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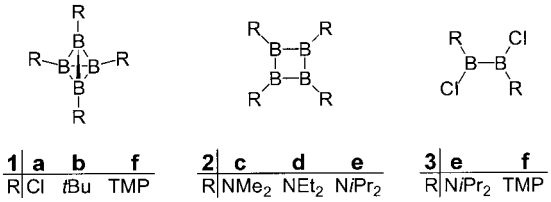
Blue Tetrakis(diisopropylamino)-*cyclo*-tetraborane and Yellow Tetrakis(tetramethylpiperidino)tetrabora-tetrahedrane**

Claus-Jürgen Maier, Hans Pritzkow, and Walter Siebert*

Dedicated to Professor Otto J. Scherer on the occasion of his 65th birthday

The chloro[1] and *tert*-butyl derivatives[2, 3] of tetraborane(4) (**1**) have a tetrahedral structure (B–B bond lengths in **1b**:[3] 1.699(6) – 1.714(4) Å), whereas an opening of the tetrahedron to a four-membered ring (**2**) is discussed for B_4Cl_4 (**1a**)[4, 5] and B_4Br_4[6] in solution. The reaction mixture obtained from di-*tert*-butyldichlorodiborane(4) and Na/K alloy was shown by



Klusik and Berndt to contain **1b** ($\delta(^{11}B) = 135.7$) and the radical anion $[B_4tBu_4]^{\bullet-}$ (**2b**$^{\bullet-}$, observed by ESR spectroscopy), for which they postulated a bent ring structure.[7] Morrison[8] could not confirm the proposed planar structure

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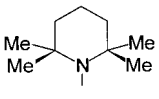
for $B_4(NMe_2)_4$ (**2c**);[9] Baudler et al. have mentioned $B_4(NEt_2)_4$ (**2d**).[10]

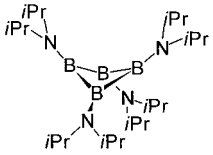
To synthesize stable tetraboranes B_4R_4, we have dehalogenated the sterically hindered diborane(4) derivatives **3e** and **3f**[11] instead of the RBX_2 compounds.[3, 10] Here we report the synthesis and structure of the bent ring **2e** and the tetrahedrane **1f**.



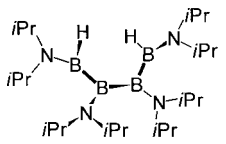
TMP

Replacement of two chloride substituents in B_2Cl_4 takes place upon reaction with diisopropylamine or lithium 2,2,6,6-tetramethylpiperidide to provide the colorless compounds **3e** and **3f**, whose constitution was established by spectroscopy and a crystal structure analysis of **3e**.[12] As is the case for other derivatives,[13] **3e** has a *gauche* conformation (the torsional angel between the two B(Cl)N*i*Pr$_2$ halves is 91°). The short B–N bond lengths of 1.380(4) Å indicate the existence of a π interaction between the boron atoms and the isopropylamino groups.

Treatment of **3e** with Na/K alloy in hexane (20 °C, 48 h) results in the formation of a gray-green reaction mixture,[11] from which blue **2e** (18 %), colorless **4** (2 %), and colorless **5e** (3 %) were isolated. The mass spectra of **2e**, **4**, and **5e** each



2e



4

R–B=B–R

5	**e**	**f**
R	N*i*Pr$_2$	TMP

contain the molecular peak with the correct isotopic distribution. The ^{11}B NMR spectrum of **2e** provides a signal at $\delta = 65$ (identical to the value observed for *cyclo*-$B_6(NMe_2)_6$[4] and *cyclo*-$B_6(NEt_2)_6$[10]), and in the ^1H NMR spectrum a doublet and a septet indicate the presence of equivalent *i*Pr$_2$N groups in **2e**. For **2e**, which is not planar because of the amino substituents, blue crystals ($\lambda_{max} = 620$ nm, $\varepsilon = 40$) were isolated from the turquoise solution in hexane.

The crystal structure analysis shows that **2e** contains a bent B_4 ring (Figure 1, folding angle B1-B2-B2′/B2-B1′-B2′ 59.3(1)°) with nearly identical B–B bond lengths (B1–B2′ 1.710(3), B1–B2 1.711(3) Å). The exocyclic B–N bond lengths

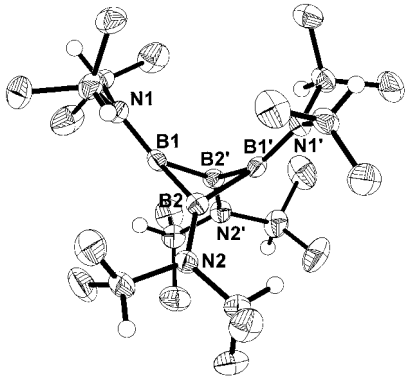


Figure 1. Structure of **2e** in the crystal. Selected bond lengths [Å] and angles [°]: B1–B2 1.711(3), B1–B2′ 1.710(3), B1–N1 1.397(2), B2–N2 1.396(2); B2-B1-B2′ 81.8(1), B1-B2-B1′ 82.1(1), B1-B2-N2 133.3(2), B1′-B2-N2 137.6(3), B2-B1-N1 138.3(2), B2′-B1-N1 133.0(2).

(av 1.396(3) Å) indicate a π interaction; the nitrogen atoms deviate significantly (0.45 Å) from the corresponding B_3 plane. Thus the atoms N1 and N1′ move towards each other, as do N2 and N2′. The inclination of N1 towards N1′ (that is, the angle between N1–B1 and B1-B2-B2′) and of N2 towards N2′ is on average 19.0°.

As the colorless products **4** and **5e** were obtained in only small amounts, they could not be characterized by NMR spectroscopy. However, a crystal structure analysis[12] confirmed the constitution of **4**, which is similar in structure to $B_4(NMe_2)_6$.[14] Diborene **5e** and other derivatives (**5**, R = *sec*-Bu_2N, 2,6-dimethylpiperidino) were first identified by Meller and Maringgele on the basis of mass spectrometry and ^{11}B NMR spectroscopy as well as trapping reactions.[15]

To investigate the steric influence of a rigid amino substituent on the formation of the product, we replaced the movable diisopropylamino groups in **3e** by the less flexible TMP ligands. As in the case of **3e**, dehalogenation of **3f** led to a gray-green reaction mixture, from which surprisingly yellow crystals were isolated. Mass spectrometry and ^{11}B NMR spectroscopy ($\delta = 67.5$) suggest the formation of a *cyclo*-tetraborane. However, the yellow color ($\lambda_{max} = 312$ nm, $\varepsilon = 15300$) indicates a tetrahedron, in analogy to **1a** and **1b**. The crystal structure analysis[12] confirmed the presence of tetrahedrane **1f** (Figure 2), in which two oppositely positioned

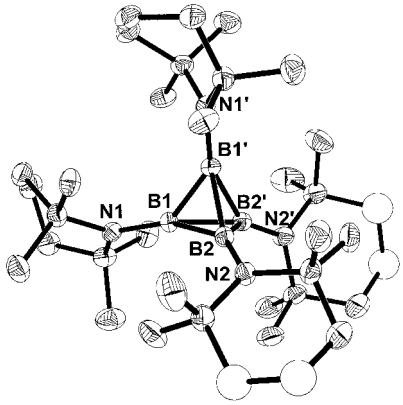


Figure 2. Structure of **1f** in the crystal. Selected bond lengths [Å] and angles [°]: B1–B1′ 1.695(6), B2–B2′ 1.701(7), B1–B2 1.765(5), B1–B2′ 1.752(5), B1–N1 1.446(4), B2–N2 1.444(4); B1′-B1-B2 60.8(2), B1′-B1-B2′ 61.6(2), B2-B1-B2′ 57.9(2), B2′-B2-B1 60.7(2), B2′-B2-B1′ 61.5(2), B1-B2-B1′ 57.6(2).

edges are short (B1–B1′ 1.695, B2–B2′ 1.701(7) Å) and the others are long (B1–B2′ 1.752, B1–B2 1.765(5) Å). The B–N bond lengths of 1.444 and 1.446(4) Å are longer than in **2e**, which indicates a weaker π interaction. We assume that, as is the case for C_4tBu_4, the "corset effect"[16] of the bulky TMP ligands causes the complete folding to the tetrabora-tetrahedrane. Theoretical investigations of $B_4(NH_2)_4$ show that the energy difference between the bent structure (D_{2d}) and the tetrahedrane structure (calculated B–B bond lengths: 1.672–1.733 Å) is very low.[17] For $B_4(NH_2)_4$ the calculations provide an energy difference of 10.8 eV between the HOMO and LUMO for the tetrahedron and 9.8 eV for the D_{2d} structure, which is in qualitative agreement with the observed colors of **1f** and **2e**.

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The isolation of **1f** proves for the first time that the TMP-substituted tetrabora-tetrahedrane is more stable than the bent *cyclo*-tetraborane isomer **2f**.

Experimental Section

3e: B_2Cl_4 (3.01 g, 18.4 mmol) and then diisopropylamine (7.45 g, 73.7 mmol) were condensed into pentane (35 mL) at $-105\,^{\circ}C$. After the mixture had warmed to room temperature, it was stirred for 15 h and then heated under reflux for 8 h. The ammonium salt (5.1 g) that had formed was removed by filtration, and the filtrate was dried under vacuum to provide colorless **3e** (5.34 g, 99%; m.p. 82 °C). ^1H NMR (200 MHz, C_6D_6, 298 K): $\delta = 1.00$, 1.06 ($2\times$ d, $^3J(H,H) = 6.7$ Hz, 12H; $CHCH_3$), 1.31, 1.33 ($2\times$ d, $^3J(H,H) = 6.7$ Hz, 12H; $CHCH_3$), 3.2–3.4 (m, 2H; $NCHCH_3$), 3.66 (sept, $^3J(H,H) = 6.7$ Hz, 2H; $NCHCH_3$); ^1H NMR (200 MHz, [D$_8$]toluene, 345 K): $\delta = 1.28$ (d, $^3J(H,H) = 6.7$ Hz, 12H; $CHCH_3$), 1.52 (d, $^3J(H,H) = 6.9$ Hz, 12H; $CHCH_3$), 3.60 (sept, $^3J(H,H) = 6.9$ Hz, 2H; $NCHCH_3$), 3.86 (sept, $^3J(H,H) = 6.7$ Hz, 2H; $NCHCH_3$). Owing to hindered rotation about the B–N and B–B bonds, four doublets, one septet, and one multiplet are observed in the ^1H NMR spectrum measured at 298 K. At 345 K the restriction to rotation is removed, and two doublets and two sharp septets appear. ^{11}B NMR (64 MHz, C_6D_6): $\delta = 38.1$; ^{13}C NMR (50 MHz, C_6D_6): $\delta = 22.1$ ($CHCH_3$), 22.3 ($CHCH_3$), 23.3 ($CHCH_3$), 46.5 ($NCHCH_3$), 54.4 (br, $NCHCH_3$); high-resolution EI-MS: *m*/*z* calcd for $^{12}C_{12}{}^1H_{28}{}^{11}B_2{}^{35}Cl_2{}^{14}N_2$: 292.1816, found: 292.1843, $\Delta m = 2.7$ mmu; elemental analyses calcd for $C_{12}H_{28}B_2Cl_2N_2$: C 49.21, H 9.63, N 9.56; found: C 48.73, H 9.41, N 9.29.

3f: B_2Cl_4 (2.20 g, 13.5 mmol) was condensed into a suspension of Li(TMP) (25.0 mmol) in hexane (50 mL) at $-100\,^{\circ}C$. The mixture was warmed to room temperature within 3 h and then stirred for 15 h. Lithium chloride was removed by filtration and washed with hexane, and the combined filtrate was concentrated to a volume of 10 mL. At $-20\,^{\circ}C$ pale yellow **3f** crystallized (1.27 g, 25%). ^1H NMR (200 MHz, C_6D_6): $\delta = 1.41$ (s, 12H; $C(CH_3)_2$), 1.49 (s, 12H; $C(CH_3)_2$), 1.68 (d, 12H; CH_2); ^{11}B NMR (64 MHz, C_6D_6): $\delta = 38.8$; ^{13}C NMR (50 MHz, C_6D_6): $\delta = 15.7$ (*p*-CH_2), 30.1, 32.3, 38.0, 39.6 (CCH_3), 33.6, 33.7 (*m*-CH_2), 57.5, 57.6 (NCC); high-resolution EI-MS: *m*/*z* calcd for $^{12}C_{18}{}^1H_{36}{}^{11}B_2{}^{35}Cl_2{}^{14}N_2$: 372.2442, found: 372.2444, $\Delta m = 0.2$ mmu.

2e: To Na/K alloy (1:2.8, ≈1 g) in hexane (20 mL) was added dropwise **3e** (350 mg, 1.13 mmol) in hexane (10 mL). After 48 h of stirring the gray-green reaction mixture was filtered, and the residue was washed with hexane (20 mL). The solvent of the green filtrate was evaporated, and the residue was dissolved in a small amount of pentane and kept at $-40\,^{\circ}C$. Blue crystals of **2e** (45 mg, 18%; m.p. 107–108 °C) and colorless crystals of **4** (≈5 mg, 2%) formed. Recondensation of the mother liquor at $20\,^{\circ}C/3\times10^{-3}$ Torr provided a colorless liquid (≈8 mg, 3%), which according to EI-MS contained **5e** (*m*/*z* 222) and silicon grease. **2e**: ^1H NMR (200 MHz, C_6D_6): $\delta = 1.24$ (d, $^3J(H,H) = 6.7$ Hz, 6H; $CHCH_3$), 3.70 (sept, $^3J(H,H) = 6.7$ Hz, 1H; $NCHCH_3$); ^{11}B NMR (64 MHz, C_6D_6): $\delta = 65$ (br); ^{13}C NMR (50 MHz, C_6D_6): $\delta = 24.7$ ($CHCH_3$), 52.7 ($NCHCH_3$); high-resolution EI-MS: *m*/*z* calcd for $^{12}C_{24}{}^1H_{56}{}^{11}B_4{}^{14}N_4$: 444.4877, found: 444.4876, $\Delta m = 0.1$ mmu. **5e**: EI-MS: *m*/*z* (%): 222 ($[M^+]$, 61.8), 207 ($[M^+ - CH_3]$, 22.5), 179 ($[M^+ - C_3H_7]$, 45.8), 43 ($[C_3H_7{}^+]$, 100). **4**: EI-MS *m*/*z* (%): 446 ($[M^+]$, 5.8), 333 ($[M^+ - C_6H_{16}BN]$, 4.4), 222 ($[C_{12}H_{28}B_2N_2{}^+]$, 100), 43 ($[C_3H_7{}^+]$, 47.5).

1f: To Na/K alloy (1:2.8, ≈1 g) in hexane (20 mL) was added dropwise **3f** (330 mg, 0.88 mmol) in hexane (10 mL). After 72 h of stirring the gray-green reaction mixture was filtered, and the residue was washed with hexane. The yellow filtrate was concentrated, and recrystallization from toluene at 5 °C provided yellow **1f** (98 mg, 37%; m.p. 292 °C). ^1H NMR (200 MHz, C_6D_6): $\delta = 1.55$–1.65 (m); ^{11}B NMR (64 MHz, C_6D_6): $\delta = 67.5$; ^{13}C NMR (50 MHz, C_6D_6): $\delta = 17.7$ (*p*-CH_2), 33.8 (*m*-CH_2), 39.8 (CCH_3), 54.5 (NCC); high-resolution EI-MS: *m*/*z* calcd for $^{12}C_{36}{}^1H_{72}{}^{11}B_4{}^{14}N_4$: 604.6129, found: 604.6138, $\Delta m = 0.9$ mmu.

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