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Structural Chemistry of Borazines[‡]

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Dedicated to Prof. Dr. K. Wade on the occasion of his 75th birthday

Keywords: Borazines / Ring distortion

The solid-state structure of $(HN{=}BF)_3$ has been redetermined. It is characterised by a stacking of the molecules, similar to hexagonal boron nitride. In contrast, $(F_3CH_2N{=}BF)_3$ shows no intermolecular interactions between the planar borazine rings. In $(Cl_2BN{=}BCl)_3$, the Cl_2B groups are almost perpendicularly oriented to the planar borazine ring and its B–Cl bonds are shorter than the Cl–B bonds to the ring boron atoms. Reactions of $(Cl_2BN{=}BCl)_3$ with Me_3SiNMe_2 allows a successive Cl/Me_2N exchange. Depending on the molar ratio, the compounds $[Cl(Me_2N)BN{=}BCl]_3$, $[(Me_2N)_2BN{=}BCl]_3$ and $[(Me_2N)_2BN{=}BNMe_2]_3$ are obtained. The latter two react with CH_2Cl_2 by B–N bond cleavage of one ring boron bonded Me_2N group with formation of an N–H bond. These molecules not only possess a strongly distorted BN hexagon with short B–NH bonds but also a nonplanar borazine ring. The nonplanarity of the borazine ring is even more pronounced in $[Me_3SiN{=}BCl]_3$. A planar borazine ring is observed for $(MeN{=}BBr)_3$. Its molecules are ordered into stacks by translation with borazine planes 4.2 Å apart from each other. Characteristic of the structure are close contacts between neighbouring bromine atoms. Due to the steric demand of pentafluorophenyl groups, the borazine ring of $(F_5C_6N{=}BBr)_3$ forms no stacks because one of the three F_5C_6 rings stands almost perpendicular to the borazine plane while the other two are twisted by 70°. Aminolysis of $(F_5C_6N{=}BBr)_3$ yields $(F_5C_6N{=}BNH_2)_3$ with NH_2 groups that are coplanar with the borazine ring. The phenyl groups of $(HN{=}BPh)_3$ are twisted by only 30–40° relative to the borazine ring. A threefold crystallographic axis stands perpendicular to the ring plane. The sixfold crystallographic axis of the unit cell generates a channel structure with an internal diameter of 4.5 Å. The two isomeric borazines, $(iPrN{=}BMe)_3$ and $(MeN{=}BiPr)_3$ are structurally rather similar although the first of these has longer B–N bonds due to the shorter N–C bonds. Moreover, the B–N–B and N–B–N bond angles are slightly different.

Introduction

Although isoelectronic and isolobal with benzene, borazine exhibits antiaromatic character.[2] In contrast to benzene with D_{6h} symmetry, borazine exhibits D_{3h} symmetry in the gas phase[3] but C_2 symmetry in the solid state.[4] The boron atoms carry a partial positive charge and the nitrogen atoms a partial negative charge which leads to BN bond polarity and this polarity determines its chemical behaviour.[5–10] Amongst the BN heterocycles, borazine and its derivatives have been extensively investigated and the chemistry of the former has been described in books[5–9] and handbooks.[10]

Renewed interest in borazines can be associated with the preparation of BN-fibres and nanotubes[11–14] as precursors in the formation of BNC- and BSiN-type materials[15–17] as well as the challenge of preparing BN-"fullerenes".[18–20] These latter compounds will be built from edge-sharing four-membered B_2N_2 rings and six-membered B_3N_3-borazine rings. Other areas consist of N- or B-metallated borazines.[21–26] Several of these borazine derivatives possess nonplanar borazine rings and also their B–N bond lengths become different, i.e. the B_3N_3 rings are distorted. We report here on the syntheses and structures of new borazine derivatives but also on the structure determination of well known borazines.

2,4,6-Trihaloborazines and Their Structures

Synthesis of Fluoroborazines $(RN{=}BF)_3$

It is well known that the thermal stability of 2,4,6-trihaloborazines $(HN{=}BX)_3$ depends on the halogen atom X and increases in the order of X = I < Br < Cl < F. The compound $(HN{=}BI)_3$ is unstable at ambient temperature,[27] $(HN{=}BBr)_3$ decomposes slowly at ambient temperature but rapidly at 90 °C[28] whereas $(HN{=}BCl)_3$ can be sublimed at 65 °C. Nevertheless, on storing the latter at 100 °C for an extended time, it decomposes with formation of HCl and a diborazinyl.[29] $(HN{=}BF)_3$ can be prepared

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from the trichloroborazine by treatment with various metal fluorides.[30–33] We followed the reaction of $(HN{=}BCl)_3$ with SbF_3 by ^{11}B NMR spectroscopy and observed a quantitative Cl/F exchange [Equation (1)]. Crystallisation from hexane yielded $(HN{=}BF)_3$, **1**, in 89% yield which can be compared with a reported yield of 40%.[30,33] However, it was difficult to grow suitable single-crystals for the structure determination. Crystallisation at –25 °C from hexane yielded mainly a powder.[34]

$$(HN{=}BCl)_3 + 3\,SbF_3 \rightarrow \underset{\mathbf{1}}{(HN{=}BF)_3} + 3\,\text{“}SbCl_2F\text{”} \qquad (1)$$

$$\underset{\mathbf{2}}{(F_3CCH_2N{=}BF)_3)}$$

A sample of $(F_3CCH_2N{=}BF)_3$ (**2**) was supplied by A. Meller.[35]

Synthesis of Chloroborazines $(RN{=}BCl)_3$

2,4,6-Trichloroborazines can be prepared by various methods. One of the most convenient of these syntheses involves the reaction of BCl_3 with a suitable trimethylsilylamine.[27] In case of the *N*-trimethylsilyl-substituted chloroborazine **4**, a two step reaction is required as shown below [Equations (2) and (3)].

$$BCl_3 + N(SiMe_3)_3 \rightarrow \underset{\mathbf{3}}{Cl_2B\text{-}N(SiMe_3)_2} + Me_3SiCl \qquad (2)$$

$$3\,Cl_2B\text{-}N(SiMe_3)_2 \rightarrow \underset{\mathbf{4}}{[ClB{=}N(SiMe_3)]_3} + 3\,Me_3SiCl \qquad (3)$$

Reaction (3) was carried out with excess BCl_3 in hexane at reflux.[36] Compound **3** can be isolated by distillation at 89 °C/11 Torr. Single-crystals, obtained from a hexane solution at –78 °C, were found to melt at 5–7 °C. Compound **3** can also be prepared by treating $NaN(SiMe_3)_2$ with BCl_3 in a 1:1 molar ratio in hexane.

The conversion of **3** into the borazine **4**[37] was achieved within two days in boiling xylene. It was isolated by sublimation at 95 °C/2 Torr and crystallisation from hexane yielded single-crystals. Both **3** and **4** hydrolyse readily in moist air.

The boron nuclei of **4** are better shielded than in **3** ($\delta^{11}B$ = 35.5 vs. 37.6 ppm). On the other hand, the ^{29}Si resonance of **4** can be observed at lower field (δ = 19.34 ppm) compared with the resonance of **3** (δ = 9.70 ppm) and the same holds for the ^{1}H NMR shifts (**4**, δ = 0.44; **3**, δ = 0.26 ppm). In contrast, the reverse is true for the ^{13}C resonances of the methyl groups as shown for **3** with $\delta^{13}C$ = 3.60 and for **4** with $\delta^{13}C$ = 3.83 ppm.

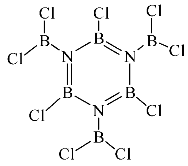
The mass spectra of **3** and **4** show only weak parent ions (≈ 3%). The fragmentation of **3** is dominated by the formation of $MeBCl_2$ as shown by the base peak at *m/e* = 145 for NSi_2Me_3. In contrast, **4** loses successively two Me_3SiCl molecules and a Cl atom, i.e. the borazine ring remains intact until the compound has lost its substituents.

We have already reported another *N*-substituted 2,4,6-trichloroborazine, $(Cl_2BN{=}BCl)_3$ **5**.[39] Its structure was deduced from NMR spectroscopic data which indicated that the Cl_2B groups are perpendicular to the borazine ring. To determine its structure we repeated its preparation from an excess of BCl_3 and $N(SnMe_3)_3$. Single-crystals were grown from $CHCl_3$/hexane solutions. This compound was also used to prepare Me_2N substituted borazines, for example $[(Me_2N)_2BN{=}BCl]_3$, **7** [Equations (4) and (5)]. Because the Me_2NB group forms B–N bonds with a high π bond character we expected that $(Me_2N)_2B$ groups would have an opposite effect on the borazine ring compared with the Cl_2B groups. Reactions of $(Cl_2BN{=}BCl)_3$ with Me_3SiNMe_2 were performed in 3:1, 6:1 and 9:1 ratios. ^{11}B NMR spectroscopy showed the formation of compounds **6**, **7** and **8** when using toluene solutions. Treatment of **6** and **7** with CH_2Cl_2 yielded compounds **9** and **10**.

$$\underset{\mathbf{5}}{(Cl_2BN{=}BCl)_3} + n\,Me_3SiNMe_2 \rightarrow [(Me_2N)_nCl_{6-n}B_3]N_3B_3Cl_3 + n\,Me_3SiCl \qquad (4)$$

$$n = 3: \mathbf{6},\ n = 6: \mathbf{7},$$

$$(Cl_2BN{=}BCl)_3 + 9\,Me_3SiNMe_2 \rightarrow \underset{\mathbf{8}}{[(Me_2N)_2BN{=}BNMe_2]_3} + 9\,Me_3SiCl \qquad (5)$$



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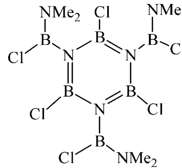

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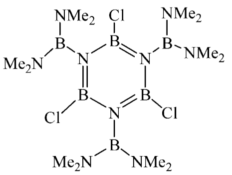

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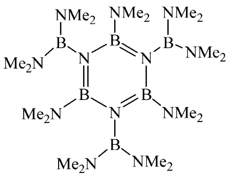

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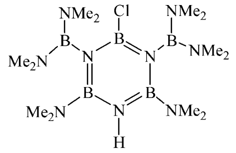

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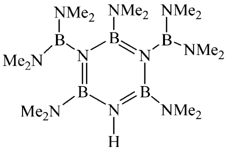

10

This shows that the substitution of the Cl atoms of $(Cl_2BN{=}BCl)_3$ occurs stepwise and that the Cl atoms of the Cl_2B groups are more reactive than those of the ClB groups, a result that is not unexpected as the boron atoms of the BCl_2 group are more Lewis acidic than the borazine boron atoms.

The reactions (4) and (5) were followed by ^{1}H and ^{11}B NMR spectroscopy. The ^{1}H NMR signals of the Me_2N groups in CH_2Cl_2 solution are found in the range from 2.56 to 2.70 ppm. Signals at 3.44 (**9**) and 3.41 ppm (**10**) showed the presence of NH groups. These were absent in the products obtained from toluene solutions. The introduction of Me_2N groups at the BCl_2 substituents leads to better shielded ^{11}B nuclei. The signals are rather broad and can be observed around 30 ppm. The ^{11}B NMR signal of the

B–Cl groups in the borazines **6** and **7** ($\delta^{11}B$ = 30–31 ppm) overlaps with the signal of the $(Me_2N)_2B$ group while the ^{11}B NMR signal of the borazine bonded Me_2N group results in a high field shift (25–26 ppm). The presence of $(Me_2N)BCl$ and $(Me_2N)_2B$ groups can be seen in some cases by the asymmetry of the signals around 30 ppm.

The mass spectra of compound **6**, **9** and **10** show the parent ions. It can be noted that the fragmentation starts in all cases with loss of a dimethylaminochloroborane molecule, a Cl atom or a Me_2N group. In case of **10**, the loss of $B(NMe_2)_3$, $B(NMe_2)_2$ and $BNMe_2$ groups is typical.

Synthesis of Bromoborazines $(RN{=}BBr)_3$

In contrast to the B-trihaloborazines $(HN{=}BX)_3$ no structure of a 1,3,5-triorganyl-2,4,6-trihaloborazine $(RN{=}BX)_3$ has so far been reported although these types of borazines are well documented.[10] We prepared $(MeN{=}BBr)_3$, **11**, by treating BBr_3 with $(Me_3Si)_2NMe$ as shown in Equation (6)[27] and obtained single crystals from hexane solutions.

$$3\,BBr_3 + 3\,(Me_3Si)_2NMe \rightarrow \underset{\mathbf{11}}{(MeN{=}BBr)_3} + 6\,Me_3SiBr \qquad (6)$$

Meller et al.[40] as well as Glemser et al.[41] have described the synthesis of $(F_5C_6N{=}BBr)_3$, **12**, from BBr_3 and $F_5C_6NH_2$ in the presence of NMe_3 as shown in Equation (7). We obtained **12** by this route in 51% yield.

$$3\,F_5C_6NH_2 + 3\,BBr_3 + 6\,NMe_3 \rightarrow \underset{\mathbf{12}}{(F_5C_6N{=}BBr)_3} + 6\,(Me_3NH)Br \qquad (7)$$

$$(F_5C_6N{=}BBr)_3 + 6\,NH_3 \rightarrow \underset{\mathbf{13}}{(F_5C_6N{=}BNH_2)_3} + 3\,(NH_4)Br \qquad (8)$$

Compound **12**, when treated with an excess of ammonia, yields the corresponding triaminoborazine **13** which was isolated in 43% yield [Equation (8)]. The replacement of the Br atoms of **12** ($\delta^{11}B$ = 30.9 ppm) by the NH_2 groups leads to a high field shift of the ^{11}B NMR signal to 25.3 ppm.

Characteristic in the IR spectrum of **13** is a strong broad band at 1399 cm^{-1} due to B_3N_3 ring vibrations. This band is 35 cm^{-1} higher than that found in **11** (1364 cm^{-1}). The band at 1342 cm^{-1} can be assigned to the exocyclic B–N vibrations in **13**.[42,43] BN deformation modes can be found at 734 cm^{-1} for **12** and at 736 cm^{-1} for **13**. Two strong bands at 3526 and 3448 cm^{-1} can be assigned to the asymmetric and symmetric NH stretching vibrations of **13**, respectively. They are at higher wavenumbers than in $(H_2NB{=}NH)_3$ (3509, 3401 and 3185 cm^{-1}).[10] The IR spectrum of **12** is consistent with the data reported by Meller.[40]

Synthesis of Borazines $(HN{=}BR)_3$ and $(R'N{=}BR)_3$

Although the thermally very stable triphenylborazines (RN=BPh) (R = H, Me, Et, Ph) are well known[10] their structures have not yet been described. We prepared $(PhB{=}NH)_3$, **14**[27] by the silazane cleavage reaction as shown in Equation (9).

$$3\,PhBCl_2 + 3\,HN(SiMe_3)_2 \rightarrow \underset{\mathbf{14}}{(HN{=}BPh)_3} + 6\,Me_3SiBr \qquad (9)$$

$$3\,iPrBBr_2 + 3\,MeN(SiMe_3)_2 \rightarrow \underset{\mathbf{15}}{(iPrB{=}NMe)_3} + 6\,Me_3SiBr \qquad (10)$$

$$3\,MeBBr_2 + 3\,iPrN(SiMe_3)_2 \rightarrow \underset{\mathbf{16}}{(MeB{=}N\,iPr)_3} + 6\,Me_3SiBr \qquad (11)$$

In order to check whether bulky groups on the boron and/or nitrogen atoms might lead to a ring distortion of the borazine as observed for **4** we prepared $(iPrN{=}BMe)_3$, **15**, and $(MeN{=}BiPr)_3$, **16** as shown in Equations (10) and (11). However, we were unsuccessful in synthesising $(tBuN{=}BMe)_3$ and $(HN{=}Bmes)_3$ by the silazane cleavage route.[44]

The aminosilane $iPrN(SiMe_3)_2$ had to be prepared in a three step reaction from $iPrNH_2$ and Me_3SiCl to give $iPrNHSiMe_3$ followed by metallation with LiBu to produce $iPrN(Li)SiMe_3$ which on reaction with Me_3SiCl gave $iPrN(SiMe_3)_2$. The compound $tBuN(SiMe_3)_2$ was prepared analogously.[44] However its reaction with $MeBBr_2$ in toluene or xylene at reflux (5 d) gave only a single ^{11}B-NMR peak with $\delta^{11}B$ = 48 ppm which indicates that no borazine had been formed. The ^{29}Si NMR spectrum showed peaks corresponding to the formation of Me_3SiBr besides two more intensive signals at $\delta^{29}Si$ = 3.2 and 8.1 ppm. The ^1H NMR spectrum showed signals at δ = 0.41 and 0.17 ppm. These signals may stem from an aminoborane MeBBr–N(tBu)$SiMe_3$ because aminoboranes of type $MeBBrNR_2$ show ^{11}B NMR signals in the order of 50 to 40 ppm.[45]

X-ray Structures

Compound $(HN{=}BF)_3$ crystallises in the trigonal space group $R\bar{3}$ and shows D_{3h} point symmetry. The C_3 axis stands perpendicular to the planar ring system and passes through its centre. Table 1 lists the relevant bonding parameters for the trihaloborazines[46–49] and Figure 1 shows the molecular structure of $(HN{=}BF)_3$. The data indicate that the B–N bond lengths of $(HN{=}BF)_3$ seem to be slightly shorter than in the chloro and bromo derivatives[44,49] although the former is very close to the others considering the standard deviations. However, the B–F bond is longer than in BF_3 [1.311(1) Å].[50] According to calculations, the partial double-bond character of the B–Hal bond decreases from Hal = fluoride (1.44) via chloride (1.20) to bromide (1.05).

The molecules of **1** are arranged in the trigonal unit cell in sheets parallel to the *ab* plane (Figure 2). Therefore, each boron atom has not only two N atoms next to it within the ring but is oriented to two N atoms of two neighbouring borazine rings and each nitrogen atom of a ring has two boron atoms as neighbours in addition to two boron atoms from neighbouring borazine rings. The distance between two borazine rings within each stack is 3.42(2) Å. This is only 0.19 Å longer than in hexagonal boron nitride (3.33 Å).[51]

Table 1. Relevant bond lengths [Å] and bond angles [°] of the trihaloborazines $(HN{=}BX)_3$.

Compound	$[BrBN{=}NH]_3$[44] (X-ray)	$[ClB{=}NH]_3$[49] (X-ray)	$[FB{=}NH]_3$ [48] (Electr. diffr.)	$[FB{=}NH]_3$ (X-ray)	$[FB{=}NH]_3$[47] (X-ray)
B–N	1.41(1)	1.41.(1)	1.43(1)	1.418(2)	1.420(9)
B–X	1.94 (1)	1.76(2)	1.36(1)	1.338(3)	1.350(8)
N–H	0.85	0.84	0.79	0.77	
N–B–N	120(1)	119(1)	119(1)	119.0(2)	119.9(8)
B–N–B	119.5(9)	121(1)	121(1)	121.0(2)	120.1(8)

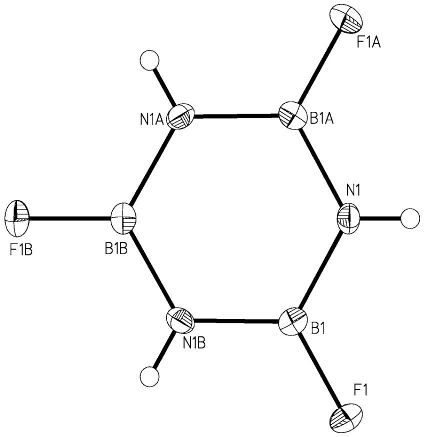

Figure 1. The molecular structure of $(HN{=}BF)_3$ in ORTEP representation. Bond lengths [Å]: N1–B1 1.418(2), B1–N1B 1.418(2), B1–F1 1.338(3), N1–H1 0.77(1). Bond angles [°]: B1–N1–B1A 121.0(2), N1–B1–F1 120.5(1), N1–B1–N1B 119.0(2).

Compound **2** forms orthorhombic colourless crystals, space group *Pnma* with $Z = 4$. This implies that the molecules have crystallographically imposed symmetry. The two C atoms and one F atom of the CF_3CH_2 group and of the *para* BF group occupy positions on a mirror plane. The B_3N_3 ring is planar and Figure 3 shows one complete molecule. B–N and B–F bond lengths are similar to those of $(HN{=}BF)_3$.

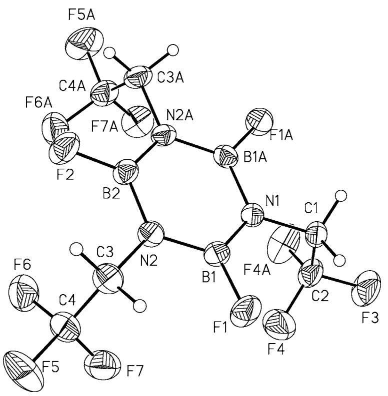

Figure 3. The molecular structure of $[F_3CCH_2N{=}BF]_3$, **2**. Selected bond lengths [Å]: N1–B2 1.421(3), N1–B1A 1.421(3), N2–B1 1.421(3), B2–N2 1.419(3). B1–F1 1.336(3), B2–F2 1.341(5), N1–C1 1.459(5), C1–C2 1.496(7), C3–C4 1.486(5), C2–F3 1.342(5), C2–F4 1.323(4), C4–F5 1.336(3), C4–F6 1.346(4), C4–F7 1.321(4). Selected bond angles [°]: B1–N1–B1A 119.1(4), N1–B1–N2 120.8(2), B1–N2 –B2 119.0(2), N2–B2–N2A 121.0(3), N1–B2–F1 119.3(2), N2–B2–F2 119.5 (2), N1–C1–C2 111.5(3), N2–C3–C4 111.6(3), B2–N2–C3 120.8(2), C3–C4–F5 110.6(3), C3–C4–F6 112.6(3), C3–C4–F7 113.5(3), B1–N1–C1 120.3(2). N1–C1–C2 111.5 (3). Selected torsion angles [°]: F2–B2–N2–C3 3.8, B2–N2–C3–C4 89.5, F1–B1–N2–C3 –3.6, F1–B1–N2–B2 174.5.

Structures of Chloroborazines $(RN{=}BCl)_3$

Bis(trimethylsilyl)aminodichloroborane **3**, the precursor of the borazine **4**, crystallises in the monoclinic system, space group *C*2/*c* with $Z = 4$. The B–N bond of the molecule lies on a twofold axis making the two Cl atoms and

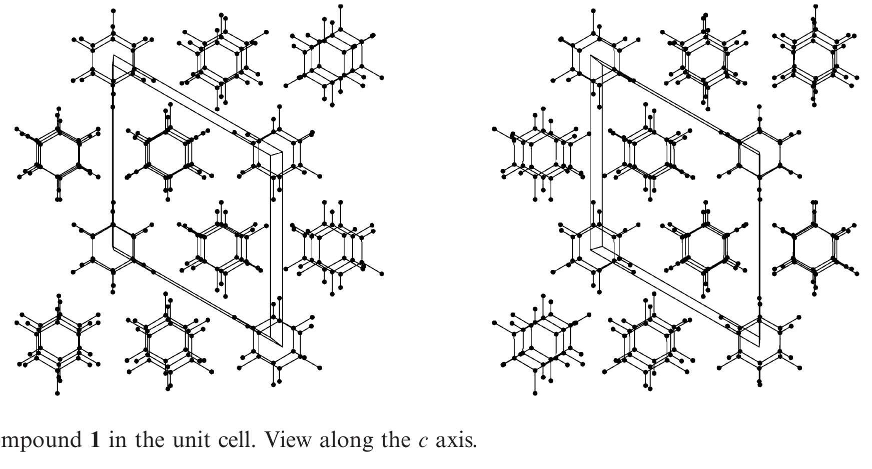

Figure 2. Packing of compound **1** in the unit cell. View along the *c* axis.

the two Me_3Si groups equivalent (see Figure 4). Both the boron and the nitrogen atom reside in a planar environment. They are connected by a short B–N bond [1.384(4) Å] indicating the presence of strong π bonding. This is emphasised by long B–Cl bonds [1.779(2) Å] which are longer than the B–Cl bond in BCl_3 [1.742(4) Å],[52,53] the borazine $(HN{=}BCl)_3$ [1.76(2) Å][49] or the B–Cl bond (1.71 Å) of the Cl_2B group in the borazine $(Cl_2BN{=}BCl)_3$. The most interesting feature of compound **3** is that the BCl_2 plane is twisted relative to the Si_2N plane by 31.8°. In spite of this, the B–N bond lengths are on the short side for monoaminoboranes.[54] The reason for the twisting is the bulkiness of the Me_3Si group as shown by the orientation of the Me_3Si groups: the Cl atoms point to the void between two methyl groups of a Me_3SiN unit (see Figure 5). This orientation has a steric effect on the Cl atoms by pushing them backwards from the Me_3SiN group which results in an acute Cl–B–Cl angle of 111.9°. The Si–C and Si–N bonds and N–Si–C bond angles show no anomalies.

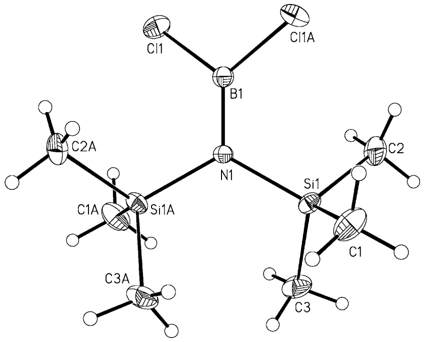

Figure 4. The molecular structure of $(Me_3Si)_2N{-}BCl_2$, **3**. View on the Cl_2BN plane. Selected bond lengths [Å]: B1–N1 1.384(4), B1–Cl1 1.779(2), N1–Si1 1.778(1), Si1–C1 1.850(2), Si1–C2 1.860(2), Si1–C3 1.868(2). Selected bonds angles: Cl1–B1–Cl1A 111.9(2), Cl1–B1–N1 124.1, B1–N1–Si1 119.42(7), N1–Si1–C1 110.13(9), N1–Si1–C2 110.6(1), N1–Si1–C3 209.5(1). Selected torsion angles [°]: C1–Si1–N1–B1 89.7, C2–Si1–N1–B1 –32.9, C3–Si1–N1–B1 –146.7. Interplanar angle [°] Cl1–B1–Cl1A/Si1–N1–Si1A 31.7.

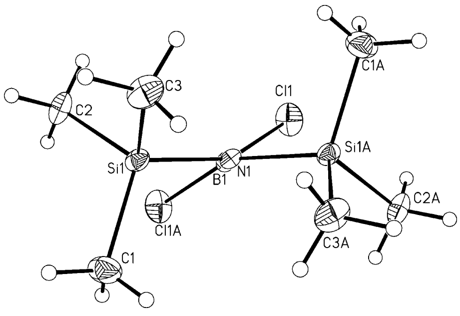

Figure 5. View along the BN axis of **3**.

Borazine **4** crystallises in the triclinic space group $P\bar{1}$ with $Z = 4$. There are two independent molecules in the unit cell. The two molecules show slightly different bonding parameters on the border of the 3σ criterion. Therefore, we will discuss only the data for one of these molecules (see Figure 6). The most significant result of the structure determination is that the borazine ring shows a significant distortion towards a chair shaped six-membered ring The Si1N1B1B3 plane is twisted with respect to the N3B3N2B2 plane by 13.5° and the Cl1B1N1N2 plane is twisted with respect to the N1B3N2N2 plane by 22.7° (see Figure 7). Although all B and N atoms reside in a planar environment, each of the BCl bonds is twisted against the mean plane of the borazine by 16.4° and the N–Si bond in the opposite direction by 8.9°.

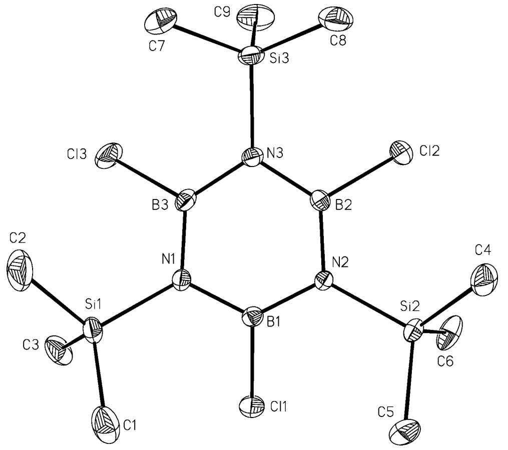

Figure 6. The molecular structure of the borazine $[(Me_3Si)_2N{=}BCl]_3$, **4**. Selected bond lengths [Å]: B1–N1 1.430(3), B1–N2 1.430(3), B2–N2 1.428(3), B2–N3 1.432(3), B3–N1 1.430(3), B3–N3 1.429(3), B1–Cl1 1.791(3), B2–Cl2 1.796(3), B3–Cl3 1.795(3), N1–Si1 1.795(2), N2–Si2 1.802(2), N3–Si3 1.795(2), Si1–C1 1.864(4), Si1–C2 1.861(4), Si1–C3 1.846(4), Si2–C4 1.857(3), Si2–C5 1.862(3), Si2–C6 1.844(4), Si3–C7 1.859(3), Si3–C8 1.854(4), Si3–C9 1.852(4). Selected bond angles [°]: N1–B1–N2 123.9(2), N2–B2–N3 124.4(2), N3–B3–N1 123.9(2), B1–N2–B2 114.3(2), B2–N3–B3 114.0(2), B3–N1–B1 114.1(2), Cl1–B1–N1 117.3(2), Cl1–B1–N2 118.3(2), Cl2–B2–N2 118.0(2), Cl2–B2–N3 117.2(2), Cl3–B3–N1 117.4(2), Cl3–B3–N3 118.1(2). Selected torsion angles [°]: Cl1–B1–N1–Si1 29.1, Cl1–B1–N2–Si2 –24.2, Cl2–B2–N2–Si2 22.0, Cl2–B2–N3–Si3 –24.3, Cl3–B3–N3–Si3 28.1, Cl3–B3–N1–Si1 –30.6. Interplanar angles [°]: Si1–N1–B1–B3/N3–B3–N2–B2 13.5, Cl1–B1–N1–N2/N1–B3–N2–B2 22.7.

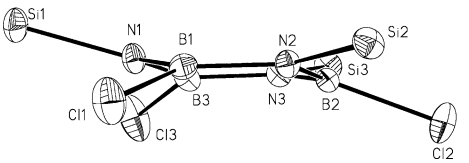

Figure 7. Side view of a molecule of **4**. Only the atoms directly bonded to the ring atoms are shown.

Compound $(Cl_2BN{=}BCl)_3$ crystallises in the tetragonal space group $P4_12_12$ with $Z = 4$. The twofold axis passes through the exocyclic B–N bond and the B–Cl bond opposite to this B–N bond. Figure 8 shows the molecular structure of the compound. In contrast to **4** the molecule possesses a planar borazine ring. The BCl$_2$ groups are twisted against the borazine ring by 84.7°.

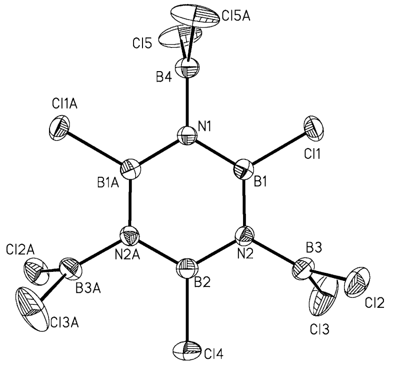

Figure 8. Molecular structure of (Cl$_2$BN=BCl)$_3$, **5**. Selected bond lengths [Å]: B1–N1 1.423(4), B1–N2 1.433(5), B2–N2 1.427(4), B2–N2A 1.427(4), B3–N2 1.456(5), B4–N1 1.458(7), B1–Cl1 1.767(4), B2–Cl4 1.770(6), B3–Cl2 1.734(5), B3–Cl3 1.718(5), B4–Cl5 1.716(3). Selected bond angles [°]: N1–B1–N2 118.5(3), N1–B1–Cl1 119.3(3), N2–B1–Cl1 119.3(3), N2–B2–N2A 121.4(4), N2–B2–Cl4 119.3(2). B2A–B2–Cl4 119.3(2), B1–N1–B4 120.6(2), B1A–N1–B4 120.6(2), Cl2–B3–Cl3 117.5(3), N2–B3–Cl2 121.8(3), N2–B3–Cl3 121.8(3), N1–B4–Cl5 121.0(2), N1–B4–Cl5A 121.0(2), Cl5–B4–Cl5A 118.0(4).

Considering the standard deviations, the ring B–N bonds are of equal lengths (average: 1.424 Å). However, the B–N bond to the BCl$_2$ groups are significantly longer [1.458(7), 1.465(5) Å]. The difference in the B–N bond lengths of 0.037 Å represents the loss of B–N π bonding due to the strongly twisted Cl$_2$B groups. Its B–Cl bonds are significantly shorter than the B–Cl bonds at the borazine ring. This indicates that the B–Cl bond of the BCl$_2$ groups have some degree of π bonding because these B–Cl bonds are shorter than in BCl$_3$. There are two types of intermolecular Cl···Cl contacts between the molecules (3.399 and 3.466 Å).

The structure of (Cl$_2$BN=BCl)$_3$ implies that the boron atoms of the BCl$_2$ groups will be preferentially attacked by nucleophiles because the BCl groups of the borazine are sterically shielded by the BCl$_2$ groups. This has been experimentally verified by the reaction of (Cl$_2$BN=BCl)$_3$ with Me$_3$SiNMe$_2$.

The borazine **9** crystallises in the monoclinic space group *C*2/*c* with *Z* = 4. Therefore, the molecule must have crystallographic symmetry as shown by the mirror plane which passes through the B–Cl and BNH units (see Figure 9). This has, of course, the consequence that the borazine ring is planar. The two bulky B(NMe$_2$)$_2$ groups are twisted against the borazine ring by 77.3°. In contrast, the two Me$_2$N groups bonded to the boron atoms of the borazine ring are twisted against the ring only by 9.8° which allows for BN π bonding as shown by the B–N bond length of 1.418(2) Å. In contrast, the interplanar angles which the Me$_2$N groups form with the BN$_3$ plane of B[(NMe$_2$)$_2$]$_3$ are 32.8°[55] i.e. the Me$_2$NB groups in **9** are less twisted against the borazine ring than in tris(dimethylamino)borane.

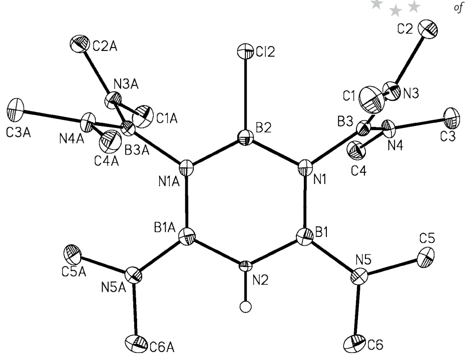

Figure 9. Molecular structure of compound **9**. Selected bond lengths [Å]: B1–N1 1.455(3), B1–N2 1.401(2), B1–N6 1.419(3), B2–N1 1.421(2), B3–N3 1.423(4), B3–N4 1.410(4), B3–N1 1.499(3), B2–Cl2 1.820(4), N2–H2A 0.86. Selected bond angles [°]: N2–B1–N5 117.8(2), N2–B1–N1 116.9(2), N1–B1–N 5 125.3(2), N1–B2–N1A 126.3(3), N1–B2–Cl2 116.9(2), N4–B3–N3 123.2(2), N1–B3–N3 117.7(2), N2–B3–N3 119.1(2), B1–N1–B2 116.4(2), B1–N1–B3 124.5(2), B1–N2–H2A 116.4, N1–B2–Cl2 116.9(2), C1–N3–C2 111.8(2), C3–N4–C4 111.8(2), C5–N5–C6 111.6(2), Selected interplanar angles [°]: N1B1N2/N5C5C6 9.9, B1N1B2/N4B3N3 77.1, C1–N2–C2/N1–B3–N3–N4 22.8, N3–B3–N4/N1–B1–B2–B3 76.8.

The B–N bonds in the borazine ring of **9** are unequal: B1–N1 1.455(3), B1–N2 1.401(2) and B2–N1 1.421(4) Å. The exocyclic B–N bonds N1–B3 and N1A–B3A are fairly long at 1.499(3) Å due to the strong twist of the B(NMe$_2$)$_2$ group against the ring. The short exocyclic B1–N5 bond [1.419(3) Å] points to a stronger π bond contribution which manifests itself also in the large B1A–N2–B1 bond angle of 127.2(2)°. Also, the N1–B2–N1A bond angle is quite open at 126.3(3)° while the B1–N1–B2 and N1–B1–N2 bond angles are smaller at 116.4(2) and 116.9(2)°. This shows that the bulky substituents distort the borazine ring in such a way that the B–N bond lengths of the borazine become longer and the respective B–N–B bond angles smaller. In particular, the long B–Cl bond at atom B2 [1.819(3) Å] indicates that the electron distribution in the ring system is no longer uniform. The B1–N2 and B1A–N2 bonds have more π bond character than the other ring B–N bonds.

Another consequence of the bulky substituents is that the B–N bond lengths and bond angles become different and this also results in a twisting of the substituents out of the borazine plane. Thus, atoms B3 and B3A are twisted out of the ring plane by 7.6° in opposite directions and the interplanar angle N3B3N4/N1N2N1A is 77.3°.

On the other hand, the Me$_2$N groups of the two B(NMe$_2$)$_2$ groups are twisted only by 22.0° (N3) and 25.1° (N4) against the N3N4B3N1 plane. Their B–N bonds at N3 and N4 are short for a triaminoborane unit at 1.423(3) and 1.410(3) Å, respectively.

The distortions noted for compound **9** become even more pronounced in compound **10**. This borazine crystallises, like **9**, in the monoclinic space group *C*2/*c* with *Z* = 4. In this case atoms N6, B2, N1 and H lie on a C_2 axis which gives the molecule C_2 point group symmetry. The three Me$_2$N groups Me$_2$N3, Me$_2$N2A and Me$_2$N6 as well the bis(dimethylamino)boryl groups are twisted in the same sense against the borazine ring which is no longer planar as shown by a torsion angle for N1–B1–N2–B2 of 11.0° (see Figure 10).

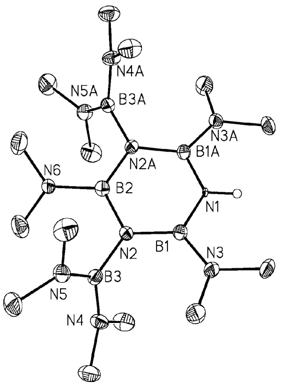

Figure 10. ORTEP plot of the borazine **10**. Hydrogen atoms omitted (except the NH hydrogen atom) for clarity. Selected bond lengths [Å]: B1–N1 1.385(5), B1–N2 1.449(6), B2–N2 1.464(5), B1–N3 1.422(6), B3–N2 1.488(6), B2–N6 1.477(8), N1–H 0.86(4), N1–C1 1.464(6), N3–C2 1.454(5), N4–C4 1.466(5), N4–C3 1.462(6), N6–C7 1.437(6). Selected bond angles [°]: B1–N1–B1A 125.8(5), N1–B1–N2 118.3(4), B1–N2–B2 120.1(4), N2–B2–N2A 120.4(5), N1–B1–N3 115.1(4), N2–B1–N3 126.6(4), B1–N2–B3 121.4(3), B2–N2–B3 120.1(4), N2–B2–N6 119.8(3), N4–B3–N5 121.8(4), N2–B3–N4 118.3(4). Selected torsion angles [°]: N1–B1–N2–B2 –11.0, B1–N2–B2–N2A 5.5. Selected interplanar angles [°]: C2–N2–C1/N1–B1–N2 12.9, N4–B3–N5/B1–N2–N2 111.5, N7–N6–N7A/N2A–B2–N2 40.7.

The bond lengths B2–N2 and B2–N2A are 1.464(5) Å, i.e. 0.04 Å longer than in **9**. The Me_2N6 group is twisted against the N2B2N2A plane by 40.9°. This results in a comparatively long B2–N6 bond [1.477(8) Å]. In contrast, the Me_2N groups on atoms B1 and B1(A) are twisted against the borazine ring by 122° and the B–N bonds lengths are 1.422(6) Å.

The shortest B–N bonds in the borazine ring of **10** are the two B–N bonds to N1 at 1.385(5) Å which is even shorter than in compound **9**. This distortion leads to quite different endocyclic bond angles: B1–N2–B2 120.1(4), N1–B1–N2 118.3(4) and B1–N1–B1A are 125.8(5) whereas N2–B2–N2a is 120.4(5)°. The longest B–N bond found involves the bis(dimethylamino)boryl group B3 with N2–B3 1.488(6) Å. Its two Me_2N groups are twisted against the B1N2B2B3 plane by 20.2 and 23.4° and the respective B–N bond lengths are 1.424(6) and 1.417(6) Å. Although the nitrogen atoms N4 and N5 are also planar, the C−N−C bond angles are sharp at 110.9(4) and 113.6(6)°.

Structures of Bromoborazines $(RN{=}BBr)_3$

The borazine $(MeN{=}BBr)_3$, **11**, crystallises in the triclinic space group $P\bar{1}$ with $Z = 4$, i.e. there are two independent molecules in the unit cell. The borazine rings are planar and B–N bond lengths span a range from 1.398 to 1.440 Å although these differences have to be considered insignificant in terms of the standard deviations which, in spite of an R_1 value of 4.42%, are rather large ($\sigma = 0.010$). The N–B–N and B–N–B bond angles span a range from 119.9(6) to 122.4(6)° and from 117.5(6) to 119.2(6)°, respectively. This indicates that the N–B–N bond angles are on average wider than the B–N–B bond angles. The B–Br bond lengths are similar to those in $(HN{=}BBr)_3$.[44] Figure 11 shows the two molecules. The molecules are stacked above one another and the planes of the borazine molecules are, on average, 4 Å apart. The shortest distances between the ring planes are 3.62 Å and the longest are 4.53 Å. The stacking results, as in hexagonal boron nitride, in weak intermolecular BN interactions. Also, intermolecular Br···Br contacts (3.85 Å) can be observed.

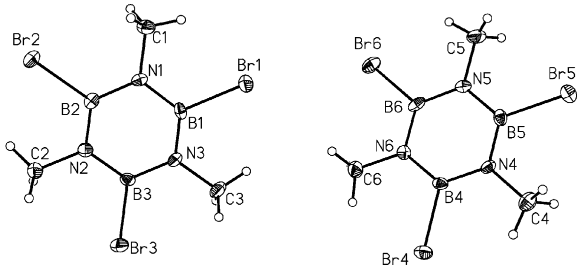

Figure 11. ORTEP plot of the two independent molecules of **11** viewed on top of the six-membered ring. Selected bond lengths [Å]: B1–N1 1.42(1), B2–N1 1.21(1), B2–N2 1.41(1), B3–N2 1.44(1), B3–N3 1.40(1), B1–N3 1.41(1), B4–N4 1.40(1), B5–N4 1.43(1), B5–N5 1.44(1), B6–N5 1.41(1), B6–N6 1.44(1), B4–N6 1.44(1), B1–Br1 1.954(8), B2–Br2 1.953(8), B3–Br3 1.939(8), B4–Br4 1.953(8), B5–Br5 1.933(8), B6–Br6 1.941(8), N1–C1 1.468(9), N2–C2 1.489(9), N3–C3 1.423(9), N4–C4 1.476(9), N5–C5 1.491(9), N6–C6 1.479(9). Selected bond angles [°]: B1–N1–B2 117.6(6), N1–B2–N2 122.0(7), B2–N2–B3 119.1(6), N2–B3–N3 119.8(7), B3–N3–B1 119.2(6), B4–N4–B5 119.2(6), N5–B6–N6 121.1(7), B6–N5–B5 119.4(6), N5–B5–N4 120.4(7), B4–N6–B6 117.6(6), N4–B5–N5 120.4(7), B5–N5–B6 119.4(6), N5–B6–N6 121.1(7), N1–B1–Br12 118.4(6), N1–B2–Br2 119.4(8), N2–B2–Br2 118.6(6), N2–B3–Br3 119.7(6).

Crystals of the borazine $(F_5C_6N{=}BBr)_3$, **12**, are monoclinic (space group *C*2/*c*, $Z = 4$). A twofold axis passes through atoms Br1, B1, N2 C7, C10 and F8 as shown in Figure 12 and the molecule therefore has point group symmetry C_2. The B–N bonds are longer than in $(HN{=}BBr)_3$[44] although the B–Br bonds are shorter. The endocyclic bond angles N–B–N are smaller than 120° (on average 119°) and the B–N–B bonds angles are larger (on average 121°). Typical is the arrangement of the pentafluorophenyl groups. They stand almost perpendicular to the borazine ring plane with interplanar angles of 86.4(1)° for the F_5C_6 group bonded to N2 and 82.2(1)° for those bonded to N1 and N1A.

A similar distortion results for the F_5C_6 ring. The C–C–C bond angles of the *ipso* C atoms C1 and C7 are only 117.3(3)° and 117.8(5)°, respectively, and the C–C–C bond angle for the *ortho* C atoms C2/C6 are 121.2(3) and 121.9(3)° for C8.

Figure 13 shows the molecular structure of the amino derivative **13** $(F_5C_6N{=}BNH_2)_3$. This borazine crystallises in the monoclinic space group *I*2/*a* with $Z = 4$ and the molecules shows point group symmetry C_2. The borazine ring is therefore planar and the N atoms of the amino groups lie in the ring plane. The pentafluorphenyl rings are twisted

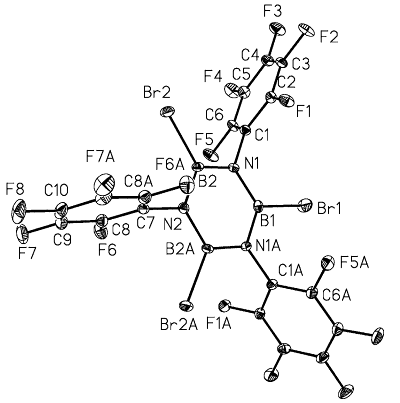

Figure 12. ORTEP plot of a molecule of (F$_5$C$_6$N=BBr)$_3$, **12**. Selected bond lengths [Å]: B1–N1 1.435(4), B2–N1 1.426(6), B2–N2 1.431(5), B1–Br1 1.907(6), B2–Br2 1.919(4). N1–C1 1.437(5), N2–C7 1.448(7). Selected bond angles [°]: N1-.B1–N1A 119.3(5), Br1–B1–N1 120.4(3), N1–B2–Br2 120.6(3), N2–B2–Br2 120.6(3), N1–B2–N2 118.8(3), B1–N1 B2 120.6(3), B1–N1–C1 118.6(3) B2–N1 C1 120.8(3), B2–N2–C7 119.3(2), B2–N2–B2A 121.3(5), C6–C1–C2 117.3(3), C9–C7–C8A 117.8(5). Selected interplanar angles [°]: B1–B2–B2A–N1–N2–N2A/C1–C6 81.4, B1–B2–B2A–N1–N2–N2A/C7–C8–C9–C8A–C9A 95.2.

against the borazine plane by 102.2° (N1) and 93.8° (N2) while the planar amino groups are twisted by only 7.4° (B1) and 8.7° (B2). Thus, the amino groups are almost coplanar with the ring and, as a consequence, the exocyclic B–N bonds are rather short at 1.392(4) and 1.410(3) Å, i.e. they show π-bond character. This is certainly the reason why the endocyclic B–N bond lengths are comparatively long, at 1.448(2) Å for B1–N1, 1.443(3) Å for B2–N1 and 1.453(2) Å for B2–N2. Similar to the F$_5$C$_6$ groups in **13** one observes a distortion of the phenyl groups. The C–C–C bond angle at the *ipso*-C atom is 116.6(2)° and at the *ortho*-C atoms it is 122.0(2)°.

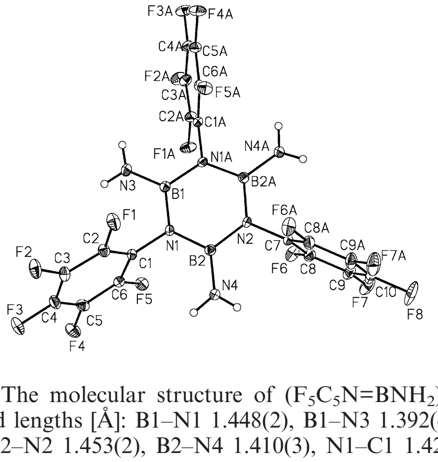

Figure 13. The molecular structure of (F$_5$C$_5$N=BNH$_2$)$_3$, **13**. Selected bond lengths [Å]: B1–N1 1.448(2), B1–N3 1.392(4), B2–N1 1.443(3), B2–N2 1.453(2), B2–N4 1.410(3), N1–C1 1.421(2), N2–C7 1.421(7). Selected bond angles [°]: N1A–B1–N1 117.2(2), B1–N1–B2 123.0(2), N1–B2–N2 116.6(2), B2–N2–B2A 123.3(2), N1–B1–N3 121.4(1), N1A–B1–N3 121,4(1), N1–B2–N4 122.1(2), N2–B2–N4 121.3(2), B1–N1–C1 117.2(2), B2–N1–C1 119.9(2). C2–C1–C6 116.4(2), C8–C7–C8A 116.6(2). Selected interplanar angles [°]: H1–H1A–N3/N1–B1–N1A 7.5, H2–H3–N4/N1–B2–N2 3.6, C1–C2–C6/B1–N1–B2 103.6, C8–C7–C8A/B2–N2–B2A 90.8.

Structures of 2,4,6-Triorganylborazines (RN=NR′)$_3$

One of the most well known and stable borazines is 2,4,6-triphenylborazine, **14**.[10] Its crystal structure was determined by I. Manners et al. in 2003.[57] They observed an orthorhombic unit cell in the space group *Pna*2$_1$. We determined the structure of **14** already in 1997[44] but report our result now because we found a different space group. It was difficult to grow suitable single-crystals because most of the long needles had diameters less than 0.01 mm. The compound crystallised in the trigonal space group *P*6*cc*. Figure 14 shows an ORTEP plot of the molecule with a view on top of the planar borazine ring down the *c* axis. A C_3 axis passes through the centre of the ring. The B–N bond lengths are 1.424(4) Å which is on the short side for B–N bond lengths in borazines. The N–B–N and B–N–B bond angles of **14** deviate from the ideal 120° of a hexagon by 3–4°. Particularly narrow is the N–B–N bond angle of 115.8(3)°. In contrast the B–N–B bond angle is 124.1°. The respective bond angles of **14** in the orthorhombic cell are closer to 120°, with B–N–B bond angles ranging from 120.6(1) to 121.1(1)° and N–B–N bond angles from 118.7(2) to 119.90(2)°.[57] Clearly, **14** can exists in two polymorphic forms.

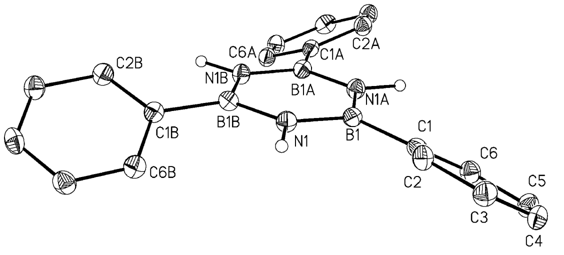

Figure 14. ORTEP plot of compound (HN=PPh)$_3$, **14**. Selected bond lengths [Å]: B1–N1 1.424(4), B1–N1A 1.424(4), B1–C1 1.573(5), N1–H1 0.81(4). Selected bond angles [°]: N1A–B1–N1 115.8(3), N1A–B1–C1 123.1(3), N1–B1–C1 121.0(3), B1B–N1–B1 124.1(3). Torsion angle [°]: C2C1B1N1 25.5.

The phenyl rings are arranged in a propeller like fashion, the interplanar angle between the phenyl groups and the borazine ring being 27.7°. This is less than in the isoelectronic 1,3,5-triphenylbenzene where the torsion angles are 36.1, 37.2 and 40.9°.[58] The difference is due to the longer ring B–N bond lengths compared with the ring C–C bond lengths.

The molecules are stacked above one another along the threefold axis (see Figure 15). Each molecule is turned around by 44.2°. The distance between two ring centres is 3.64 Å which is 0.31 Å longer than in hexagonal BN.

The arrangement of the molecules in the hexagonal unit cell induces a structural peculiarity. Six stacks of the molecules are arranged around the threefold axis in space to form a channel as shown in Figure 15. Not taking H atoms into account, the channel diameter is 7.5 Å (or 4.5 Å taking the van der Waals radius of H into account).

The borazine (*i*PrN=BMe)$_3$, **15**, crystallises in the monoclinic space group $P2_1/n$ with $Z = 4$. While the borazine ring is planar (maximum deviation from the mean plane is

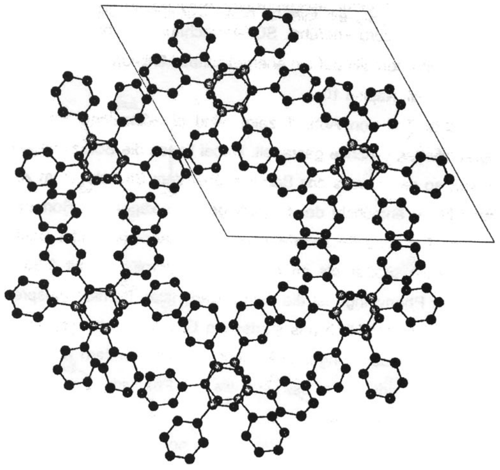

Figure 15. The channel structure created from stacks of molecules along a sixfold axis.

0.02 Å), the carbon atoms bonded to the B and N atoms deviate from the ring plane, the methyl groups by 4–5° and the central C atom of the isopropyl groups by 1–2°. Figure 16 shows the molecular structure of **15**. The N–B–N bond angles are close to 118° and the B–N–B angles close to 122°. B–C bond lengths range from 1.590(4) to 1.600(4) Å. Compared with the B–N bond lengths of $(HN{=}BMe)_3$ [1.39(4) Å][10] the B–N bonds are longer [1.442, 1.444(3) Å]. We assume that this lengthening is due to the steric effect of the isopropyl groups.

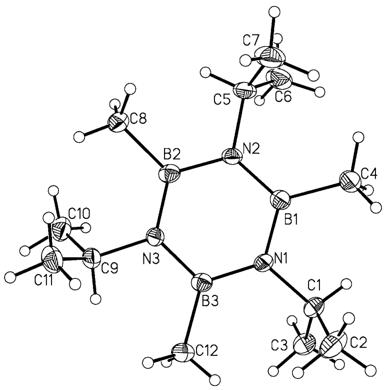

Figure 16. Molecular structure of (*i*PrN=BMe)$_3$, **15**. Selected bond lengths [Å]: N1–B11.444(3), N1–B3 1.443(3), N2–B1 1.441(3), N2–B2 1.442(3), N3–B2 1.440(3), N3–B3 1.445(3), B1–C4 1.590(4), B2–C8 1.600(4), B3–C12 1.596(4), N1–C1 1.498(3), N2–C5 1.494(3), N3–C9 1.497(3). Selected bond angles [°]. N2–B1–N1 117.4(2), N1–B1–C4 119.7(2), N2–B1–C4 122.8(2), N3–B2–N2 118.1(2), N3–B2–C8 122.3(2), N1–B3–C12 122.7(2), N1–B3–N3 118.2(2), N1–B3–C(12) 122.7(2), N3–B3–C12 119.1(2), B3–N1–B1 121.9(2), B1–N1–C12 116.7(2), B3–N1–C1 121.2(2), B1–N2–B2 122.2(2), B2–N2–C5 116.5(2), B1–N2–C5 121.2(2), B2–N3–B3 121.3(2), B2–N3–C9 121.5(2), B3–N3–C9 117.2(2). Selected torsion angles [°]: N3–B3–N1–B1 7.4, B1–N2B2–N3 –7.9.

The molecules are situated along the *b* axis. They are stacked on top of each other due to translation. The axis through the centre of the borazine ring forms an angle of 35.2° with the *b* axis.

The unit cell parameters of the isomeric borazine (MeN=B*i*Pr)$_3$, **16**, suggest that it crystallises in the tetragonal system. However, we were not able to find a structural solution in a tetragonal space group. A solution was, however, possible for the orthorhombic system in the $P2_12_12$ space group to give what we consider a preliminary result.[59] Figure 17 shows the molecular structure with the disordered isopropyl groups. The site occupation factor suggests a value of 0.5 for the disordered C atoms C4, C7 and C10. For this reason we will discuss shortly only the bonding parameters of the B_3N_3 ring and compare the data with those of the isomer **15**. The B–N bonds of **16** seem to be slightly longer than in **15** and B–N–B bond angles are slightly larger. Consequently, the N–B–N bond angles are smaller than in the isomer **16**. A steric effect resulting from the shorter N–C bond to the *i*Pr group may be responsible for the longer B–N bond in **17**. However, the differences are small and are more significant for the bond angles than for the bond lengths.

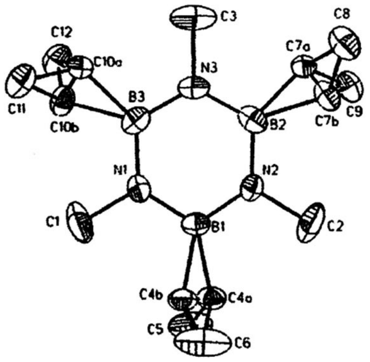

Figure 17. Molecular structure of **16** showing the site disordered position of the CH atoms of the isopropyl groups.

Discussion and Conclusions

The parent borazine $(HB{=}NH)_3$ was first prepared by Stock and Poland[60] in 1926 and its structure was determined by electron diffraction in 1938.[61] It revealed a planar six-membered ring with equal B–N bond lengths and slightly different endocyclic bond angles (119, 121°). This molecular structure was also observed in the solid-state, however the symmetry of the borazine molecule turned out to be C_2.[4] E. Wiberg[62] coined the name "inorganic benzene" for borazines because benzenes and the isoelectronic borazines usually have planar six-membered rings, although they are chemically quite different. Since then, numerous calculations at various levels of theory have been reported attempting to prove or disprove the aromatic character of borazine. Today, there is evidence that borazines may have an "antiaromatic" character.[2]

The N atoms of borazines show Lewis basicity as demonstrated, for instance, by the ease of formation of 1:1 adducts with halides of aluminium, gallium or tin[63] whereas the B atoms show Lewis acidic character as revealed by the formation pyridine adducts[56,64] or the formation of borazinium cations such as $(Me_3B_3N_3H_4)^+$.[63,65,66]

More recently, it has been shown that the BN bonds of borazines can become quite unequal by binding one N atom to a Li, Al, Si, P, As or Sb atom.[21–24] Also, borazinium cations, e.g. $(Me_3B_3N_3H_4)^+$, show three different BN bond lengths.[63–66]

The ring planarity can be lost particularly with the introduction of bulky substituents. At the moment, the most striking examples are compounds **4**, $Me_3B_3N_3H_2Ti(OtBu)_3$[24] and $[(EtB{=}NR)_3Cr(CO)_3]$.[67] In addition, there are now some examples where ring planarity is retained but the substituents are bent up and/or down from the ring plane as shown for compounds **15** and **16**. In conclusion, the shape of the borazine ring depends on the steric demand of the substituents and the electronegativity of the groups attached either to the N atoms as well as on the B atoms. From this point of view, a more systematic study of substituent effects on the structure of borazines will almost certainly provide interesting results.

Experimental Section

General: All experiments were performed under anhydrous conditions in an atmosphere of either nitrogen or argon using Schlenk techniques. The solvents were dried by standard methods and stored under N_2 using special storage flasks. If not stated otherwise, all reagents were of commercial grade. The compounds 2,4,6-tribromo-1,3,5-trimethylborazine,[10] 2,4,6-tribromo-1,3,5-tris(pentafluorophenyl)borazine, m.p. 253 °C,[40,41] were prepared according to literature procedures. $(F_3CCH_2N{=}BF)_3$ was supplied by Meller.[35]

NMR: Bruker ACP 200 (^{1}H, ^{11}B, ^{13}C), Jeol GSX 270 (^{1}H, ^{11}B, ^{29}Si), Jeol EX 400 (^{1}H, ^{11}B, ^{13}C): standards: $SiMe_4$, C_6D_6, BF_3OEt_2 ext. IR: Nicolet 520 FTIR spectrometer, usually hostaflon/nujol mulls for solids. MS: Atlas CH7 or Finnigan MAT90, usually at 70 eV; Siemens P4 diffractometer equipped with an area detector and an LT2 device. Mo-K_α-radiation, graphite monochromator. Data reduction, structure solution, absorption correction and refinement: SAINT, SADABS, SHELXTL and SHELX93.[68] Thermal ellipsoids shown in the figures represent a 25% probability. CH hydrogens were placed in calculated positions and refined as a riding model. Positions of N bonded H atoms were taken from the difference Fourier maps and their positions were refined isotropically. All non-hydrogen atoms were refined with anisotropic thermal parameters. Elemental analyses were performed at the microanalytical laboratory of the department.

2,4,6-Trifluoroborazine (1): A 100 mL Schlenk bulb was charged with freshly sublimed SbF_3 (14 g, 78 mmol) and toluene (30 mL). At –78 °C stirring was started and a solution of $(HN{=}BCl)_3$[69] (0.68 g, 3.7 mmol), dissolved in toluene (25 mL), was drop wise added to the suspension. After warming to ambient temperature the reaction was followed by ^{11}B NMR spectroscopy: the signal of $(HN{=}BCl)_3$ at δ = 30.4 ppm disappeared quickly and within an hour only the signal of **1** at δ = 25.0 ppm could be observed showing that the solution contained only **1**. After filtration (G4 frit) and storing the filtrate for one day at –25 °C a colourless solid had formed consisting of tiny, needle shaped single crystals of **1**. Yield 0.44 g, (3.3 mmol, 89%), m.p. 121 °C. NMR (C_6D_6): ^{11}B NMR: δ = 25.1 ppm. IR (nujol): $\tilde{\nu}$ = 3509 (m), 1531 (w), 1514 (vst), 1505 (vst), 1401 (m), 1333 (m), 1125 (w), 935 (m), 735 (w), 727 (w), 685 (w), 660 (m) cm^{-1}.

[Bis(trimethylsilyl)amino]dichloroborane (3):[36] a) A 250 mL three-necked round-bottomed flask fitted with a dry-ice reflux condenser was charged with a solution of $N(SiMe_3)_3$ (5.95 g, 25.5 mmol) in hexane (50 mL). BCl_3 (43.0 g, 30.0 mL), condensed in a dry-ice cooled dropping funnel, was then diluted with hexane (50 mL). At –60 °C this solution was dropped into the stirred solution of the aminosilane. After addition the mixture was allowed to attain room temperature and was then heated to reflux for 4 h. All volatiles were then removed from the solution at 25 °C/12 Torr. Distillation of the remaining oil at b.p. 82 °C/11 Torr yielded **3** (4.51 g, 73%) as a colourless liquid, m.p. 5 °C.

b) BCl_3 (3.44 g, 2.4 mL, 29.3 mmol) was condensed at –78 °C into a 250 mL round-bottomed flask and diluted with hexane (60 mL). At –60 °C a solution of $NaN(SiMe_3)_2$ (5.38 g, 29.3 mmol) in hexane (100 mL) was added while stirring. Stirring was continued overnight at ambient temperature. The insoluble NaCl was then removed by filtration and the hexane distilled from the filtrate (25 °C, 12 Torr). The residue was then distilled using a Vigreux column. **3** (3.83 g, 54%) was collected at b.p. 75 °C/5 Torr. It was subsequently dissolved in hexane (2 mL) hexane. Single-crystals separated on storing the solution at –25 °C. NMR in C_6D_6: ^{1}H NMR: δ = 0.26 ppm (s, $^1J_{H,C}$ = 18 Hz; $^2J_{H,Si}$ = 39 Hz). ^{13}C NMR (100 MHz): δ = 37.6, 3.83 ppm (s, $^1J_{C,H}$ = 18 Hz, $^1J_{C,Si}$ = 29 Hz). ^{11}B NMR (64 MHz): δ = 37.6 ppm (s, $h_{1/2}$ = 140 Hz). ^{29}Si NMR: δ = 9.70 ppm (d, $^1J_{Si,C}$ = 29 Hz). IR (NaCl): $\tilde{\nu}$ = 3041 (w), 2971 (m), 2960 (st), 2894 (m), 1409 (m), 1377 (m), 1321 (st), 1289 (vst), 1268 (st), 1257 (vst), 942 (st), 922 (vst), 875 (st), 850 (st), 803 (m), 770 (m), 695 (m), 684 (m), 637 (w), 620 (m), 552 (w), 534 (m), 472 (w), 395 (m), 302 (w) cm^{-1}. $C_6H_{18}BCl_2NSi_2$ (242.1): calcd. C 29.77, H 7.49, N 5.79; found C 27.41, H 6.88, N 5.65.

2,4,6-Trichloro-1,3,5-tris(trimethylsilyl)borazine (4):[70] A solution of **3** (4.51 g, 18.6 mmol) in xylene (100 mL) was heated at reflux for 2 d. A single ^{11}B signal at δ = 35.5 ppm was then present. Me_3SiCl and the solvent were subsequently removed in vacuo. The solid residue was subjected to sublimation (95 °C/2 Torr). Yield of **4**: 1.59 g, 64%. Compound **4** was dissolved in toluene (10 mL). At –25 °C **4** crystallised from the solution as colourless prisms, m.p. 140 °C. NMR (C_6D_6): ^{1}H NMR (400 MHz): δ = 0.44 ppm (s, $^1J_{H,C}$ = 17 Hz). ^{13}C NMR (100 MHz): δ = 3.60 ppm (s, $^1J_{H,C}$ = 17 Hz). ^{11}B NMR (64 MHz): δ = 35.5 ppm (s, $h_{1/2}$ = 370 Hz). ^{29}Si NMR (53.7 MHz): δ = 19.34 ppm. IR (nujol/hostaflon): $\tilde{\nu}$ = 3048 (w), 2997 (w), 2960 (m), 2901 (w), 1363 (st), 1335 (vst), 1255 (st), 1155 (m), 1141 (st), 1095 (w), 1067 (w), 1053 (w), 1042 (w), 1027 (w), 921 (st), 848 (vst), 779 (st), 685 (m), 677 (m), 670 (m), 643 (w), 638 (w), 619 (w), 597 (w), 513 (w), 475 (w), 399 (w), 364 (w), 350 (w), 297 (w), 270 (m) cm^{-1}. $C_9H_{27}B_3Cl_3N_3Si_3$ (400.38): calcd. C 27.00, H 6.80, N 10.49; found C 27.51, H 6.59, N 10.33.

[Bis(trimethylsilyl)amino]chloro(methyl)borane: $MeBCl_2$ (5.3 g, 55 mmol) was condensed into a 250 mL three-necked flask equipped with an dry-ice reflux condenser and hexane (10 mL) was added. The stirred solution was then kept at –60 °C and a suspension of $LiN(SiMe_3)_2$ (8.2 g, 49 mmol) in hexane (100 mL) was added. The mixture was stirred overnight at ambient temperature. After filtration and washing with hexane (2 × 10 mL) all volatiles were removed from the filtrate at 25 °C/10 Torr. Colourless crystals separated at –25 °C from a concentrated hexane solution (10 mL). The yield was not determined; m.p. –8 to –5 °C. The crystal quality was not good enough for an X-ray structure analysis. NMR (C_6D_6): ^{1}H NMR (400 MHz): δ = 0.21 (s, $^2J_{H,Si}$ = 5 Hz, 18 H), 0.76 ppm (s, 3 H). ^{13}C NMR (100 MHz): δ = 4.1 (SiMe), 13.9 ppm (br., BMe). ^{11}B NMR (64 MHz): δ = 49.1 ppm. ^{29}Si NMR (53.7 MHz): δ = 6.48 ppm. IR (CsBr plates): ṽ = 3735 (w, br.), 3662 (w, br.), 3412 (w), 2984 (st), 2958 (vst), 2900 (w), 2864 (m), 2801 (w), 1940 (w), 1877 (w), 1726 (w), 1648 (w), 1431 (m), 1411 (m), 1338 (vst), 1323 (vst), 1290 (vst), 1277 (vst), 1265 (vst), 1256 (vst), 1196 (w), 1162 (w), 1148 (w), 1051 (st), 1026 (vst), 944 (m), 905 (st), 889 (st), 847 (vst), 768 (st), 688 (st), 625 (m), 614 (st), 553 (w), 533 (w), 499 (w), 477 (m), 450 (m), 386 (m), 303 (m) cm^{-1}. $C_7H_{21}BClNSi_2$ (221.69): calcd. C 37.93, H 9.55, N 6.32; found C 37.34, H 9.03, N 6.41.

Attempted Decomposition of $(Me_3Si)_2NB(Cl)Me$: $(Me_3Si)_2NB(Cl)$-Me (9.6 g, 40 mmol) was dissolved in toluene (100 mL) and heated at reflux for 10 d. No change in the ^{11}B and ^{1}H spectra could be detected. The toluene was then removed in vacuo and replaced by xylene (100 mL). This solution was then heated to reflux for two weeks. No change in the NMR spectra could be noted. The xylene was then removed in vacuo and the pure compounds heated to reflux (≈ 195 °C). No formation of Me_3SiCl was observed.

2,4,6-Trichloro-1,3,5-tris[chloro(dimethylamino)boryl]borazine (6): To a solution of $(Cl_2BN{=}BCl)_3$ (0.48 g, 1.12 mmol) in hexane (10 mL) was added at –78 °C to a solution of Me_3SiNMe_2 (397 mg, 3.39 mmol) in hexane (5 mL). A solid formed which dissolved during warming to ambient temperature. After three hours stirring, the hexane and Me_3SiCl were removed in vacuo. 427 mg (96%) of $[Me_2N(Cl)BN{=}BCl]_3$ are left as a yellow oil. NMR (C_6D_6): ^{1}H NMR (400 MHz): δ = 2.62 (s, 9 H, NMe), 2.67 (s, 9 H, NMe). ^{13}C NMR (100 MHz): δ = 39.35, 39.42. ^{11}B NMR (64 MHz): δ = 8 ppm ($h_{1/2}$ = 400 Hz). IR (Nujol, hostaflon): ṽ = 2981 (st), 2777 (m), 2509 (st), 1649 (m), 1510 (st), 1459 (vst), 1416 (vst), 1387 (st), 1349 (m), 1220 (w), 1196 (m), 1144 (st), 1131 (st), 1077 (w), 1024 (st), 965 (vst), 910 (w), 901 (m), 842 (w), 831 (m), 817 (w), 790 (m), 731 (w), 721 (m), 700 (m), 654 (m), 630 (w), 621 (m), 611 (w), 579 (m), 541 (w), 431 (w), 389 (w), 352 (w) cm^{-1}. $C_6H_{18}B_6Cl_6N_6$ (451.8): calcd. C 15.95, H 4.02, N 18.60, Cl 47.08; found C 16.15, H 4.46, N 17.53, Cl 46.50.

1,3,5-Bis[bis(dimethylamino)boryl]-2,4,6-trichloroborazine (7) and 6-Chloro-2,4-dimethylamino-1,3-bis(dimethylaminoboryl)borazine (9): A solution of $(Cl_2BN{=}BCl)_3$ (640 mg, 1.84 mmol) in hexane (10 mL) was cooled to –78 °C. While stirring, Me_3SiNMe_2 (1.34 g, 1.44 mL, 11.5 mmol) was added with a syringe. The precipitate that formed was found to dissolve on warming to room temperature. After stirring for 3 h, Me_3SiCl and hexane were removed in vacuo (1 Torr). The oily product, dissolved C_6D_6, showed only one ^{11}B NMR signal (most likely **7**). However, when it was dissolved in dichloromethane (2 mL) and the solution cooled to –25 °C, 0.53 g of **9** (1.3 mmol, 73%) separated as colourless prisms; m.p. 125 °C. NMR of 9 (in C_6D_6): ^{1}H NMR (400 MHz): δ = 2.57 (s, 6 H, NMe), 2.60 (s, 12 H, NMe), 2.70 (s, 6 H, NMe), 3.44 ppm (s, 1 H, NH). ^{13}C NMR (100 MHz): δ = 38.1 (s), 39.4(s), 39.5 ppm (s). ^{11}B NMR (64 MHz): δ = 24.9 with a shoulder at 25.3 (B1, B1A), 29.9 ppm (B2, B4, B4A); (ratio 2:3). IR (nujol, hostaflon): ṽ = 3525 (w), 3483 (w), 2983 (st), 2788 (st), 1349 (m), 1220 (m), 1196 (w), 1144 (w), 1129 (st), 1066 (m), 1029 (w), 959 (m), 913 (m), 906 (w), 845 (m), 830 (st), 807 (w), 798 (w), 736 (w), 713 (m), 701 (w), 654 (w), 637 (w), 631 (w), 616 (w), 616 (w), 566 (w), 546 (w), 520 (w), 478 (w),

Table 2. X-ray data of compounds **1**–**5**, **9**.

Compound	**1**	**2**	**3**	**4**	**5**	**9**
Formula	$H_3B_3F_3N_3$	$C_6H_6B_3F_{12}N_3$	$C_6H_{18}BCl_2NSi_2$	$C_9H_{27}B_3Cl_3N_3Si_3$	$B_6Cl_9N_3$	$C_{12}H_{37}B_5ClN_9$
M_r [g mol^{-1}]	134.48	380.58	242.10	400.39	425.94	397.01
Cryst. size [mm]	0.10 × 0.15 × 0.40	0.24 × 0.30 × 0,33	0.2 × 0.25 × 0.6	0.15 × 0.2 × 0.5	0.23 × 0.3 × 0.5	0.3 × 0.4 × 0.6
Cryst. system	trigonal	orthorhombic	monoclinic	triclinic	tetragonal	monoclinic
Space group	$R\bar{3}c$	$Pnma$	$C2/c$	$P\bar{1}$	P4(1)2(1)2	$C2/c$
a [Å]	11.388(3)	9.481(2)	14.972(5)	10.874(3)	9.8256(1)	11.4420(6)
b [Å]	11.388(3)	15.336(3)	8.663(4)	12.099(2)	9.8256(1)	17.7561(9)
c [Å]	6.835(2)	9.744(2)	10.354(2)	18.188(4)	16.4708(2)	12.6638(6)
α [°]	90	90	90	78.303(9)	90	90
β [°]	90	90	96.40(1)	89.893(7)	90	115.18(1)
γ [°]	120	90	90	67.258(9)	90	90
V [Å^3]	767.7(4)	1416.9(5)	1334.5(8)	2153.3(9)	1590.13(3)	2328.3(2)
Z	6	12	4	4	4	4
ρ(calcd.) [Mg m^{-3}]	1.745	1.784	1.205	1.235	1.779	1.133
μ [mm^{-1}]	0.184	0.217	0.624	0.588	1.560	0.180
F(000)	396	744	512	840	816	856
Index range	$-9 \le h \le 4$, $13 \le k \le 0$, $-3 \le l \le 5$	$-1 \le \mathrm{h} \le 11$, $-18 \le k \le 1$, $-1 \le l \le 11$	$-18 \le h \le 18$, $-10 \le k \le \le 10$, $-13 \le l \le 8$	$-13 \le h \le 13$, $-16 \le k \le 13$, $-22 \le l \le 23$	$-12 \le h \le 12$, $-12 \le k \le 12$, $-18 \le l \le 21$	$-14 \le h \le 14$, $-21 \le k \le 21$, $-8 \le l \le 16$
2θ [°]	52.38	50.00	57.24	57.34	58.40	58.40
T [K]	173	193	153(5)	193(3)	213(3)	183
Refl. collected	228	1766	3502	12104	8287	6585
Refl. unique	135	1295	1192	6504	1731	1970
Refl. observed (4σ)	127	836	908	5466	1658	1321
R (int.)	0.0303	0.0294	0.0264	0.0198	0.0638	0.0351
No. variables	18	131	59	397	84	130
Weighting scheme[a] x/y	0.02790/1.4390	0.0457/0.6152	0.0442/1.7617	0.0260/1.8470	0.0654/1.4860	0.0567/4.6672
GOOF	1.109	1.021	1.114	1.151	1.092	1.142
Final R (4σ)	0.0339	0.0454	0.0333	0.0385	0.0505	0.0385
Final $wR2$	0.0825	0.1089	0.0876	0.0850	0.1286	0.0988
Larg. res. peak [e Å^{-3}]	0.168	0.200	0.355	0.286	0.446	0.260

[a] $w^{-1} = \sigma^2 F_o^2 + (xP)^2 + yP$; $P = (F_o^2 + {}^2F_c^2)/3$.

399 (w), 326 (w) cm^{-1}. $C_{12}H_{37}B_5ClN_9$ (396.92): calcd. C 36.30, H 9.39, N 31.75, Cl 8.93; found C 36.59, H 9.25, N 30.56, Cl 8.70.

1,3-Bis[bis(dimethylamino)boryl]-4,6-bis(dimethylamino)borazine (10): To a stirred solution of $(Cl_2BN{=}BCl)_3$ (670 mg, 1.95 mmol) in hexane (10 mL) was added Me_2NSiMe_3 (2.06 g, 2.81 mL, 17.5 mmol) with a syringe at –78°. The colourless precipitate that formed subsequently dissolved on warming the mixture to room temperature. After stirring for an additional 3 h the solvents and Me_3SiCl were removed in vacuo. The resultant yellow oil was dissolved in CH_2Cl_2 (2 mL) and the solution stored at –25 °C. Colourless prisms of **10** separated as single-crystals. Yield 670 mg (1.66 mmol, 85 %); m.p. 133 °C. NMR (C_6D_6): ^{1}H NMR (400 MHz): δ = 2.56 (s, 6 H, NMe), 2.60 (s, 12 H, NMe), 2.66 (s, 24 H, NMe), 3.41 ppm (s, 1 H, NH). ^{13}C NMR (100 MHz): δ = 38.0 s, 39.3 s, 39.4 ppm, s. ^{11}B NMR (64 MHz): δ = 26.1 ($h_{1/2}$ = 400 Hz, B1, B1A, B2), 30.8 ($h_{1/2}$ = 350 Hz, B3, B3A), ratio 3:2 – MS [70 eV, m/z (rel. Intensity); ^{11}B, ^{35}Cl]: 362 (30), 317 (40), 307 (100), 263 (79), 252 (15), 168 (2), 124 (35), 99 (20), 44 (60). $C_{14}H_{43}B_5N_{10}$ (405.62): calcd. C 41.46, H 10.68, N 34.53; found C 40.25, H 9.89, N 34.23.

2,4,6-Tribromo-1,3,5-trimethylborazine (11):[27] ^{1}H NMR (DMSO): δ = 6.95 (NH), 7.24, 8.17 ppm (Ph). ^{13}C NMR (DMSO): δ = 127.5, 129.6, 133.2, 136.4 ppm.

2,4,6-Triamino-1,3,5-tris(pentafluorphenyl)borazine (13): A two-necked Schlenk bulb connected to a dry-ice reflux condenser was charged at –78 °C with a solution of dry NH_3 (7.7 g, 450 mmol) and CH_2Cl_2 (25 mL). With stirring a solution of $(F_5C_6N{=}BBr)_3$ (7.51 g, 12 mmol) in CH_2Cl_2 (30 mL) was added. The mixture was allowed to attain room temperature and the reaction followed by ^{11}B NMR spectroscopy. The starting material signal at δ = 30.9 ppm disappeared within 3 h and was replaced by a signal at δ = 26.1 ppm. At that time only a single for **13** could be observed at δ = 26.1 ppm. All volatiles were then evaporated in vacuo and the residue extracted with toluene (20 mL). After filtration and washing with toluene (10 mL) crystals separated on cooling to –25 °C. Yield 3.2 g (43 %); m.p. 259 °C (dec.). NMR (C_6D_6): ^{1}H NMR (400 MHz): 2.56 ppm (s, br.). ^{11}B NMR (64 MHz): δ = 25.3 ppm (s, $h_{1/2}$ = 190 Hz). ^{19}F NMR (376 MHz): δ = 2.7 (m, 2 *m*-F), 7.7 (m, 1 *p*-F), 16.9 ppm (m, 2 *o*-F). IR (Nujol, hostaflon): ṽ = 3687 (w), 3663 (m w), 3547 (m), 3526 (st), 3469 (m), 3448 (st), 1651 (m), 1610 (vst), 1515 (vst), 1509 (vst), 1489 (st), 1425 (st), 1408 (vst), 1399 (vst), 1342 (st), 1308 (st), 1282 (w), 1249 (w), 1200 (w), 1153 (m), 1126 (w), 1062 (m), 1036 (st), 1026 (m), 1000 (vst), 992 (vst), 941 (w), 913 (w), 882 (w), 831 (w), 806 (m), 785 (m), 736 (st), 688 (m), 681 (m), 660 (m), 607 (w), 569 (m), 463 (m), 449 (m), 440 (m), 391 (st) cm^{-1}. $C_{18}H_6B_3F_{15}N_6$ (623.69): calcd. C 34.66, H 0.97, N 13.47; found C 34.29, H 1.02, N 12.90.

2,4,6-Triphenylborazine (14): Prepared as described in ref.[27] In order to remove soluble by-products, the raw material was washed 3 times with toluene (20 mL). Crystallisation from hot hexane (500 mL for 12 g of triphenylborazine) gave a powder containing thin needles, most of them not suitable for X-ray crystallography although some had acceptable diameters (0.09 to 0.12 mm) which were selected for the structure determination. NMR spectroscopic data: ^{11}B NMR: δ^{11}B (C_6D_6) = 34.8 ppm.

Table 3. X-ray data of compounds **10**–**15**.

Compound	**10**	**11**	**12**	**13**	**14**	**15**
Formula	$C_{14}H_{43}B_5N_{10}$	$C_3H_9B_3Br_3N_3$	$C_{18}B_3Br_3F_{15}N_3$	$C_{18}H_6B_3F_{15}N_6$	$C_{18}H_{18}B_3N_3$	$C_{12}H_{10}B_3N_3$
M_r [g mol^{-1}]	405.63	359.29	815.37	623.72	308.78	248.82
Cryst. size [mm]	0.15 × 0.2 × 0.2	0.2 × 0.4 × 0.4	0.20 × 0.20 × 0.30	0.12 × 0.15 × 0.18	0.2 × 0.2 × 0.4	0.4 × 0.3 × 0.3
Cryst. system	monoclinic	triclinic	monoclinic	monoclinic	hexagonal	monoclinic
Space group	*C*2/*c*	$P\bar{1}$	*C*2/*c*	*I*2/*a*	*P*6*cc*	$P2_1/n$
a [Å]	12.43(1)	7.960(2)	16.7592(3)	11.6547(3)	17.195(3)	15.386(8)
b [Å]	10.17(1)	9.392(2)	15.6197(4)	14.9327(3)	17.195(3)	6.026(3)
c [Å]	19.61(1)	15.467(3)	11.7494(3)	13.0087(1)	7.203(2)	19.14(1)
α [°]	90	90.36(3)	90.00	90.00	90	90
ß [°]	90.32(3)	91.77(3)	128.395(1)	93.426(1)	90	111.78(4)
γ [°]	90	114.48(3)	90.00	90.00	120	90
V [Å^3]	2477.8(35)	1051.6(4)	2410.6(1)	2259.94(8)	1844.4(7)	1648(1)
Z	4	4	4	4	4	4
ρ(calcd.) [Mg m^{-3}]	1.087	2.269	2.247	1.833	1.112	1.003
μ [mm^{-1}]	0.067	11.456	5.154	0.198	0.064	0.057
F(000)	888	672	1536	1224	648	552
Index range	$-16 \le h \le 16$, $12 \le k \le 12$, $-21 \le l \le 26$	$-7 \le h \le 10$, $12 \le k \le 12$, $-19 \le l \le 19$	$-21 \le h \le 21$, $18 \le k \le 19$, $-14 \le l \le 14$	$-14 \le h \le 14$, $17 \le k \le 18$, $-16 \le l \le 16$	$-1 \le h \le 16$, $18 \le k \le 1$, $-8 \le l \le 7$	$0 \le h \le 17$, $-6 \le k \le 0$, $-21 \le l \le 19$
2θ [°]	57.94	58.64	57.86	57.04	45.38	47–08
T [K]	203(3)	193	193	183(2)	210	293(2)
Refl. collected	6792	6175	6803	6393	3266	2547
Refl. unique	2049	3253	2417	2242	841	2445
Refl. observed (4σ)	1065	2184	2062	1781	654	1594
R (int.)	0.0852	0.0253	0.0293	0.0211	0.0764	0.0255
No. variables	140	218	194	205	77	172
Weighting scheme[a] *x*/*y*	0.0264/6.9083	0.0720/0	0.0783/4.7293	0.0483/2.1213	0.0654/0.0	0.0393/0.8257
GOOF	1.242	0.972	1.083	1.040	1.134	1.067
Final *R* (4σ)	0.0822	0.0445	0.0473	0.0380	0.0477	0.0521
Final *wR*2	0.1476	0.1134	0.1208	0.0924	0.1082	0.1159
Larg. res. peak [e Å^{-3}]	0.249	1.411	1.228	0.209	0.150	0.144

[a] $w^{-1} = \sigma^2 F_o^2 + (xP)^2 + yP$; $P = (F_o^2 + {}^2F_c^2)/3$.

1,3,5-Triisopropyl-2,4,6-trimethylborazine (15): *N*-Isopropyl-hexamethyldisilazane (15.5 mL, 62.5 mmol) was placed in a three-necked flask (200 mL) equipped with a dry-ice cooled reflux condenser and a dropping funnel. The system was flushed with nitrogen gas and a slow stream of nitrogen was maintained. The flask was then cooled with liquid nitrogen. $MeBBr_2$ (5.75 mL, 62.2 mmol) was slowly added (over 10 min). On warming, the reaction started at about –80 °C and the mixture quickly reached 60 °C. After the main reaction had subsided, the solution was kept at reflux at 95 °C for 24 h. Me_3SiBr was then removed by distillation. Isolation of the product was by distillation; b.p. 120 °C/0.05 Torr. It crystallised as needles. Yield 2.52 g (49 %); m.p. 58 °C. NMR: ^1H NMR ($CDCl_3$): δ = 0.62 (s, 9 H, BMe), 1.32 (d, CH_3, 18 H), 3.83 ppm (sept, 3 H). ^{13}C NMR (C_6D_6): δ = 23.6 (C-CH_3), 50.5 ppm (CH), BCH_3 not observed. ^{11}B NMR ($CDCl_3$): δ = 36.2 ppm. $C_{12}H_{30}B_3N_3$ (248.82): calcd. C 57.93, H 12.15, N 16.89; found C 56.93, H 11.72, N 16.45.

2,4,6-Triisopropyl-1,3,5-trimethylborazine (16): Prepared in analogy to **15** from iPrBBr_2 (15.4 g,72 mmol) and $MeN(SiMe_3)_2$ (15.9 mL, 72 mmol). Yield 5.9 g, m.p. 40–45 °C. NMR ($CDCl_3$): ^1H NMR: δ = 0.67 (s, 9 H, Me), 1.35 (d, 18 H, CMe_3), 4.01 ppm (sept, 3 H, CH). ^{13}C-NMR: δ = 3.8 (BC), 24.1 (C-CH_3), 46.9 ppm (NC). ^{11}B-NMR: δ = 36.6 ppm. $C_{12}H_{30}B_3N_3$ (248.82): calcd. C 57.93, H 12.15, N 16.89; found C 57.07, H 11.74, N 16.96.

Structure Determinations: Crystals were put in perfluoroether oil (if necessary cooled to –30 °C) and a suitable specimen was selected, fixed on top of a glass fibre and then on the goniometer head which was flushed with cold nitrogen gas (usually –80 °C). The unit cell was determined from reflections on five sets of 15 frames using the program SMART. Data were collected in the hemisphere mode on 1200 frames and two different sets of settings. All non-hydrogen atoms were refined anisotropically. CH hydrogen atoms were placed in calculated positions and refined isotropically, riding on the respective C atom. NH hydrogen positions were taken from the difference Fourier map and refined isotropically. The data of the Br-containing borazines as well as some of the B-chloroborazines were corrected for absorption. Tables 2 and 3 show relevant crystallographic data and data related to data collection and refinement.

CCDC-678182 (for **1**), -678183 (for **2**), -678184 (for **3**), -678185 (for **4**), -678186 (for **5**), -678187 (for **9**), -678188 (for **10**), -678189 (for **11**), -678190 (for **12**), -678191 (for **13**), -678192 (for **14**), -678193 (for **15**) contain the supplementary crystallographic data. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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