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Synthesis and Structure of *per*-Methylated B_6N_7-Azaboraphenalene[‡]

Henry P. Ederle[a] and Heinrich Nöth*[a]

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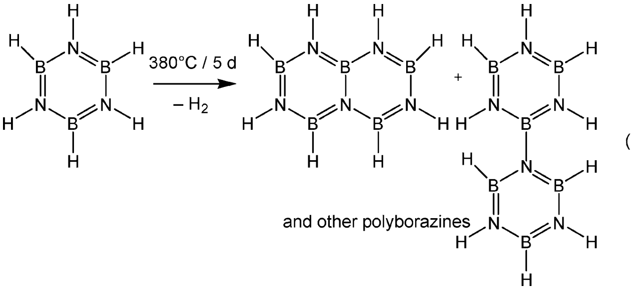
Tricyclic nonamethyl-B_6N_7-phenalene, $Me_9B_6N_7$ (**1**) was prepared from $N(BCl_2)_3$ and $MeB(NHMe_2)_2$ in the presence of NEt_3. Its B_3N_3 rings are twisted against each other by 8 and 11° and the B–N bond lengths vary from 1.412(9) to 1.482(9) Å. The tricyclic ring is rather stable as shown by its mass spectrum, which is dominated by the loss of Me groups as well as by the formation of doubly charged fragments of the tricycle.

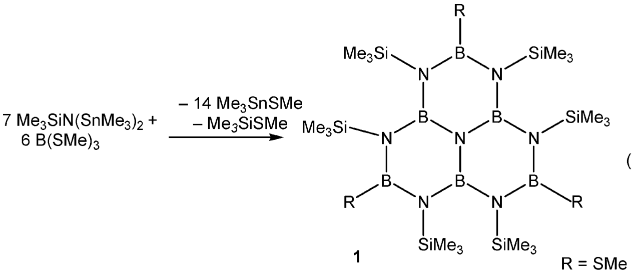
Introduction

Within the last decennium, research related to the various forms of boron nitride has become a topic of high interest due to its properties as a material.[2] Moreover, fibres and plastic materials based on borazines as building blocks have been produced, which serve as precursors for boron nitride.[3] The first polyborazines to be characterized by mass spectroscopy were the BN analogues of diphenyl and naphthalene.[4] Both resulted from the pyrolysis of borazine or the photoinduced condensation of gaseous borazine.[5,6] The structure of the naphthalene analogue was determined by Beck and Sneddon.[7] Equation (1) shows the characterized products of the borazine thermolysis.[4]

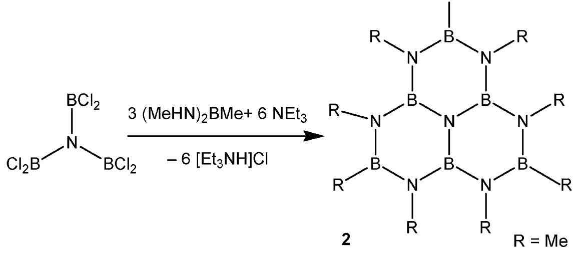


(1)

Willcockson et al.[8] observed that the reaction of trichloroborazine $(ClB{=}NH)_3$ with MeMgCl not only generated the trimethyl derivative $(MeB{=}NH)_3$ but also the B-tetramethylazaboranaphthalene $(MeB)_4(NH)_4BN$. They could also isolate two additional products, which they believed to be the anthracene and phenalene BN analogues. Other diborazines were reported by Meller and Füllgrabe.[9] The first well-defined BN-phenalene derivative was obtained by treating tris(methylthio)borane with trimethylsilyl bis(trimethylstannyl)amine,[10] as shown in Equation (2). We now found a more efficient route to permethylated azaboraphenylene **2**, as shown in Equation (3).



(2)



(3)

The reaction of $N(BCl_2)_3$[11] with the aminoborane $MeB(NHMe)_2$ in a molar ration of 1:3 and in the presence of NEt_3 yielded nonamethyl derivative **2** of the heptaazahexaboraphenalene in 50–60% yield. Colourless single crystals of **2** separated from its hexane solution at –78 °C.

The tris(dichloroboryl)amine should be a suitable starting compound for preparing various kinds of condensed BN compounds containing NB_3 units. We tested this approach by treating $N(BCl_2)_3$ with $Me_2Si(NHMe)_2$ in order to achieve the synthesis of tricyclic $N_7B_3Si_3$ system **3** as shown in Equation (4). The raw product showed a ^{11}B resonance at δ = 29 ppm. This corresponds to ^{11}B atoms in a BN_3 environment. However, there were more ^1H NMR signals than expected for the new heterocycle. Recrystallization yielded no pure product. It may well be that SiN cleavage with formation of Me_3SiCl also occurs besides the

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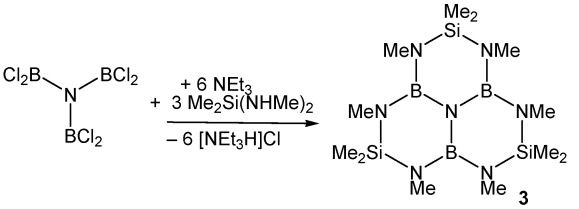
[a] Department of Chemistry and Biochemistry
University of Munich
Butenandtstr. 3–15, 81377 München, Germany

expected HCl elimination (trapped by Et_3N as $[Et_3NH]Cl$), and indeed, some Me_3SiCl was detected in the ^1H NMR spectrum.



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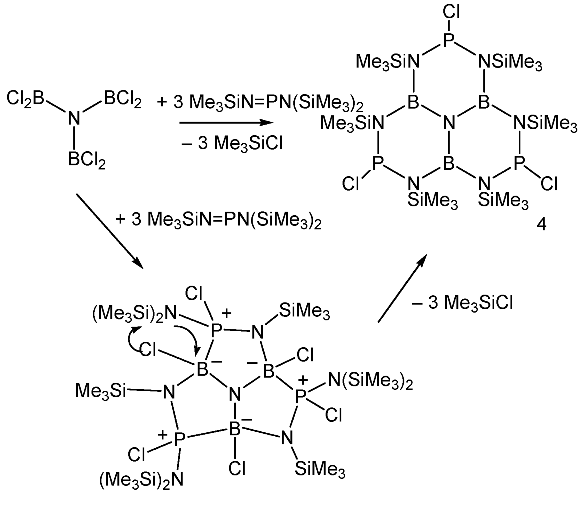


(5)

We were also not successful in generating a hexaoxopentaboraazaphenalene $(PhB)_3O_6B_3N$ by treating phenyl boronic acid with $N(BCl_2)_3$ in the presence of triethylamine. $N(BCl_2)_3$ reacted with the trimethylsilyliminophosphane $Me_3SiN{=}P(SiMe_3)_2$ in a 1:3 ratio where we expected the formation of compound **4** as depicted in Equation (5). Eight ^{11}B NMR signals showed that no single product was generated. Heating the residue of the reaction products to 150 °C resulted in the formation of Me_3SiCl, but in spite of observing only a single ^{11}B resonance for compound **4** the ^{11}B NMR spectrum was still complex.

NMR Spectra

Table 1 shows the chemical shifts for azaboraphenalens **1** and **2** as well as those of the permethylated borazine $(MeB{=}NMe)_3$.

Table 1. NMR spectroscopic data of compounds **1**, **2** and $(MeB{=}NH)_3$.[a]

	$\delta^{31}B$	$\delta^{14}N$	$\delta^{12}C$	$\delta^{1}H$
$R_9B_6N_7$ (**2**)	38.2 ($C\mathit{B}N_2$)	–265 ($C\mathit{N}B_2$)	–1 br. (BMe)	0.53 (BMe)
	27.9 (BN_3)	–281 ($\mathit{N}B_3$)	34.7 (NMe)	2.78 (NMe)
$R_3{}^*R'_6B_6N_7$ (**1**)	39.4 ($C\mathit{B}N_2$)	–		
	39.4 (BN_3)	–		
$(MeB{=}NMe)_3$	35.8 ($C\mathit{B}N_2$)	–275 ($C\mathit{N}B_2$)	0.0 (BMe)	0.46 (BMe)
			34.5 (NMe)	2.82 (NMe)

[a] R = Me, R′ = MeS, R* = Me_3Si.

There are two well-defined ^{11}B NMR signals in the expected intensity ratio (1:1) for compound **1** The signal of the better shielded boron nucleus (δ =27.9 ppm) results from the BN_3 units, whereas the signal at lower field (δ =38.2 ppm) represents the CBN_2 units [compare with 29.6 ppm for $B(NMe_2)_3$, 35.8 ppm for $(MeB{=}NMe)_3$ and 21.7 ppm for $MeB(NHMe)_2$].[12] The data of **1** suggest that BN–π-bonding is more pronounced for the BN_3 units than for the CBN_2 units.

In contrast to silyl-substituted B_6N_7 heterocycle **1**, which shows only a broad and asymmetric ^{11}B NMR signal, the ^{11}B NMR signals of **2** are well resolved and the boron nuclei are better shielded. Its $MeBN_2$ units are observed at lower field relative to the permethylborazine by 2.4 ppm. The ^{14}N NMR spectra reveal that the central N atom of **2** is deshielded by 10 ppm compared with the MeN nitrogen groups of $(MeB{=}NMe)_3$.[12] This is not unexpected because there are three boron atoms competing for BN–π-bonding in **2**, whereas there are only two boron atoms in $(MeB{=}NMe)_3$ that compete for the lone electron pair of the MeN groups. The ^1H and ^{13}C NMR spectroscopic data show no special features.

X-ray Structure

Compound **1** crystallizes in the orthorhombic space group *Iba*2 with eight molecules in the unit cell. Therefore, the molecule shows neither a twofold nor a threefold rotation axis nor a mirror plane as a view on top of the molecule might suggest (see Figure 1; for bonding values see Tables 2 and 3.). The reason for this is that the B and N atoms of the heterocycle are not arranged in a plane because the borazine subunits are twisted against each other (see Figure 2). The largest torsion angles in the B_6N_7 unit are –167.8(7)° for B2N1B5N5, –159.5.(7)° for B5N1B3N3 and 171.0(7)° for B3N1B1N7. Most of the other torsion angles BNBN or NBNB are found in the range from –8.2(1) to 14.0(7)°. Torsion angles incorporating the C atoms are larger, for instance, –156.0(7)° for C3N3B3N1. The largest deviation form the mean plane of the three borazine units is 0.11 Å for atom N2 on the ring N1N2B2N34B3N1 and 0.13 Å for N7 and B5 in the rings B1N7B6N6B5N1 and N1B5N5B4N4B3. Therefore, the borazine rings are not planar. In spite of this, the B–N bond lengths are generally shorter in **1** than those in **2**. The reason for this is that the torsion angles in **2** are larger than those in **1**. As expected, the steric influence on the central B_3N unit is negligible, as shown by the corresponding B–N bond lengths [N1–B1 1.454(8), N1–B3 1.441(8) and N1–B5 1.448(9) Å] and B–N–B bond angles [B1–N1–B3 119.1(5), B1–N1–B5 119.5(5) and B3–N1–B5 121.6(6)°]. The shortest B–N bonds are 1.411(9) Å for B5–N7 and B6–N7. The B–N bond lengths in compound **2** compared with those in compound **1** are 0.018–0.38 Å longer. This is obviously a consequence of the stronger distortions in **2**, which are responsible for decreased BN–π-bonding in **2**. The B–N–B bond angles in **1** and **2** are in general somewhat smaller than 120°, whereas most N–B–N bond angles are larger than 120° (up to 126°).

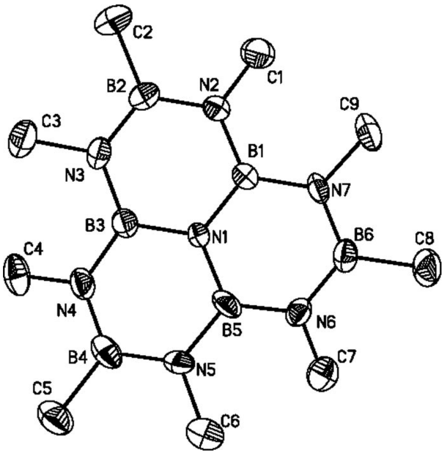


Figure 1. ORTEP plot of the molecular structure of compound **1**. Thermal ellipsoids are shown on a 25% probability level.

Table 2. Torsion angles [°] of compounds **1** and **2**.

Compound	1	2		1	2
N5–B3–N1–B1	–11.3	18.5	N3–B3–N5–R[a]	26.2	–59.1
B3–N1–B1–N2	8.2	15.8	N5–B3–N3–B2	–162.0	148.6
N1–B3–N5–R	–156.2	122.8	N2–B2–N3–B3	–9.4	17.9

[a] R = Me or $SiMe_3$.

Table 3. Selected B–N bonds [Å] of compounds **1** and **2**.

Compound	2	1		2	1
N1–B2	1.441(9)	1.443(4)	B2–N3	1.412(9)	1.448(3)
B2–N2	1.416(9)	1.434(4)	B2–C/Si	1.581(1)	1.855(3)
B3–N3	1.433(9)	1.471(5)	N3–C/Si	1.469(1)	1.767(3)

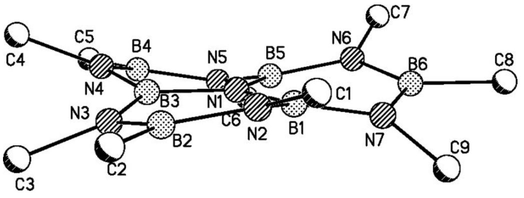


Figure 2. Side view on molecule **2** with H atoms omitted for clarity.

The average B–N bond length in **2** is 1.437 Å. This matches with 1.433 Å for $(HB{=}NH)_3$[13] and 1.433 Å for $(Me_2NB{=}NH)_3$.[14] The packing of molecules **2** in the unit cell is shown in Figure 3. There are stacks of molecules packed above one another, but the packing is by far not as close as that in hexagonal boron nitride. This is shown for some of the shortest intermolecular distances: N1–C8 3.877 Å, B5–N7 4.621 Å, N2–B6 4.533 Å, N2–C8 3.792 Å, N4–B4 4.060 Å and B4–B4 4.235 Å.

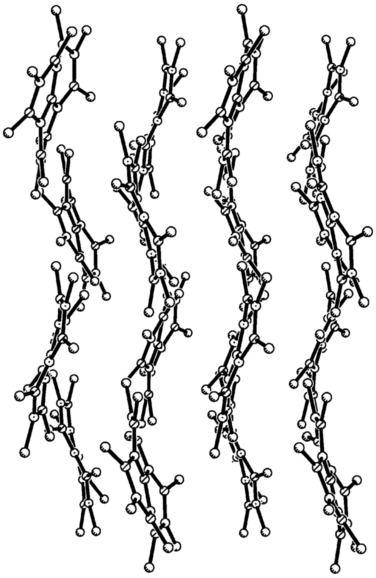
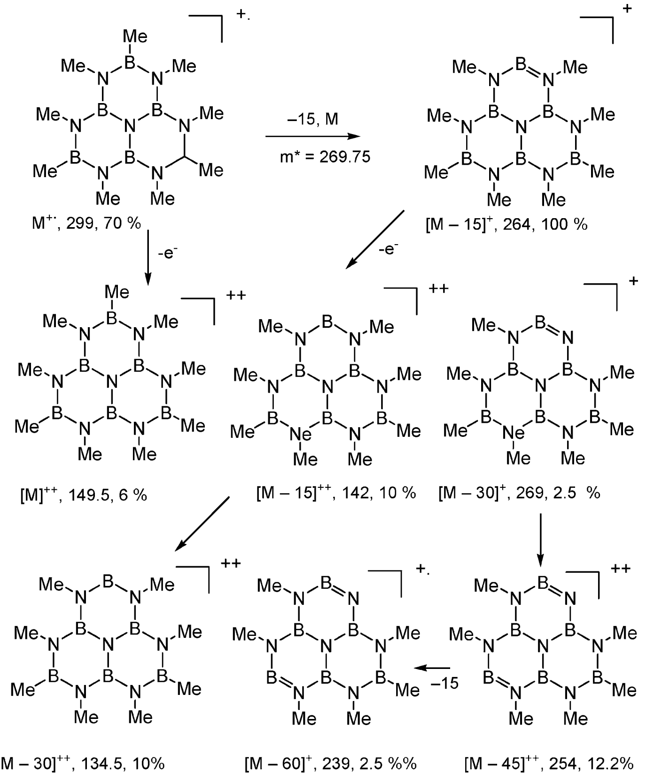


Figure 3. Packing of molecules **2** in the unit cell. View down the *b* axis.

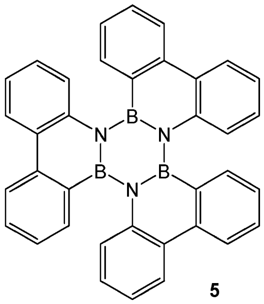
Mass Spectrum

The parent ion of compound **2** in the FAB mass spectrum (70 eV) is observed with a relative intensity of 70%, which shows that the molecule is quite stable (see Scheme 1). The fragmentation pattern is characterized by the loss of methyl groups, which most likely occurs by breaking the B–C bond, which is weaker than the N–C bond. Moreover, one can also observe the formation of



Scheme 1. Typical fragments in the mass spectrum of **1**.

doubly charged fragments. This latter fragmentation does not occur very often with borazines, particularly not with simple $(XB{=}NR)_3$ molecules. However doubly charged fragments were observed for borazines carrying condensed benzene rings or other heterocycles, as shown for **5** and **6**.[15] The formation of doubly charged fragments of **2** gives good evidence for a significant delocalisation of electrons in this ring system.



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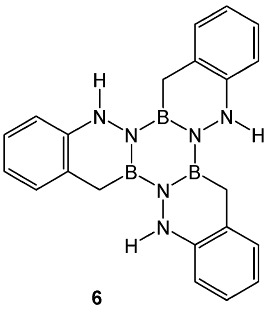

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Discussion and Conclusion

This study has shown that the $N(BCl_2)_3$ molecule provides access to permethylated borazaphenalene **2**, and there is no doubt that other derivatives can be prepared in the same manner. The ring system of this compound is isoelectronic with the phenalene anion. Although the reactions with $PhB(OH)_2$, $Me_2Si(NHMe)_2$ and $Me_3SiN{=}P{-}N(SiMe_3)_2$, which were not studied in detail, were unsuccessful as far as the formation of pure condensed heterocycles are concerned, a more detailed study may eventually lead to the expected reaction products. Both the X-ray structure as well as the mass spectrum indicates the high thermal stability of **2**. Moreover, compounds of type $B(NHR)_3$, $B(NRSiMe_3)_3$or $B[N(SiMe_3)_2]_3$ may also act as precursors for the formation of new types of condensed BN heterocycles, for example, by reactions with B-halogenated diborylamines and similar species. Moreover, compounds like **1** may eliminate Me_3SiSMe and generate even higher condensed species.

Experimental Section

General: All experiments were conducted under anhydrous conditions under an atmosphere of dry nitrogen gas by using Schlenk techniques. Solvents were used in an anhydrous state. $N(BCl_2)_3$ was prepared from BCl_3 and $N(SnMe_3)_3$.[7]

1,2,3,4,5,6,7,8,9-Nonamethyl-hexahydro-1*H*,4*H*,7*H*-1,3,4,6,7,9,9b-heptaaza-2,3a,5,6a,8,9a-hexaboraphenalene (2): To a stirred solution of $MeB(NHMe)_2$ (860 mg, 10 mmol) and Et_3N (2.1 g, 20.7 mmol) in hexane (20 mL) was added at –78 °C a solution of $N(BCl_2)_3$ (850 mg, 3.3 mmol) in hexane (10 mL). A solid $[(Et_3NH)Cl]$ formed rapidly. After allowing the suspension to attain ambient temperature stirring was continued for 3 h. The supernatant solution showed two signals in the ^{11}B NMR spectrum at δ = 38 and 28 ppm. The insoluble material was separated by centrifugation. The solution was then cooled to –78 °C. Colourless crystals separated within a few days. These were recrystallized from pentane at –10 °C. Yield: 0.79 g, 80%. M.p. 179–181 °C. $C_9H_{27}N_7B_6$ (298.08): calcd. C 36.23, H 9.13, N 32.88; found C 35.04, H 9.21, N 32.03.

Structure Determination: Crystals of **2** were grown from pentane at –10 °C. The selected crystal was fixed on a glass fibre with perfluoroether oil and transferred to the goniometer head, which was cooled to –60 °C by a stream of nitrogen gas. The unit cell was determined from the reflections on three sets of 15 exposures each taken at different angles. Data collection was performed in the hemisphere mode as implemented in the program SMART The program SAINT was used for data reduction, and the program SHELX94 for structure solution and refinement. Table 4 contains relevant data. CCDC-718394 contains 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.

Table 4. Crystallographic data and data related to structure solution and refinement of compound **2**.

	2
Formula	$C_9H_{27}B_6N_7$
Mol. mass [g/mol]	425.0
Crystal system	orthorhombic
a [Å]	19.860(6)
b [Å]	22.001(7)
c [Å]	8.017(3)
α [°]	90
β [°]	90
γ [°]	90
V [Å^3]	3503(2)
Space group	*Iba*2
ρ [g/cm^3]	1.131
μ [1/cm]	0.064
F(000)	1280
Crystal size [mm]	0.25 × 0.23 × 0.2
Temperature [K]	273
Scan width/background [°]	1/0.9
Scan speed [°/min]	1.8–29.3
Scan range 2θ [°]	2.0–45.0
Rezip. grid	*h*, *k*, *+/–l*
Reflect. measured	2460
Reflect. independ.	2310
Reflect. observ., 2σ	1830
R (obs. refl.)	0.00726
R_w	0.00593
R (all data)	0.00910
R_w	0.00602
GOOF	3.12
Param. refined	198
Larg. residue [e/Å^3]	0.34

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