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Tetra(pyrrolidino)diborane(4), [(C₄H₈N)₂B]₂, as a New Improved Alternative Synthetic Route to Bis(pinacolato)diborane(4) – Crystal Structures of the Intermediates

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Keywords: Boranes / Tris(pyrrolidino)borane / Tetra(pyrrolidino)diborane(4) / Solvolysis / Bis(pinacolato)diborane(4)

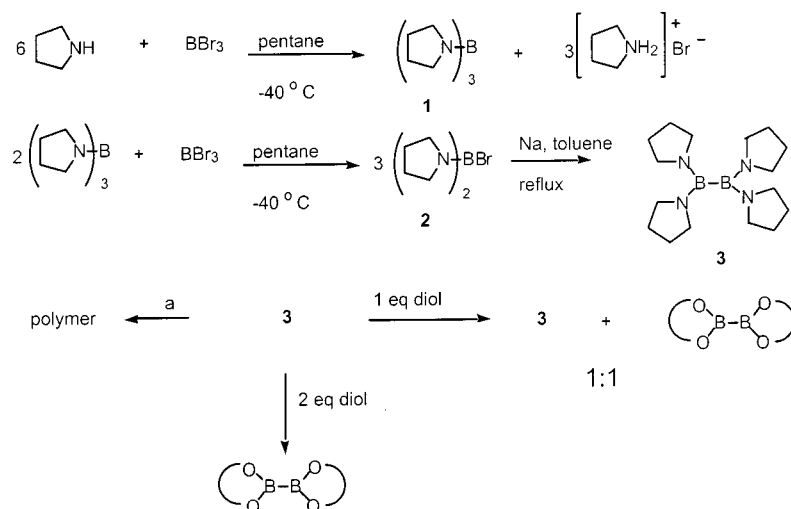
The compound tetra(pyrrolidino)diborane(4) (**3**) is an important new and alternative precursor for the preparation and synthesis of bis(pinacolato)diborane(4). The latter is the major intermediate among the diborane derivatives used for many addition and insertion reactions into multiple bonds.

The crystal structure of **3** and its precursor, tris(pyrrolidino)borane, **1**, were determined. In addition the solvolysis reactions and solution behavior of **3** with alcohols were examined.

Introduction

Derivatives of diboranes,^[1] in particular tetraalkoxydiboranes, have become increasingly important as a result of the accelerating use of the Suzuki coupling reaction in the synthesis of complex molecular species.^[2] The preparation of arylboronates from tetraalkoxydiboranes,^[3] and the addition of tetraalkoxydiboranes across alkenes,^[4] alkynes,^[5] di-

ynes,^[4e,5c] enynes,^[4e] allenes,^[4e,10a,10b] 1,3-butadienes,^[4e,6] methylenecyclopropanes,^[7] allylic acetates,^[8] α,β -unsaturated compounds^[4d,9] and various other substrates^[10] have contributed to the development of the chemistry of diboranes.^[11] Tetraalkoxydiboranes are generally prepared from tetradialkylaminodiboranes, by Wurtz coupling of the corresponding bis(dialkylamino)haloboranes,^[12] or by reaction of bis(dialkylamino)dichlorodiboranes with lithium



a. CDCl₃ or acetone, 1 day; or CO/toluene 4h. Diol=pinacol or 2-ethoxy-1,3-propanediol

Scheme 1. Synthesis and reactions of **3**

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amides.^[13] The tetraalkoxydiboranes are then obtained by solvolysis of the tetradialkylaminodiboranes with alcohols.^[14]

While many tetradialkylaminodiboranes have been prepared by the above methods, few structures have been reported. In this paper we describe an improved synthesis of

3,^[12b] its crystal structure, solution structure and solvolysis reactions, which have not been reported on previously. Compound **3**, we believe, is an important new and alternative precursor for the preparation of bis(pinacolato)diborane(**4**) which is the major intermediate among the diborane derivatives used for many addition and insertion reactions (see the extended reference list in the manuscript). This crucial compound can be obtained from tetra(dimethylamino)diborane(**4**), as described by Nöth.^[15] This is the only synthetic route for this compound reported in the literature. There are several distinct disadvantages with this route. The preparation of bis(pinacolato)diborane(**4**) by the published route requires the use of dimethylamine, a dangerous gas above 7° C that is not easy to handle. In addition, dimethylamine is on the list of restricted chemicals, and thus is not available in many parts of the world. Alternatively, pyrrolidine is a stable liquid (87–88° C), easy to handle and is not on any restricted list of chemicals. Further, we have determined that **3**, which is a solid, is more stable to air and hydrolysis than tetra(dimethylamino)diborane(**4**), which is a very sensitive liquid [Various (R₂N)₂BX compounds, where R = Et, *i*Pr, etc and X = Cl, Br, failed to give B–B compounds in the dehalogenation step]. However, dipyrrolidino behaved like dimethylamine, in that bis(pyrrolidino)bromoborane, **2**, was debrominated by sodium to give **3**. The precursor, tris(pyrrolidino)borane, **1**, is readily prepared from one equiv. of BBr₃ in pentane at –40° C and six equiv. of pyrrolidine. After filtering the bromide salt, distillation afforded **1**. Bis(pyrrolidino)bromoborane was prepared from one equiv. of BBr₃ in pentane at –40° C and two equiv. of **1** (Scheme 1). We have determined the stability of **3** in various solvents and found that the compound, while readily converted into tetraalkoxydiboranes by alcohols, polymerizes in the presence of acetone, chloroform, THF and CO/toluene. It is very stable to inert solvents like benzene, toluene and hydrocarbons.

Results and Discussion

Compound **1** crystallizes with four molecules in the asymmetric unit cell, two of which are shown in (Figure 1). The molecular entities have a planar BN₃ core, but they differ slightly in the conformation of the peripheral ring fragments. The latter are bent above and below the BN₃ plane, and are affected by severe disorder problems (in two of the four species). This is consistent with the low crystal density and loose intermolecular organization which facilitate the assumedly dynamic conformational behavior of the saturated rings at 110 K (Even at this low temperature the observed disorder of these rings could not be accounted for by a suitable combination of several static structures with partial occupancies and acceptable geometries. However, this order may still be static with several closely related positions, as this might also give rise to overlapped atoms that are not easy to resolve into separate positions). The bond lengths and angles involving B and N are similar to those previously observed in related triazaborane structures.^[16]

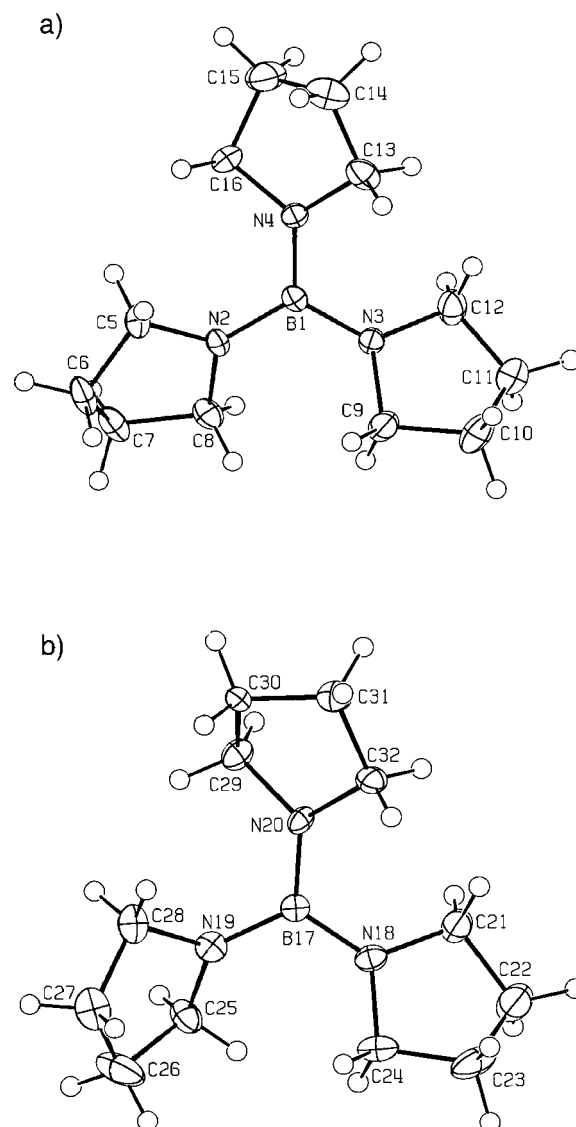


Figure 1. View of the molecular structure of **1** showing the atom numbering scheme (only the two ordered species of the asymmetric unit are shown). Ellipsoids represent thermal displacement parameters at the 50% probability level. The conformational lability of these species is reflected in the larger volume and higher anisotropy of the peripheral C-atoms. Selected bond lengths (Å) and angles (°) include: B1–N2 1.457(5), B1–N3 1.434(5), B1–N4 1.429(5), B17–N18 1.430(5), B17–N19 1.449(5), B17–N20 1.430(5), mean C–N 1.465, mean C–C 1.529; sum of angles at B1 360.0; sum of angles at B17 359.9.

The crystal structure is illustrated in (Figure 2). It shows a layered arrangement of the roughly flat molecules parallel to the *ab* plane of the unit-cell, that is stabilized by weak van der Waals forces between the lipophilic surfaces of adjacent species.

The molecular structure of **3** is shown in (Figure 3). It has a crystallographic twofold rotational axis which coincides with the B–B bond. As in related compounds, it maintains the trigonal planar geometry around the boron atoms. However, the observed B–B distance of 1.739(4) Å is slightly longer than in previously reported analogues.^[12b,13,17] This may be due to the bulky pyrrolidino

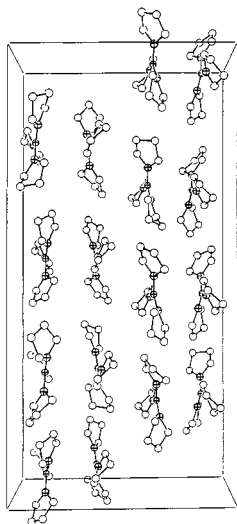


Figure 2. Crystal structure of **1** viewed approximately down the *a* axis (*b* is vertical) which shows the contents of a single unit-cell and the hypercentric layered molecular organization.

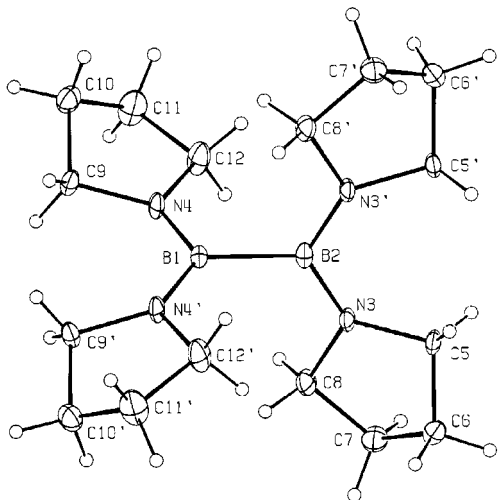


Figure 3. View of the molecular structure of **3**, showing the atom numbering scheme. Ellipsoids represent thermal displacement parameters at the 50% probability level. The molecules are located in the crystal on twofold symmetry axes; primed atoms are related to nonprimed atoms by symmetry transformation: $1 - x, y, 1/2 - z$. Selected bond lengths (Å) and angles ($^{\circ}$) include: B1–B2 1.739(4), B1–N3 1.424(2), B1–N4 1.427(2), mean C–N 1.472, mean C–C 1.523, N4–B1–N4' 121.7(2), N3–B2–N3' 120.8(2), N4–B1–B2 119.1(1), N3–B2–B1 119.6(1), N4–B1–B2–N3 $-103.6(1)$, N4–B1–B2–N3' 76.4(1).

groups around the boron atoms. The molecule adopts a staggered conformation around the B–B bond (Figure 4) in order to avoid collision between the inner hydrogen atoms. The N–B–B–N torsion angles are 76.4 and 103.6° .^[12b] The crystal structure is stabilized by weak van der Waals forces between the lipophilic surfaces of adjacent molecules, and readily cleaves along the interfaces between the molecular layers (Figure 4).

Compound **3** is monomeric in solvents like benzene or in hydrocarbons. It is more stable in air than tetra(dimethylamino)diborane(4). In terms of chemical reactivity

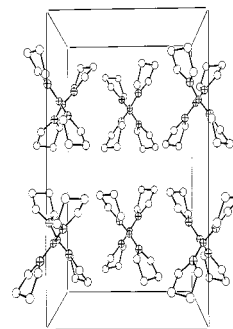


Figure 4. View of the crystal structure of **3** down the *b* axis of the unit cell (contents of $1\frac{1}{2}$ unit cells are shown). Note the staggered disposition of the five-membered rings with respect to the B–B bond, and the layered organization of the molecular entities in the crystals of this material.

and solvolysis, the pyrrolidino compound behaves in a similar manner to the tetradimethylamino analogue, but is more reactive than other tetradialkylamine derivatives. It reacts with one equiv. of pinacol to give a 1:1 mixture of bis(pinacolato)diborane(4),^[15] and starting material. However, with two equiv. of pinacol, pure bis(pinacolato)diborane(4) is obtained in an 83% yield (Scheme 1). With two equiv. of 2-ethoxy-1,3-propanediol, the corresponding 2,2'-bis(5-ethoxy-1,3-dioxo-2-boracyclohexane), $[(C_5H_{10}O_3)B]_2$, is produced. Allowing a solution of freshly prepared **3** in $CDCl_3$, acetone or in CO in toluene, for 4 h results in the disappearance of starting material and the precipitation of a new compound, as indicated by 1H , ^{13}C , ^{11}B NMR, GCMS and GPC analysis (Scheme 1). GPC analysis of the new compound indicates that it is a polymer ($M_w = 19,458$; $M_n = 19,139$; $M_w/M_n = 1.02$).^[18] The small signals in the variable-temperature NMR spectra (Figure 5) at around $\delta = 1.75$ and 2.95 are not impurities, but rather arise from the formation of a polymer, the structure of which has not yet been determined. However, a variable-temperature

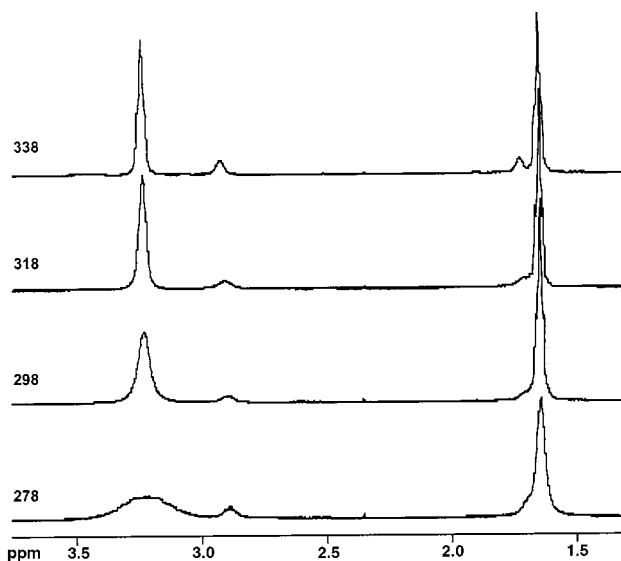


Figure 5. Variable-temperature (K) 1H NMR spectra of **3** in $CDCl_3$.

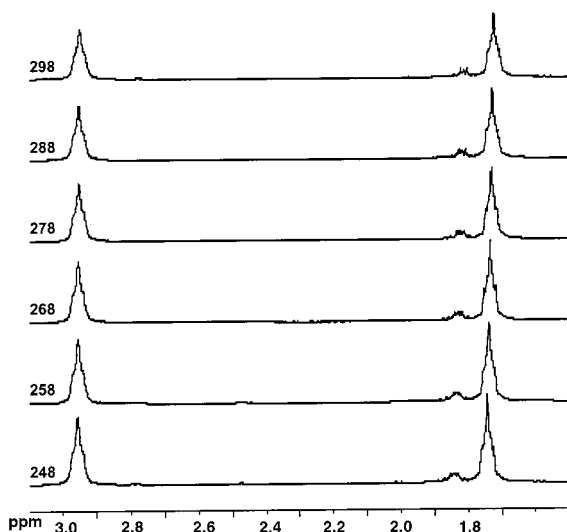


Figure 6. Variable-temperature (K) ^1H NMR spectra of the polymer in CDCl_3 .

NMR spectroscopic study of the polymer in CDCl_3 has been performed (Figure 6). The signal of the monomer at $\delta = 1.64$ is shifted downfield in the polymer, while the signal at $\delta = 3.23$ is shifted upfield.

The ^1H NMR spectrum of **3** at 25 °C initially shows two broad singlets at $\delta = 1.64$ and 3.23. In the ^{13}C NMR spectrum, the C1 carbon atom of the pyrrolidino ring cannot be seen at room temperature. These phenomena may be due to the proximity of C1 to the boron atom, as well as the tumbling effect that takes place for large molecules in solution. Such spectra could also result from the restricted rotation around the B–B or B–N bond, or from both. However, when a CDCl_3 solution of **3** is heated from 278 to 338 K, the broad signals in the ^1H NMR spectrum are resolved into triplets ($^3J = 6.5$ Hz) (Figure 5), whereas C1 in the ^{13}C NMR spectrum is resolved into a singlet at $\delta = 49.43$. For the monomer, temperatures lower than 278 K result in the broadening of both signals in the ^1H NMR spectrum, and all splitting is lost, while for the polymer, lower temperatures give enhanced signals.

Conclusion

We have discovered that tetra(pyrrolidino)diborane(4) (**3**) is an excellent new precursor for the preparation of bis(pinacolato)diborane(4). Its crystal structure has been determined, as well as that of tris(pyrrolidino)borane. We have shown that **3** is stable in benzene, toluene and hydrocarbons, but tends to polymerize in acetone, chloroform, THF, and CO/toluene. We found that most bis(dialkylamino)-haloboranes are not suitable for the coupling reaction and give primarily the tris(dialkylamino)boranes and very low yields of the B–B product. Thus, tetra(pyrrolidino)diborane(4) is a valuable precursor for the preparation of bis(pinacolato)diborane(4) (obtained in an 83% yield), and is an alternative to $\text{B}_2(\text{NMe}_2)_4$.

Experimental Section

General Remarks: All reactions were carried under a nitrogen atmosphere using vacuum line and glove box techniques. Solvents were purified by distillation from appropriate drying agents under a nitrogen atmosphere. Starting materials were purchased from commercial suppliers and used without further purification. – ^1H and ^{13}C NMR spectra were recorded in CDCl_3 solution using a Varian Unity (300 or 75 MHz) spectrometer with Me_4Si as an internal standard. ^{11}B NMR spectra were recorded with a Bruker MSL-400 (128 MHz) spectrometer using $\text{BF}_3\cdot\text{OEt}_2$ as an external standard. – GC/MS spectra were obtained on a HP GCD PLUS instrument in EI mode on a 30 m methylsilicone column.

($\text{C}_4\text{H}_8\text{N}$)₃\text{B} (1): Pyrrolidine (86 g, 1.21 mol) and pentane (150 mL) was put into a dry 500 mL flask, closed with a rubber septum, under a nitrogen atmosphere. The flask was placed in a dry ice bath (-78°C). Tribromoborane (51.25 g, 0.20 mol) was added slowly under nitrogen into a flask containing pentane (50 mL) which had been cooled to about -40°C . This solution was added dropwise, with stirring, to the cooled amine-pentane solution. After an additional 3 h, the solution was allowed to warm to room temperature. The mixture was filtered under a nitrogen atmosphere, and pentane was added to transfer the solid to the filter funnel. The pentane was removed from the clear solution under vacuum, and the residue was distilled under vacuum to give colorless crystals (35.80 g, 81%). M.p. 40°C , b.p. $105^\circ\text{C}/1.5\text{Torr}$. – ^1H NMR (CDCl_3): $\delta = 1.66$ (t, 12 H, CH_2 , $^3J_{\text{H-H}} = 6.6$ Hz), 3.04 (t, 12 H, CH_2N , $^3J_{\text{H-H}} = 6.6$ Hz). – $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): $\delta = 24.61$ (CH_2), 46.84 (CH_2N). – ^{11}B NMR (CDCl_3): $\delta = 23.75$. – MS (EI), m/z (%) = 221 (20.4) [M^+], 192 (10.14), 178 (12.19), 151 (100), 123 (12.00), 109 (10.36), 82 (32.06), 70 (15.39), 40 (21.65). – $\text{C}_{12}\text{H}_{24}\text{N}_3\text{B}$: calcd. C 65.17, H 10.94, N 19.00; found C 64.96, H 10.81, N 18.81.

($\text{C}_4\text{H}_8\text{N}$)₂\text{BBr} (2): A solution of tribromoborane (16.29 g, 0.065 mol) in pentane (50 mL) was added to a vigorously-stirred solution of tris(pyrrolidino)borane (30 g, 0.13 mol) in pentane (150 mL) at -50 to -40°C , over a period of 20 min.. After an additional 3 h, the solution was allowed to warm to room temperature. The pentane was removed by rapid distillation at 1.5 Torr and the residue was distilled at 0.5 Torr giving the product as a pure liquid (39.51 g, 84%). B.p. $90^\circ\text{C}/0.5\text{Torr}$. – ^1H NMR (CDCl_3): $\delta = 1.71$ (t, 8 H, CH_2 , $^3J_{\text{H-H}} = 6.75$ Hz), 3.31 (t, 8 H, CH_2N , $^3J_{\text{H-H}} = 6.75$ Hz). – $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): $\delta = 26.56$ (CH_2), 50.01 (CH_2N). ^{11}B NMR (CDCl_3): $\delta = 24.51$ – $\text{C}_8\text{H}_{16}\text{N}_2\text{BBr}$: calcd. C 41.60, H 6.98, N 12.13; Br, 34.60; found C 41.31, H 7.21, N 11.46; Br, 34.93.

[($\text{C}_4\text{H}_8\text{N}$)₂\text{B}]₂ (3): A solution of bis(pyrrolidino)bromoborane (21.8 g, 0.094 mol) in dry toluene (6 mL) was added slowly to highly-dispersed molten sodium (2.6 g, 0.11 mol) in dry toluene (20 mL) at 110°C . After 4 h, the resulting solids were filtered under a nitrogen atmosphere. The toluene was removed from the filtrate by vacuum distillation and the residue distilled at $160^\circ\text{C}/0.5\text{Torr}$ to give the product as a clear liquid, which on cooling gave colorless crystals (7.1 g, 50%). M.p. 75°C , b.p. $160^\circ\text{C}/0.5\text{Torr}$. – ^1H NMR (CDCl_3) at 338 K: $\delta = 1.64$ (broad t, 16 H, CH_2 , $^3J = 6.5$ Hz), 3.23 (broad t, 16 H, CH_2N). – $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3) at 338 K: $\delta = 26.53$ (CH_2), 49.43 (CH_2N). ^{11}B NMR (CDCl_3): $\delta = 33.96$. – MS (EI): m/z (%) = 302 (23.4) [M^+], 230 (100), 203 (46.6), 202 (39.2), 163 (64), 151(100), 133 (24.5), 107 (29.7), 82 (100), 70 (93.4). – $\text{C}_{16}\text{H}_{32}\text{N}_4\text{B}_2$: calcd. C 63.61, H 10.67, N 18.54; found C 63.53, H 10.69, N 18.27.

[($\text{C}_5\text{H}_{10}\text{O}_3$)\text{B}]₂: A solution of tetra(pyrrolidino)diborane(4) (3.0 g, 0.01 mol) in benzene (20 mL) was added to a vigorously stirred

Table 1. Crystal data and structure refinement for **1** and **3**

Compound	1	3
Empirical formula	C ₁₂ H ₂₄ BN ₃	C ₁₆ H ₃₂ B ₂ N ₄
Molecular mass	221.15	302.08
Color	Colorless	Colorless
Temperature (K)	110(2)	110(2)
Wavelength (Å)	0.71070	0.71070
Crystal dimension (mm)	0.55 × 0.45 × 0.15	0.35 × 0.25 × 0.20
Crystal system	Monoclinic	Orthorhombic
Space group	<i>P</i> 2 ₁ / <i>n</i>	<i>Pbcn</i>
<i>a</i> (Å)	9.3780 (1)	10.6990 (4)
<i>b</i> (Å)	33.3540 (1)	9.3420 (5)
<i>c</i> (Å)	16.3120 (1)	17.6500 (8)
α (deg)	90	90
β (deg)	91.34	90
γ (deg)	90	90
<i>V</i> (Å ³)	5100.90 (2)	1764.12 (14)
<i>Z</i>	16	4
<i>D</i> _{calcd.} (g cm ⁻³)	1.152	1.137
<i>F</i> 000	1952	664
μ (mm ⁻¹)	0.069	0.067
θ limits (deg)	2.22/25.34	3.80/25.36
Reflns unique	9151	1602
No. of data measured	15872	1873
Restraints	0	0
<i>hkl</i> limits	0,11/0,40/ -19,19	0,12/0,11/0,21
No. of variables	578	101
No. of data with $[I > 2\sigma(I)]^{[a]}$	4774	1234
Final ^[b] <i>R</i> indices $[I > 2\sigma(I)]^{[a]}$		
<i>R</i> 1/ <i>wR</i> 2	0.0824	0.0754
	0.2320	0.1948
Largest diff peak and hole (e/ Å ³)	0.692 and - 0.725	0.727 and - 0.313
GOF	1.05	1.06

[^a] $[I > 3\sigma(I)]$ for **1**. - [^b] $R_I = \frac{\sum |F_o - |F_{c||}}{\sum |F_o|}$ $wR2 = \frac{\{\sum [w(F_o^2 - F_c^2)^2]\}}{\{\sum [w(F_o^2)^2]\}}^{1/2}$.

solution of 2-ethoxy-1,3-propanediol (2.4 g, 0.02 mol) in benzene (10 mL) at 25 °C. A solution of 3 M HCl/ether (15 mL) was added to the resulting mixture. After 6 h, the mixture was filtered and the benzene was removed under vacuum to give the product as an oily material, which was purified by silica gel chromatography eluting with 10% ether/petroleum ether (2.0 g, 78%). - ¹H NMR (CDCl₃): δ = 1.13 (t, 6 H, CH₃, ³*J* = 7.0 Hz), 3.50 (q, 4 H, CH₂, ³*J* = 7.0 Hz), 3.53 (m, 2 H, CH, ³*J* = 5.0 Hz), 3.87 (dd, 8 H, CH₂, ³*J* = 5.0 Hz). - ¹³C{¹H} NMR (CDCl₃): δ = 15.31 (CH₃), 64.36 (OCH₂CH₃), 63.19 (CH₂), 71.50 (CH). - ¹¹B NMR (CDCl₃): δ = 27.49. - MS (EI): *m/z* (%) = 213 [M⁺ - 45] (1.11), 171 (6.6), 143 (9.7), 129 (10.3), 115 (14.7), 101 (21.1), 72 (100), 45 (20.6), 29 (61.6). - C₁₀H₂₀O₆B₂: calcd. C 46.55, H 7.76; found C 46.13, H 7.55.

X-ray Crystallographic Study: Single crystals of **1** and **3** suitable for X-ray diffraction analysis were obtained from a saturated pentane solution at \approx -20 °C. The crystal data and structure refinement for both are summarized in Table 1. (C₄H₈N)₃B (**1**). Crystals of this low-melting compound are extremely sensitive to air and moisture, and were coated with a layer of hydrocarbon oil in order to minimize deterioration. The X-ray diffraction measurements were carried out at ca. 110 K on a Nonius-Kappa CCD diffractometer, using Mo-*K*_α (λ = 0.7107 Å) radiation and 0.9° ϕ and Ω scans. The structure was solved by direct methods (SIR-92)^[19] and refined by full-matrix least-squares based on *F*² for all reflections (SHELXL-97).^[20] All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms were located in calcu-

lated positions to correspond to standard bond lengths and angles, and were included in the refinement with isotropic displacement parameters using a riding model. Even at 110 K, the molecular structure of this compound is affected by severe conformational disorder of the five-membered rings. The asymmetric unit of the observed structure consists of four molecular entities that exhibit somewhat different conformations and varied degrees of disorder. The latter is reflected in the large-amplitude thermal displacement parameters of the C atoms, and could not be modeled; it is particularly evident in two out of the four crystallographically independent species. The dynamic nature of the structure gives rise to a large percentage of weak reflections in the diffraction pattern (revealing the appearance of several superlattice peaks as well), and affects the precision of this determination.

[(C₄H₈N)₂B]₂ (**3**): The analyzed crystal of **3** was coated with a layer of hydrocarbon oil in order to minimize deterioration and mounted on a glass fiber. The X-ray diffraction measurements were carried out as for **1**, using 1.0° Phi and Omega scans; solution and refinement were as for **1**.

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-165578 (**1**) and CCDC-165579 (**3**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

Acknowledgments

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