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SPECIAL ISSUE

Is There B–N Bond-Length Alternation in 1,2:3,4:5,6-Tris(biphenylylene)borazines?

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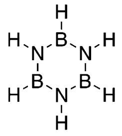
In memory of Detlef Schröder

The alternation of the B–N bonds in the central borazine ring of the overcrowded 1,2:3,4:5,6-tris(biphenylylene)borazine (**2a**) and its tribromo derivative (**2g**) is investigated by computational methods and compared with their experimentally obtained crystal structures. The calculations are performed with a meta-generalized-gradient-approximation (GGA) density functional (Tao–Perdew–Staroverov–Scuseria (TPSS)) without and with dispersion corrections, including Becke–Johnson damping, in conjunction with a polarized triple-ζ basis set. These data show a small bond-length alternation (BLA) of around 0.01 Å in **2a** and **2g**. This outcome is in good agreement with X-ray diffraction data for **2g**, but at variance with earlier X-ray diffraction measurements that gave a BLA of 0.06 Å for **2a**. A re-investigation of the crystal structure of **2a** reveals a positional disorder that precludes a discussion of the B–N bond lengths. The synthesis of **2g** is the first example of an electrophilic aromatic substitution of an aryl borazine with elemental bromine. Successful bromination was also demonstrated for hexaphenylborazine.

Introduction

As bond-length equalization is one criterion of aromaticity,[1–4] bond-length alternation (BLA) in annulated benzenoid molecules has been investigated extensively.[5–18] Extreme examples are "starphenylene"[5] and tris(bicyclo[2.1.1]hexeno)benzene,[11] the central six-membered rings of which exhibit cyclohexatriene-like geometries with BLA of 0.14 and 0.089 Å, respectively. But even in a relatively simple polycyclic aromatic hydrocarbon such as triphenylene, a BLA of 0.059 Å in the central ring is observed.[19,20] This has been explained by cyclic π effects.[21]

The aromatic character of "inorganic" benzene,[22–27] borazine $B_3N_3H_6$ (**1**), is still debated (Scheme 1).[28–49] The B–N bond lengths in **1** alternate to a very small extent and their average (electron diffraction: 1.4355(21) Å;[50] X-ray: 1.429(1) Å[51]) lies between the values for a typical B–N single bond (for example, in ammonia borane: 1.6576(16) Å[52] (microwave spectroscopy) and 1.564(6) Å[53] (X-ray)) and a B=N double bond (e.g., in aminoborane: 1.391(2) Å[54] (microwave spectroscopy)). A survey of the geometries of borazine molecules deposited in the Cambridge Structural Database (CSD) revealed that BLA in borazine derivatives is usually small (see the Supporting Information for details).



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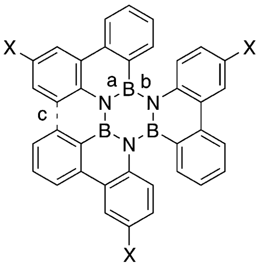

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Scheme 1. Borazine (**1**) and 1,2:3,4:5,6-tris(biphenylylene)borazine (**2a**, X = H).

An unusual borazine derivative in this regard is 1,2:3,4:5,6-tris(biphenylylene)borazine (**2a**), the borazine analogue of hexabenzotriphenylene,[21,55–59] which was synthesized first by Köster et al. in 1965 (Scheme 1).[60,61] The crystal and molecular structure of **2a** was reported by Roberts et al. in 1974.[62] The steric overcrowding due to the biphenyl rings precludes a planar geometry for **2a**, and a propeller-like structure with the borazine ring distorted from planarity is preferred.[62] The B–N bond lengths were reported to alternate: the shorter B–N bonds (average 1.430 Å vs. 1.488 Å) were found between pairs of atoms bridged by the biphenylylene substituent.[62] The resulting BLA of 0.06 Å is larger than that found in hexabenzotriphenylene (0.04 Å),[21] but similar to that of triphenylene (0.06 Å).[20]

We have recently reported an alternative synthesis for **2a** and found that the molecule has interesting photophysical properties.[63] Although the geometry of **2a** computed at the B3LYP/6-31G* level of theory was overall in good agreement

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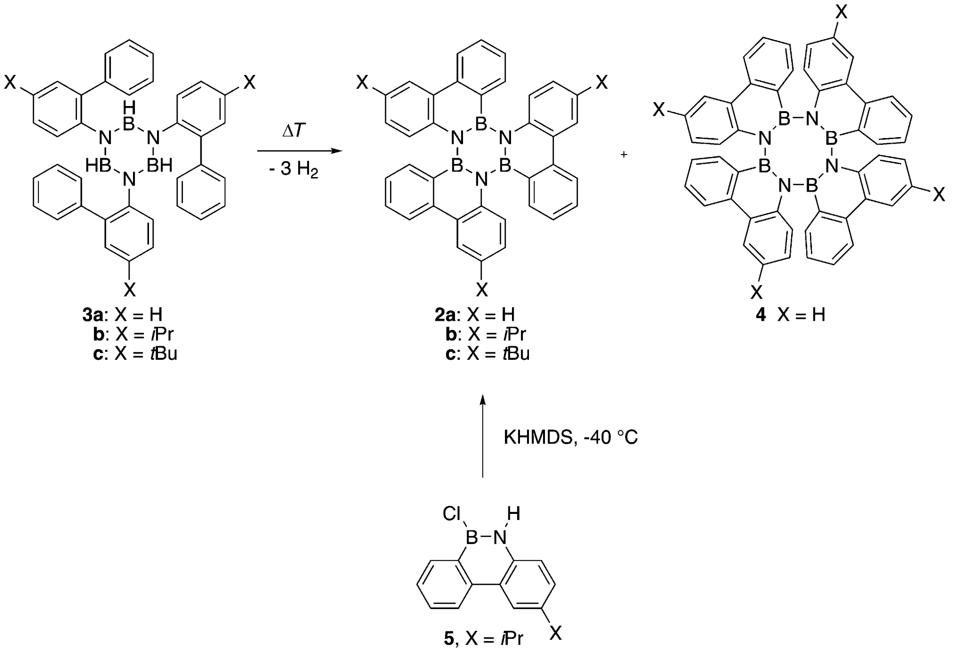
with experiment, the bond-length alternation (0.01 Å) was significantly smaller than the one derived experimentally (0.06 Å).

One may argue that the B3LYP/6-31G* level of theory is not of sufficient quality to produce highly accurate geometric parameters for the overcrowded **2a**. However, the B3LYP functional in conjunction with similar-quality basis sets reproduced the experimental structure and BLA in hexabenzotriphenylene[21] and triphenylene[64] well. Moreover, more sophisticated computational methods do not bring experiment and theory in accord, as demonstrated below. In view of the importance of an accurate computational description of molecular structures, the discrepancy in bond-length alternation between experiment and theory prompted the present study. Herein, we report for the first time the synthesis and structural characterization of a derivative of **2a** that was obtained by electrophilic aromatic substitution, a reaction that has not been reported previously for aryl-substituted borazines. In addition, the geometries of **2a** and its derivative were studied using more sophisticated computational treatments of **2a**. Our results indicate that the bond-length alternation in **2a** is significantly smaller than concluded previously.



Scheme 2. Synthetic routes to **2**.

Results and Discussion

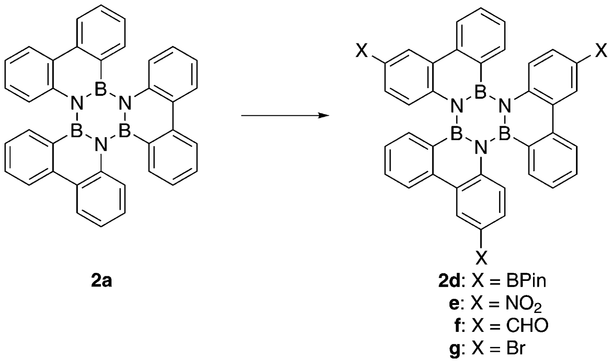
Syntheses

High-temperature dehydrogenation of **3a** at 405 °C was described by Köster et al.[60,61] to produce **2a** in a yield of 16% (Scheme 2). We were able to increase the yield to 25% by strict control of the argon flow that blows off the released hydrogen. During the course of the reaction the crystalline by-product **4** also formed in 6% yield, as we reported previously.[63]

To reveal a motif-inherent bond-length alternation, it is necessary to synthesize derivatives of **2a** for structural characterization. However, the high temperature required for the dehydrogenation step is expected to severely limit the scope of substituents that would be tolerated. Indeed, the high-temperature synthesis of isopropyl derivative **2b** failed. The synthesis of the *tert*-butyl derivative was impossible as the precursor borazine **3b** could not be obtained. Attempts to lower the reaction temperature required for dehydrogenation using Hartwig's[65] iridium(I) complex resulted in mixtures that could not be characterized any further.

Another synthetic route to **2b** uses base-induced dehydrohalogenation[63] of 10-chloro-3-isopropyl-9-aza-10-boraphenanthrene (**5**). Although the synthesis of **5** is straightforward, the dehydrohalogenation step failed.

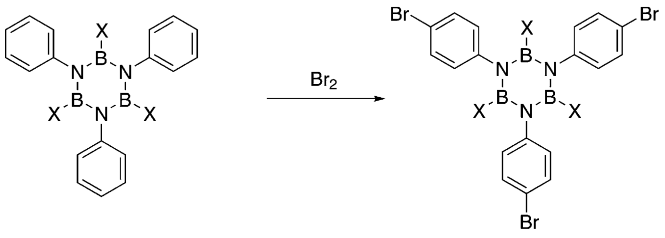
As **2a** is sensitive to water and Lewis acids in solution, we focused on its mild direct functionalization (Scheme 3). Transition-metal-mediated borylation of **2a** to yield **2d** using bis(pinacolato)diboron/Ir^{I}[66] led to the recovery of the starting material. Some of the classical electrophilic aromatic substitution reactions (acid-free nitration[67,68] and Vilsmeier–Haack formylation[69]) gave rise to complex mixtures instead of the expected derivatives **2e** and **2f**. Only the bromination of **2a** yielded tribromo derivative **2g** in reasonable quantities. Treatment of **2a** at room temperature with an excess amount of bromine without catalyst in dichloromethane produces derivative **2g** in 35% yield according to mass spectrometry and heteronuclear two-dimensional NMR spectroscopy. The proton spectrum displays seven signal groups and thus points to a structure with



Scheme 3. Attempted functionalization of **2a**.

threefold symmetry. Two sets consisting of four and three hydrogen atoms can be identified by ^{1}H,^{1}H-COSY and TOCSY, which indicates that only one of the rings in the biphenylyl system carries a bromine atom. Owing to efficient relaxation induced by boron nuclei, adjacent carbon atoms are not seen in carbon NMR spectra.

The preferred bromination of the nitrogen-bound phenyl ring is expected as it is more electron rich owing to the mesomeric effect of the borazine nitrogen atoms. To the best of our knowledge, this is the first example of an electrophilic aromatic bromination of an aryl borazine. This reaction is not limited to **2a**: the three nitrogen-bound phenyl rings of hexaphenylborazine (**6**) can be brominated to give the corresponding tribromo derivative **6a** (Scheme 4). As the structure cannot be confirmed by X-ray crystallography, a ^{1}H,^{15}N HMBC NMR spectrum was recorded. The data clearly show a correlation between the *ortho* protons of the brominated aryl ring and the borazine nitrogen. A good indicator for the reaction success is the strong BN stretching band detected by IR spectroscopy around 1360 cm^{-1}. Upon bromination of *N*,*N*′,*N*″-triphenylborazine (**7**) this band disappears, which indicates decomposition of the borazine core during the reaction.



6: X = Ph
7: X = H

6a: X = Ph
7a: X = H

Scheme 4. Bromination of aryl borazines **6** and **7**.

Computational treatment

The repulsion between hydrogen atoms of the biphenylyl systems results in the propeller-like structure of **2a**. The distances between the adjacent rings are 3.1–3.2 Å, a range that is just below the sum of the van der Waals radii of carbon (3.4 Å).[70] It may be argued that the bond-length alternation in **2a** as determined by X-ray diffraction[62] arises from steric overcrowding of the biphenylyl substituents at the borazine ring. The accurate treatment of such close contacts between aromatic units can be achieved nowadays by density functional methods using the corrections for dispersion interactions without (D3) and with Becke–Johnson damping (D3(BJ)) as introduced by Grimme and co-workers.[71,72] Grimme and Mück-Lichtenfeld have shown recently for cyclophanes with π–π distances shorter than the sum of the van der Waals radii that the combination of common density functionals, such as the Tao–Perdew–Staroverov–Scuseria (TPSS)[73] meta-generalized-gradient-approximation, and the D3 and D3(BJ) corrections provides geometries in very good agreement with X-ray crystallography.[74]

Table 1. Computed distances (in Å) in **2a** and its derivative **2g** using the TPSS meta-GGA functional without and with D3 dispersion corrections, including Becke–Johnson damping D3 (BJ) in conjunction with the def2-TZVP basis set. See Scheme 1 for a definition of distances a–c.

Level	Distance a	Distance b	Distance c
		X = H (**2a**)	
TPSS	1.453	1.464	3.150
TPSS-D3	1.451	1.462	3.131
TPSS-D3(BJ)	1.449	1.461	3.097
		X = Br (**2g**)	
TPSS	1.453	1.464	3.142
TPSS-D3	1.451	1.462	3.122
TPSS-D3(BJ)	1.449	1.460	3.088
exptl[a]	1.445	1.453	3.097

[a] Averaged.

We hence used these techniques also for the computation of the structures of **2a** and its derivative **2g** (Table 1).

The results obtained without dispersion correction parallel the earlier B3LYP/6-31G* data: again, the bond-length alternation is around 0.01 Å and therefore much smaller than that in experiment. Switching on the dispersion correction (D3) slightly shortens the BN distances, but does not change the difference in bond lengths: it remains at 0.01 Å. Likewise, additional BJ damping very slightly shortens the BN distances further, but the degree of alternation does not change. Only distances between neighboring aromatic systems shrink by 0.05 Å. Hence, the calculations show that the bond-length alternation in **2a** is smaller than that derived earlier from X-ray diffraction and is not influenced markedly by the close contact of the organic aromatic π systems present. The same also holds true for derivative **2g** that has not been structurally characterized previously.

Single-crystal X-ray crystallography

In light of the theoretical results above, we have carried out an X-ray diffraction study on **2g** for the first time, and also re-investigated the crystal structure of **2a** at low temperature and with Mo instead of Cu radiation. Suitable crystals for **2a** were obtained from the melt of **3a**. The same space group and unit cell as in the previous report were obtained for **2a**.[62] In that earlier study, the authors noted that both potential models for the assignment of the B and N positions in the borazine ring had been tested; the one with the lower *R* value (0.084) was finally selected as the best model. In our refinements, we in addition employed a model in which the B and N atoms were treated as being disordered over all six ring positions. With this approach, the *R* value dropped significantly (to 0.048) and the occupancy factors for the ring sites were refined to a B/N ratio of about 1:1 (i.e., each position is shared by boron and nitrogen by equal amounts). This strongly suggests the presence of positional disorder in the borazine ring, which is also facilitated by the molecular symmetry (close to C_3) of the compound: The overall geometry of the molecule (i.e., the relative positions of the biphenylyl groups), and hence the intermolecular interactions within the crystalline framework, are not affected by the occupation scheme of the borazine ring. Consequently, bond lengths and in particular their alternation cannot be reliably discussed using the X-ray data owing to disorder.

Crystals of **2g** suitable for X-ray crystallography were obtained by slow evaporation of the solvent dichloromethane. Compound **2g** crystallizes in the space group $P2_1/c$ along with one molecule of dichloromethane in the asymmetric unit (see Table 2 and Figure 1).

Table 2. Crystal data and structure refinement for **2g**.

empirical formula	$C_{37}H_{23}B_3Br_3Cl_2N_3$
formula mass	852.64
T [K]	100(2)
λ [Å]	1.54178
crystal system	monoclinic
space group	$P2_1/c$
a [Å]	14.2604(2)
b [Å]	8.21000(10)
c [Å]	28.3417(4)
α, β, γ [°]	90, 94.821(1), 90
V [Å^3]	3306.45(8)
Z, ρ_{calcd} [Mg m^{-3}]	4, 1.713
μ [mm^{-1}]	6.274
F(000)	1680
crystal size [mm^3]	0.50×0.06×0.04
θ range for data collection [°]	3.13 to 66.65
index ranges	$-16 \leq h \leq 16$
	$-7 \leq k \leq 9$
	$-33 \leq l \leq 32$
reflections collected/unique	29 199/5726 ($R_{int} = 0.0337$)
completeness to $2\theta = 66.65°$ [%]	98.0
absorption correction	numerical
max./min. transmission	0.7937/0.1428
structure solution	direct methods
refinement method	full-matrix least-squares on F^2
data/restraints/parameters	5726/0/433
GOF on F^2	1.042
final R indices ($I > 2\sigma(I)$)	$R_1 = 0.0293$, $wR_2 = 0.0714$
R indices (all data)	$R_1 = 0.0351$, $wR_2 = 0.0743$
largest diff. peak and hole [e A^{-3}]	0.860 and −0.861

In contrast to **2a**, the boron- and nitrogen-atom positions could now be clearly located within the borazine ring. It seems that it is the presence of the three bromine atoms in the periphery of the molecule that prevents the occurrence of disorder in **2g**: The bromine atoms participate in the intermolecular interactions in the crystal and therefore also imply a distinct occupation scheme in the borazine ring. The average B–N bond lengths in **2g** are 1.445 and 1.453 Å, respectively, and thus the BLA is now less than 0.01 Å. This is in good agreement with the theoretical treatments that arrive at a BLA slightly above 0.01 Å.

Conclusion

The experimental and computational results reported here allow the following conclusions to be drawn:

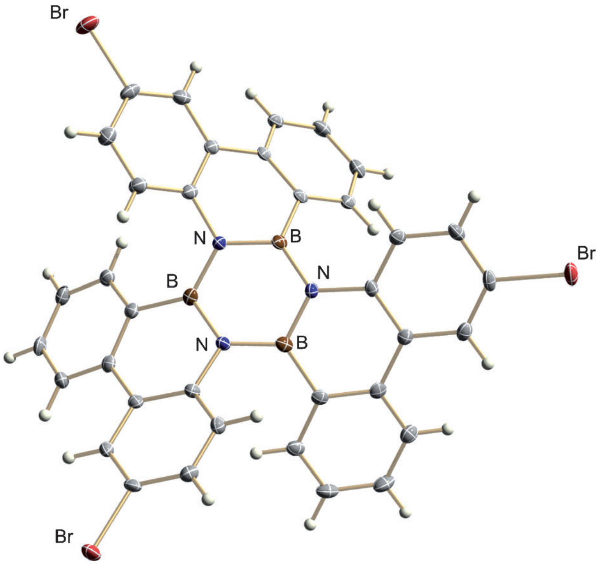


Figure 1. Structure of **2g** in the solid state. A dichloromethane molecule was omitted for clarity. Ellipsoids are drawn at the 50% probability level.

1) The previously determined pronounced BLA of 0.06 Å in the overcrowded 1,2:3,4:5,6-tris(biphenylylene)borazine (**2a**) results from a misinterpretation of the diffraction data. A re-investigation of the crystal structure of **2a** arrives at disorder that precludes discussion of the boron–nitrogen bond lengths.
2) The sterically overcrowded **2a** can be functionalized further with high chemoselectivity using Br_2 (to give **2g**), whereas a number of other methods used for functionalization of aromatic rings fail.
3) X-ray crystallography of **2g** demonstrates that the BLA in the 1,2:3,4:5,6-tris(biphenylylene)borazine system is small.
4) Computations using modern density functional methods with appropriate corrections for dispersion interactions, TPSS-D3 and TPSS-D3(BJ), calculate a structure for **2g** that is in very good agreement with experiment. Based on the good performance for **2g**, the computed BLA of the closely related parent **2a** can safely be assumed to be similarly small.

Experimental Section

General

All experiments were performed under anhydrous conditions using argon as the protective gas. Dry dichloromethane was collected from a MBraun solvent purification system (SPS-800) and xylene was distilled from P_2O_5 prior to use. All NMR spectra were recorded on Bruker DRX 250 and Avance II 400 spectrometers. The spectra were referenced to residual solvent signals (^1H, ^{13}C: $SiMe_4$) and externally (^{11}B: $BF_3{\cdot}OEt_2$). The NMR spectra were measured at room temperature in CD_2Cl_2 and [D_8]THF that were purchased from Deutero GmbH. IR spectra were recorded on a Bruker Tensor 27, elemental analysis was performed using a EuroEA system, LDI mass spectra were performed on a Bruker AutoFlex with a steel plate, and APCI mass spectra were acquired on a Bruker Esquire3000plus. High-resolution mass spectrometry was performed on a Finnigan MAT MAT95 (HRMS EI) or Bruker maxis4G (HRMS APCI) instrument. Melting points were determined with a Büchi B-540 heat block. The borane–triethylamine complex (Sigma–Aldrich), bromine, and 2-aminobiphenyl (Acros) were purchased and used as received. FWHM is the full width at half-maximum, which was determined by a Lorentzian fit with TopSpin 2.1 (Bruker).

1,2:3,4:5,6-Tris(biphenylylene)borazine (2 a)

This compound was synthesized according to Köster et al.[61] with minor modifications. In a Schlenk tube, *N*-tri(biphenylyl)borazine (**6**; 5.773 g, 10.75 mmol) prepared as described previously[75] was heated to 405 °C with an argon flow of 2.3 sccm min^{-1}. During heat-up the compound melted and a viscous, colorless oil was released. At 405 °C the melt became brownish and after 1 h a colorless precipitate was formed. After 6.5 h the almost-solid melt was brought to room temperature. The resulting brown tar was suspended 4 times with dichloromethane (40 mL) and the slurry was dissolved in dichloromethane (total volume: 800 mL). After filtration the filter was filled with off-white crystals (432 mg) that were identified as **4**.[63] The solvent of the filtrate was evaporated and the resulting orange foam was suspended in acetone (30 mL). This suspension was centrifuged for 5 min at 13.4 krpm. The supernatant was discarded and fresh acetone was added. After the threefold repetition of this centrifugation procedure the sediment was air-dried and finally isolated as an off-white, fine powder (1.275 g, 22 %). ^{1}H NMR (400 MHz, [D$_8$]THF): $\delta = 8.28$ (m, 6 H), 7.64 (m, 3 H), 7.50–7.56 (m, 6 H), 7.37 (m, 3 H), 7.06–7.11 ppm (m, 6 H); MS (LDI-TOF): *m/z* (%): 531 (100) [M^+].

3,11,19-Tribromohexabenzo[*a,b,g,i,m,o*]-1a,5a,9a-triaza-4a,8a,12a-triboratriphenylene (2 g)

Borazine **2 a** (115.3 mg, 0.22 mmol) was dissolved in dichloromethane (125 mL) and elemental bromine (1.01 mL, 19.8 mmol) was added at room temperature over 2.5 min. The red solution was clipped from the argon and stirred overnight. Then the solution was cooled and decolorized within 5 min using saturated Na$_2$SO$_3$ solution (50 mL). The solvent was removed and the yellow residue was suspended in acetone (4 mL) and centrifuged (5 min at 13.4 krpm). The supernatant was removed and replaced by fresh acetone. After treatment in an ultrasonic bath the suspension was centrifuged once more (5 min, 13.4 krpm). The sediment was then dried under vacuum and obtained as a colorless solid (58.2 mg, 35 %). For elemental and X-ray analysis the sample was purified on a column chromatography system using hexane and dichloromethane as eluent and silica gel as the stationary phase. M.p. 312–315 °C; ^{1}H NMR (400 MHz, [D$_8$]THF): $\delta = 8.46$ (d, ^4J(H,H) = 2 Hz, 3 H), 8.30 (d, ^3J(H,H) = 8 Hz, 3 H), 7.58–7.61 (m, 6 H), 7.50 (m, 3 H), 7.26 (dd, ^3J(H,H) = 9 Hz, ^4J(H,H) = 2 Hz, 3 H), 7.16 ppm (t, ^3J(H,H) = 8 Hz, 3 H);^{13}C{^{1}H} NMR (101 MHz, [D$_8$]THF): $\delta = 140.3$, 140.1, 135.0, 132.3, 130.2, 130.0, 128.3, 128.2, 127.1, 124.2, 116.9 ppm; ^{11}B{^{1}H} NMR (80 MHz, [D$_8$]THF): $\delta = 36.1$ ppm (FWHM = 1000 Hz); IR (KBr): 1363 cm^{-1} (B–N); UV/Vis (CH$_2$Cl$_2$): $\lambda_{max} = 325$, 234 nm; fluorescence (CH$_2$Cl$_2$): $\lambda_{ex} = 246$, 324 nm; $\lambda_{em} = 388$ nm; MS (APCI ion trap): *m/z*: 809 [M^++CH$_3$CN+H], 768 [M^++H]; elemental analysis calcd (%) for C$_{37}$H$_{23}$B$_3$Cl$_2$N$_3$: C 52.12, H 2.72, N 4.93; found: C 52.10, H 2.71, N 4.68.

10-Chloro-6-*i*Pr-9-aza-10-boraphenanthrene (5)

5-*i*Pr-2-aminobiphenyl (4.311 g, 20.4 mmol) that was synthesized as described previously[76,77] was dissolved in dry xylene (125 mL) and BCl$_3$ (34 mL, 34 mmol, 1 M in hexanes) was added at 0 °C over 7 min. After stirring at 0 °C for 30 min and for 30 min at room temperature a ^{11}B{^{1}H} NMR spectrum ($\delta = 6.8$ ppm (FWHM = 13 Hz)) of the reaction mixture indicated the formation of the amine–boron adduct. AlCl$_3$ (545 mg, 4.1 mmol) was added to this mixture and was heated under reflux for 15 h. After the evaporation of the solvent, the residue was distilled at 90 °C under vacuum (10^{-3} mbar). The colorless oil solidifies upon standing (1.353 g, 26 %). ^{1}H NMR (400 MHz, C$_6$D$_6$): $\delta = 8.49$ (dd, ^3J(H,H) = 8 Hz, ^4J(H,H) = 1 Hz, 1 H), 8.09 (d, ^4J(H,H) = 2 Hz, 1 H), 7.06 (dd, ^3J(H,H) = 8 Hz, ^4J(H,H) = 2 Hz, 1 H), 6.91 (br s, 1 H), 6.41 (d, ^3J(H,H) = 8 Hz, 1 H), 2.84 (sept, ^3J(H,H) = 7 Hz, 1 H), 1.23 ppm (d, ^3J(H,H) = 7 Hz, 6 H); ^{13}C{^{1}H} NMR (101 MHz, C$_6$D$_6$): $\delta = 142.5$, 140.0, 136.6, 134.8, 132.1, 126.72, 126.68, 123.3, 122.5, 121.9, 119.2, 34.4, 24.5 ppm; ^{11}B{^{1}H} NMR (80 MHz, C$_6$D$_6$): $\delta = 34.5$ ppm (FWHM = 168 Hz); MS (EI quadrupole, 70 eV): *m/z* (%): 255 (44) [M^+], 240 (100) [M^+−Me], 213 (28) [M^+−C$_3$H$_6$]; HRMS (EI sector field, 70 eV): *m/z*: calcd for C$_{15}$H$_{15}$BClN [M^+]: 255.09861; found: 255.09824.

N-Tris(5-*i*Pr-biphen-2-yl)borazine (3 b)

5-*i*Pr-2-aminobiphenyl (9.800 g, 46.38 mmol)[76,77] was mixed with triethylaminoborane (6.81 mL, 46.38 mmol) and heated for 6.5 h at 205 °C. The product was recrystallized from hexanes (60 mL) and isolated as an off-white powder (6.267 g, 61 %). M.p. 123–125 °C; ^{1}H NMR (250 MHz, CD$_2$Cl$_2$): $\delta = 6.05$–7.41 (m, 24 H), 4.13 (br s, 3 H), 2.94 (sept, ^3J(H,H) = 7 Hz, 3 H), 1.28 ppm (d, ^3J(H,H) = 7 Hz, 18 H); ^{1}H{^{11}B} NMR (250 MHz, CD$_2$Cl$_2$): $\delta = 6.07$–7.44 (m, 24 H), 4.29 (br s, 3 H), 2.96 (m, 3 H), 1.30 ppm (d, ^3J(H,H) = 6 Hz, 18 H); ^{13}C{^{1}H} NMR (101 MHz, CD$_2$Cl$_2$): $\delta = 146.3$, 143.5, 141.0, 137.8, 130.7, 129.0, 126.8, 126.3, 34.0, 24.2 ppm; ^{11}B{^{1}H} NMR (80 MHz, CD$_2$Cl$_2$): $\delta = 33.5$ ppm (FWHM = 953 Hz); IR (KBr): 1401 (B<C-N), 2555 cm^{-1} (B–H); MS (APCI-TOF): *m/z*: 664 [M^++H]; HRMS (APCI-TOF): *m/z*: calcd for C$_{45}$H$_{49}$B$_3$N$_3$ [M^+] (monoisotopic): 664.42208; found: 664.42204.

N-Tris(4-bromophenyl)-*B*-triphenylborazine (6 a)

Hexaphenylborazine (170 mg, 0.32 mmol) that was prepared from *N*-triphenyl-*B*-trichloroborazine and phenylmagnesium bromide[78] was dissolved in dichloromethane (125 mL). At room temperature, bromine (1.48 mL, 28.80 mmol) was added to the colorless solution over 3.5 min and was stirred for 18 h. The mixture was washed twice with saturated Na$_2$SO$_3$ solution (50 mL) and dried over Na$_2$SO$_4$. After the evaporation of the solvent the crude solid was subjected to column chromatography on a column chromatography system using hexane and dichloromethane as eluent and silica gel as the stationary phase (R_f(CH$_2$Cl$_2$) = 0.81). The product was isolated as an off-white powder (87 mg, 35 %). M.p. 330–333 °C; ^{1}H NMR (400 MHz, [D$_8$]THF): $\delta = 6.94$ (m, 6 H), 6.86 (m, 15 H), 6.67 ppm (m, 6 H); ^{13}C{^{1}H} NMR (101 MHz, [D$_8$]THF): $\delta = 164.8$, 133.0, 132.1, 131.1, 127.3, 127.2, 118.1 ppm; ^{11}B{^{1}H} NMR (80 MHz, [D$_8$]THF): $\delta = 34.8$ ppm (FWHM = 714 Hz); MS (APCI-iontrap): *m/z*: 774 [M^++H]; IR (KBr): 1369 cm^{-1} (B–N); UV/Vis (CH$_2$Cl$_2$): $\lambda_{max} = 231$ nm; fluorescence (CH$_2$Cl$_2$): $\lambda_{ex} = 257$ nm; $\lambda_{em} = 282$ nm; HRMS (APCI-TOF): *m/z*: calcd for C$_{36}$H$_{28}$B$_3$Br$_3$N$_3$ [M^++H] (monoisotopic): 772.01093; found: 772.00676.

X-ray diffraction

Suitable single crystals were coated with paratone oil and mounted using a nylon loop. Data collection was performed on a Smart APEX II diffractometer (**2a**) using $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å) at 153 K, and a Smart APEX II Duo diffractometer (**2g**) equipped with a Cu microfocus tube ($\lambda = 1.54178$ Å) at 100 K, respectively. Raw data were integrated with the program SAINT, and absorption effects were corrected numerically using SADABS.[79] The structures were solved by a combination of direct methods (SHELXS) and iterative difference Fourier syntheses (SHELXL).[80] All non-hydrogen atoms were refined anisotropically, while the hydrogen atoms were placed at calculated positions and refined using a riding model. As mentioned before, the atoms within the borazine ring in **2a** were refined using a model of positional disorder for the boron and nitrogen atoms. Further details of the refinements and crystallographic data are listed in Table 2 (**2g**) and in the Supporting Information (**2a**). Plots were generated using the program ORTEP-3.[81] CCDC-930452 (**2a**) and CCDC-930451 (**2g**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Computations

The non-empirical meta-GGA functional introduced by Tao, Perdew, Staroverov, and Scuseria (TPSS)[73] was employed for all geometry optimizations using the def2-TZVP basis set in conjunction with the resolution-of-the-identity (RI) approximation and the recommended fitting basis sets.[82,83] To take into account the dispersion interaction that is not included in the TPSS functional, Grimme's dispersion correction with and without Becke–Johnson damping (D3 and D3(BJ)) was employed.[71,72] All calculations were performed with the Turbomole program using tightened SCF (10^{-8} au) and geometry convergence criteria (10^{-4}).[84]

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