# Structural and Spectroscopic Properties of Aryl Substituted Aminoboranes as Model Compounds and Synthons for B/C/N Materials and New Fluorescent Systems

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Dedicated to Professor Michael Veith on the Occasion of His 65th Birthday

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Abstract. Tetraphenylaminoborane (1) and carbazonyldiphenylborane (2) are examples for isolated BN bonds completely substituted by aryl ligands, which enable  $\pi$ -interactions. Such systems can serve as building blocks for new fluorescent polymers and are also suitable precursors for B/C/N materials. The compounds were characterized by multinuclear NMR spectroscopy, UV/Vis spectroscopy, and single-crystal X-ray diffractometry. Both compounds 1 and 2 are principal structures for tricoordinate, aryl substituted BN bonds. Compound 1 crystallizes in the monoclinic crystal system in the space group *P*2<sub>1</sub>, with two formula units per unit cell with *a* = 9.8236(9) Å, *b* = 9.2743(8) Å, *c* = 10.7426(10) Å;  $\alpha = 90^{\circ}$ ,  $\beta = 107.228(4)^{\circ}$ ,  $\gamma = 90^{\circ}$ , Z = 2, V = 10.7426(10) Å;  $\alpha = 90^{\circ}$ ,  $\beta = 107.228(4)^{\circ}$ ,  $\gamma = 90^{\circ}$ , Z = 2, V = 10.7426(10) Å;  $\alpha = 90^{\circ}$ ,  $\beta = 107.228(4)^{\circ}$ ,  $\gamma = 90^{\circ}$ , Z = 2, V = 10.7426(10) Å;  $\alpha = 90^{\circ}$ ,  $\beta = 107.228(4)^{\circ}$ ,  $\gamma = 90^{\circ}$ , Z = 2, V = 10.7426(10) Å;  $\alpha = 90^{\circ}$ ,  $\beta = 107.228(4)^{\circ}$ ,  $\gamma = 90^{\circ}$ , Z = 2, V = 10.7426(10) Å;  $\alpha = 90^{\circ}$ ,  $\beta = 107.228(4)^{\circ}$ ,  $\gamma = 90^{\circ}$ , Z = 2, V = 10.7426(10) Å;  $\alpha = 90^{\circ}$ ,  $\beta = 107.228(4)^{\circ}$ ,  $\gamma = 90^{\circ}$ , Z = 2, V = 10.7426(10) Å;  $\alpha = 90^{\circ}$ ,  $\beta = 107.228(4)^{\circ}$ ,  $\gamma = 90^{\circ}$ , Z = 2, V = 10.7426(10) Å;  $\alpha = 90^{\circ}$ ,  $\beta = 107.228(4)^{\circ}$ ,  $\gamma = 90^{\circ}$ , Z = 2, V = 10.7426(10) Å;  $\alpha = 90^{\circ}$ ,  $\beta = 107.228(4)^{\circ}$ ,  $\gamma = 90^{\circ}$ , Z = 2, V = 10.7426(10)

## Introduction

Materials of the system boron/carbon/nitrogen are of general interest for fundamental research and also because of their use in various applications. These are, for example, carbon derivatives that are coordinated threefold, like graphene [1, 2], graphite, fullerenes and carbon nanotubes [3]. Within these systems it is interesting to investigate the effects that occur if a  $C_2$ fragment is replaced by an isoelectronic BN unit. Therefore, substitution patterns of tricoordinate as well as tetracoordinate systems are feasible and make these systems interesting starting materials in regard of their physical and electronic properties. The understanding of the influence of steric and electronic effects if aryl substituents are linked to the BN bond in BNsubstituted aromatic compounds is of general interest regarding the development of new BC<sub>x</sub>N materials, since  $\pi$ -interactions are feasible with boron as well as nitrogen atoms. For this reason we characterized tetraphenylaminoborane (1) and carbazonyldiphenylborane (2) as selected model compounds for tricoordinate, fully aryl substituted BN systems.

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934.81(15) Å<sup>3</sup> (final *R* indices  $[I > 2 \sigma(I)]$ :  $R_1 = 0.0597$ ;  $wR_2 = 0.1489$ ) and compound **2** crystallizes in the monoclinic crystal system of the space group *C2/c*. The unit cell contains four formula units as a set of two pairs of diastereomers. The cell parameters are a = 17.404(4) Å, b = 11.020(2) Å, c = 9.4195(19) Å;  $a = 90^{\circ}$ ,  $\beta = 91.45(3)^{\circ}$ ,  $\gamma = 90^{\circ}$ , Z = 4, V = 1805.9(6) Å<sup>3</sup> (final *R* indices  $[I > 2 \sigma(I)]$ :  $R_1 = 0.038$ ;  $wR_2 =$ 0.0847). The UV/Vis spectra of **1** and **2** reveal strong absorptions (240 nm and 285 nm) for **1** and broad features (260 nm and 290 nm) for **2**. The <sup>11</sup>B NMR spectroscopic data of **1** (48.7 ppm) and **2** (53.0 ppm) clearly indicate tricoordinate BN systems in solution with a weaker BN  $\pi$ -interaction compared to dialkylborylamines.

These compounds can formally be considered as molecular building blocks for BN substituted fullerenes [4, 5] and heterographenes, and as molecular units for the generation of self organized superstructures on surfaces [6, 7]. Their structural motifs are depicted in Figure 1.

Since aryl ligands have UV active  $\pi$ -interactions, an important aim of this study is also to characterize the influence of a boryl substitution of highly fluorescent groups like the carbazolyle ligand for the development of new fluorescent devices, as for example OLEDs [8], cf. Figure 2.

The structural and spectroscopic data of the heteroaromatic compounds **1** and **2**, both depicted in Figure 3, which can be considered as examples of an arylated, BN-substituted ethylene, were hitherto unknown. They were prepared according to standard procedures described in Equation (1) and characterized by <sup>1</sup>H, <sup>13</sup>C, and <sup>11</sup>B NMR spectroscopy, UV/Vis spectroscopy, and single crystal XRD.

$$Ar_{2}NH + N(C_{2}H_{5})_{3} + Ph_{2}BBr \xrightarrow{-(C_{2}H_{5})_{3}NHBr} Ar_{2}N-BPh_{2}$$

$$[Ar = Ph \text{ for (1) or } Ar_{2}NH = Carbazole \text{ for (2)}]$$
(1)

Compound **1** is a completely phenylated derivative of aminoborane  $H_2B=NH_2$ , which exists as a monomer only under extreme conditions [3,9,10]. The isoelectronic ethylene,  $H_2C=CH_2$ , however, is stable as a monomer under normal conditions. Fit-



Figure 1. Tetraphenylaminoborane (1) and carbazolyldiphenylborane (2) as molecular building blocks for tricoordinate BCN compounds, for example heterographenoid structures [Figure 1a)] and fulleroid structures [Figure 1b)].



Figure 2. Concept for the synthesis of new boryl substited fluorescent systems linked by  $\pi$ -systems.



Figure 3. Tetraphenylaminoborane (1) and Carbazolyldiphenylborane (2).

ting a BN bond in aromatic systems, for example by replacing the hydrogen atoms with phenyl groups, will result in a change in the binding situation and, in principle it is likely that the  $p_z$ orbitals of the boron and nitrogen atoms may interact with  $\pi$ orbitals of the phenyl substituents. This type of intramolecular stabilization and also the steric demand of the ligands are two effects that can be considered to be either responsible to prevent an oligomerization of polar BN units. Thus, an important question is up to what extent the BN bond is influenced by the possibility of aromatic  $\pi$ -interactions. The model compounds 1 and 2 characterized in this study are of use as molecular synthons for BN substituted graphenes, fullerenes and nanotubes, as exemplified in Figure 1. Although the structures of the carbon analogues like tetraphenylethylene [11, 12] and diphenylmethylenefluorene [13] have already been reported, the structures of the corresponding BN compounds, tetraphenylaminoborane (1) and carbazolyldiphenylborane (2), are still unknown. In these cases, C<sub>2</sub> fragments of a conjugated  $\pi$ -system are substituted by an isoelectronic BN group and enable investigation of the influence of the substitution of a C=C unit by a B=N unit in conjugated aromatic systems.

Compounds 1 and 2 can also be further functionalized e.g. by C–C coupling reactions to enable the preparation of BN aromatic systems. In addition, such molecular systems are valuable starting materials for functionalized graphene films and enable new routes as precursors for  $BC_xN$  materials, which are currently accessible by methods like e.g. decomposition of pyridine-borane or acetonnitile-BCl<sub>3</sub> [14, 15]. The approach presented in this study provides compounds for the molecular buildup of hetereographene units selectively substituted by BN groups in contrast to the synthesis of the high temperature routes of  $BC_xN$  materials [16, 17]. Therefore, compounds 1 and 2 were characterized as the most simple models for a B= N bond in an aromatic environment and the spectroscopic and structural data of those systems are reported.

## **ARTICLE**

### **Results and Discussion**

Compounds 1 and 2 were prepared according to Equation (1) in a straightforward reaction of diphenylbromborane and the corresponding amine in toluene by using trimethylamine as scavenger for hydrogen bromide. A different approach to obtain 1 is reported in [18], whereas no data for 2 were available so far. The compounds were characterized by multinuclear NMR spectroscopy, UV/Vis spectroscopy as well as single crystal XRD.

# *Tetraphenylaminoborane ["Diphenylaminodiphenylborane"]* (1)

A solution of compound **1** in CDCl<sub>3</sub> reveals one signal in the <sup>11</sup>B NMR spectrum at 48.66 ppm, which indicates a threefold coordination of the boron atoms and a monomer species in solution. The <sup>13</sup>C NMR spectrum reveals 10 signals, which can be interpreted as four carbon atoms of rotating phenyl groups at the Ph<sub>2</sub>B group (128.05 ppm, 131.44 ppm, 136.00 ppm, 136.1 ppm) and six carbon atoms of non rotating phenyl rings (NPh<sub>2</sub>, 108.22 ppm, 114.12 ppm, 117.82 ppm, 127.63 ppm,

130.94 ppm, 136.93 ppm). These attributions are in accordance with the starting materials [Ph<sub>2</sub>BBr: four signals at 137.5 (C2,6), 133.0 (C4), 127.9 (C3,5) and 139.2 (C1) ppm; Ph<sub>2</sub>NH: 143.15 (C1), 121.42 (C2), 121.03 (C2,6) and 117.85 (C3,5) ppm], and it is obvious that three resonances of the carbon atoms of the phenyl groups are strongly shifted to high field (108.22 ppm, 114.12 ppm, 117.82 ppm). This phenomenon clearly shows that the NMR shift of the carbon atoms of the NPh<sub>2</sub> units is affected by the ring current of the phenyl groups attached to the BPh<sub>2</sub> group. These results indicate that in solution, the phenyl groups at the boron atom are in a more symmetrical conformation, whereas the phenyl groups at the nitrogen atom show a signal splitting because of a hindered rotation.

Single crystals of **1** suitable for X-ray structure determination could be obtained from toluene solution. The compound crystallizes in a monoclinic crystal system in the space group  $P2_1$  with two formula units per unit cell. The structural features are depicted in Figure 4:

The molecular structure of **1** is depicted in Figure 4b and clearly indicates a monomeric aminoborane. The boron atoms



**Figure 4.** a) Unit cell and packing diagram [view along *a* axis]; b), c) molecular structure of tetraphenylaminoborane (1). Selected bond lengths / Å, bond angles /°, dihedral angles /° and interplanar angles /° of tetraphenylaminoborane (1): N(1)–B(1) 1.441(2); N(1)–C(1) 1.479(2); N(1)–C(7) 1.493(2); B(1)–C(19) 1.515(3); B(1)–C(13) 1.520(2); C–C 1.340(7)–1.407(3); bond angles: B(1)–N(1)–C(1) 121.88(14); B(1)–N(1)–C(7) 121.80(15); C(1)–N(1)–C(7) 116.33(15); N(1)–B(1)–C(19) 121.69(15); N(1)–B(1)–C(13) 120.73(15); C(19)–B(1)–C(13) 117.58(15); C(2)–C(1)–N(1) 121.45(16); C(6)–C(1)–N(1) 120.04(16); C(12)–C(7)–N(1) 121.8(2), C(8)–C(7)–N(1) 118.7(2); C(18)–C(13)–B(1) 119.69(17); C(14)–C(13)–B(1) 122.71(18); C(20)–C(19)–B(1) 121.86(17); C(24)–C(19)–B(1) 119.93(16); C–C–C 117.59(18)–121.3(2); dihedral angles: C(19)–B(1)–N(1)–C(7) –11.204(260); C(19)–B(1)–N(1)–C(1) 168.201(160), C(13)–B(1)–N(1)–C(1) –11.442(256); C(13)–B(1)–N(1)–C(7) 169.153(162); interplanar angles (Notation: plane 1//plane 2): C(13)B(1)C(19)//C(13)B(1)N(1) 11.345(143); C(19)C(24)C(23)C(22)C(21)C(20)//(13)B(1)N(1) 45.205(119); C(7)C(8)C(9)C(10)C(11)C(12)//C(13)B(1)N(1) 50.797(156); C(1)C(2)C(3)C(4)C(5)C(6)//C(19)B(1)N(1) 60.050(162); C(13)C(14)C(15)C(16)C(17)C(18)//C(7)B(1)N(1) 47.629(164).

c)



as well as the nitrogen atoms show a trigonal planar coordination (sum of bond angles at B(1) and N(1) =  $360^{\circ}$ ). The BN bond length of 1.441(2) Å is considerably longer than the standard value of 1.37 Å for a monomeric aminoborane [3, 9, 10], and the BC bond length of 1.515(3) Å and 1.520(2) Å does not reveal a significant aryl-boron interaction. The situation at the nitrogen atom N(1) is similar regarding the CN bond length in the range of 1.479(2)-1.493(2) Å. The BN bond length is closer to the expected values for borazines (1.44 Å) than to the expected value for aminoboranes (1.37 Å), and also similar to those in triaminoboranes [B(NHMe)<sub>3</sub> (1.41 Å)] [3, 18]. Since the molecule is substituted by four phenyl groups in a sterically demanding manner, the planes C(1)-N(1)-C(7)and C(13)-B(1)-C(19) are not fully coplanar (dihedral angle approx. 11.4°). The interplanar angles of the phenyl rings and the BN bond are in the range of 45-60°, and thus, there is no completely conjugated  $\pi$ -system because of an insignificant small overlap of the  $\pi$ -orbitals at the boron and nitrogen atoms, and no significant interactions with the aromatic  $\pi$ -system of the phenyl rings. The contortion of the phenyl groups and the BN bond thus can be attributed mainly to steric reasons. These effects comply with reports in literature [19] describing that aminoboranes have a  $\pi$ -contribution of 30–60 %, depending on the character of the substituents according to MO calculations and NMR spectra. According to [19], the phenyl groups are contorted out of the BN plane with an angle of 45° to minimize steric effects.

The analogue isoelectronic carbon compound of 1, tetraphenylethylene, reveals comparable crystal structure features like the same space group and similar cell parameters [ $P2_1$ ; a =9.798(2) Å, b = 9.715(2) Å, c = 10.781(2) Å and  $\beta =$ 107.94(1)°] [11, 12]. Also the molecular structure in the solid state resembles the corresponding analogs (C=C bond length: 1.356 Å, C=C-Ph length: 1.491–1.503 Å; dihedral angle of the C=C bond: 8.6°). In tetraphenylethylene, the C=C double bond of the ethylene unit is also slightly elongated compared to a standard value of 1.33 Å [3].

#### Carbazolyldiphenylborane (2)

Carbazolyldiphenylborane (2) was prepared in a similar manner as compound 1. The <sup>11</sup>B NMR spectrum of a toluene solution shows a single signal at 53.0 ppm, which clearly indicates tricoordinated boron atoms. Thus, this compound is monomeric in solution, too. The <sup>11</sup>B NMR signal of compound **2** is shifted to low field relative to compound 1, which indicates an electronically less shielded boron atom and thus the BN  $\pi$ -bonding is reduced. This effect can be attributed to the incorporation of the nitrogen atom in an aromatic ring system, and thus the BN  $\pi$ -back donation is weaker. This effect is also verified by the <sup>13</sup>C NMR spectrum, since the <sup>13</sup>C NMR signals for carbazole (110.92 ppm, 119.79 ppm, 120.67 ppm, 123.70 ppm, 126.17 ppm, 139.83 ppm) are nearly at the same positions relative to the <sup>13</sup>C NMR signals of carbazolyldiphenylborane (110.54 ppm, 119.43 ppm, 120.31 ppm, 123.33 ppm, 125.82 ppm), and indicate therefore a comparatively small disturbance of the aromatic system by the BN  $\pi$ -interaction. A comparable high field shift as in (diphenylamino)diphenylborane cannot be noted, which indicates that no substituents are affected by the ring currents of other phenyl groups attached to the BN bond. For the BPh2 groups attached to the boron atom, three signals are detected (127.93 ppm, 131.07 ppm, 134.69 ppm), which indicate a free rotation of these phenyl rings in the <sup>13</sup>C NMR spectrum. The NMR signal of the ipso-carbon atoms is not detectable because of the quadrupole broadening caused by the boron atom. No significant features are observed in the <sup>1</sup>H NMR spectrum and all signals are in the aromatic range (7.26–8.16 ppm).

Colorless single crystals of compound 2 suitable for X-ray structure determination were obtained from a toluene solution.

Carbazolyldiphenylborane (2) crystallizes in a monoclinic crystal system of the space group C2/c. The unit cell contains four formula units as a set off two pairs of diastereomers. Selected structural features, dihedral and interplanar angles of carbazolyldiphenylborane are given in Figure 5. The molecular structure of 2 reveals a crystallographically imposed  $C_2$  axis



**Figure 5.** a) Unit cell and packing diagram [view along *b* axis]; b) molecular structure of carbazolylborane (**2**). Selected bond lengths /Å, bond angles /°, dihedral angles /° and interplanar angles of carbazolyldiphenylborane (**2**): N(1)–B(1) 1.443(2); N(1)–C(1) 1.4373(14), B(1)–C(7) 1.5756(15); C(6)–C(6#) 1.447(2); other aromatic C–C distances: 1.380(3)–1.4125(17); bond angles: C(1)–N(1)–C(1#) 105.87(12); C(1)–N(1)–B(1) 127.06(6); N(1)–B(1)–C(7) 120.65(7); C(7)–B(1)–C(7#) 118.70(14), C(5)–C(6)–C(6#) 132.06(7); C(1)–C(6)–C(6#) 107.58(7); C(2)–C(1)–N(1) 129.80(10); C(6)–C(1)–N(1) 109.49(10); other C–C–C angles: 117.18(12) – 121.77(11); dihedral angles: C(1)–N(1)–B(1)–C(7) 29.356(15); N(1)–B(1)–C(7)–C(8) 42.257(14); C(12)–C(7)–B(1)–C(7) 37.177(13); interplanar angles (notation: plane 1//plane 2): C(1)N(1)C(1#)// C(7)B(1)C(7#) 29.358, C(7)C(8)C(9)C(10)C(11)C(12)//B(1)N(1)C(1) 61.201.

of symmetry along the BN bond, as indicated in Figure 5b. The BN bond length of 1.443(2) Å is located between the calculated values for a BN single bond (1.52 Å) and a BN double bond (1.32 Å) and the same arguments as for 1 can be considered in this case [3]. The BN bond length observed for 2 [N(1)-B(1): 1.443(2) Å] is nearly the same with the one of tetraphenylaminoborane (1) [N(1)–B(1): 1.441(2) Å], although the dihedral angle of 2 along the BN bond of approx. 30° is significantly increased compared to a value of  $\sim 11^{\circ}$  for 1 and indicates a weaker BN  $\pi$ -interaction in 2. The analogue isoelectronic carbon compound of 2, 9-(diphenylmethyliden)fluorene, was already described by Bock and Ruppert [13]. The selected bond length and angles of 9-(diphenylmethyliden)fluorene [C=C: 1.349(3); C=C-Ar: 1.491(3)-1.520(2); dihedral angle along the C=C bond:  $3^{\circ}$ ] reveal a stronger  $\pi$ -interaction in the exocyclic ethylene type C=C double bond and a smaller dihedral angle [in the range of  $\sim 3^{\circ}$  compared to those of  $\sim 30^{\circ}$ for 2] and thus a less contorted system. From these effects observed in these two similar structures it can be reasoned that the nonplanarity of the carbazolyl- and diphenylboryl groups linked by a BN bond can be attributed to the more ionic system in the case of **2**.

#### *UV/Vis Spectra of Tetraphenylaminoborane (1) and Carbazonyldiphenylborane (2)*

In order to characterize the UV/Vis spectroscopic properties of systems with fully aryl-substituted BN bonds, the spectra of compounds 1 and 2 were recorded and are depicted in Figure 6 a and b together with the spectra of carbazole and diphenylamine. As it can be seen from the spectrum of compound 2, the



Figure 6. a). UV/Vis Spectrum of 1; b) UV/Vis Spectrum of 2.

absorption in the UV region is enhanced in the case of carbazolylborane (2) making this compound also interesting for the synthesis of cabazolyl-based polymers and OLEDs.

The UV spectrum of tetraphenylaminoborane (1, bold line) shows two strong absorptions at 242 nm and 285 nm. The signal at 242 nm, which is not present in the UV spectrum of diphenylamine (dotted line), can be attributed to the phenyl groups at the boryl rest of 1.

Relative to carbazole (dotted line), compound **2** (bold line) shows a more pronounced absorption in the range of 240-260 nm and 280 -300 nm. New signals could be observed at 258 nm and 284 nm in the same range as the signals of carbazole.

#### Comparison of Compounds 1 and 2

Compounds 1 and 2 are similar regarding the substance class of monomeric aryl-substituted aminoboranes, but they differ in their spectroscopic properties and structural data. The most important data are summarized in Table 1.

Although tetraphenylaminoborane (1) reveals a more crowded arrangement of the phenyl ligands, the dihedral  $C_2BNC_2$  angle is smaller than in 2. Steric reasons can not be made responsible for this effect, since compound 1 could easily reduce steric hindrance by an increase of the C2BNC2 dihedral angle, and thus the observed structural effects are mainly due to electronic influence of the substituents and the different nature of the BN bond within these two systems. A comparison of the corresponding carbon systems of 1 and 2 reveals in general that the analogous C=C bond is only moderately distorted, which can be attributed to steric effects of the aryl substituents (tetraphenylethylene [11, 12]: C=C 1.356 Å, dihedral angle ~9°; trans-stilbene [20]: C=C 1.334 Å, dihedral angle ~3.4-6.9°; 9-(diphenylmethylidene)fluorene [13]: C=C 1.349(3) Å, dihedral angle  $\sim 3^{\circ}$ ]. The structural parameters of these carbon analogs of 1 and 2 indicate that an ethylene type bonding with an arrangement close to coplanarity is in general present, and the shortening of the C=C bond observed by comparison of trans-stilbene and tetraphenylethylene clearly indicates steric reasons. The dihedral angle observed for 2 in the range of about 30° is significantly larger than those of the carbon analog 9-(diphenylmethylidene)fluorene [13] of only ca. 3° and can not be explained by steric reasons.

The <sup>11</sup>B NMR spectroscopic data of Table 1 indicate clearly that both compounds are monomeric in solution and the signal of **2** is shifted about 4.3 ppm to low field because of a less pronounced BN  $\pi$ -interaction relative to **1**. The chemical shift of **2** is actually closer to the range of arylboronhalides than normal aminoboranes [21]. Because of the incorporation of the nitrogen atom in the hereroaromatic carbazolyle ring system in compound **2**, the  $\pi$ -back donation of the nitrogen atom to the boron atom is weaker in this case. The solid-state structures of **1** and **2** are also in accordance with this trend. Although the BN bond lengths are rather similar to **1** and **2**, differences in the dihedral angle (~11° vs. ~30°) and in the shorter CN bond length of the heteroaromatic carbazolyl substituent reveal a lower  $\pi$ -back donation of the nitrogen atom to the boron atom



Table 1. Summary of	the important	data of tetraphen	ylaminoborane (1	) and	carbazolyldi	phenylborane	(2)
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compound	<sup>11</sup> B NMR /ppm	B–N /Å	C−B /Å	C–N /Å	interplanar angle C(2)B–NC(2) /°	fluorescence (244 nm)
1	48.7	1.441(2)	1.515(3)–1.520(2)	1.479(2)–1.493(2)	11.4	blue-white
2	53.0	1.443(2)	1.5756(15)	1.4373(14)	29.4	green

in compound 2. The structural data of 1 and 2 do not indicate significant boron–carbon  $\pi$ -interaction with the B–Ph groups either. Additionally, the B-CPh bonds are significantly larger in 2 [1.5756(15) Å] than in 1 [1.515(3)-1.520(2) Å], and the phenyl groups are tilted out of a coplanar arrangement in both compounds [2, approx. 60°; cf. Figure 4 and 1, approx. 45-60°; cf. Figure 5]. It would be expected, that at least a partial interaction of the boron atom, as e.g. observed in the structure of phenylborondichloride PhBCl<sub>2</sub> with a B-C<sub>Ph</sub> bond length of 1.54 Å and a coplanar arrangement of the aryl group and the BCl<sub>2</sub> fragment [22], would enable an electronic stabilization of the boron atom in compound 2 because of a weakened BN bond, which is indicated by the chemical shift of the <sup>11</sup>B NMR signal and the dihedral angle of the BN bond of  $\sim 30^{\circ}$ , but this is not observed. The structural arrangement of 2 (phenyl groups closer to an orthogonal arrangement with the  $p_z$  orbital of the boron atom) can lead to [1,4]-B-H interactions (distances in the range of 2.7-3.0 Å), which have to be studied in more detail by high resolution multidimensional NMR spectroscopy [23]. For the above discussed reasons, a comparison of the borafluorene analogs of 2 and related compounds (cf. Figure 7) is currently carried out [23].

ally, an enhancement of the fluorescence can be observed in the case of boryl substitution of the carbazole unit. These findings make the carbazolyl boranes also interesting for applications in light harvesting and light emitting devices.

It has to be distinguished that although the ionicity in compounds 1 and 2 is increased by substitution of a C=C bond by a B=N bond, the conformation of compound 1 is still close to planarity regarding the heteroethylene type BN bond, whereas the distortion of 2 is significantly increased relative to 1 and the carbon analog described in [11–13, 20]. This effect can be attributed to an aromatic interaction of  $\pi$ -electrons of the nitrogen atom in the carbazolyl substituent, thus leading to a weak BN bond and a higher dihedral angle, which therefore can not solely be attributed to packing effects. The structural data of 2 indicate that the inclusion of the nitrogen atom in the aromatic ring system favors over the BN  $\pi$ -bonding. The experimental data are also supported by ab initio DFT calculations of the arrangement and electronic structure of 1 and 2 and similar systems [24].

In general, the substitution of a C=C unit by a B=N unit leads to compounds revealing many common structural properties, but if for example the nitrogen atom is part of an aromatic



Figure 7. Borafluorene derivatives with a inverse BN bond connectivity compared to compound 2.

#### Conclusions

In this report we could show that in aryl-substituted BN bonds the aryl-boron interaction is rather weak and the  $\pi$ -system of the phenyl rings is in general not interacting with the boron atoms. The structural results of **1** indicate that, if a sp<sup>2</sup> type BN bond is linked with four phenyl groups, the analogy to the corresponding carbon compound tetraphenylethylene is quite obvious and steric reasons can be made responsible for the non planarity of the BN bond in compound **1**. By UV irradiation a blue-white fluorescence is observed in this system. If the nitrogen atom of the BN bond is included in an aromatic ring system like carbazole, the interaction with the diphenyl boron unit is rather weak, as indicated by the <sup>11</sup>B NMR spectra as well as the crystallographic data of compound **2**. Addition-

system like in compound **2**, the B=N bond is significantly weakened. Therefore, heterographenoid molecular structures depicted e.g. in Figure 1a are expected to have a higher stability than molecular fullerenoid structures e.g. like those shown in Figure 1 b, where the B=N bond is part of a five membered aromatic system. Further studies will show if higher aromatic systems can be obtained from these compounds by C–C coupling reactions and how the  $\pi$ -bonding is disturbed within the inverse systems of **2** and related structures depicted in Figure 7 a–c [24].

## **Experimental Section**

**General:** All procedures were carried out by using modified Schlenk techniques in an argon atmosphere. Solvents were dried by standard procedures and degassed prior to use. Diphenylamine, triethylamnine

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#### Table 2. Structural data of 1 and 2.

Identification code	Tetraphenylaminoborane (1)	Carbazolyldiphenylborane (2)
Empirical formula	C <sub>24</sub> H <sub>20</sub> BN	C <sub>24</sub> H <sub>18</sub> BN
Formula weight	333.22	331.20
Temperature	100(2) K	293(2) K
Wavelength	0.71073 Å	0.71073 Å
Crystal System	monoclinic	monoclinic
Space Group	$P2_1$	C2/c
Unit cell dimensions	a = 9.8236(9) Å	a = 17.404(4) Å
	b = 9.2743(8) Å	b = 11.020(2) Å
	c = 10.7426(10) Å	c = 9.4195(19)  Å
	$\beta = 107.228(4)^{\circ}$	$\beta = 91.45(3)^{\circ}$
Volume	934.81(15) Å <sup>3</sup>	1805.9(6) Å <sup>3</sup>
Z	2	4
Density (calculated)	1.184 Mg·m <sup>-3</sup>	1.218 Mg·m <sup>-3</sup>
Absorption coefficient	$0.067 \text{ mm}^{-1}$	$0.069 \text{ mm}^{-1}$
<i>F</i> (000)	352	696
Crystal size	$0.5 \times 0.5 \times 0.5$ mm	$0.5 \times 0.5 \times 0.5$ mm
Theta range for data collection	1.98 to 34.02°.	3.06 to 28.06°.
Index ranges	$-15 \le h \le 12, -14 \le k \le 12, -16 \le l \le 15$	$-22 \le h \le 22, -14 \le k \le 14, -12 \le l \le 12$
Reflections collected	13750	8489
Independent reflections	6121 [R(int) = 0.0299]	2062 [ $R(int) = 0.0554$ ]
Completeness to theta 0-34.02°	94.3 %	93.6 %
Absorption correction	None	None
Refinement method	Full-matrix least-squares on $F^2$	Full-matrix least-squares on $F^2$
Data / restraints / parameters	6121 / 1 / 315	2062 / 0 / 155
Goodness-of-fit on $F^2$	1.057	0.968
Final <i>R</i> indices $[I > 2\sigma(I)]$	$R_1 = 0.0597, wR_2 = 0.1489$	$R_1 = 0.0381, wR_2 = 0.0847$
R indices (all data)	$R_1 = 0.0797, wR_2 = 0.1634$	$R_1 = 0.0678, wR_2 = 0.0934$
Absolute structure parameter	-1(3)	
Largest diff. Peak and hole	0.419 and $-0.474 \text{ e}\cdot\text{\AA}^{-3}$	0.174 and $-0.120 \text{ e} \cdot \text{\AA}^{-3}$

and carbazole were obtained from commercial suppliers (Aldrich) and used as received, and diphenylborbromide was prepared according to literature methods [22]. NMR spectra were recorded in  $C_6D_6$  solution by using a Bruker ACP 200 S spectrometer (TMS as external standard; <sup>1</sup>H: 200MHz; <sup>13</sup>C: 55.0 MHz; <sup>11</sup>B: 64.2 MHz). Regarding the hazard potential of compounds **1** and **2**, there is no specific knowledge available and the usual precautions for aromatic compounds should be taken. UV/Vis spectra were recorded in CH<sub>2</sub>Cl<sub>2</sub> (~10 mg of sample dissolved in 5 mL) by a Perkin–Elmer Lambda 35 UV/Vis spectrometer. Deviations in elemental analyses are attributed to the formation of carbides and nitrides during combustion.

The data for the crystal structure of compound **1** and **2** (Table 2) were collected at the specified temperatures with a Bruker AXS X8 Apex CCD diffractometer with a LT cooling device (Mo- $K_{\alpha}$ ,  $\lambda = 0.71073$  Å, graphite monochromator) Frames of 0.5° oscillation were exposed; deriving data in the Theta range of 2 to 34° with a completeness of ~ 95 %. Structure solution and full-matrix least square refinement with anisotropic thermal parameters for all non hydrogen atoms were performed using SHELX [25]. Further details of the crystal structure investigations are available from the Cambridge Crystallographic Data Centre by quoting the depository numbers CCDC-746398 for **1** and CCDC-746399 for **2**. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1 EZ, UK [Fax: + 44-1223-336-033; E-Mail: deposit@ccdc.cam.ac.uk.]

**Tetraphenylaminoborane** ["Diphenlamino-diphenylborane"] (1): A solution of diphenylbromborane (16.90 g, 69.01 mmol) in toluene (50 mL) was added to a solution of diphenylamine (11.68 g, 69.01 mmol) and triethylamine (7.68 g, 75.91 mmol) in toluene (200 mL). Triethylammoniumbromide precipitated immediately and the temperature of the mixture rose slightly. After complete addition, the mixture was heated to reflux for 30 minutes and a complete reaction was confirmed by <sup>11</sup>B NMR spectroscopy. The precipitate was removed by filtration and washed with toluene. The solvent was removed from the filtrate until crystallization started. Storage of the filtrate at 5 °C resulted in the formation of single crystals suitable for X-ray structure determination.

C<sub>24</sub>H<sub>20</sub>BN (M<sub>r</sub> = 333.24 g·mol<sup>-1</sup>): calcd. C 86.50, N 4.20, H 6.06; found C 86.61, N 4.32, H 5.56 %. <sup>11</sup>**B** NMR (CDCl<sub>3</sub>):  $\delta$  = 48.66. <sup>13</sup>**C** NMR (CDCl<sub>3</sub>):  $\delta$  = 108.22 (Ph–N), 114.12 (Ph–N), 117.82 (Ph–N), 127.63 (Ph–N), 128.05 (Ph–B), 130.94 (Ph–N), 131.44 (Ph–B), 136.00 (Ph–B), 136.1 (Ph–B, ipso), 136.93 (Ph–N, ipso). <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  = 6.31–7.95 (m, Ph).

**Carbazolyl-diphenylborane (2):** A solution of diphenylbromborane (7.29 g, 29.78 mmol) in toluene (50 mL) was added dropwise to a solution of carbazole (5 g, 29.90 mmol) and triethylamine (5 mL, 35.91 mmol) in toluene (100 mL). The yellow suspension was heated to reflux for 6 hours. Triethylammoniumbromide precipitated, which was removed by filtration and washed with toluene. The solvent was removed from the filtrate until crystallization started. Long, transparent crystals formed at 5 °C, which were recrystallized from toluene. C<sub>24</sub>H<sub>18</sub>BN (M = 331.22 g·mol<sup>-1</sup>): calcd. C 87.03, N 4.23, H 5.48; found C 89.56, N 4.32, H 5.64 %. <sup>11</sup>B NMR (CDCl<sub>3</sub>):  $\delta = 52.99$ . <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta = 110.54$  (Cz), 119.43 (Cz), 120.31 (Cz), 123.33 (Cz), 125.82 (Cz), 127.93 (Ph–B), 131.07 (Ph–B), 134.69 (Ph–B), 139.45 (Ph–B). <sup>11</sup>H NMR (CDCl<sub>3</sub>):  $\delta = 7.26$ –8.16 (m, Ph).



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