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

Hermann SACHDEV*, Nina ZAHN, Volker HUCH

Dedicated to Prof. Dr. M. Veith on the occasion of his 65th birthday

Abstract:

Tetraphenylaminoborane (**1**) and carbazonyldiphenylborane (**2**) are examples for isolated BN- bonds completely substituted by aryl ligands enabling π - 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 and single crystal X-ray diffractometry. Both compounds (**1**) and (**2**) are principal structures for threefold coordinate, arylsubstituted BN- bonds. Compound (**1**) crystallizes in the monoclinic crystal system in the space group P2(1), with two formula units per unit cell with $a = 9.8236(9) \text{ \AA}$, $b = 9.2743(8) \text{ \AA}$, $c = 10.7426(10) \text{ \AA}$; $\alpha = 90^\circ$, $\beta = 107.228(4)^\circ$, $\gamma = 90^\circ$, $Z = 2$, $V = 934.81(15) \text{ \AA}^3$ (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 $a = 17.404(4) \text{ \AA}$, $b = 11.020(2) \text{ \AA}$, $c = 9.4195(19) \text{ \AA}$; $\alpha = 90^\circ$, $\beta = 91.45(3)^\circ$, $\gamma = 90^\circ$, $Z = 4$, $V = 1805.9(6) \text{ \AA}^3$ (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 in the range of 240 nm and 285 nm (**1**) and broad features 260 nm and 290 nm (**2**). The ^{11}B NMR-data of (**1**) [48.7 ppm] and (**2**) [53.0 ppm] clearly indicate threefold coordinate BN- systems in solution with a weaker BN- π - interaction compared to dialkylborylamines.

Keywords: Boron / NMR spectroscopy / Aromaticity / Amines / X- ray structure determination

Introduction:

Materials in the system boron- carbon- nitrogen are of general interest for fundamental research and also because of their use in applications. These are, for example, carbon forms that are coordinated threefold, like graphene [1, 2], graphite, fullerenes and carbon nanotubes [3]. Within these systems it is interesting to investigate the effects if a C_2 - fragment is replaced by an isoelectronic BN- unit. Therefore, substitution patterns of threefold coordinate systems as well as fourfold coordinate systems are feasible and make these systems interesting starting materials regarding their physical and electronic properties. A still open question in BN- substituted aromatic compounds is the understanding of the influence of steric and electronic effects if arene substitutes are linked to the BN- bond, since π - interactions are feasible with the boron- as well as the nitrogen- centres. For this reason we characterized tetraphenylaminoborane (**1**) and carbazonyldiphenylborane (**2**) as selected model compounds for threefold coordinate, fully aryl- substituted BN- systems. These compounds can also 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], and the structural motifs are depicted in fig. 1.

Figure 1:

Tetraphenylaminoborane (**1**) and carbazolyldiphenylborane (**2**) as molecular building blocks for threefold coordinate BCN- compounds, for example heterographenoid structures [fig. 1a)] and fulleroid structures [fig. 1b)]

Since the aryl ligands have UV active π - interactions, this study is also of importance to characterize the influence of a boryl substitution of highly fluorescent groups like the carbazole ligand for the development of new fluorescent devices, as for example OLED's [8], cf. fig. 2.

Fig. 2:

Concept for the synthesis of new boryl substituted fluorescent systems linked by π - systems

The structural and spectroscopic data of the two heteroaromatic compounds (**1**) and (**2**), both depicted in fig. 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 eq. 1 and characterized by ^1H , ^{13}C , ^{11}B NMR- spectroscopy, UV-VIS- spectroscopy and single crystal XRD.

Equation 1:

[Ar = Ph for (**1**) or Ar₂NH = Carbazole for (**2**)]

Fig. 3: Tetraphenylaminoborane (1**) and Carbazolyldiphenylborane (**2**)**

Compound (**1**) is a completely phenylated derivative of aminoborane $\text{H}_2\text{B}=\text{NH}_2$, which exists as a monomer only under extreme conditions [3, 9, 10]. The isoelectronic ethene, $\text{H}_2\text{C}=\text{CH}_2$, however, is stable as a monomer under normal conditions. Fitting 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 π - orbitals of the phenyl substituents. This type of intramolecular stabilisation and also the steric demand of the ligands are two effects which can be considered to be either responsible to prevent an oligomerisation of polar BN- units. Thus, an important question is to what extend the possibility of aromatic π - interactions influences the BN- bond. The model compounds characterized in this study are of use as molecular synthons for BN- substituted graphenes,

fullerenes and nanotubes, as exemplified in fig. 1. Although the structures of the carbon analogues like tetraphenylethylene [11, 12] and diphenylmethylenefluorene [13] already have been reported, the structures of the corresponding BN- compounds tetraphenylaminoborane (1) and carbazolyldiphenylborane (2) were still unknown. In these cases, C₂-fragments of a conjugated π - system are substituted by an isoelectronic BN- group and enable an investigation of the influence of the substitution of a C=C- unit by a B=N- unit in conjugated aromatic systems.

The 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 a new routes as precursors for BC_xN- materials, which are currently accessible by methods like e.g. decomposition of pyridine-borane or acetonitrile-BCl₃ [14, 15]. The approach presented in this study provides molecules for a molecular built-up of heterographene units selectively substituted by BN- groups in contrast to the synthesis of the high temperature routes of BC_xN- materials [16, 17]. Therefore, the 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.

Results and discussion

The 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 (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 CDCl₃ reveals one signal in the ¹¹B NMR spectrum at 48.66 ppm indicating a threefold coordination of the boron atoms and a monomer species in solution. The ¹³C NMR spectrum reveals 10 peaks, and this number can be interpreted as 4 carbon atoms of rotating phenyl groups at the Ph₂B group (128.05 ppm, 131.44 ppm, 136.00 ppm, 136.1 ppm) and 6 carbon atoms of non-rotating phenyl rings (NPh₂, 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 (Ph₂BBr: 4 peaks at 137.5 (C_{2,6}), 133.0 (C₄), 127.9 (C_{3,5}) and 139.2 (C₁) ppm; Ph₂NH: 143.15 (C₁), 121.42 (C₂), 121.03 (C_{2,6}) and 117.85 (C_{3,5}) ppm), and it can be seen 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 NPh₂- units is affected by the ring current of the phenyl groups attached to the BPh₂- 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 due to a hindered rotation.

Single crystals of (1) suitable for X-ray structure determination could be obtained from toluene solution. The compound crystallises in a monoclinic crystal system in the space group P2(1) with two formula units per unit cell. The structural features are depicted in fig. 4:

Fig. 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)

bond lengths [Å]: 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; angle [°]): 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)

The molecular structure of (1) is depicted in figure 4b), clearly indicating a monomeric aminoborane. The boron atoms as well as the nitrogen atoms show a trigonal planar coordination (sum of bond angles at B(1) and N(1): 360°). The BN- bond length of 1.441(2) Å is considerably longer compared to 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 comparable to those in triaminoboranes [B(NHMe)₃ (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 quite coplanar (dihedral angle approx. 11.4°). The interplanar angles of the phenyl rings and the BN- bond are in the of 45 to 60°, and thus, there is no completely conjugated π - system due to an insignificant small overlap of the π - orbitals at the boron and nitrogen atoms, and no significant interactions with the aromatic π - 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 an π - 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 [P2₁; a = 9.798(2) Å, b = 9.715(2) Å, c = 10.781(2) Å and β = 107.94(1)°] [11, 12]. Also the molecular structure in the solid state resembles the corresponding analogies (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 ethene 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 ¹¹B NMR spectrum of a toluene solution shows a single signal at 53.0 ppm, clearly indicating threefold coordinate boron atoms. Thus, this compound is monomeric in solution, too. The ¹¹B NMR signal of compound (2) is shifted to low field compared to compound (1), indicating that the boron atom is electronically less shielded and thus the BN- π - bonding is reduced. This effect can be attributed to the incorporation of the nitrogen atom in an aromatic ring system, and thus the BN- π - back donation is weaker. This effect is also verified by the ¹³C NMR spectrum, since the ¹³C 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 compared to the ¹³C NMR signals of carbazolyldiphenylborane (110.54 ppm, 119.43 ppm, 120.31 ppm, 123.33 ppm, 125.82 ppm), therefore indicating a comparatively small disturbance of the aromatic system by the BN- π - interaction. A comparable high field shift as in (diphenylamino)diphenylborane cannot be noted, indicating that there are no substituents 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), indicating a free rotation of these phenyl rings in the ¹³C 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 ¹H NMR spectrum and all signals are in the aromatic range (7.26-8.16 ppm).

Colourless single crystals of compound (**2**) suitable for X-ray structure determination were obtained from a toluene solution.

Fig. 5: a) unit cell and packing diagram [view along b- axis]; b) molecular structure of carbazolyldiphenylborane (2)

Selected bond lengths [Å], bond angles [°], dihedral angles [°] and interplanar angles of carbazolyldiphenylborane (**2**)

bond length [Å]: 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 angle [°]): 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.

Carbazolyldiphenylborane (**2**) crystallizes in a monoclinic crystal system of the space group C2/c. The unit cell contains 4 formula units as a set of two pairs of diastereomers. Selected structural features, dihedral and interplanar angles of carbazolyldiphenylborane are given in fig. 5. The molecular structure of (**2**) reveals a crystallographically imposed C₂ axis of symmetry along the BN- bond, as indicated in fig 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 identical with 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 ~11° for (**1**) and indicates a weaker BN- π - 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°] reveal a stronger π - interaction in the exocyclic ethylene type C=C- double bond and a smaller dihedral angle [in the range of ~3° compared to those of ~30° for (**2**)] and thus a less contorted system. From these effects observed in these two similar structures it can be reasoned that the non- planarity of the carbazoly- 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- spectroscopic properties of systems with fully aryl substituted BN- bonds, the spectra of compound (**1**) and (**2**) were recorded and are depicted in figures 6 a) and 6 b) together with the spectra of carbazole and diphenylamine. As it can be seen from the spectrum of compound (**2**), the absorption in the UV- region is enhanced in the case of carbazolyldiphenylborane (**2**) making this compound also interesting for the synthesis of cabazoly- based polymers and OLED's.

Fig. 6a) UV-VIS Spectrum of (1)

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

Fig. 6 b) UV-VIS Spectrum of (2)

Compared 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 (1) and (2):

The compounds (**1**) and (**2**) are comparable regarding the substance class of monomeric arylsubstituted aminoboranes, but they differ in their spectroscopic properties and structural data. The most important data are summarized in tab. 1.

Table 1: Summary of the important data of Tetraphenylaminoborane (1) and Carbazolyldiphenylborane (2):

compound	^{11}B NMR [ppm]	B-N [$\text{\AA}$]	C-B [$\text{\AA}$]	C-N [$\text{\AA}$]	interplanar angle C(2)B-NC(2) [$^\circ$]	fluorescence (244 nm)
(1)	48.7	1.441(2)	1.515(3)- 1.520(2)	1.479(2)- 1.493(2)	11.4	blueish-white
(2)	53.0	1.443(2)	1.5756(15)	1.4373(14)	29.4	green

Although tetraphenylaminoborane (**1**) reveals a more crowded geometry of the phenyl ligands, the dihedral angle is smaller in (**1**) than in (**2**). Steric reasons can not be made responsible for this effect, since compound (**1**) could easily release steric hindrance by an increase of the C_2BNC_2 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 this two systems. A comparison of the corresponding carbon systems of (**1**) and (**2**) reveals in general, that the $\text{C}=\text{C}$ - bond is only moderately distorted, which can be attributed to steric effects of the aryl substituents (tetraphenylethylene [11, 12]: $\text{C}=\text{C}$ 1.356 $\text{\AA}$, dihedral angle $\sim 9^\circ$; trans- stilbene [20]: $\text{C}=\text{C}$ 1.334 $\text{\AA}$, dihedral angle $\sim 3.4 - 6.9^\circ$; 9-(diphenylmethylidene)fluorene [13]: $\text{C}=\text{C}$ 1.349(3) $\text{\AA}$, dihedral angle $\sim 3^\circ$). The structural parameters of these carbon analogs of (**1**) and (**2**) indicate that an ethylene type bond geometry with a geometry close to coplanarity is in general present, and the shortening of the $\text{C}=\text{C}$

bond observed by comparison of trans-stilbene and tetraphenylethylene clearly indicates steric reasons. The dihedral angle observed for (2) in the range of $\sim 30^\circ$ is significantly larger than those of the carbon analogon 9-(diphenylmethyldene)fluorene [13] of only $\sim 3^\circ$ and can not be explained by steric reasons.

The ^{11}B NMR data of tab. 1 indicate clearly that both compounds are monomer in solution and the signal of (2) is shifted about 4.3 ppm to low field due to a less pronounced BN- π - interaction compared to (1). The chemical shift of (2) is actually closer to the range of arylboronhalides than normal aminoboranes [21]. Due to the incorporation of the nitrogen atom in the heteroaromatic carbazoly ring system in compound (2), the π - 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- lengths are rather similar to (1) and (2), but differences in the dihedral angle ($\sim 11^\circ$ vs. $\sim 30^\circ$) and in the shorter CN- bond length of the heteroaromatic carbazoly substituent reveals a lower π - back donation of the nitrogen atom to the boron atom in compound (2). The structural data of (1) and (2) do not indicate significant boron- carbon- π - interaction with the B-Ph-groups either. Also, the B- C_{Ph} - bonds are significantly larger in (2) [1.5756(15) Å] than in (1) [1.515(3)-1.520(2) Å], and also the phenyl groups are tilted out of a coplanar arrangement in (2) [approx. 60° ; cf. fig. 4] and in (1) [approx. $45 - 60^\circ$; cf. fig. 5]. It would be expected, that at least a partial interaction of the boron atom, as eg. observed in the structure of phenylborondichloride PhBCl_2 with a B- C_{Ph} - bond length of 1.54 Å and a coplanar arrangement of the aryl group and the BCl_2 - fragment [22], would enable an electronic stabilisation of the boron atom in compound (2) due to a weakened BN- bond indicated by the chemical shift of the ^{11}B NMR signal and the dihedral angle of the BN- bond of $\sim 30^\circ$, but 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 borafuorene- analogues of (2) and related compounds (cf. fig. 7) are currently investigated [23].

Conclusion

In this report we could show that in aryl substituted BN- bonds the aryl boron interaction is rather weak and the π - system of the phenyl rings in general is not interacting with the boron atoms. The structural results of (1) indicate if a sp^2 - 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). A bluish-white fluorescence is observed in this system by UV irradiation. If the nitrogen atom of the BN- bond is included in an aromatic ring system like in carbazole, the interaction with the diphenyl boron unit is rather weak, as indicated by the ^{11}B NMR- spectra as well as the crystallographic data of compound (2). Also, an enhancement of the fluorescence can be observed in the case of a boryl substitution of the carbazole unit. This findings make the carbazoly boranes also interesting for applications in light harvesting and light emitting devices.

It has to be distinguished that although the ionicity is increased in compound (1) and (2) by substitution of a $\text{C}=\text{C}$ - bond by a $\text{B}=\text{N}$ - 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 compared to (1) and the carbon analogon described in [11-13, 20]. This effect can be attributed to an aromatic interaction of π - electrons of the nitrogen atom in the carbazoly 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 favours over the BN- π bonding. The experimental data are also supported by ab initio- DFT- calculations of the geometry and electronic structure of (1) and (2) and comparable systems [24].

In general, the substitution of a $\text{C}=\text{C}$ - unit by a $\text{B}=\text{N}$ - unit leads to compounds revealing many common structural properties, but if for example the nitrogen atom is part of a aromatic system like in compound (2), the $\text{B}=\text{N}$ - bond is significantly weakened. Therefore, heterographenoid molecular structures depicted e.g. in fig. 1a) are expected to have a higher stability than molecular fullerenoid structures e.g. like those shown in fig. 1 b), where the $\text{B}=\text{N}$ - 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 π - bonding is disturbed within the inverse systems of (2) and related structures depicted in fig. 7 a)-c) [24].

Fig. 7: Borafluorene derivatives with a inverse BN- bond connectivity compared to compound (2)

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Experimental Section

General: All procedures were carried out by using modified Schlenk techniques in an inert gas atmosphere (argon 4.6). Solvents were dried by standard procedures and degassed prior to use. Diphenylamine, triethylamine 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; 1H : 200MHz; ^{13}C : 55.0 MHz; ^{11}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 methylenechloride (~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) were collected at the specified temperatures with a Bruker AXS X8 Apex CCD diffractometer with a LT cooling device ($Mo-K_{\alpha}$, $\lambda = 0.71073 \text{ \AA}$, 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 Center 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 Crytallographic Data Centre, 12, Union Road, Cambridge CB2 1 EZ, UK [Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

Synthesis of Tetraphenylaminoborane [“Diphenlamino-diphenylborane] (1)

A solution of 16.90 g (69.01 mmol) diphenylbromborane in 50 ml toluene was added to a solution of 11.68 g (69.01 mmol) diphenylamine and 7.68 g (75.91 mmol) triethylamine in approx. 200 ml toluene. A precipitate of triethylammoniumbromide formed 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 ^{11}B NMR-spectroscopy. The precipitate was removed by filtration and washed with toluene. The solvent was removed from the filtrate until crystallisation set in. Storage of the filtrate at $5^\circ C$ resulted in the formation of single crystals suitable for x-ray structure determination.

NMR ($CDCl_3$): δ ^{11}B : 48.66 ppm; δ ^{13}C : 108.22 ppm (Ph-N), 114.12 ppm (Ph-N), 117.82 ppm (Ph-N), 127.63 ppm (Ph-N), 128.05 ppm (Ph-B), 130.94 ppm (Ph-N), 131.44 ppm (Ph-B), 136.00 ppm (Ph-B), 136.1 ppm (Ph-B, ipso), 136.93 ppm (Ph-N, ipso); δ 1H : 6.31-7.95 (m, Ph) $C_{24}H_{20}BN$ ($M_r = 333.24 \text{ g/mol}$): calcd C 86.50, N 4.20, H 6.06; found C 86.61, N 4.32, H 5.56.

Synthesis of Carbazolyl-diphenylborane (2)

A solution of 7.29 g (29.78 mmol) diphenylbromborane in toluene (50 ml) was added dropwise to a solution of 5 g (29.90 mmol) carbazole and 5 ml (35.91 mmol) triethylamine in toluene (100 ml). The yellow suspension was refluxed for 6 hours. Precipitated triethylammoniumbromide was removed by filtration and washed with toluene. The solvent was removed from the filtrate until crystallisation set in. A fraction of transparent longish crystals started to form at $5^\circ C$ and was recrystallized from toluene. NMR ($CDCl_3$): δ ^{11}B : 52.99 ppm; δ ^{13}C : 110.54 ppm, 119.43 ppm, 120.31 ppm, 123.33 ppm, 125.82 ppm, 127.93 ppm, 131.07 ppm, 134.69 ppm, 139.45 ppm; δ 1H : 7.26-8.16 (m, Ph); $C_{24}H_{18}BN$ ($M = 331.22 \text{ g/mol}$): calcd C 87.03, N 4.23, H 5.48; found C 89.56, N 4.32, H 5.64.

Table 2: Structural data of (1) and (2):

Identification code	(1) Tetraphenylaminoborane	(2) Carbazolyldiphenylborane
Empirical formula	C ₂₄ H ₂₀ B N	C ₂₄ H ₁₈ B N
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 α = 90°. b = 9.2743(8) Å β = 107.228(4)°. c = 10.7426(10) Å γ = 90°.	a = 17.404(4) Å α = 90°. b = 11.020(2) Å β = 91.45(3)°. c = 9.4195(19) Å γ = 90°.
Volume	934.81(15) Å ³	1805.9(6) Å ³
Z	2	4
Density (calculated)	1.184 Mg/m ³	1.218 Mg/m ³
Absorption coefficient	0.067 mm ⁻¹	0.069 mm ⁻¹
F(000)	352	696
Crystal size	.5 x .5 x .5 mm ³	.5 x .5 x .5 mm ³
Theta range for data collection	1.98 to 34.02°.	3.06 to 28.06°.
Index ranges	-15 ≤ h ≤ 12, -14 ≤ k ≤ 12, -16 ≤ l ≤ 15	-22 ≤ h ≤ 22, -14 ≤ k ≤ 14, -12 ≤ l ≤ 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 R indices [I > 2σ(I)]	R1 = 0.0597, wR2 = 0.1489	R1 = 0.0381, wR2 = 0.0847
R indices (all data)	R1 = 0.0797, wR2 = 0.1634	R1 = 0.0678, wR2 = 0.0934
Absolute structure parameter	-1(3)	
Largest diff. Peak and hole	0.419 and -0.474 e.Å ⁻³	0.174 and -0.120 e.Å ⁻³

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FULL PAPER

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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 Prof. Dr. M. Veith on the occasion of his 65th birthday

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Entry for the Table of Contents

Tetraphenylaminoborane (**1**) and carbazonyldiphenylborane (**2**) serve as examples for isolated BN- bonds completely substituted by aryl ligands enabling π - interactions. Such systems are building blocks for new fluorescent polymers and are also suitable precursors for B-C-N materials.

((Key Topic))

Hermann SACHDEV*, **Nina ZAHN**,
Volker HUCH Page No. – Page
No.

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