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# Synthesis and characterization of new azido(*o*-phenylenedioxy)-boranes and azidobicyclononylboranes†

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The boron azides azido(*o*-phenylenedioxy)borane, (1,2-$C_6H_4O_2$)B($N_3$) **1**, and azidobicyclononylborane, $C_{16}H_{28}NB_2(N_3)$ **3**, have been prepared by the reaction of the corresponding chloroborane with trimethylsilyl azide. Both reactions were also carried out in the presence of pyridine. The resulting donor–acceptor complexes **1**·$C_5H_5N$ **2** and **3**·$C_5H_5N$ **5** and the boron azides (**1**, **3**) have been characterized by analytical and spectroscopic methods. The molecular structures of **1**, **3** and **5** have been confirmed by a single crystal X-ray diffraction study. The formation of **3** has been observed by a low temperature $^{11}$B NMR study and a probable mechanism is discussed.

## Introduction

In 1954 Wiberg and Michaud[1] reported the synthesis of the first azide of the element boron. They obtained the highly explosive boron triazide by the reaction of diborane with $HN_3$ in an ether solution at low temperature. Since the preparation of boron triazide the chemistry of boron azides has developed slowly. In 1963 Paetzold[2] reported the synthesis of trimeric $(BCl_2N_3)_3$ from the reaction of $LiN_3$ with $BCl_3$ in $CH_2Cl_2$ solution. Boron dihalide azides were also prepared by Wiberg *et al.*[3] in 1972. They generated $(BX_2N_3)_3$ (X = F, Cl or Br) by the reaction of $BX_3$ with trimethylsilyl azide in $CH_2Cl_2$. Several alkyl- and aryl-boron azides have also been prepared using similar methods.[4–6]

Although boron azides have now been known for more than 40 years their characterization by common spectroscopic methods is rather limited. To our knowledge, only the structures of trimeric boron dichloride azide, *arachno*-$B_{10}H_{12}(N_3)$-$NH_2$ and $H_3N_3B_3(N_3)_3$ have explicitly been determined by single crystal structure analysis.[7–9] The structures of boron triazide and $BCl_2N_3$, which was isolated in a low temperature argon matrix, have been studied using infrared spectroscopy and *ab initio* calculations.[10,11] The gas-phase structure of dimethylboron azide has also been determined by electron diffraction.[12]

In this paper we report the reaction of chloro(*o*-phenylenedioxy)borane and 9-borabicyclononyl chloride (9-BBN-Cl) with trimethylsilyl azide. Both reaction products have been characterized by IR, Raman and multinuclear NMR spectroscopy and their molecular structures confirmed by single crystal X-ray diffraction study. The reaction of 9-BBN-Cl with trimethylsilyl azide has been observed by a low temperature $^{11}$B NMR study and a probable mechanism is given. Both reactions were also carried out in the presence of pyridine and the spectroscopic characterization of the obtained adducts is reported. The molecular structure of one of these has been determined by a single crystal X-ray diffraction analysis.

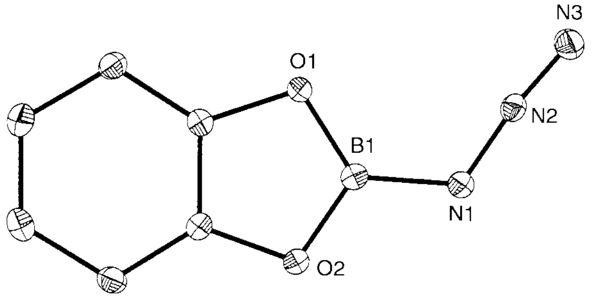
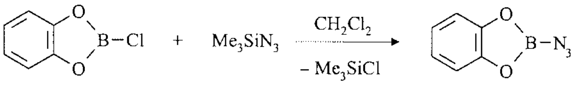


**Fig. 1** An ORTEP[16] plot of the molecular structure of compound **1** with thermal ellipsoids at 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): N(1)–B(1) 1.433(3), N(1)–N(2) 1.243(2), N(2)–N(3) 1.120(2), O(1)–B(1) 1.380(3) and O(2)–B(1) 1.379(2); N(3)–N(2)–N(1) 173.1(2).

## Results and discussion

### 1 Reaction of chloro(*o*-phenylenedioxy)borane with trimethylsilyl azide

Azido(*o*-phenylenedioxy)borane **1** is obtained in high yields as a colorless solid from the reaction of chloro(*o*-phenylenedioxy)borane with trimethylsilyl azide in $CH_2Cl_2$ solution, eqn. (1). The IR spectrum of **1** shows the characteristic absorption band caused by the asymmetric stretching vibration of the azide group at 2169 cm$^{-1}$, in the Raman spectrum at 2165 cm$^{-1}$. The resonance in the $^{11}$B NMR spectrum was found at $\delta$ 26.1, a typical region for pseudohalogen substituted phenylenedioxyboranes.[13] The $^{14}$N NMR spectrum shows three resonances at $\delta$ −317 (Nα), −181 (Nγ) and −148 (Nβ) due to the covalently bonded azide group (connectivity B–Nα–Nβ–Nγ). The assignment was made on the arguments given by Witanowski *et al.*[14] and other reported chemical shifts of boron azides.[15] Azido(*o*-phenylenedioxy)borane **1** has also been characterized by a single crystal X-ray diffraction study. Suitable single crystals were grown by recrystallization from toluene. A view of the molecular structure of **1** is shown in Fig. 1.



(1)

1

Azido(*o*-phenylenedioxy)borane **1** crystallizes in the space group *Pbca* with eight formula units in the unit cell. The B(1)–N(1) distance of 1.433(3) Å is between the length of a B–N single [1.54 Å] and double bond [1.37 Å] and the found B–O distance of 1.38 Å is shorter than a typical B–O single bond.

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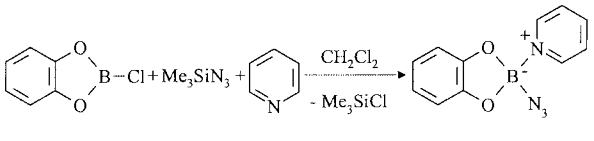
† *Supplementary data available*: rotatable 3-D crystal structure dagram in CHIME format. See http://www.rsc.org/suppdata/dt/1999/4283/

The B–O distances compare well with those of other phenylenedioxyboranes.[17,18] The relatively short bond distances display the interaction of the lone pairs of the α-nitrogen atom of the azide group and the oxygen atoms with the empty $p_z$ orbital of the electron deficient boron atom.

Chloro(*o*-phenylenedioxy)borane was also treated with trimethylsilyl azide in the presence of the Lewis base pyridine, eqn. (2). The donor–acceptor complex was obtained as a colorless oil. It is soluble in chloroform, methylene chloride, benzene and toluene but insoluble in hexane. The IR spectrum is dominated by a very strong absorption band at 2132 cm$^{-1}$ caused by the asymmetric stretching mode of the azide group. The Raman spectrum of **2** shows the asymmetric stretching mode of the azide group at 2131 cm$^{-1}$ as a weak absorption. The $^{11}$B NMR resonance was found at δ 9.9 which is the typical area of a four-co-ordinated boron. The $^{14}$N NMR spectrum displays three resonances for the azide group, at δ −315 (Nα), −202 (Nγ) and −141 (Nβ), and one broad resonance for the pyridine nitrogen atom at δ −110.

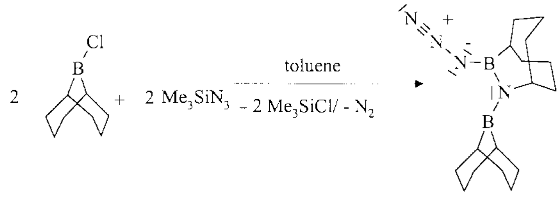


(2)

2

## 2 Reaction of 9-borabicyclononyl chloride (9-BBN-Cl) with trimethylsilyl azide

A suspension of 9-BBN-Cl in toluene was treated at −78 °C with trimethylsilyl azide. The analysis of the obtained product **3** showed that the expected 9-BBN-N$_3$ had not been formed. The actually observed reaction is given in eqn. (3). A mechanism for the formation of **3** is discussed later in this article. Compound **3** could be isolated as a colorless, air sensitive, solid in high yields (80%). It is highly soluble in toluene, benzene, methylene chloride, chloroform and diethyl ether, insoluble in pentane. The IR and Raman spectra show beside many other bands the characteristic absorption at 2132 (IR) or 2137 (Raman) cm$^{-1}$ caused by the asymmetric stretching vibration of the azide group. The $^{11}$B NMR signals were found at δ 62.5 (B2) and 43.0 (B1). Compound **3** was also characterized by $^{14}$N NMR spectroscopy. For the covalently bonded azide group three resonances have been observed at δ −142 (Nβ), −179 (Nγ) and −287 (Nα) (connectivity B–Nα–Nβ–Nγ). The resonance for the nitrogen atom bound to both boron atoms was found at δ −237. Recrystallization of **3** from toluene afforded crystals which were suitable for a single-crystal X-ray diffraction study. A view of the molecular structure of **3** is shown in Fig. 2.



(3)

3

Compound **3** crystallizes in the monoclinic space group *C*2/*c* with eight formula units in the unit cell. The angle at the boron-bonded nitrogen atom of the azide group [N(3)–N(2)–B(1)] is 123.3(2)°, the B(1)–N(1)–B(2) angle is 124.1(2)°. The N(2)–N(3)–N(4) angle of 172.4(3)° is less than 180° as expected for a covalent bonded azide. The N(3)–N(4) [1.123(3) Å] and the N(3)–N(2) [1.222(3) Å] bond lengths are comparable with those found in **1**. These bond distances have lengths between those of a N–N double [1.24 Å] and a triple bond [1.10 Å].[19] The B(1)–N(2) [1.457(3) Å], B(1)–N(1) [1.420(3) Å] and B(2)–N(1) [1.440(3) Å] bond lengths are all between that of a B–N single [1.58 Å] and double bond [1.37 Å].

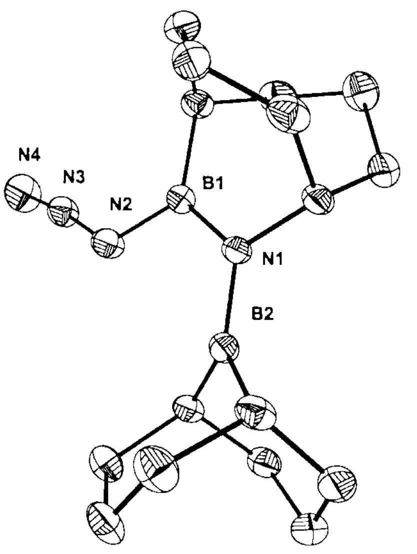


**Fig. 2** An ORTEP plot of the molecular structure of **3** with thermal ellipsoids at 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å): N(1)–B(1) 1.420(3), N(2)–B(1) 1.457(3), N(1)–B(2) 1.440(3), N(2)–N(3) 1.222(3) and N(3)–N(4) 1.123(3).

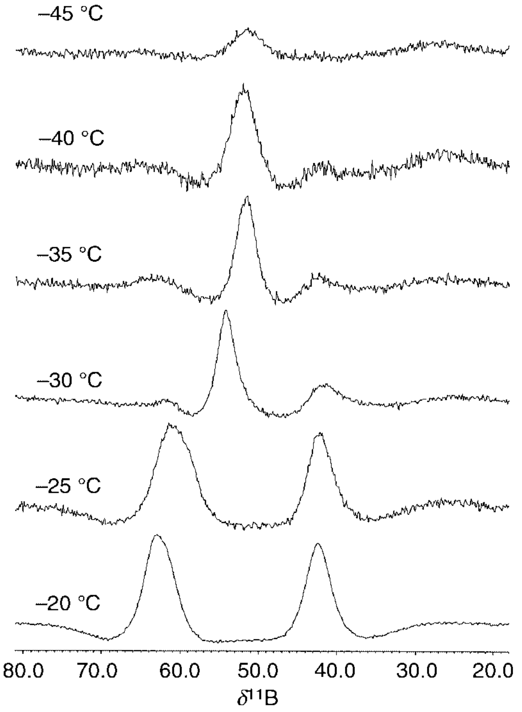


**Fig. 3** Low temperature $^{11}$B NMR spectra of the reaction of 9-BBN-Cl with trimethylsilyl azide in toluene solution.

The isolation of the unexpected product **3** prompted us to observe the reaction of 9-BBN-Cl with trimethylsilyl azide in toluene by a low temperature $^{11}$B NMR study (Fig. 3). The recorded $^{11}$B NMR spectra show the formation of an intermediate compound below −25 °C. The observed resonance at δ 54 is tentatively assigned to the formation of 9-BBN-N$_3$ **4**. It should be noticed that 9-BBN-Cl is insoluble in toluene at low temperatures and therefore no resonance of the starting material (δ 80) can be observed. At −25 °C two resonances corresponding to product **3** at δ 63 and 43 are visible and the resonance at δ 54 disappeared.

The reaction of 9-BBN-Cl with trimethylsilyl azide was also carried out in the presence of pyridine, eqn. (4). The reaction

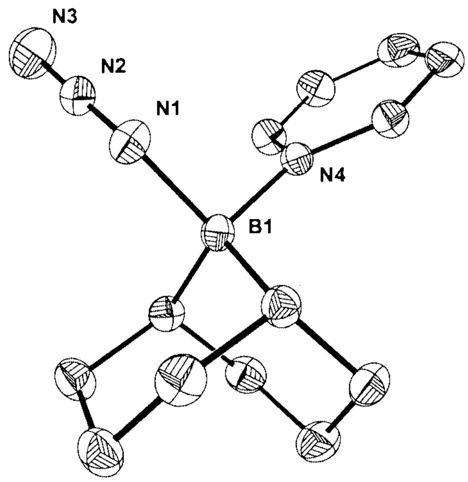
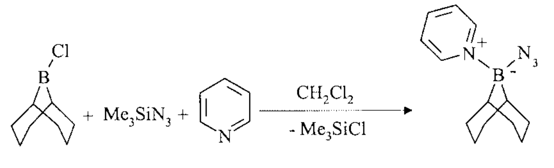


**Fig. 4** An ORTEP plot of the molecular structure of compound **5** with thermal ellipsoids at 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): N(1)–B(1) 1.588(3), B(1)–N(4) 1.637(3), N(1)–N(2) 1.196(3) and N(2)–N(3) 1.140(3); N(1)–N(2)–N(3) 176.3°(3).



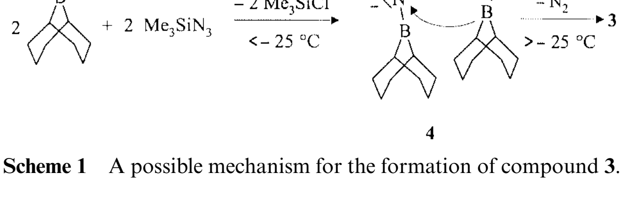
(4)

**5**

product **5** was isolated in high yields (85%) as a colorless solid, which is nicely soluble in chloroform and methylene chloride but insoluble in toluene and pentane. The IR spectrum contains a strong band at 2093 cm$^{-1}$, the Raman spectrum a weak band at 2089 cm$^{-1}$, which is assigned to the asymmetric stretching vibration of the azide group. The $^{11}$B NMR shows one resonance at $\delta$ 6.0, a typical region for four-co-ordinated boron atoms. The $^{14}$N NMR spectrum displays four resonances at $\delta$ −136 (N of pyridine), −138 (Nβ), −211 (Nγ) and −303 (Nα) which are comparable with those found for **2**. The molecular structure of **5** has also been confirmed by a single X-ray diffraction study (Fig. 4).

Compound **5** crystallizes in the space group $P2_1/c$ with four formula units in the unit cell. It shows a tetrahedral co-ordination geometry around the boron atom. The nearly linear azide group [N(1)–N(2)–N(3) 176°] is bonded to the boron atom by a typical B–N single bond (1.58 Å). The B(1)–N(1) (1.59 Å) and B(1)–N(4) (1.64 Å) distances are considerably longer than those found in **1** and **3**. This increase can be explained by the fact that the boron atom of **5** is in contrast to those in **1** and **3** four-co-ordinated and therefore the lone pairs of the nitrogen atoms cannot interact with the boron atom. The N(2)–N(3) bond is, at 1.140(3) Å, shorter than the N(1)–N(2) bond [1.196(3) Å] and these bond distances have lengths between those of a N–N double [1.24 Å] and a triple bond [1.10 Å].

On the basis of the results of the low temperature $^{11}$B NMR study and the isolation of the adduct **5** we propose a "synchronous" mechanism for the formation of **3**, as shown in Scheme 1.



**4**

**Scheme 1** A possible mechanism for the formation of compound **3**.

The first step of the reaction is the formation of the 9-BBN-N$_3$ **4** from 9-BBN-Cl with trimethylsilyl azide at a temperature below −30 °C. The corresponding resonance for **4** can be observed at $\delta$ 54 in the $^{11}$B NMR spectrum. The next proposed step is the reaction of two molecules of **4** with elimination of dinitrogen as shown in Scheme 1. The α-nitrogen atom of the azide group attacks the electron deficient boron atom of another molecule, the B–C bond breaks, the carbon atom migrates to the α-nitrogen atom of the azide group leading to the elimination of dinitrogen. We believe these steps are synchronous and very fast and therefore no resonance of a four-co-ordinated boron atom was observed in the $^{11}$B NMR spectrum. In the presence of pyridine, which is a stronger Lewis base than the α-nitrogen atom of the azide group, **4** forms a pyridine adduct **5** and a rearrangement is no longer possible.

## Experimental

### General

All manipulations of air and moisture sensitive materials were carried out under dinitrogen using standard Schlenk techniques, or in an inert gas dry-box containing dinitrogen. Solvents were dried and degassed by standard methods. Trimethylsilyl azide and chloro(*o*-phenylenedioxy)borane were purchased (Aldrich) and used as received. The 9-BBN-Cl was prepared as described.[20] Raman spectra were recorded on a Perkin-Elmer 2000 NIR FT-Raman spectrometer, IR spectra as neat solids between CsI plates on a Nicolet 520 FT-IR spectrometer. The elemental analyses were performed with a C, H, N-Analysator Elementar Vario EL. The NMR spectra were recorded as $C_6D_6$ solutions on JEOL GSX 270 and EX 400 instruments. Chemical shifts are with respect to $(CH_3)_4Si$ ($^1$H, $^{13}$C), $BF_3{\cdot}OEt_2$ ($^{11}$B), and $CH_3NO_2$ ($^{14}$N). For the determination of the melting points, samples were heated in sealed capillaries in a Büchi B540 instrument.

**CAUTION:** although all the discussed compounds were obtained as non-explosive materials, experiments with azides should be handled with care.

### Preparations

**$C_6H_4O_2BN_3$ 1.** A colorless solution of $C_6H_4O_2BCl$ (0.31 g, 2 mmol) in $CH_2Cl_2$ (10 cm$^3$) was treated with 0.4 mL (3 mmol) trimethylsilyl azide at −78 °C. The solution was allowed to warm slowly and stirred for 12 h at room temperature. The solvent and all volatile products were removed by vacuum evaporation leaving a white solid. The solid was purified by recrystallization from toluene. Yield 0.26 g (80%), mp 62–64 °C. IR (powder between CsI plates): 3075w, 2169s ($\nu_{asym}$-N$_3$), 1600w, 1625w, 1465vs, 1421vs, 1336s, 1286m, 1235vs, 1136s, 1006m, 917m, 869m, 849m, 807m, 743vs, 580w and 428m. Raman (100 mW): 3070 (6), 3035 (2), 2165 (3, $\nu_{asym}$-N$_3$), 1625 (4), 1613 (2), 1466 (3), 1428 (2), 1358 (4), 1342 (4), 1271 (1), 1256 (5), 1216 (3), 1147 (2), 1009 (7), 858 (1), 811 (10), 742 (1), 588 (2), 439 (7), 329 (2) and 283 (3). $^{11}$B NMR [$C_6D_6$]: $\delta$ 26.1 (s). $^{14}$N NMR [$C_6D_6$, $\Delta\nu_{1/2}$/Hz]: $\delta$ −148 (60, Nβ), −181 (170, Nγ) and −317 (635, Nα). $^1$H NMR ($C_6D_6$): $\delta$ 6.80 (m, 4 H). $^{13}$C NMR ($C_6D_6$): $\delta$ 112.3, 122.9 and 148.0; Calc. for $C_6H_4BN_3O_2$: C, 44.78; H, 2.51; N, 26.11. Found: C, 44.15; H, 2.81; N, 25.17%.

**$C_{11}H_9O_2BN_4$ 2.** A colorless solution of $C_6H_4O_2BCl$ (0.31 g, 2 mmol) in $CH_2Cl_2$ (10 cm$^3$) was treated with 0.4 mL (3 mmol) trimethylsilyl azide and 0.16 mL pyridine (2 mmol) at −78 °C. The solution was allowed to warm slowly and stirred for 12 h at room temperature. All volatile residues were removed by vacuum evaporation leaving a yellow oil. The oil was vacuum distilled (65–67 °C, 0.01 Torr) and a colorless oil collected. Yield 0.35 g (70%), mp 85–87 °C. IR (oil between CsI plates): 3100w, 3065w, 2132vs ($\nu_{asym}$-N$_3$), 1863s, 1734m, 1578w, 1482vs, 1458s, 1386m, 1332m, 1235s, 1057vs, 914s, 866m, 749s, 700s,

**Table 1** Crystal data and structure refinements for compounds **1**, **3** and **5**

| | **1** | **3** | **5** |
|---|---|---|---|
| Empirical formula | $C_6H_4BN_3O_2$ | $C_{16}H_{28}B_2N_4$ | $C_{13}H_{19}BN_4$ |
| Formula weight | 160.93 | 298.04 | 242.13 |
| $T$/K | 193 | 293(2) | 293(2) |
| Crystal system | Orthorhombic | Monoclinic | Monoclinic |
| Space group | *Pbca* | *C*2/*c* | *P*2$_1$/*c* |
| $a$/Å | 7.6720(2) | 24.819(6) | 7.793(2) |
| $b$/Å | 6.5437(2) | 7.422(1) | 11.786(4) |
| $c$/Å | 28.2086(9) | 19.099(3) | 14.763(6) |
| $\beta$/° | | 106.29(2) | 103.65(3) |
| $V$/Å$^3$ | 1416.16(7) | 3377(1) | 1317.7(8) |
| $Z$ | 8 | 8 | 4 |
| $\mu$/mm$^{-1}$ | 0.144 | 0.069 | 0.075 |
| Reflections collected | 7184 | 4088 | 2359 |
| Independent reflections | 1429<br>($R_{\text{int}} = 0.0348$) | 2648<br>($R_{\text{int}} = 0.0201$) | 2058<br>($R_{\text{int}} = 0.0391$) |
| Observed reflections | 1159 | 1967 | 1316 |
| $R1$, $wR2$ | 0.0486, 0.0991<br>[$I > 4\sigma(I)$] | 0.0559, 0.1319<br>[$I > 2\sigma(I)$] | 0.0512, 0.1006<br>[$I > 2\sigma(I)$] |
| (all data) | 0.0645, 0.1061 | 0.0776, 0.1493 | 0.0909, 0.1205 |

647m, 604w and 429m. Raman (100 mW): 3084 (6), 3070 (5), 2131 (1, $\nu_{\text{asym}}$-N$_3$), 1626 (3), 162 (1), 1487 (1), 1460 (2), 1367 (3), 1238 (1), 1152 (2), 1097 (2), 1026 (10), 1008 (7), 799 (42), 649 (37), 567 (1), 367 (1) and 261 (3). $^{11}$B NMR [C$_6$D$_6$]: $\delta$ 9.9 (s). $^{14}$N NMR [C$_6$D$_6$, $\Delta\nu_{1/2}$/Hz]: $\delta$ −110 (850, N of pyridine), −141 (145, Nβ), −202 (290, Nγ) and −315 (850, Nα). $^1$H NMR (C$_6$D$_6$): $\delta$ 8.55 (m, 2 H), 7.09 (m, 1 H), 6.85 (m, 4 H) and 6.58 (m, 2 H). $^{13}$C NMR (C$_6$D$_6$): $\delta$ 152.2, 144.5, 128.2, 125.3, 120.3 and 109.8. Calc. for $C_{11}H_9BN_4O_2$: C, 55.04; H, 3.78; N, 23.34. Found: C, 55.50; H, 4.08; N, 22.17%.

**$C_{16}H_{28}B_2N_4$ 3.** Compound **3** was prepared from 9-BBN-Cl (0.31 g, 2 mmol) with 0.4 mL (3 mmol) trimethylsilyl azide in toluene (10 cm$^3$) following the method described for **1**. The product was purified by recrystallization from toluene. Yield 0.24 g (80%), mp 71–73 °C (decomp.). IR (powder between CsI plates): 2985w, 2922vs, 2840s, 2132vs ($\nu_{\text{asym}}$-N$_3$), 1468vs, 1447vs, 1416vs, 1380vs, 1359vs, 1325vs, 1304vs, 1283vs, 1259vs, 1167s, 1105m, 1009m, 937w, 784w, 689w, 620w, 584w and 452w. Raman (100 mW): 2951 (5), 2914 (10), 2137 (3, $\nu_{\text{asym}}$-N$_3$), 1451 (4), 1436 (5), 1344 (3), 1300 (2), 1287 (3), 1190 (2), 1013 (2), 980 (2), 777 (4) and 550 (2). $^{11}$B NMR [C$_6$D$_6$]: $\delta$ 62.5 (s, B2) and 43.0 (s, B1). $^{14}$N NMR [C$_6$D$_6$, $\Delta\nu_{1/2}$/Hz]: $\delta$ −142 (190, Nβ), −179 (280, Nγ), −237 (520, N1) and −287 (635, Nα). $^1$H NMR (C$_6$D$_6$): $\delta$ 3.96 (m, 1 H) and 1.51– 2.50 (m, 27 H). $^{13}$C NMR (C$_6$D$_6$): $\delta$ 52.4, 33.9, 32.5, 27.2, 26.9, 23.5 and 22.2. Calc. for $C_8H_{14}BN_2$: 64.48; H, 9.47; N, 18.79. Found: C, 63.99; H, 9.95; N, 18.07%.

**$C_{13}H_{19}BN_4$ 5.** Compound **5** was prepared from 9-BBN-Cl (0.31 g, 2 mmol) with 0.4 mL (3 mmol) trimethylsilyl azide and 0.16 mL pyridine (2 mmol) in CH$_2$Cl$_2$ (10 cm$^3$) following the method described for **1**. The product was purified by recrystallization from chloroform. Yield 0.41 g (85%), mp 115–117 °C (decomp.). IR (powder between CsI plates): 2987vs, 2960vs, 2830vs, 2093s ($\nu_{\text{asym}}$-N$_3$), 1620s, 1460s, 1411m, 1316s, 1297s, 1259s, 1206s, 1083vs, 1046s, 933m, 849w, 771s, 700vs, 632s, 632s, 530w and 294m. Raman (100 mW): 3098 (3), 3075 (3), 2914 (6), 2891 (6), 2852 (4), 2089 (1, $\nu_{\text{asym}}$-N$_3$), 1620 (4), 1578 (1), 1451 (3), 1434 (2), 1316 (1), 1293 (3), 1226 (4), 1081 (2), 1027 (10), 932 (1), 755 (2), 650 (2), 634 (1), 541 (2), 384 (1) and 271 (3). $^{11}$B NMR [CDCl$_3$]: $\delta$ 6.0 (s). $^{14}$N NMR [CDCl$_3$, $\Delta\nu_{1/2}$/Hz]: $\delta$ −136 (250, N4), −138 (200, Nβ), −211 (220, Nγ) and −303 (520, Nα). $^1$H NMR (CDCl$_3$): $\delta$ 9.19–7.72 (m, 5 H) and 1.18– 2.10 (m, 14 H). $^{13}$C NMR (CDCl$_3$): $\delta$ 144.2, 141.4, 126.2, 31.5, 30.1, 23.8 and 21.7. Calc. for $C_{13}H_{19}BN_4$: C, 64.49; H, 7.91; N, 23.14. Found: C, 64.49; H, 7.91, N, 22.33%.

### X-Ray crystallography

Data for compound **1** were collected on a Siemens SMART Area detector using Mo-Kα radiation. The structure was solved by direct methods (SHELXS)[21] and refined by means of full-matrix least square procedures using SHELXL 93[22] (Table 1). Data for **3** and **5** were collected on a Nonius CAD 4 diffractometer using Mo-Kα radiation. The structures were solved by direct methods (SHELXS 86) and refined by means of full-matrix least square procedures using SHELXL 93 (Table 1). Compound **3** has disordered CH$_2$ groups (C3–C3a/C7–C7a/C15–C15a) and was therefore split and refined with distance restraints.

CCDC reference number 186/1691.

See http://www.rsc.org/suppdata/dt/1999/4283/ for crystallographic files in .cif format.

## Acknowledgements

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