Synthetic, Structural, Photophysical and Computational Studies on 2-Arylethynyl-1,3,2-Diazaboroles

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New 2-arylalkynyl benzo-1,3,2-diazaboroles, 2-(4'-$XC_6H_4C{\equiv}C$)-1,3-Et_2-1,3,2-$N_2BC_6H_4$ (X =Me **2**; MeO **3**; MeS **4**; Me_2N **5**), were prepared from B-bromodiazaborole, 2-Br-1,3-Et_2-1,3,2-$N_2BC_6H_4$, with the appropriate lithiated arylacetylene, $ArC{\equiv}CLi$. Molecular structures of **2, 3** and **5** were determined by X-ray diffraction studies. UV-vis and luminescence spectroscopic studies on these diazaboroles reveal intense blue/violet fluorescence with very large quantum yields of 0.89-0.99 for **2**-**5**. The experimental findings were complemented by DFT and TD-DFT calculations. The Stokes shift of only 2600 cm^{-1} for **5**, compared to Stokes shifts in the range of 5800 - 7400 cm^{-1} for **1**-**4**, is partly explained by the different electronic structures found in **5** compared to **1**-**4**. The HOMO is mainly located on the aryl group in **5** and on the diazaborolyl group in **1**-**4** whereas the LUMOs are largely aryl in character for all compounds. Thus, in contrast to other conjugated systems containing three-coordinate boron centers such as $B(Mes)_2$, (Mes = 2,4,6-$Me_3C_6H_2$), in which the boron serves as a π-acceptor, the 10-π electron benzodiazaborole moiety appears to function as a π-donor moiety.

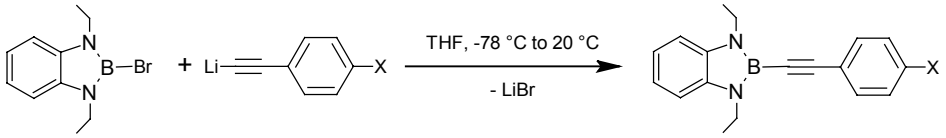
Introduction

Conjugated molecules and polymers containing three-coordinate boron exhibit interesting optical and electronic properties making them appropriate for use in functional materials.[1] Three-coordinate boron generally behaves as a π-acceptor, due to its vacant p_z orbital, but as boron is more electropositive than carbon, the boryl moiety can be a σ-donor. Much of the work in this area has involved dimesitylboryl ($B(Mes)_2$) moieties (Mes- = 2,4,6-$Me_3C_6H_2$-), as these confer stability to the unsaturated boron center via steric effects of the *ortho* methyl groups. Such compounds exhibit sizable second and third-order nonlinear optical (NLO)

coefficients,[2,3] large two-photon absorption (TPA) cross-sections,[4] and can been used as efficient electron-transporting and/or emitting layers in organic light emitting diodes (OLEDs).[5] Three-coordinate boron-containing compounds are effective colorimetric and luminescent sensors for anions, especially fluoride ions.[6] Recently, a number of conjugated molecules with boryl side-groups were shown to display very large Stokes shifts and high quantum yields both in solution and the solid state, which was attributed to the lack of close packing.[7]

Materials with phenylethynyl scaffolds as π-electron conducting units have been intensively studied mainly because of their luminescence and nonlinear optical properties, potential application as emitters in electroluminescent devices and as sensors, and liquid crystal phase behavior. Marder,[8,9] Bunz[10] and others[11] have examined optical and other physical properties of oligo- and poly-(*p*-arylene)ethynes, including those substituted by donor- and/or acceptor groups.

At Bielefeld, we have a long-standing interest in the chemistry of 1,3,2-diazaboroles.[12,13] 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 substituents, which gave intense luminescence when irradiated with UV light.[14,15] We recently reported the synthesis and photophysical properties of 2-(PhC≡C)-1,3-Et_2-1,3,2-$N_2BC_6H_4$, **1**.[16] Herein we report the syntheses, photophysical properties and computational studies of derivatives with a series of substituents of increasing π-electron-donating strength, i.e. Me, OMe, SMe, NMe_2, attached at the *para* position of the phenyl group of compound **1**.



1 : X = H
2 : X = Me
3 : X = OMe
4 : X = SMe
5 : X = NMe_2

Chart 1. Compounds discussed in this study.

Results and discussion

Synthesis

Reaction of 2-bromo-1,3-diethyl-1,3,2-benzodiazaborole with equimolar amounts of the *in situ* generated lithium-derivatives of the appropriate arylalkynes in THF in the temperature range -78°C to 20°C led to the generation of benzodiazaboroles, 2-(4'-$XC_6H_4C{\equiv}C$)-1,3-Et_2-1,3,2-$N_2BC_6H_4$ (X = Me, **2**; MeO **3**; MeS **4**; Me_2N **5**) (Chart 1). The products were isolated by short path distillation and recrystallization of the solid distillates from n-pentane/dichloromethane mixtures as colorless crystalline solids in 42-69% yields. All of the compounds synthesized here can be stored at -5°C under an argon atmosphere for several weeks without decomposition. In the $^{11}B\{^1H\}$ NMR spectra for the 1,3,2-diazaboroles **2-5** synthesized here, singlets are observed between 20.5 and 21.2 ppm in agreement with a singlet at δ = 21.2 ppm reported for **1**.[16]

X-ray crystallography

The molecular structures of the diazaboroles **2**, **3** and **5** were determined by single-crystal X-ray diffraction studies. Selected bond lengths and angles are listed in Table 1, with data for **1** added for comparison. While crystals of **1**, **2** and **5** contain one independent molecule, the crystal structure of the methoxy derivative **3** contains two independent molecules A and B, one of similar conformation to molecules of **1**, **2** and **5** wherein the angles between the arene and heterocycle ring planes are in the range of 65.8 to 78.4°. The second independent molecule B in the crystal of **3** has a different conformation, featuring an interplanar angle between the arene ring and heterocycle of 13.4 ° as determined by the angle between the two normals at the rings.

As shown in Table 1, the bond lengths and angles are virtually identical even in the case of the nearly planar conformation of molecule B for **3**. The similar parameters found in both conformers (A and B) for **3** show that the ring rotation has little influence on bond lengths, despite the fact that π conjugation between the rings would be highly favored in molecule B.

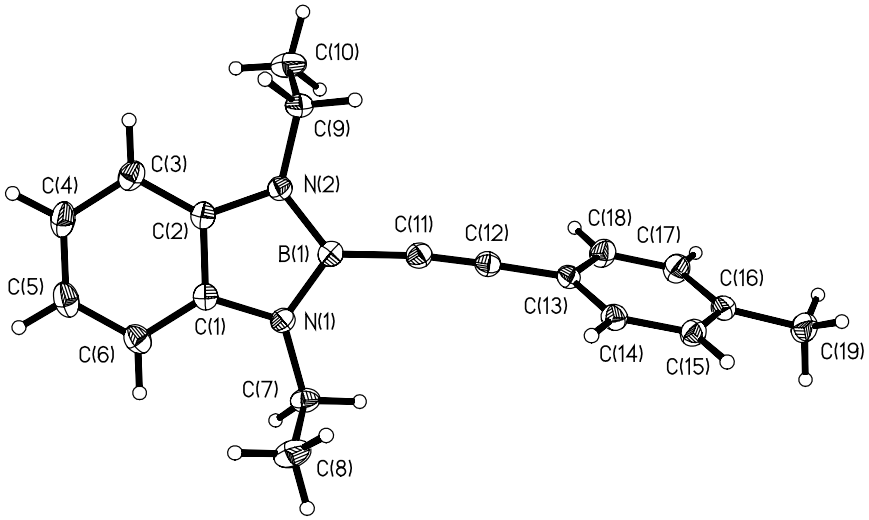


Figure 1. Molecular structure of **2** in the crystal. Ellipsoids are drawn at 50% probability level here and in Figures 2 and 3.

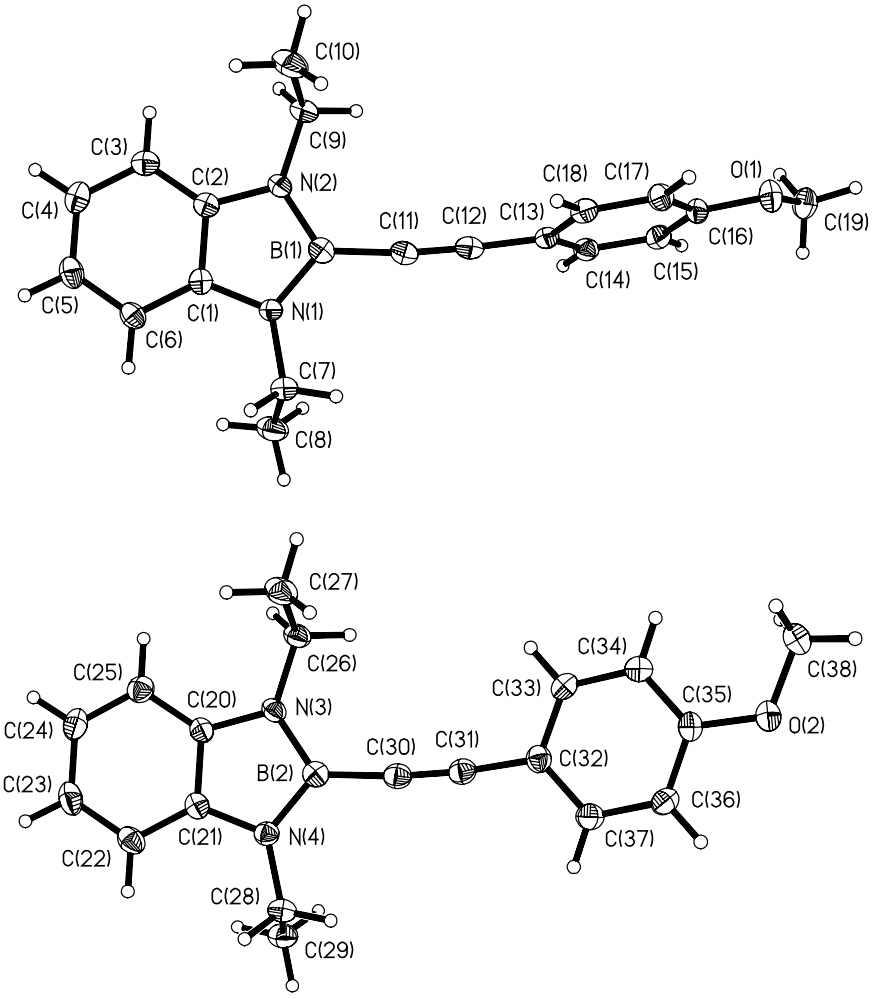


Figure 2. Molecular structure of **3**, showing the molecules in the unit cell, A (top) and B (bottom).

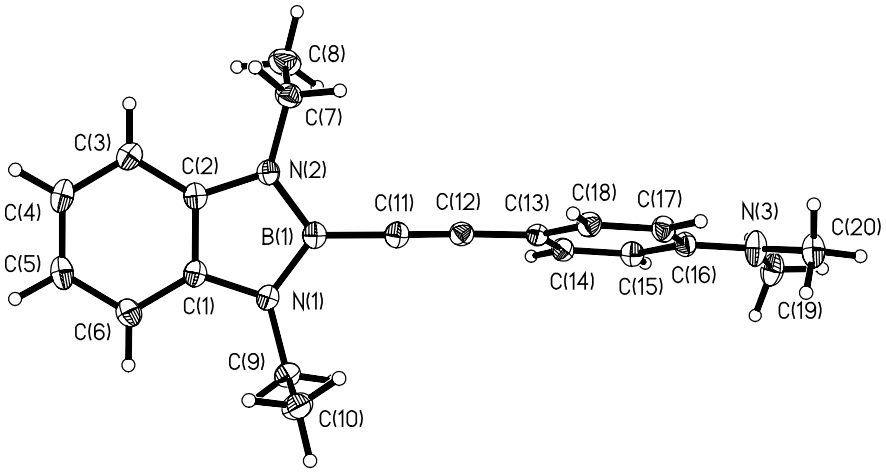


Figure 3. Molecular structure of **5**. Selected angles (°) C(16)-N(3)-C(20) 119.7(1), C(16)-N(3)-C(19) 119.6(1), C(19)-N(3)-C(20) 118.5(1), C(15)-C(16)-N(3)-C(19) -6.2, C(17)-C(16)-N(3)-C(20) 11.1.

Table 1. Selected bond lengths and angles for **1-3** and **5**.

	1[a]	**2**	**3** (A)	**3** (B)	**5**
Bond lengths (Å)					
B-C	1.524(2)	1.530(1)	1.524(2)	1.523(2)	1.525(2)
B-N*	1.429(1)	1.431(1)	1.431(2)	1.427(2)	1.430(1)
C≡C	1.208(1)	1.207(1)	1.207(2)	1.212(2)	1.209(1)
C-C(≡C)	1.439(1)	1.438(1)	1.440(2)	1.435(2)	1.435(1)
Benzene ring					
C(13)-C(14/18)*	1.400(1)	1.400(1)	1.399(2)	1.395(2)	1.401(1)
C(14)-C(15)/C(17)-C(18)*	1.384(1)	1.389(1)	1.385(2)	1.380(2)	1.380(1)
C(15/17)-C(16)*	1.388(1)	1.394(1)	1.393(2)	1.389(2)	1.411(1)
C(16)-(C/O/N)		1.509(1)	1.361(2)	1.371(2)	1.380(1)
Angles (°)					
B-C≡C	175.6(1)	174.0(1)	173.8(2)	172.8(2)	179.4(1)
C-C≡C	178.8(1)	178.0(1)	176.1(2)	174.0(2)	178.3(1)
Interplanar angles (°)	65.8	70.4	78.4	13.4	76.4

[a]Reference 16.

*averaged values

Several compounds related to **1** but containing three-coordinate boron attached to a phenylethynyl group have been structurally characterised.[15,16] However, aside from the molecular structures of **1-3** and **5** herein, there is only one set of crystal structures from which we can examine the structural effects of substituents on the phenyl group of the B-C≡C-Ar moiety, namely $Mes_2BC{\equiv}CMes$ and $Mes_2BC{\equiv}CC_6H_4NMe_2$, which may be viewed as Mes_2B analogues of **2** and **5**.[3,17] As in **2** and **5**, the bonds in the B-C≡C-C_{Ar} moiety are essentially unaffected by whether the substituent is Me or NMe_2. A slight increase in the quinoidal distortion of the *para*-substituted arene ring is observed for **5**.

UV-visible and luminescence spectroscopy

The optical properties of compounds **2-5** in THF solutions are summarized in Table 2 along with reported data for **1**. Compounds **1-5** show absorption maxima in the UV spectra at 307-325 nm and emission maxima in the near UV-visible region at 355-410 nm with extremely high quantum yields ranging from 0.89 to 0.99 (Table 2, Figs. 4,5). Diazaborole **4** has the lowest quantum yield (0.89), together with the largest Stokes shift, which may be explained by the heavy-atom effect of the S-Me group.[9] There is a correlation between the absorption maxima and the Hammett constant[18] σ_p of the substituent in the diazaboroles **1-5**, but there is no such trend between σ_p and the emission maxima.

The smallest Stokes shift of 2600 cm^{-1} for the Me_2N-substituted compound **5** is markedly different from the Stokes shifts of 5800-7400 cm^{-1} for the other diazaboroles listed in Table 2 and of 6200-9500 cm^{-1} recently reported for closely related diazaboroles where the boron is directly linked to thienyl or aryl groups. One explanation (*vide infra*) is that the HOMO and LUMO orbitals in **5** are quite different from those in other diazaborazoles **1-4** due to the strong electron-donating NMe_2 group in **5**.

Table 2. Photophysical data

	λ_{max} (abs, nm)	λ_{max} (abs, cm^{-1})	ε ($mol^{-1}cm^{-1}dm^3$)	λ_{max} (em, nm)	Φ_{fl}	Stokes shift (cm^{-1})	σ_p
1[a]	306	32700	-	393	-	7200	0.00
2[b]	307	32600	22300	388	0.99	6800	-0.31
3[b]	307	32600	26700	374	0.97	5800	-0.78
4[b]	315	31700	31800	410	0.89	7400	-0.80
5[b]	325	30800	44700	355	0.97	2600	-1.70

[a] Reference 16, solvent n-hexane

[b] This work, solvent THF, reference POPOP (Φ = 0.93)

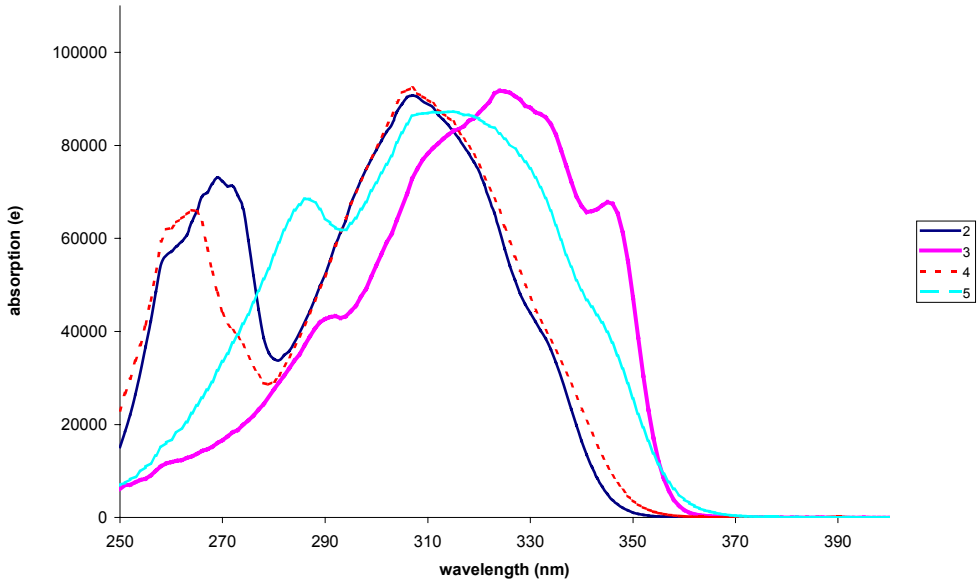


Figure 4. Absorption spectra of compounds **2-5**

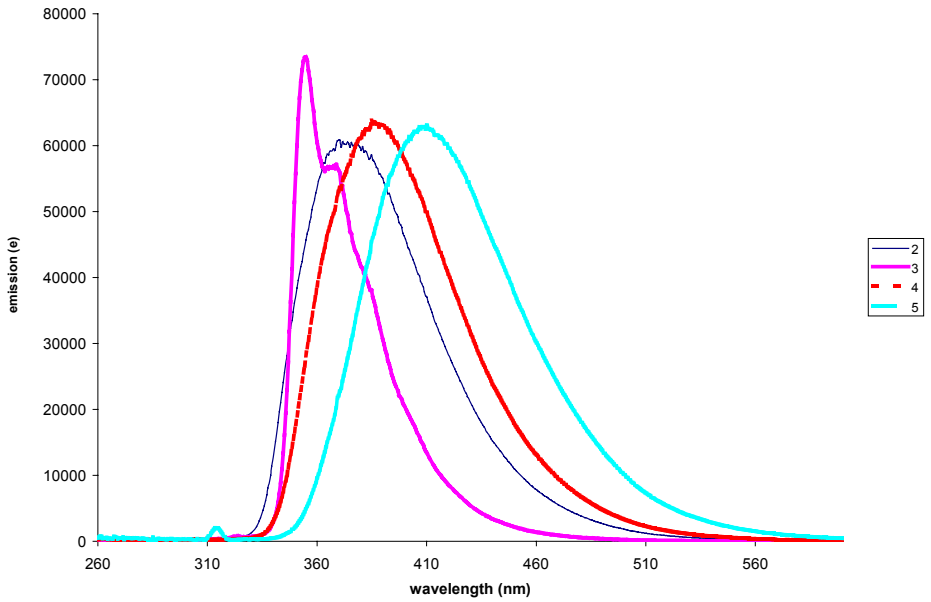


Figure 5. Emission spectra of compounds **2-5**

DFT computations

Geometries of model compounds **1a-5a**, with methyl groups instead of the ethyl groups in **1-5**, were optimized via DFT calculations at the B3LYP/6-31G* level of theory. Global minima occur when both the benzodiazaborole and benzene rings are coplanar. Model geometries with the diazaborole and benzene rings constrained to be mutually perpendicular were also optimized, confirmed as true local minima and are denoted as **1b-5b**. The energy differences between the two conformers were in the range of 0.6-0.8 kcal mol^{-1}. The highest energy geometry between the two minima **1a** and **1b** was located with diazaborole and benzene rings at 85° to each other and was found to be a mere 0.005 kcal mol^{-1} higher than **1b**. These energy values indicate that the rotation barriers between these rings are negligible, and that all rotamers will be populated in solution at ambient temperature. The sum of the angles at the nitrogen in the dimethylamino group in the experimental and optimized geometries are 357.8°, 359.9° and 357.3° for **5**, **5a** and **5b** respectively, close to 360° expected for a planar geometry, which maximizes conjugation of the N-lone pair with the aromatic π-system as expected.

Table 3 lists selected geometrical parameters for **1a**, **1b**, **5a** and **5b** and shows that the different ring orientations have little influence on the geometries. This is in agreement with the negligible geometrical differences found for the two independent in the crystal of the methoxy derivative **3**. Comparison between the experimental X-ray and optimized geometries (Tables 1 and 3) reveal very good agreements in the geometrical parameters. The modest quinoidal distortion in the solid state structure of **5** is also well reproduced in the DFT calculations.

Table 3. Selected bond distances and angles for model geometries of **1** and **5**.

	1a	**1b**	**5a**	**5b**
Bond distances (Å)				
B-C	1.516	1.519	1.513	1.517
B-N	1.439	1.438	1.441	1.440
C≡C	1.221	1.220	1.222	1.221
C-C(≡C)	1.426	1.428	1.422	1.425
Benzene ring				
C-C	1.409	1.409	1.409	1.408
	1.392	1.393	1.386	1.387
	1.397	1.397	1.416	1.416
C-(H/N)	1.087	1.089	1.382	1.386
Angles (°)				
B-C≡C	180.0	180.0	180.0	180.0
C-C≡C	180.0	180.0	180.0	180.0
Torsion angles (°)				
N-B-(C≡C)-C-C	0.0	90.0	0.0	90.0

The calculated absorption maxima from TD-DFT computations on the model geometries clearly depend on the orientations between the two ends of the triple bond link. These absorptions arise from strong, low energy HOMO-LUMO transitions. The observed absorption values for **1**-**4** are in good agreement with computed data from their model geometries assuming that all conformers are present in solution where the planar and perpendicular forms represent the two extreme conformers. However, for **5** the agreement between computed and observed values is poor, being much closer to the planar form **5a** than for **5b**. This can be explained by the use of the polar solvent THF in our experimental study vs. gas phase calculations, and the fact that compound **5** is considerably more polar than **1**-**4** as shown by the calculated dipole moments in Table 4, and thus its measured absorption maximum could be significantly affected. The computed oscillator strengths are in accord with the observed extinction coefficients for all diazaboroles **1**-**5**.

Table 4. Comparison of computed (TD-DFT) data for model geometries of **1-5** with observed UV absorption data for **1- 5**.

	λ_{max} (nm)	Oscillator strength (*f*)	Dipole moment[a] (μ,D)		λ_{max} (abs, nm)	ε ($mol^{-1}cm^{-1}dm^3$)
1a	336	0.65	1.69	**1**	306	-
1b	272	0.51	1.71			
2a	335	0.73	1.40	**2**	307	22300
2b	275	0.84	1.40			
3a	328	0.85	3.21	**3**	307	26700
3b	272	0.64	3.09			
4a	342	0.93	2.42	**4**	315	31800
4b	278	1.31	2.37			
5a	331	1.19	5.21	**5**	325	44700
5b	277	1.47	4.87			

[a]dipole is oriented with the negative end towards the diazaborolyl moiety in all cases.

Table 5 lists the orbital energies and orbital compositions for the HOMO and LUMO of all ten model geometries; the model geometries for **2**-**4** all have similar orbital compositions as the model geometries for **1**. In contrast, the electronic structure of the dimethylamino compound **5** is different to those for **1**-**4**. Figures 6 and 7 show the HOMOs and LUMOs for the four model geometries of **1** and **5**. While the HOMO in **1** is largely diazaborolyl (73-75%) in character, the LUMO in **1** is mainly located on the aryl moiety (52-55%). The HOMO-LUMO transitions for **1**-**4** are thus π(borolyl) → π*(aryl) charge transfer in nature. They indicate that the excited singlet state geometries for **1**-**4** have large dipole moments. In contrast, the HOMO in **5** has considerable aryl character (38% in **5a** and 82% in **5b**) while the LUMO in **5** is also of mainly aryl character (49% in **5a** and 80% in **5b**). The HOMO-LUMO transition for **5** is π(aryl) → π*(aryl) in nature. As both HOMO and LUMO are mainly located on the aromatic ring, compound **5** may not have a large dipole moment in its singlet excited state. The excited state of **5** would not be as dependent on the polar nature of the

solvent as the excited states of **1-4**. The significantly lower degree of charge transfer character could explain why the Stokes shift of 2600 cm^{-1} for **5** is considerably smaller than those of 5800-9500 cm^{-1} for related diazaboroles studied here and elsewhere.[16]

What is clearly evident from the computational results is that, in contrast to well-known BAr_2 systems (e.g. Ar = Mes), in which the BAr_2 unit serves as a strong π-acceptor, the 10 π-electron benzodiazaborole unit, isoelectronic with indenyl anion, is electron rich. Thus, in compounds **1-4**, the benzodiazaborole serves as the π-electron donor. It would therefore be interesting to explore, in future studies, the photophysical properties of a series of compounds analogous to **1-5** but bearing a strong π-acceptor, e.g. CN, CO_2R, $B(Mes)_2$ at the para position of the phenyl ring.

Table 5. Orbital energies and compositions for model geometries.

	X	HLG[a] (eV)	Orbital	E (eV)	$C_6H_4(NMe)_2$ (%)	B (%)	C≡C (%)	aryl (%)	X (%)
1a	H	4.06	LUMO	-1.16	11	9	25	55	0
			HOMO	-5.22	75	8	10	8	0
2a	Me	4.07	LUMO	-1.09	11	10	24	52	2
			HOMO	-5.16	73	7	11	9	0
3a	OMe	4.15	LUMO	-0.92	13	11	25	47	3
			HOMO	-5.07	67	6	12	12	3
4a	SMe	3.99	LUMO	-1.14	11	9	24	53	4
			HOMO	-5.13	64	6	11	12	7
5a	NMe_2	4.11	LUMO	-0.70	14	12	25	43	6
			HOMO	-4.81	44	3	14	24	14
1b	H	4.42	LUMO	-0.87	2	3	23	72	0
			HOMO	-5.29	82	10	7	1	0
2b	Me	4.47	LUMO	-0.79	2	3	23	69	3
			HOMO	-5.26	82	10	8	1	0
3b	OMe	4.64	LUMO	-0.58	2	3	24	66	4
			HOMO	-5.22	82	10	8	1	0
4b	SMe	4.41	LUMO	-0.86	2	3	22	69	5
			HOMO	-5.27	82	10	8	1	0
5b	NMe_2	4.38	LUMO	-0.70	2	3	24	62	8
			HOMO	-5.08	1	1	17	48	34
			HOMO-1	-5.12	81	10	8	1	0

[a]HLG = HOMO-LUMO Gap

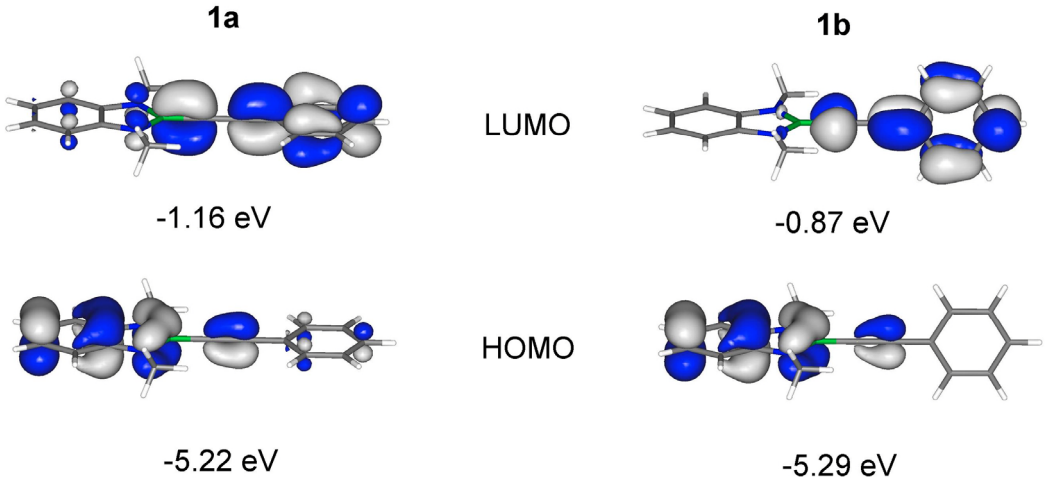


Figure 6. The frontier molecular orbitals for **1a** and **1b**. Contour values are plotted at ± 0.04 $(e/bohr^3)^{1/2}$.

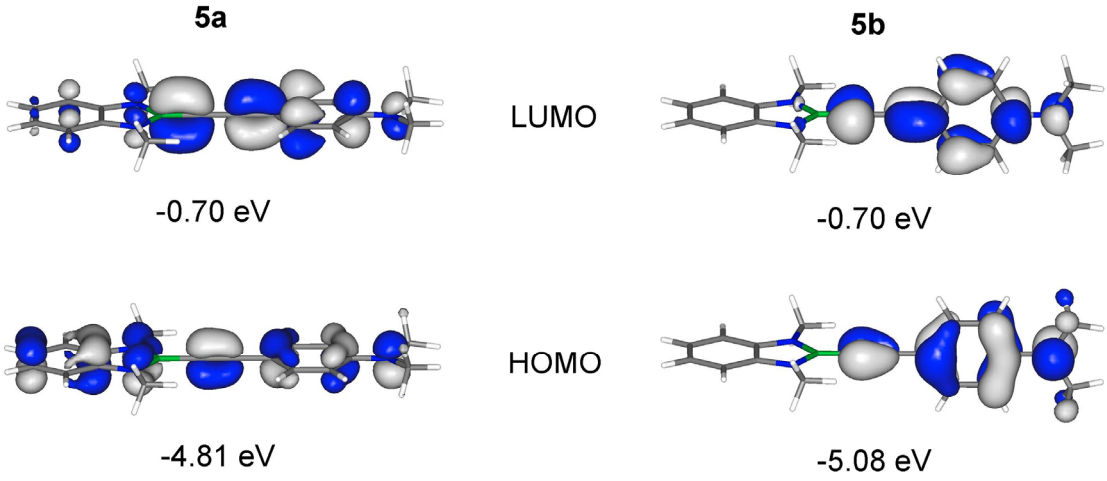


Figure 7. The frontier molecular orbitals for **5a** and **5b**. Contour values are plotted at ± 0.04 $(e/bohr^3)^{1/2}$.

Experimental section

All manipulations were performed under an atmosphere of dry, oxygen-free argon using standard Schlenk techniques. All solvents were dried by standard methods and freshly distilled prior to use. The compounds 2-bromo-1,3-diethyl-1,3,2-benzodiazaborole,[19] 4-methoxy-phenylacetylene,[20] 4-methylthio-phenylacetylene[21] and 4-dimethylamino-phenylacetylene[20,21] were prepared according to literature methods. 4-Methyl-phenylacetylene was employed as received from commercial sources (Aldrich). NMR spectra were recorded in $CDCl_3$ solutions at room temperature on a Bruker AM Avance DRX 500 spectrometer (^1H, ^{11}B, ^{13}C) using $SiMe_4$ and $BF_3{\cdot}OEt_2$ as external standards. The expected ^{13}C peaks corresponding to the ethynyl carbons were not detected above the noise levels. Absorption is measured with a UV/VIS double-beam spectrometer (Shimadzu UV-2550), using the solvent as a reference. The setup used to acquire excitation-emission spectra (EES) was similar to that employed in commercial static fluorimeters: The output of a continuous Xe-lamp (75W, LOT Oriel) was wavelength-separated by a first monochromator (Spectra Pro ARC-175, 1800 l/mm grating, Blaze 250 nm) and then used to irradiate a sample. The fluorescence was collected by mirror optics at right angles and imaged on the entrance slit of a second spectrometer while compensating astigmatism at the same time. The signal was detected by a back-thinned CCD camera (RoperScientific, 1024×256 pixels) in exit plane of the spectrometer. The resulting images were spatially and spectrally resolved. As the next step, one averaged fluorescence spectrum was calculated from the raw images and stored in the computer. This process was repeated for different excitation wavelengths. The result is a two-dimensional fluorescence pattern with the y-axis corresponding to the excitation, and the x-axis to the emission wavelength. Figure 8 shows sample spectra obtained with this technique. Here, the wavelength range is λ_{ex} = 230-450 nm (in 1 nm increments) for the UV light and λ_{em} = 100-700 nm for the detector. The time to acquire a complete EES is typically less than 15 min. Post-processing of the EES includes subtraction of the dark current background, conversion of pixel to wavelength scales, and multiplication with a reference file to take the varying lamp intensity as well as grating and detection efficiency into account. For all measurements, samples were contained in quartz cuvettes of 10×10 mm^2 (Hellma type 111-QS, suprasil, optical precision). They were prepared with distilled and dried THF, with concentrations varying from 1 to 8 μM according to their optical density. The quantum yields were determined against POPOP (p-bis-5-phenyl-oxazolyl(2)-benzene) (Φ= 0.93) as the standard.

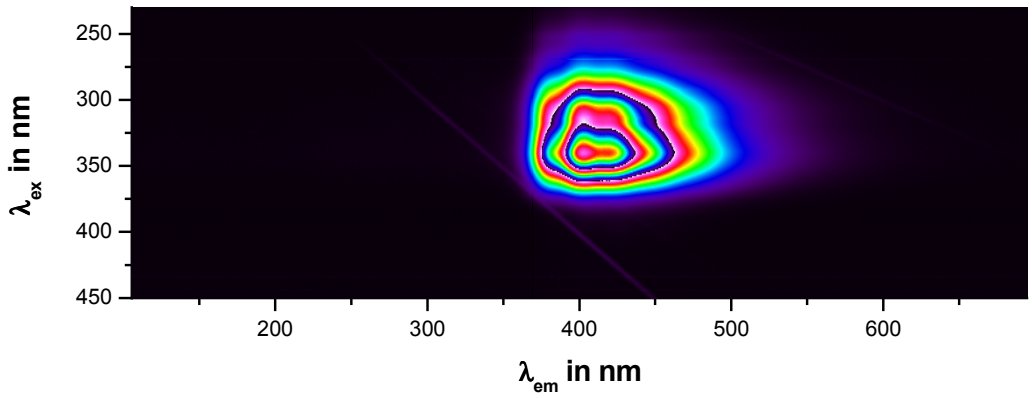


Figure 8. Example of an EES spectrum

2-(4´-Methylphenylethynyl)-1,3-diethyl-1,3,2-benzodiazaborole **2**

A chilled solution (-78°C) of 4-methyl-phenylacetylene (0.43 g,1.7 mmol) in THF (30 mL) was treated with a 1.5 M solution of n-butyllithium in hexane (1.14 ml, 1.7 mmol) and the mixture was stirred for 3 h at -78°C and another 0.5 h at ambient temperature. After cooling to -78°C, a solution of 2-bromo-1,3-diethyl-1,3,2-benzodiazaborole (0.20 g, 1.70 mmol) in THF (5 mL) was added dropwise to the solution of the lithium acetylide. Stirring of the mixture was continued for 2.5 h at -78°C and then overnight at room temperature. The resulting solution was evaporated to dryness. The resulting residue was triturated with CH_2Cl_2 and filtered. The filtrate was liberated from solvents and the residue was subsequently purified by short path distillation at 10^{-3} bar. Product **2** was collected as a colorless solid, which was crystallized from n-pentane at -20°C for 3 d to yield 0.32 g (65%) of **2** as analytically pure colorless crystals.

Found C, 78.98; H, 7.22; N, 9.65% $C_{19}H_{21}N_2B$ requires C, 79.18; H, 7.34; N, 9.70%; ^{1}H-NMR: δ = 1.39 (t, $^3J_{H,H}$ = 7.2 Hz, 6H, $CH_2C\underline{H}_3$), 2.38 (s, 3H, $C_6H_4C\underline{H}_3$), 3.93 (q, $^3J_{H,H}$ = 7.2 Hz, 4H, $C\underline{H}_2CH_3$), 7.03 (m, 2H, CH-benzodiazaborole), 7.08 (m, 2H, CH-benzodiazaborole), 7.18 (d, $^3J_{H,H}$ = 8.2 Hz, 2H, C_6H_4), 7.49 (d, $^3J_{H,H}$ = 8.2 Hz, 2H, C_6H_4); ^{13}C{^{1}H}-NMR: δ = 16.2 (s, $CH_2\underline{C}H_3$), 21.6 (s, $C_6H_4\underline{C}H_3$), 38.2 (s, $\underline{C}H_2CH_3$), 106.8 (s, B-C≡$\underline{C}$), 108.8 (s, CH-benzodiazaborole), 118.8 (s, CH-benzodiazaborole), 120.1 (s, C-Ph), 129.2 (s, C-Ph), 132.0 (s, C-Ph), 137.0 (s, C-benzodiazaborole), 139.0 (s, $\underline{C}$-CH_3); ^{11}B{^{1}H}-NMR: δ = 21.1 (s); MS (EI) m/z = 288 [M^+], 273 [M^+-CH_3].

2-(4´-Methoxy-phenylethynyl)-1,3-diethyl-1,3,2-benzodiazaborole **3**

A well stirred, chilled solution (-78°C) of 4-methoxy-phenylacetylene (2.00 g,15.1 mmol) in THF (50 mL) was combined with a 1.6 M solution of n-butyllithium in hexane (9.5 ml, 15.1

mmol). Stirring was continued at -78°C for 1 h and then 0.5 h at room temperature. The mixture was chilled to -78°C and subsequently treated dropwise with a solution of 2-bromo-1,3-diethyl-1,3,2-benzodiazaborole (3.82 g, 15.1 mmol) in THF (20 mL). The solution was stirred for 1 h at -78°C and overnight at ambient temperature. The solvent was removed *in vacuo* and the residue was dissolved in CH_2Cl_2 (20 mL) and filtered. The filtrate was freed from volatile components and the residue was purified by short-path distillation at 10^{-3} bar. Crystallization of the solid distillate from a CH_2Cl_2/hexane mixture afforded 3.30 g (69%) of colorless crystalline product **3**.

Found C, 74.04; H, 7.15; N, 8.91% $C_{19}H_{21}N_2BO$ requires C, 75.02; H, 6.96; N, 9.21%; ^{1}H-NMR: δ = 1.37 (t, $^3J_{H,H}$ = 7.2 Hz, 6H, $CH_2C\underline{H}_3$), 2.82 (s, 3H, O-C$\underline{H}_3$), 3.90 (q, $^3J_{H,H}$ = 7.2 Hz, 4H, C$\underline{H}_2CH_3$), 6.87 (d, $^3J_{H,H}$ = 8.8 Hz, 2H, CH-phenyl), 7.00 (m, 2H, CH-benzodiazaborole), 7.05 (m, 2H, CH-benzodiazaborole), 7.51 (d, $^3J_{H,H}$ = 8.8 Hz, 2H, H- m-CH-phenyl); ^{13}C{^{1}H}-NMR: δ = 16.1 (s, $CH_2\underline{C}H_3$), 38.2 (s, $\underline{C}H_2CH_3$), 55.3 (s, O-$\underline{C}H_3$), 108.7 (s, CH-benzodiazaborole), 114.0 (s, C-Ph), 115.7 (s, C-Ph), 118.8 (s, CH-benzodiazaborole), 133.6 (s, C-Ph), 136.9 (s, C-benzodiazaborole), 160.6 (s, $\underline{C}$-OCH$_3$); ^{11}B{^{1}H}-NMR: δ = 21.1 (s); MS (EI) m/z = 304 [M^+], 289 [M^+-CH_3].

2-(4´-Methylthio-phenylethynyl)-1,3-diethyl-1,3,2-benzodiazaborole **4**

A well stirred chilled solution (-78°C) of 4-methylthio-phenylacetylene (0.20 g, 1.35 mmol) in THF (30 mL) was treated with a 1.6 M solution of n-butyllithium in hexane (0.87 ml, 1.36 mmol). The resulting mixture was stirred for 3 h at -78°C and another 0.5 h at room temperature before it was cooled to -78°C again. A solution of 2-bromo-1,3-diethyl-1,3,2-benzodiazaborole (0.34 g, 1.7 mmol) in THF (5 mL) was slowly added and stirring was continued for 2 h, and then overnight at room temperature. Evaporation of the reaction mixture to dryness was followed by extraction of the obtained residue with CH_2Cl_2. The filtered CH_2Cl_2 extract was freed from solvent, and the crude product was purified by short-path distillation at 10^{-3} bar. The solid distillate was crystallized from n-pentane (-20°C, 3 d) to give 0.18 g (42%) of **4** as colorless needles.

Found C, 70.27; H, 6.60; N, 8.69% $C_{19}H_{21}N_2BS$ requires C, 71.26; H, 6.61; N, 8.69%; ^{1}H-NMR: δ = 1.37 (t, $^3J_{H,H}$ = 6.9 Hz, 6H, $CH_2C\underline{H}_3$), 2.50 (s, 3H, S-C$\underline{H}_3$), 3.90 (q, $^3J_{H,H}$ = 6.9 Hz, 4H, C$\underline{H}_2CH_3$), 7.02 (m, 2H, CH-benzodiazaborole), 7.06 (m, 2H, CH-benzodiazaborole), 7.21 (d, $^3J_{H,H}$ = 8.5 Hz, 2H, CH-phenyl), 7.47 (d, $^3J_{H,H}$ = 8.5 Hz, 2H, CH-phenyl); ^{13}C{^{1}H}-NMR: δ = 14.5 (s, S-$\underline{C}H_3$), 15.3 (s, $CH_2\underline{C}H_3$), 37.3 (s, $\underline{C}H_2CH_3$), 107.9 (s, CH-benzodiazaborole), 117.9 (s, CH-benzodiazaborole), 118.4 (s, C-Ph), 124.8 (s, C-Ph), 131.4 (s, C-Ph), 136.0 (s,

C-benzodiazaborole),139.2 (s, C-SCH_3); $^{11}B\{^1H\}$-NMR: δ = 20.9 (s); MS (EI) m/z = 320 [M^+].

2-(4′-Dimethylamino-phenylethynyl)-1,3-diethyl-1,3,2-benzodiazaborole **5**

Analogously, a sample of 4-dimethylamino-phenylacetylene (2.00 g,13.8 mmol) was first lithiated using a 1.6 M solution of n-butyllithium in hexane (8.7 ml, 13.9 mmol) and then further reacted with an equimolar amount of 2-bromo-1,3-diethyl-1,3,2-benzodiazaborole (3.49 g, 13.8 mmol) in 20 mL of THF. After evaporation of solvent and volatile components from the reaction mixture the residue was crystallized from dichloromethane (-20°C, 2 d) to give 2.37 g (54%) of product **5** as colorless needles.

Found C, 75.05; H, 7.58; N, 13.02% $C_{20}H_{24}BN_3$ requires C, 75.72; H, 7.63; N, 13.25%; ^{1}H-NMR: δ = 1.38 (t, $^3J_{H,H}$ = 6.9 Hz, 6H, CH_2CH_3), 3.0 (s, 6H, N-CH_3), 3.91 (q, $^3J_{H,H}$ = 6.9 Hz, 4H, CH_2CH_3), 6.65 (d, $^3J_{H,H}$ = 9.1 Hz, 2H, CH-phenyl), 7.01 (m, 2H, CH-benzodiazaborole), 7.05 (m, 2H, CH-benzodiazaborole), 7.49 (d, $^3J_{H,H}$ = 9.1 Hz, 2H, CH-phenyl); $^{13}C\{^1H\}$-NMR: δ = 16.1 (s, CH_2CH_3), 38.1 (s, CH_2CH_3), 40.2 (s, N-CH_3), 108.6 (s, CH-benzodiazaborole), 109.8 (s, C-Ph), 111.7 (s, C-Ph), 118.8 (s, CH-benzodiazaborole), 133.3 (s, C-Ph), 137.0 (s, C-benzodiazaborole), 150.4 (s, C-$N(CH_3)_2$); $^{11}B\{^1H\}$-NMR: δ = 21.2 (s); MS (EI) m/z = 317 [M^+], 302 [M^+-CH_3].

Computational Studies

All *ab initio* computations were carried out with the Gaussian 03 package.[22] The model and full geometries discussed here were optimised via DFT calculations using the B3LYP/6-31G* level of theory[23,24] with no symmetry constraints or with a constrained dihedral angle between the two rings of 90°. Frequency calculations carried out on these optimized geometries showed no imaginary frequencies. The electronic structure and TD-DFT computations were also carried out at the same level of theory. The MO diagrams and orbital contributions were generated with the aid of Gabedit[25] and GaussSum[26] packages respectively.

Crystallographic Studies

Crystallographic data were collected with a Nonius KappaCCD diffractometer with Mo-Kα (graphite monochromator, λ = 0.71073 Å) at 100 K.

Crystallographic programms used for structure solution and refinement were from SHELXS-97 and SHELXL-97.[27] The structures were solved by direct methods and were refined by using full-matrix least equares on F^2 of all unique reflections with anisotropic thermal parameters for all non-hydrogen atoms. Hydrogen atoms were included at calculated positions with U(H) = 1.2 U_{eq} for CH_2 groups and U(H) = 1.5 U_{eq} for CH_3 groups. Crystal data of the compounds are listed in Table 6. Supplementary crystallographic data for this paper can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Table 6. Crystallographic data of compounds **2**, **3** and **5**.

Compound	**2**	**3**	**5**
Empirical formula	$C_{19}H_{21}BN_2$	$C_{19}H_{21}BN_2O$	$C_{20}H_{24}BN_3$
M_r [g mol^{-1}]	288.19	304.19	317.23
Crystal dimensions [mm]	0.26 x 0.26 x 0.24	0.30 x 0.30 x 0.18	0.30 x 0.30 x 0.25
Crystal system	monoclinic	orthorhombic	monoclinic
Space group	$P2_{1/}n$	Pbca	$P2_{1/}n$
a [Å]	14.2697(3)	8.3709(3)	11.0573(2)
b [Å]	8.3197(2)	16.8468(5)	11.5078(2)
c [Å]	14.6128(2)	48.0255(16)	14.1544(3)
ß [°]	107.3256(11)	90	94.3123(13)
Z	4	16	4
ρ_{calc} [g cm^{-3}]	1.156	1.193	1.173
μ [mm^{-1}]	0.067	0.073	0.069
F (000)	616	2592	680
Θ[°]	3 – 30	3 – 27.5	3 – 27.5
No. refl. collected	35625	28284	27595
No. refl. unique	4828	7576	4108
R (int)	0.038	0.055	0.032
No. refl. [I > 2σ (I)]	3873	4774	3437
Refined parameters	203	421	221
GOF	1.061	0.969	1.042
R_F [I > 2σ (I)]	0.0424	0.0449	0.0385
wR_{F2} (all data)	0.1162	0.1087	0.1033
$\Delta\rho_{max/min}$ [e Å^{-3}]	0.268/ –0.198	0.181/ –0.260	0.216/ –0.221
CCDC			

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