 321 nm (ε = 9509 $L\,mol^{-1}\,cm^{-1}$). In thf, only slight shifts of these absorption bands are registered. The band with the lowest energy is attributed to the HOMO→LUMO transition. The HOMO–1→LUMO transition is attributed to the band at 296 nm (Table 6). In the fluorescence spectrum of **5a** in cyclohexane a band at λ = 371 nm is observed, which experiences a small redshift in thf to λ = 389 nm. These data correspond to Stokes shifts of 5300 cm^{-1} (*c*-C_6H_{12}) and 5800 cm^{-1} (thf).

Similarly, in cyclohexane solutions of **5b**, two bands at λ = 296 nm (ε = 22628 $L\,mol^{-1}\,cm^{-1}$) and 328 nm (ε = 9931 $L\,mol^{-1}\,cm^{-1}$) were observed, which are assigned to the HOMO–1→LUMO and the HOMO→LUMO transitions. The luminescence spectrum is characterized by an intense emission at 386 nm, which led to Stokes shifts of 5000 cm^{-1} in cyclohexane as well as in thf. Again the lack of solvatochromism is consistent with a nonpolar excited state.

DFT Calculations

Table 2 contains selected calculated geometrical parameters for 1,3-diethyl-1,3,2-benzodiazaborole (B), 2-[*N*-3′,6′-di-*tert*-butylcarbazolyl]-1,3-diethyl-1,3,2-benzodiazaborole (BC, **3a**) and 2[5′-*N*-carbazolyl-2′-thienyl]-1,3-diethyl-1,3,2-benzodiazaborole (BTC, **5a**), in addition to the experimental structural data of **3a** and **5a** (Figure 6).

The geometry of benzodiazaborole ring of BC undergoes no significant changes in comparison to B and agrees nicely with experimental data found in numerous diazaboroles and also in **3a** and **5a**. The calculated value of the NC bond length in carbazole (1.386 Å) marginally increases in BC (1.401 Å) [exp. av. 1.403(5) Å]. The endocyclic angle NBN in BC [107.3°, exp. 107.2(3) Å] is more obtuse than in the free molecule B, whereas the endocyclic angle CNC in BC [107.0°, exp. 108.4(3)°] is slightly compressed relative to the calculated angle in carbazole (109.3°). Interestingly, both rings of BC are not oriented in the same plane, but instead enclose a dihedral angle of 63.7° (exp. av. 66.6°), which does not allow for a significant (BN) π interaction. In keeping with this, the bond B(1)–N(3) (1.468 Å) [exp. av. 1.468(6) Å] is markedly longer than typical BN double bonds (exp. av. 1.412 Å).[15a] Accordingly, at least in the electronic ground state, there exists no essential π-electronic communication between both ring systems.

Table 2. Selected experimental and calculated [B3LYP/6-311G(d,p)] bond lengths [Å] and angles [°] for molecules B, BC (**3a**) and BTC (**5a**).

	$B_{calcd.}$	$BC_{calcd.}$ (**3a**)	$BC_{exp.}$ (**3a**)	$BTC_{calcd.}$ (**5a**)	$BTC_{exp.}$ (**5a**)
B(1)–N(1)	1.436	1.434	1.438(6)	1.442	1.432(2)
B(1)–N(2)	1.436	1.435	1.422(5)	1.442	1.437(2)
C(1)–C(2)	1.414	1.415	1.415(6)	1.416	1.406(2)
N(1)–C(1)	1.396	1.398	1.399(5)	1.398	1.402(2)
N(2)–C(2)	1.396	1.398	1.406(5)	1.398	1.398(2)
B(1)–N(3)		1.468	1.457(5)		
B(1)–C(11)				1.558	1.557(2)
C(11)–S(1)				1.754	1.735(1)
C(14)–S(1)				1.758	1.735(1)
C(14)–N(3)				1.398	1.405(2)
N(3)–C(11)		1.401	1.404(5)		
N(3)–C(22)		1.401	1.402(5)		
N(3)–C(15)				1.405	1.406(2)
N(3)–C(26)				1.403	1.407(2)
N(1)–B(1)–N(2)	106.8	107.3	107.2(3)	106.6	106.7(1)
C(2)–N(2)–B(1)	108.0	107.7	108.0(3)	108.0	108.3(1)
C(1)–N(1)–B(1)	108.0	107.7	107.9(3)	108.1	107.7(1)
N(3)–B(1)–H(1)	126.6				
N(2)–B(1)–N(3)		126.4	127.2(4)		
N(2)–B(1)–C(11)				128.0	127.8(1)
C(11)–S(1)–C(14)				92.4	92.8(1)
C(11)–N(3)–C(22)		107.0	106.5(3)		
C(15)–N(3)–C(26)				108.0	108.1(1)
N(2)–B(1)–N(3)–C(26)		63.7	55.9 (av. 66.6)		
N(1)–B(1)–C(11)–S(1)				–45.3	–33.1
S(1)–C(14)–N(3)–C(26)				–60.2	–39.3

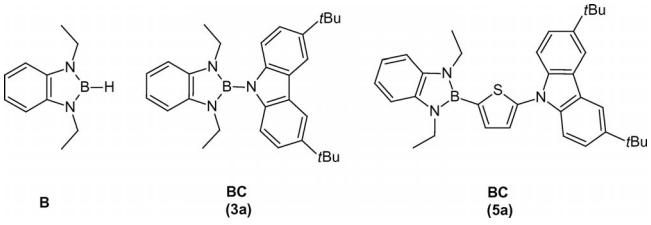

Figure 6. Compounds B, BC (**3a**) and BTC (**5a**).

TD-DFT computations carried out on the optimized geometry of BC (**3a**), which is presumably not markedly different from the geometry of **3b**, gave a lowest energy of 320 nm for an allowed $S_1 \leftarrow S_0$ electronic absorption with an oscillator strength f = 0.0328, which corresponds to the HOMO–LUMO transition. This calculated value differs from the observed absorption maximum at 334 nm by 14 nm. The redshift may be due to the fact that, in solution, an ensemble of rotational isomers exists, including planar geometries.

In Table 3, TD-DFT [B3LYP/6-311(d,p)] calculated ionization energies [eV] and MOLEKEL visualizations of the MOs for molecules B, C (**2-*H***) and BC (**3a**) are given. The HOMO [π_I(*crb*)] of (BC) is assigned to the antibonding interaction between the sp^2 carbon atoms and nitrogen lone pair in the π plane (6.62 eV). The corresponding HOMO (7.01 eV) in the free carbazole is thus destabilized by 0.39 eV because of the positive inductive effect of the diazaborole fragment. The HOMO (π_3–π_{NBN}) in free B, which

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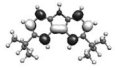
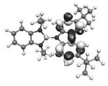
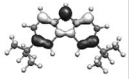
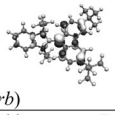
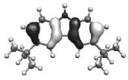
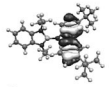
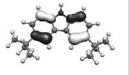
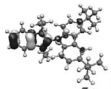
Table 3. TD-DFT [B3LYP/6-311G(d,p)] calculated ionization energies, ε^{KS} and the MOLEKEL[18] MO visualization for molecules B, C (carbazole **2**-*H*) and BC (**3a**). (*ΔSCF values, **ε^{KS}, all values in eV).

MO	B	C (**2**-H)	BC (**3a**)
LUMO	*0.10*** 	*0.88*** 	*0.94*** 
HOMO	*5.60*** 7.63*  π_3–π_{NBN}	*5.51*** 7.01*  π_I	*5.41*** 6.62*  $\pi_I(crb)$
HOMO–1	*5.99*** 8.06  $\pi_{C=C}^{-}$–$n_N^{\pi-}$	*5.78*** 7.37  π_{II}	*5.83*** 7.15  $\pi_{II}(crb)$
HOMO–2	*7.70*** 9.60  $[\pi_{C=C}+n_N^{\pi}]^-$	*6.79*** 8.49  π_{III}	*5.88*** 7.32  $\pi_{C=C}^{-}$–π_{NBN}–$n_N^{\pi}(crb)$

corresponds to the antibonding combination of the orbitals of the sp^2 carbon atoms, and the bonding NBN π orbital (7.63 eV) is destabilized to 7.32 eV by the carbazole because of a +M effect, albeit to a slightly smaller extent (0.31 eV). The intense absorption band in the experimental UV/Vis spectrum at 296 nm can be assigned to a transition from the HOMO–1 (π_{II}) (7.15 eV), which is also centred on the carbazole part, to the LUMO of the molecule, with an oscillator strength of 0.1424. In line with the two observed transitions, the calculated corresponding energy of the HOMO–LUMO transition is 3.88 eV (319.70 nm), whereas that between HOMO–1 and LUMO is 4.40 eV (218.84 nm). In Table 4, the calculated and observed electronic transitions are compiled (for calculated values of the HOMO–LUMO gap of studied compounds see the Supporting Information).

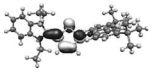
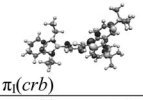
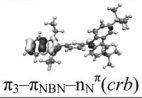
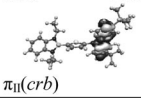
Table 4. Calculated [B3LYP/6-311G(d,p)] UV spectrum for BC (**3a**).

E	λ	*f*	Transition
3.88	319.70	0.0328	HOMO→LUMO
4.40	281.84	0.1424	HOMO–1→LUMO
4.42	280.54	0.0061	HOMO–2→LUMO
4.53	273.45	0.2108	HOMO→LUMO+1
4.77	259.86	0.0002	HOMO–3→LUMO
4.94	250.97	0.1026	HOMO–2→LUMO
4.95	250.31	0.2133	HOMO→LUMO+2
5.07	244.44	0.2404	HOMO–2→LUMO+1
5.15	240.70	0.0099	HOMO–3→LUMO+1
5.19	238.69	0.0004	HOMO→LUMO+4

For compound BTC (**5a**), the experimentally determined bond lengths and valence angles (Table 2) are not significantly different from those calculated with the exception of the C(1)–C(2) bond, where the calculated value of 1.416(2) Å is slightly longer than the experimental one [1.406(2) Å]. The same holds for the S–C bonds within the thiophene fragment [calcd. 1.754 and 1.758 Å vs. exp. 1.735(2) Å]. The interplanar angles between the three rings of this molecule in the gas phase (–45.3 and –60.2°), however, differ essentially from those determined in the crystal of **5a** (–33.1 and –39.3°).

Table 5 displays the MO visualization and the corresponding ionization energies. As previously observed for molecule BC (**3a**) (6.62 eV), the first ionization energy of BTC (**5a**) (6.54 eV) corresponds to the HOMO $\pi_I(crb)$, which is located on the carbazole part. Thus, the formal insertion of the thiophene spacer between the diazaborole and carbazole fragments leads to only a small destabilization (0.08 eV).

Table 5. TD-DFT [B3LYP/6-311 G(d,p)] calculated ionization energies, ε^{KS} and the MOLEKEL[18] MO visualization for molecules B, TC and BTC (**5a**). (* ΔSCF values, **ε^{KS}, all values in eV).

MO	B	TC	BTC (**5a**)
LUMO	*0.10*** 	*0.97*** 	*1.02*** 
HOMO	*5.60*** 7.63*  π_3–π_{NBN}	*5.55*** 6.91*  $\pi_I(crb)$	*5.45*** 6.54*  $\pi_I(crb)$
HOMO–1	*5.99*** 8.06  $\pi_{C=C}^{-}$–$n_N^{\pi-}$	*5.92*** 7.42  $\pi_{II}(crb)$	*5.68*** 7.01  π_3–π_{NBN}–$n_N^{\pi}(crb)$
HOMO–2	*7.70*** 9.60  $[\pi_{C=C}+n_N^{\pi}]^-$	*6.75*** 7.90  $\pi_{III}(crb)$	*5.88*** 7.06  $\pi_{II}(crb)$

The HOMO–1 $\pi_{II}(crb)$ of **3a** (7.15 eV), which is a part of the more complex molecule **5a**, is destabilized to 7.06 eV and becomes the HOMO–2 in this species. The HOMO–1 [π_3–π_{NBN}–$n_N^{\pi}(crb)$] of **5a** is ionized by an energy of 7.01 eV. This is an antibonding combination of π_3 of benzene with the two adjacent nitrogen atom lone pairs delocalized to the p orbital of the boron atom in interaction with the carbazole nitrogen atom lone pair.

The low-energy HOMO–LUMO transition of 340.35 nm (3.64 eV, f = 0.3107) corresponds to a charge transfer from the carbazole part to the thiophene unit of the molecule. The next observed absorption at 312.78 nm is assigned to the HOMO–1 to LUMO transition (3.96 eV, f = 0.1187) and reflects a charge transfer from the benzodiazaborole part to the central thiophene ring. In Table 6, the calculated electronic transitions of **5a** are presented. Because of the opposite directions of the charge-transfer processes, no significant net increase in the dipole moments results. This idea is underlined by the lack of solvatochromism.

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Table 6. Calculated [B3LYP/6-311G(d,p)] of BTC (**5a**).

E [eV]	$\lambda_{calcd.}$ [nm]	f	Transition
3.64	340.35	0.3107	HOMO→LUMO
3.87	320.19	0.0958	HOMO→LUMO+1
3.96	312.78	0.1187	HOMO–1→LUMO
4.12	301.13	0.0012	HOMO–2→LUMO
4.31	287.46	0.0022	HOMO–1→LUMO+1
4.37	283.45	0.0119	HOMO–3→LUMO
4.41	281.30	0.1534	HOMO–2→LUMO+1
4.77	259.80	0.0446	HOMO→LUMO+2
4.83	256.71	0.0005	HOMO–3→LUMO+1
4.96	249.93	0.1080	HOMO–1→LUMO+2

Conclusions

1,3,2-Benzodiazaboroles with *N*-carbazolyl substituents of the boron atom, **3a**,**b**, have nonplanar geometries in the crystalline phase, as evidenced by X-ray crystallography, as well as in the gas phase, according to DFT calculations. Obviously, there exists no appreciable π communication between both ring units in the molecule. In keeping with this, no marked charge transfer was observed during excitation with UV light. Small Stokes shifts and the absence of solvatochromism are in accord with electron transitions within the carbazole part of the molecules. In *N*-carbazolylthienylbenzodiazaborole **5a**, it was calculated that the low-energy HOMO–LUMO transition of 340.35 nm (3.64 eV) corresponds to a charge transfer from the carbazole part to the thiophene unit, while the absorption band at 312.78 nm (3.96 eV) is assigned to the HOMO–1→LUMO transition and reflects a charge transfer from the benzodiazaborole fragment to the central thiophene ring. Experimental values for these transitions in **5a** (λ = 323; 296 nm) are slightly blueshifted. Emission was observed at λ = 371 nm (in *c*-C_6H_{12}), which results in a Stokes shift of 5300 cm^{-1}. In thf, this value increases to 5800 cm^{-1}.

Experimental Section

All manipulations were performed under an atmosphere of dry, oxygen-free argon by using standard Schlenk techniques. All solvents were dried by standards methods and freshly distilled prior to use. The compounds 2-bromo-1,3-diethyl-1,3,2-benzodiazaborole (**1a**),[12] 1,3-bis(2,6-diisopropylphenyl)imidazolium chloride[19a] and *N*-(2-thienyl)-3,6-di-*tert*-butyl-carbazole[14] were prepared according to literature methods. The protocol for N,N′-diphenyl-o-phenylenediamine reported in ref.[19b] was modified. 1,2-Dibromobenzene, aniline, palladium acetate and $NaOC(CH_3)_3$ were purchased commercially (Aldrich). NMR spectra were recorded at room temperature on a Bruker AM Avance DRX 500 spectrometer (^1H, ^{11}B, ^{13}C) by using TMS and $BF_3{\cdot}Et_2O$ as external standards. Mass spectra were taken with a VG autospec sector field mass spectrometer (Micromass). The UV/Vis spectra were recorded on a Thermo Evolution 300 UV/Vis spectrometer and the emission spectra on a Hitachi F-4500 Fluorescence spectrometer. From the microanalyses, low C values were repeatedly obtained with different samples, which may be due to boron carbide formation during the combustion process.

2-Bromo-1,3-diphenyl-1,3,2-benzodiazaborole (1b)

Step 1, *N*,*N*′-Diphenyl-*o*-phenylenediamine: A mixture of 1,3-bis(2,6-diisopropylphenyl)imidazolium chloride (0.721 g, 1.70 mmol), sodium *tert*-butanolate (0.244 g, 2.54 mmol) and palladium acetate (0.190 g, 0.848 mmol) were combined with toluene (20 mL), and the slurry was heated for 1 h at 80 °C. Homogenization of the suspension was achieved in an ultrasound bath over 5 min; *o*-dibromobenzene (20.0 g, 84.7 mmol), aniline (16.5 g, 17.8 mmol), sodium *tert*-butanolate (24.4 g, 254.0 mmol) and the catalyst solution were then poured into toluene (150 mL). The obtained mixture was heated to boil for 5 h. After cooling to room temperature, a saturated aqueous NH_4Cl solution (30 mL) was added, followed by the dropwise addition of glacial acetic acid (10 mL). The organic layer was separated, washed twice with brine (20 mL) and then evaporated to dryness. The solid residue was recrystallized from methanol. The obtained crystalline product was washed with ethanol (5 × 10 mL) and *n*-hexane (2 × 30 mL) and then dried in vacuo. *N*,*N*′-diphenyl-*o*-phenylene diamine was obtained as a light-violet solid. Yield: 19.19 g (87%). ^1H NMR (C_6D_6): δ = 5.12 (s, 2 H, NH), 6.70 (d, J_{HH} = 8.0 Hz, 4 H, NH–C=C*H*–CH=CH), 6.78 (t, J_{HH} = 7.8 Hz, 2 H, NH–C=CH–CH=C*H*), 6.84 (m, 2 H, NH–C=CH–C*H*), 7.06 (t, J_{HH} = 7.8 Hz, 4 H, NH–C=CH–C*H*=CH), 7.18 (m, 2 H, NH–C=C*H*–CH) ppm. $^{13}C\{^1H\}$ NMR (C_6D_6): δ = 117.5 (s, NH–CH=*C*H–*C*H=CH), 120.9 (s, NH–*C*H=CH–CH=*C*H), 123.4 (s, *p*-Ph*C*), 128.4 (s, *o*-Ph*C*), 129.7 (s, *m*-Ph*C*), 135.5 (s, Ph*C*-N), 144.5 (s, N_2C_2) ppm. MS/EI: *m*/*z* = 260.1 $[M]^+$.

Step 2, Path A: Solution of boron tribromide (6.40 g, 25.4 mmol) in toluene (40 mL) and *N*,*N*′-diphenyl-*o*-phenylene diamine (6.01 g, 23.1 mmol) in toluene (40 mL) were slowly added to a chilled slurry (0 °C) of calcium hydride (2.94 g, 69.8 mol) in toluene (75 mL). After completion, the slurry was stirred for 3 h at room temperature and filtered. The filtrate was freed from solvent and volatiles. The remaining dark-brown oil was purified by short-path distillation at 10^{-6} bar to afford **1b** as a clear, colourless, viscous oil. Yield: 7.89 g (98%). **Path B:** A solution of *n*-butyllithium in *n*-hexane (11.3 mL of a 1.6 M solution, 18.0 mmol) was added dropwise to a chilled solution (–78 °C) of *N*,*N*′-diphenyl-*o*-phenylene diamine (2.08 g, 8.0 mmol) in toluene (30 mL). After completion, the reaction mixture was stirred for 1 h at –78 °C and then for 1 h at 70 °C, whereby a yellow solid precipitated. It was cooled to 0 °C, before boron tribromide (2.12 g, 8.5 mmol) was added by syringe. The mixture was stirred continuously at room temperature overnight. It was filtered, and the filtercake was washed with toluene (2 × 10 mL). The filtrate was evaporated to dryness, and the remaining brown oil was purified as described above. Yield: 2.01 g (72%). ^1H NMR ($CDCl_3$): δ = 7.06 (m, 2 H, C*H*=CH–CH=C*H*), 7.14 (m, 2 H, CH=C*H*–C*H*=CH), 7.42 (t, J_{HH} = 7.3 Hz, 2 H, p-Ph–C*H*), 7.49 (d, J_{HH} = 7.5 Hz, 4 H, o-Ph–C*H*), 7.55 (t, J_{HH} = 7.7 Hz, 4 H, m-Ph–C*H*) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 110.4 (s, *C*H=CH–CH=*C*H), 120.6 (s, CH=*C*H–*C*H=CH), 126.8 (s, *p*-Ph*C*), 127.2 (s, *o*-Ph*C*), 129.3 (s, *m*-Ph*C*), 136.9 (s, Ph*C*-N), 138.8 (s, N_2C_2) ppm. $^{11}B\{^1H\}$ NMR ($CDCl_3$): δ = 23.8 (s) ppm; (C_6D_6): δ = 24.0 (s) ppm.

2-*N*-(3′,6′-Di-*tert*-butylcarbazolyl)-1,3-diethyl-1,3,2-benzodiazaborole (3a): An *n*-pentane solution of *tert*-butyllithium (1.6 M, 3.8 mL, 6.08 mmol) was added dropwise with stirring at room temperature to the slurry of 3,6-di-*tert*-butylcarbazole (1.70 g, 6.08 mmol) in *n*-pentane (60 mL). After 1 h of stirring at room temperature, the slurry was treated with a sample of 2-bromo-1,3-diethyl-1,3,2-benzodiazaborole (1.54 g, 6.08 mmol). The slurry was stirred for 2 h at room temperature. It was filtered, and, after 15 h at –20 °C, colourless crystals of **3a** separated from the filtrate. Yield: 2.12 g (77%). ^1H NMR ($CDCl_3$): δ = 1.20 (t, J_{HH} = 6.9 Hz, 6 H, NCH_2CH_3), 1.50 (s, 18 H, *t*Bu), 3.70 (q, J_{HH} = 6.9 Hz, 4 H, CH_3CH_2N), 7.17 (m, 2 H, C*H*=CH–CH=C*H*), 7.26 (m, 4 H, CH=C*H*–C*H*=CH and *t*Bu-CCH–C*H*), 7.48 (d, J_{HH} = 8.2 Hz, 2

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H, *t*Bu-C–C*H*–CH), 8.18 (d, J_{HH} = 1.9 Hz, C–C*H*–C) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 15.7 (s, CH_3CH_2N), 32.0 [s, $C(CH_3)_3$], 34.7 [s, $C(CH_3)_3$], 37.4 (s, CH_3CH_2N), 109.5, (s, *C*H=CH-CH=*C*H), 111.0 (s, *t*Bu-C–CH–*C*H), 116.2 (s, *t*Bu-C–*C*H–C), 119.1 (s, CH=*C*H–*C*H=CH), 123.6 (s, *t*Bu-C–*C*H–CH), 125.0, 141.0 142.6 (3s, C-carbazole), 136.6 (s, N_2C_2) ppm. $^{11}B\{^1H\}$NMR ($CDCl_3$): δ = 24.6 ppm. IR (ATP, diamond): $\tilde{\nu}$ = 2960 (s), 2901 (m), 2865 (m), 1604 (m), 1488 (m), 1469 (s), 1450 (s), 1420 (s), 1376 (m), 1360 (m), 1324 (w), 1301 (m), 1259 (s), 1231 (m), 1200 (w), 1083 (s), 1016 (s), 875 (m), 794 (s), 732 (s), 642 (w), 620 (m), 600 (w), 552 (w), 466 (m) cm^{-1}. MS/EI: *m*/*z* = 451.5 (95) $[M]^+$, 436.5 (100) $[M - CH_3]^+$. $C_{30}H_{38}BN_3$ (451.47): calcd. C 79.76, H 8.48, N 9.30; found C 79.21, H 8.50, N 8.44.

2-*N*-(3′,6′-Di-*tert*-butylcarbazolyl)-1,3-diphenyl-1,3,2-benzodiazaborole (3b): A slurry of 3,6-di-*tert*-butylcarbazole (0.90 g, 3.2 mmol) in *n*-pentane (50 mL) was combined at 20 °C with an *n*-hexane solution of *n*-butyllithium (1.6 M, 3.2 mmol) and stirred for 2 h. A solution of 2-bromo-1,3-diphenyl-1,3,2-benzodiazaborole (7.50g, 3.2 mmol) in benzene (50 mL) was then added. After stirring for 15 h, all the volatile components were removed in vacuo, and the residue was continuously extracted (3 h) with *n*-hexane (70 mL). After this, the volatiles were removed in vacuo, and the colourless residue was crystallized from toluene (25 mL) at 4 °C to yield 1.28 g (2.3 mmol, 73%) of **3b** as a colourless microcrystalline solid. ^1H NMR ($CDCl_3$): δ = 1.41 (s, 18 H, *t*Bu), 7.04 (d, J_{HH} = 8.6 Hz, 2 H, *t*Bu-CCH–C*H*), 7.13 (m, 2 H, *p*-H-Ph), 7.16 (dd, J_{HH} = 8.6, 1.7 Hz, 2 H, *t*Bu-C–C*H*–CH), 7.19 (m, 2 H, C*H*=CH–CH=C*H*), 7.25 (m, 8 H, *o*-, *m*-H Ph), 7.45 (m, 2 H, CH=C*H*–C*H*=CH), 7.99 (d, J_{HH} = 1.7 Hz, 2 H, C C*H*–C-*t*Bu) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 31.9 [s, $C(CH_3)_3$], 34.6 [s, $C(CH_3)_3$], 110.5 (s, *C*H=CH–CH=*C*H), 111.6 (*t*BuCCH–*C*H), 115.6 (C*C*H–C-*t*Bu), 120.6 (s, CH=*C*H–*C*H=CH), 123.6 (s, *t*Bu-C–*C*H–CH), 125.7 (s, *o*-, *m*-Ph*C*), 126.0 (s, *p*-Ph*C*), 125.2, 140.2, 142.5 (3s, C-carbazole), 136.3 (s, N_2C_2), 139.2 (s, Ph*C*-N) ppm. ^{11}B $\{^1H\}$ NMR ($CDCl_3$): δ = 25.6 ppm. IR (ATP, diamond): $\tilde{\nu}$ = 3037 (w), 2958 (m), 2860 (w), 2360 (m), 2342 (m), 1585 (m), 1499 (m), 1485 (m), 1469 (s), 1411 (m), 1380 (s), 1330 (w), 1257 (m), 1229 (s), 1185 (w), 1071 (w), 1026 (w), 878 (w), 811 (s), 742 (s), 695 (s), 648 (m), 614 (m), 510 (m) cm^{-1}. MS/EI: *m*/*z* = 547.3 (100) $[M]^+$, 532.2 (83) $[M - CH_3]^+$. $C_{38}H_{38}BN_3$ (547.54): calcd. C 83.36, H 7.00, N 7.67; found C 82.57, H 7.06, N 7.68.

5′-*N*-(Carbazolyl-2′-thienyl)-1,3-diethyl-1,3,2-benzodiazaborole (5a): A solution of *N*-2′-thienyl-3,6-*tert*-butylcarbazole (1.20 g, 3.3 mmol) in ethyl ether (50 mL) was slowly combined with an *n*-hexane solution of *n*-butyllithium (1.6 M, 2.1 mL, 3.4 mmol) at room temperature. After 1 h, 2-bromo-1,3-diethyl-benzodiazaborole (**1a**) (0.85 g, 3.36 mmol) was added in one portion. After 20 h of stirring at room temperature, all volatile compounds were removed in vacuo, and *n*-hexane (40 mL) was added. The obtained slurry was filtered. After 3 d, product **5a** was separated from the chilled filtrate (4 °C) as an off-white solid (1.20 g, 2.2 mmol, 68% yield). ^1H NMR ($CDCl_3$): δ = 1.48 (t, J_{HH} = 7.2 Hz, 6 H, NCH_2CH_3), 1.54 (s, 18 H, *t*Bu), 4.08 (q, J_{HH} = 7.2 Hz, 4 H, NCH_2CH_3), 7.14 (m, 2 H, C*H*=CH–CH=C*H*), 7.21 (m, 2 H, CH=C*H*–C*H*=CH), 7.40 (d, J_{HH} = 4.6 Hz, 1 H, S–C–CH–CH–CN), 7.56 (d, J_{HH} = 4.6 Hz, 1 H, S–C–CH–CH–CN), 7.59 (s, 4H *t*Bu-C–C*H*–C*H*), 8.20 (s, 2 H, C–C*H*–C) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 16.3 (s, CH_3CH_2N), 32.0 [s, $C(CH_3)_3$], 34.8 [s, $C(CH_3)_3$], 38.0 (s, CH_3CH_2N), 108.9 (s, CH=*C*H–*C*H=CH), 109.7 (s, *t*Bu-C–CH–*C*H), 116.2 (s, *t*Bu-C–*C*H–C), 119.0 (s, CH=*C*H–*C*H=CH), 123.9 (s, *t*Bu-C–*C*H–CH), 124.6 (s, SC–CH–CH–CN), 132.9 (s, S–C–CH–CH–N), 123.6, 140.1, 143.6 (3s, C-carbazole), 137.1 (s, N_2C_2), 143.8 (s, S–*C*–N), ppm. ^{11}B $\{^1H\}$NMR ($CDCl_3$): δ = 25.8 (s) ppm. IR (ATP, diamond): $\tilde{\nu}$ = 3037 (w), 2960 (s), 2926 (m), 1678 (m), 1602 (s), 1549 (s), 1488 (m), 1469 (s), 1397 (s), 1363 (s), 1263 (m), 1233 (s), 1045 (m), 880 (w), 809 (s), 735 (s), 730 (s), 653 (m), 614 (m), 510 (m) cm^{-1}. MS/EI: *m*/*z* = 533.3 (100) $[M^+]^+$, 518.35 (36) $[M - CH_3]^+$. $C_{34}H_{40}BN_3S$ (533.58): calcd. C 76.53, H 7.56, N 7.88; found C 74.56, H 7.74, N 7.50.

5′-*N*-(3′-6′-Di-*tert*-butylcarbazolyl-2′-thienyl)-1,3-diphenyl-1,3,2-benzodiazaborole (5b): An *n*-hexane solution of *n*-butyllithium (1.6 M, 1.5 mL, 2.4 mmol) was added in one portion to a solution of *N*-2′-thienyl-3,6-*tert*-butylcarbazole (0.88 g, 2.4 mmol) in ethyl ether (50 mL) at room temperature. After 1 h, a solution of 2-bromo-1,3-diphenyl-1,3,2-benzodiazaborole (6.30 g, 2.4 mmol) was added. The solution was stirred for 16 h, and then all the volatile compounds were removed in vacuo. The residue was suspended in *n*-pentane (40 mL) and filtered. Crystals were grown from the filtrate after 30 min at 4 °C. They were collected and recrystallized from *n*-pentane (30 mL). After two days at 4 °C, product **5b** was obtained as an off-white solid (0.94 g, 1.5 mmol, 62% yield). ^1H NMR ($CDCl_3$): δ = 1.47 (s, 18 H, *t*Bu) 6.90 (d, J_{HH} = 3.8 Hz, 1 H, S–C–CH–CH), 6.96 (m, 3 H, C*H*=CH–CH=C*H*, and S–C–CH–CH), 7.04 (m, 2 H, CH=C*H*–C*H*=CH), 7.32 (d, J_{HH} = 8.7 Hz, 2 H, *t*Bu-C–CH–C*H*), 7.45 (dd, J_{HH} = 8.7, 1.7 Hz, 2 H, *t*Bu-C–C*H*–CH), 7.47 (m, 2 H, *p*-H-Ph), 7.53 (m, 4 H, *m*-H-Ph), 7.57 (m, 4 H, *o*-H-Ph), 8.08 (d, J_{HH} = 1.7 Hz, 2 H, *t*Bu-C–C*H*–C) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 32.0 [s, $C(CH_3)_3$], 34.7 [s, $C(CH_3)_3$], 109.7 (s, *C*H=CH–CH=*C*H), 110.0 (s, *t*Bu-C–CH–*C*H), 116.1 (s, *t*Bu-C–*C*H–C), 120.0 (s, CH=*C*H–*C*H=CH), 123.7 (s, *t*Bu-C–*C*H–CH), 125.4 (s, SC–CH–CH–CN), 127.4 (s, NC–CH=CH–*C*H), 128.6, 129.9 (2s, NC–*C*H=*C*H–CH), 135.9 (s, S–C–CH–CH–N), 123.4, 140.1, 143.4 (3s, C-carbazole), 138.4 (s, N_2C_2), 144.5 (s, S–*C*–N) ppm. ^{11}B $\{^1H\}$NMR ($CDCl_3$): δ = 21.3 ppm. IR (ATP, diamond): $\tilde{\nu}$ = 3037 (w), 2959 (s), 2898 (m), 1589 (s), 1541 (s), 1456 (m), 1362 (s), 1228 (s), 1063 (m), 880 (w), 839 (s), 740 (s), 697 (m), 510 (m) cm^{-1}. MS/EI: *m*/*z* = 629.3 (100) $[M]^+$, 614.2 (36) $[M - CH_3]^+$. $C_{42}H_{40}BN_3S$ (629.68 g/mol): calcd. C 80.11, H 6.40, N 6.67; found C 77.60, H 6.19, N 6.46.

X-ray Crystallography: Single crystals of **3a** and **5a** were coated with a layer of hydrocarbon oil, attached to a glass fibre and cooled to 100 K for data collection. Crystallographic data were collected with a Nonius Kappa CCD diffractometer with Mo-K_α radiation (graphite monochromator), λ = 0.71073 Å. Crystallographic programs used for the structure solution and refinement were from SHELX-97.[20] The structure was solved by direct methods and was refined by using full-matrix least-squares on F^2 of all unique reflections with anisotropic thermal parameters for all non-hydrogen atoms, with the exception of the disordered solvent in **3a**. Hydrogen atoms were included at calculated positions with $U(H) = 1.2U_{eq}$ for CH_2 groups and $U(H) = 1.5U_{eq}$ for CH_3 groups. Crystal data for the compounds are listed in Table 7. CCDC-780597 (**3a**) and -780598 (**5a**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from Cambridge Crystallographic Data Centre via www.ccd.cam.ac.uk/data_request/cif or as ESI.

Computational Methods: All calculations were performed by using the Gaussian 03[21] program package with the 6-311G(d,p) basis set. DFT has been shown to predict various molecular properties successfully.[22] All geometry optimizations were carried out with the B3LYP[23] functional and were followed by frequency calculations in order to verify whether the stationary points obtained were true energy minima. Ionization energies (IE) were calculated with ΔSCF–DFT, which means that separate SCF calculations were performed to optimize the orbitals of the ground state and the appro-

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Table 7. Crystallographic data for **3a** and **5a**.

	3a	**5a**
Empirical formula	$C_{30}H_{38}BN_3$ + C_5H_{12}	$C_{34}H_{40}BN_3S$
M_r [g mol^{-1}]	523.59	533.56
Crystal dimensions [mm]	0.30 × 0.30 × 0.05	0.26 × 0.22 × 0.12
Crystal system	monoclinic	monoclinic
Space group	$P2_1$	$P2_1/c$
a [Å]	12.3812(1)	21.0380(5)
b [Å]	31.5523(3)	13.0890(3)
c [Å]	16.8248(1)	10.9130(3)
β [°]	99.5623(5)	94.7240(12)
V [Å^3]	6481.4(1)	2996.5(2)
Z	8	4
$\rho_{calcd.}$ [g cm^{-1}]	1.073	1.183
μ [mm^{-1}]	0.062	0.135
F(000)	2288	1144
θ [°]	3–25	3–30
No. reflections collected	126296	57361
No. unique reflections	11617	8648
R(int)	0.047	0.063
No. reflections [$I > 2\sigma(I)$]	10443	6276
Refined parameters	1343	360
GOF	1.044	1.030
R_f [$I > 2\sigma(I)$]	0.0577	0.0494
wR_F^2(all data)	0.1621	0.1237
$\Delta\rho_{max/min}$ [e Å^{-3}]	0.894/–0.468	0.407/–0.272

priate ionic state ($IE = E_{cation} - E_{neutral}$). The advantages of the most frequently employed ΔSCF–DFT method of calculations of the first ionization energies have been demonstrated previously.[24] The TD-DFT[25] approach provides a first principal method for the calculation of excitation energies within a density functional context by taking into account the low-lying ion calculated by the ΔSCF method. Finally, the so-called "corrected" IEs were evaluated by applying a uniform shift, $x = -IE_v^{exp.} - \varepsilon^{KS}{}_{HOMO}$, where $\varepsilon^{KS}{}_{HOMO}$ is the B3LYP/6-311G(d,p) Kohn–Sham energy of the highest occupied MO of the molecule in the ground state and IE_v is the lowest-calculated ionization energy of this species, as was suggested previously by Stowasser and Hoffmann[26] and in our studies on different methods for the calculation of IEs.[27] MOLEKEL[18] has been used as a visualization tool for MOs.

Supporting Information (see footnote on the first page of this article): Tables of atomic coordinates for [B3LYP/6-311G(d,p)] optimized geometries, values of total energies, optimized geometrical parameters and ionization energies (IEs) of B, C, T, BC, TC and BTC are presented.

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