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Reactions and Structure of Electron-Precise Triborane(5) and Tetraborane(6) Derivatives

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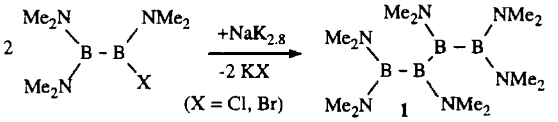
An improved synthesis of $B_3(NMe_2)_5$ (**2**), $B_4(NMe_2)_6$ (**1**), and $B_6(NMe_2)_8$ (**4**) is reported. From each compound two of the four terminal dimethylamino groups are readily replaced by halogen atoms yielding α,ω-dihalides $B_n(NMe_2)_nX_2$ (n = 3, 4; X = Cl, Br, I). These are used in turn to replace the substituent X by groups like RO, RS, RHN, R_2P, and R. Crystal structure determinations on several of these compounds reveal as a common feature planar $(C_2N)BB_2$ and $(C_2N)B(B)X$ groups which are arranged in an approximately orthogonal manner to one another with NBBN dihedral angles ranging from 69 to 104.6°. Consequently, there is no significant π bonding between the boron atoms.

While there is a rich versatile chemistry of polyboranes B_pH_{p+q} characterized by electron-deficient bonding[2] comparatively little knowledge exists of electron-precise polyboranes of the general formula B_nX_{n+2}. Bonding in these compounds can be described conveniently by classical localized covalent bonds. Most of the present knowledge of these compounds is confined to diborane(4) derivatives, and B_2F_4, B_2Cl_4, $B_2(OMe)_4$, $B_2(NMe_2)_4$, and B_2R_4 are prominent examples[3]. The only well-defined electron-precise polyborane species containing more than two boron atoms are B_3F_5[4], $B_n(NMe_2)_{n+2}$[5], and the cyclic $B_6[NMe_2]_6$[6]. The latter is the only member of these compounds whose molecular structure has been determined by X-ray methods. Amongst these polyboranes the dimethylamino derivatives are the most readily accessible. Therefore, we expected that they might be well suited to develop a chemistry of electron-precise polyporanes, and we report in this paper our results achieved in this context.

Synthesis of (Dimethylamino)polyboranes

The synthesis of (dimethylamino)polyboranes is accomplished by dehalogenation of $B_2(NMe_2)_3X$ compounds or of mixtures composed of $B_2(NMe_2)_3X$ or $B_2(NMe_2)_2X_2$ with $(Me_2N)_2BX$ (X = Cl)[5]. Hexakis(dimethylamino)tetraborane(6) (**1**) is best prepared according to eq. (1) from $B_2(NMe_2)_3Cl$ in yields up to 23%; however, when $B_2(NMe_2)_3Br$ is used the yield is improved to 38%, and this result is in accordance with earlier observations that (dimethylamino)boron bromides are more readily dehalogenated than the respective boron chlorides[5]. Optimization of the codehalogenation of $B_2(NMe_2)_3Cl$ and $B(NMe_2)_2Cl$ with sodium-potassium alloy as described in eq. (2) raises the yield of pentakis(dimethylamino)triborane(5) (**2**) from the reported 5[5] to 23%. Additional members of the series $B_n(NMe_2)_{n+2}$, **3** (n = 2, 8.5%) and **4** (n = 6, 0.5%) have also been isolated.



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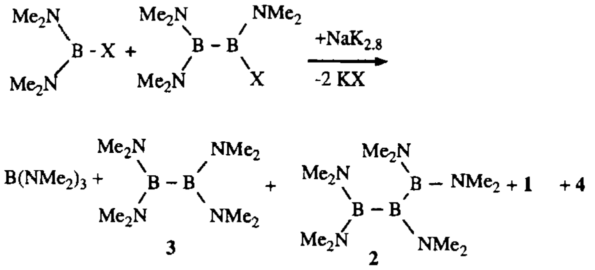

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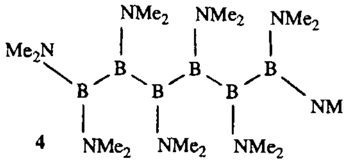

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While compounds **1** to **3** can be separated by fractional distillation in vacuo the hexaborane **4** can only be isolated by short-path distillation as a very viscous brown oil. The components of the dark brown, glassy residue which is left after fractional distillation have not yet been identified.

It is imperious that distillation of the (dimethylamino)polyboranes is carried out at the lowest possible temperature because the compounds **1**, **2**, and **4** decompose on heating by releasing $B(NMe_2)_3$ as the most volatile compound.

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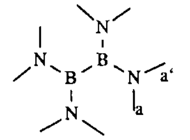
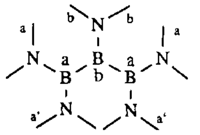
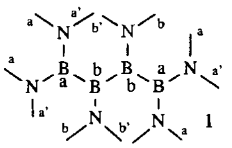
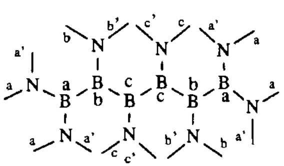
Therefore, it would be important to develop a chromatographic method in order to improve separation. This method would probably also make other not yet identified aminopolyboranes available. However, our efforts have so far proven unsuccessful: depending on the stationary phases used either the compounds are not be released from the column (Al_2O_3, SiO_2) or no clean separation has been achieved (RP-18 in reversed-phase chromatography).

NMR Spectra of (Dimethylamino)polyboranes

The (dimethylamino)polyboranes can be readily characterized by their ^1H-, ^{11}B-, and ^{13}C-NMR spectra. Data are compiled in Table 1.

Table 1. NMR data of (dimethylamino)polyboranes recorded in C_6D_6 solutions at 28°C

	$\delta^{11}B$	$\delta^{13}C$	δ^1H
 3	36.8	41.3	2.64
 2	36.9(2)(a) 60.2(1)(b)	41.4 (a,a') 46.1 (b)	2.65 (2) (a,a') 2.86 (1), (b)
 1	37.1(1)(a) 61.3(1)(b)	41,4 (a,a') 46.0 (b,b')	2.67 (1) (a, a') 2.87 (1) (b, b')
 4	37.5(1)(a,a') 62.4(2)(b,c)	41.6 (a,a') 45.9 (b,b') 46.5 (c,c')	2.71 (2) (a,a') 2.73 (1) (b,b') 2.90 (1) (c,c')

As has been noted previously[5] the ^{11}B resonances fall into two regions: signals $\delta^{11}B$ at ca. 37 can be assigned to the terminal $(Me_2N)_2B$ groups while the signals found at $\delta^{11}B$ ca. 61 arise from the internal Me_2NB groups. The two groups can also be discerned by the ^{13}C resonances of the respective dimethylamino substituents: the carbon atoms of the $(Me_2N)_2B$ groups are much better shielded than those of the Me_2NB groups, and this holds also for the ^1H-NMR signals. These data suggest a stronger BN-π bond of the internal amino groups to its boron atom which withdraws electron density from the nitrogen atoms more effectively than the boron atom of the $(Me_2N)_2B$ part of the molecules. The number of ^1H- as well as of ^{13}C-NMR signals indicate free rotation at ambient temperature about the B−B as well as the terminal B−N bonds.

Reaktions with Amines and Phenol

Since dehalogenation of aminoboron halides $(R_2N)_2BHal$ containing sterically more demanding amino groups than the Me_2N group produces $B_2(NR_2)_4$ compounds only in low yield[1,8], no attempts have been made to prepare other kinds of $B_n(NR_2)_{n+2}$ polyboranes by this method than the dimethylamino derivatives. Therefore, transamination was considered to be the method of choice to generate a series of $B_n(NR_2)_{n+2}$ compounds. Although dimethylamine was liberated on heating piperidine (pipH) with either **2** or **1** neither $B_3(pip)_5$ nor $B_4(pip)_6$ could be detected as a reaction product, and no ^{11}B-NMR signal at δ ca. 60 was observed after the Me_2NH evolution had ceased indicating the absence of a $B-BNR_2-B$ moiety. However, a fair amount of $B_2(pip)_4$ was isolated in each case demonstrating that the boron chain of **1** and **2** had been broken down to a diborane(4) unit. In addition, an ^{11}B-NMR signal at δ ca. 27 proves the presence of $B(pip)_3$[9] as the second reaction product but this compound was not isolated. B−B bond cleavage also resulted in the transamination of **2** with pyrrolidine (pyrH) at 100°C. The reaction mixture consisted of $B(pyr)_3$ and $B_2(pyr)_4$ according to ^{11}B-NMR analysis.

Efforts to transform $B_3(NMe_2)_5$ into $B_3(OPh)_5$ by treating **2** with phenol in varying proportions even in the presence of HCl failed. The product which has been formed almost quantitatively even at 0°C with respect to phenol is the borate $(Me_2NH_2)[B(OPh)_4]$. Thus, B−B bond cleavage occurs with phenol at an even lower temperature than required for transamination.

Halogenation of $B_n(NMe_2)_{n+2}$

It is well-known that one R_2N group per $(Me_2N)_2B$ unit can be replaced by a chlorine atom in $B_2(NMe_2)_4$[10]. Total exchange of all amino groups for halogen atoms in order to achieve the syntheses of B_2X_4 (X = Cl, Br) is not possible on a preparative scale. Similarly, neither **1** nor **2** could be used to synthesize B_4X_6 or B_3X_5 irrespective of the halogenating agent. However, reactions according to eqs. (3) and (4) lead to α,ω-dihalogeno(dimethylamino)polyboranes in good yields.

$$B_n(NMe_2)_{n+2} + 2\,BX_3 \longrightarrow B_n(NMe_2)_nX_2 + B(NMe_2)X_2 \quad (3)$$

$$B_n(NMe_2)_{n+2} + 2\,YBX_2 \longrightarrow B_n(NMe_2)_nX_2 + YB(NMe_2)X \quad (4)$$

n	3			4		
X	Cl	Br	I	Cl	Br	I
	5	**6**	**7**	**8**	**9**	**10**

The dichloro compound **5** is easily prepared from **2** and BCl_3, a reaction that also leads to **8** if $B_4(NMe_2)_6$ is used[5]. However, **8** is more conveniently obtained from **1** by using $EtBCl_2$ as the halogenating agent.

The dibromo compounds **6** and **9** are prepared by allowing **2** or **1** to react with either BBr_3 or $MeBBr_2$. Since $MeBBr(NMe_2)$ is more volatile than $BrB(NMe_2)_2$, methylboron dibromide is the reagent of choice. Similarly, iodination of **1** and **2** is best achieved with $MeBI_2$.

The chloride **5** is a colorless liquid. All other α,ω-dihalogeno(dimethylamino)polyboranes are crystalline. The iodides **7** and **10** are only sparingly soluble even in boiling hexane or toluene.

The structures of compounds **5** to **10** are in accordance with their NMR spectra (see Table 2). Each of the (dimethylamino)dihalogenotri- and -tetraboranes exhibit two ^{11}B-NMR signals. These can be unambiguously assigned for **5** to **7** by their 2:1 intensity ratio. The δ^{11}B data reveal that the influence of the halogen atom on the shielding of the boron nucleus is not very pronounced but is largest for the iodides. This corresponds nicely with the shift difference found earlier for the series of aminoboron halides $(Me_2N)_2BCl$, $(Me_2N)_2BBr$, and $(Me_2N)_2BI$ (3 ppm)[11]. In contrast to **1** and **2**, the ^{1}H and ^{13}C resonances of compounds **5** to **7** indicate hindered rotation about the terminal B−N bonds. This is an expected feature since the introduction of a halogen atom increases the Lewis acidity at the respective boron center and generates stronger BN-π bonding. For symmetry reasons there is no splitting of the signals of the internal dimethylamino group in the triborane compounds **5** to **7**. This would be in accord with a free rotation about the B−N bond. However, there is no reason to believe why there should be a different situation as observed for **8** to **10** (v.i.).

Nucleophilic Substitution Reactions

The (dimethylamino)dihalogenopolyboranes **5** to **10** offer themselves for a nucleophilic displacement of their halogen atoms. Thus, treatment of **6** with alkali metal alkoxides and aryl oxides leads to replacement of the bromine atoms by OR groups according to eq. (5). As reagents have been used LiOMe, NaO*t*Bu, and *o*,*o*′-$(Me_3C)_2C_5H_3OLi$ but only the first two gave access to the 1,3-dialkoxytris(dimethylamino)triboranes(5) **11** and **12**, while the rather bulky lithium 2,6-di-*tert*-butylphenoxide did not react at all. Therefore, steric effects play an important part in these nucleophilic substitution reactions. Similarly, 1,4-di-*tert*-butoxytetrakis(dimethylamino)tetraborane(6) (**13**) was prepared from **9** and NaO*t*Bu.

In a similar manner alkylthio and arylthio groups can be introduced. For that purpose, thiophenol and cyclohexanethiol were allowed to react with **6** or **9** in the presence of triethylamine as an auxiliary base as described by eq. (6). The obtained compounds **14** and **15** are colorless, unpleasently smelling, crystalline materials. There is no doubt that many other α,ω-bis(alkyl- or arylthio)-(dimethylamino)polyboranes can be prepared by this method.

Since transaminations were unsuccessful in generating new kinds of aminopolyboranes, the reaction of **6** and **9** with several lithium amides was studied in order to obtain "mixed" aminopolyboranes as exemplified by compounds **16** to **18**. Subsitution reactions proceeded smoothly as described by eqs. (7) and (9). However, lithium 2,2,6,6-tetramethylpiperidide did not react at all with either **5** or **6**, indicating steric overcrowding of the transition state. At 100°C a reaction ensued but with degradation of the polyboron chain since no ^{11}B-NMR signal could be detected in the diagnostic region at δ ca. 60.

The versatility of nucelophilic substitution reactions for the preparation of new electron-precise polyboranes is further demonstrated by the synthesis of the phosphanylpolyboranes **20** and **21** from $LiPPh_2$ and **6** or **9**. Similarly, hexakis(dimethylamino)-1,6-bis(diphenylphosphanyl)hexaborane(8) (**21**) was prepared from $B_6(NMe_2)_6Cl_2$ and $LiPPh_2$ However, attempts to synthesize monophosphanylpolyboranes $Ph_2P(Me_2N)B-[BNMe_2]_n-B(NMe_2)X$ failed. This result is conceivable because the terminal $B(NMe_2)X$ groups are well separated, and the reactivity of the halogen atoms X should therefore not differ significantly.

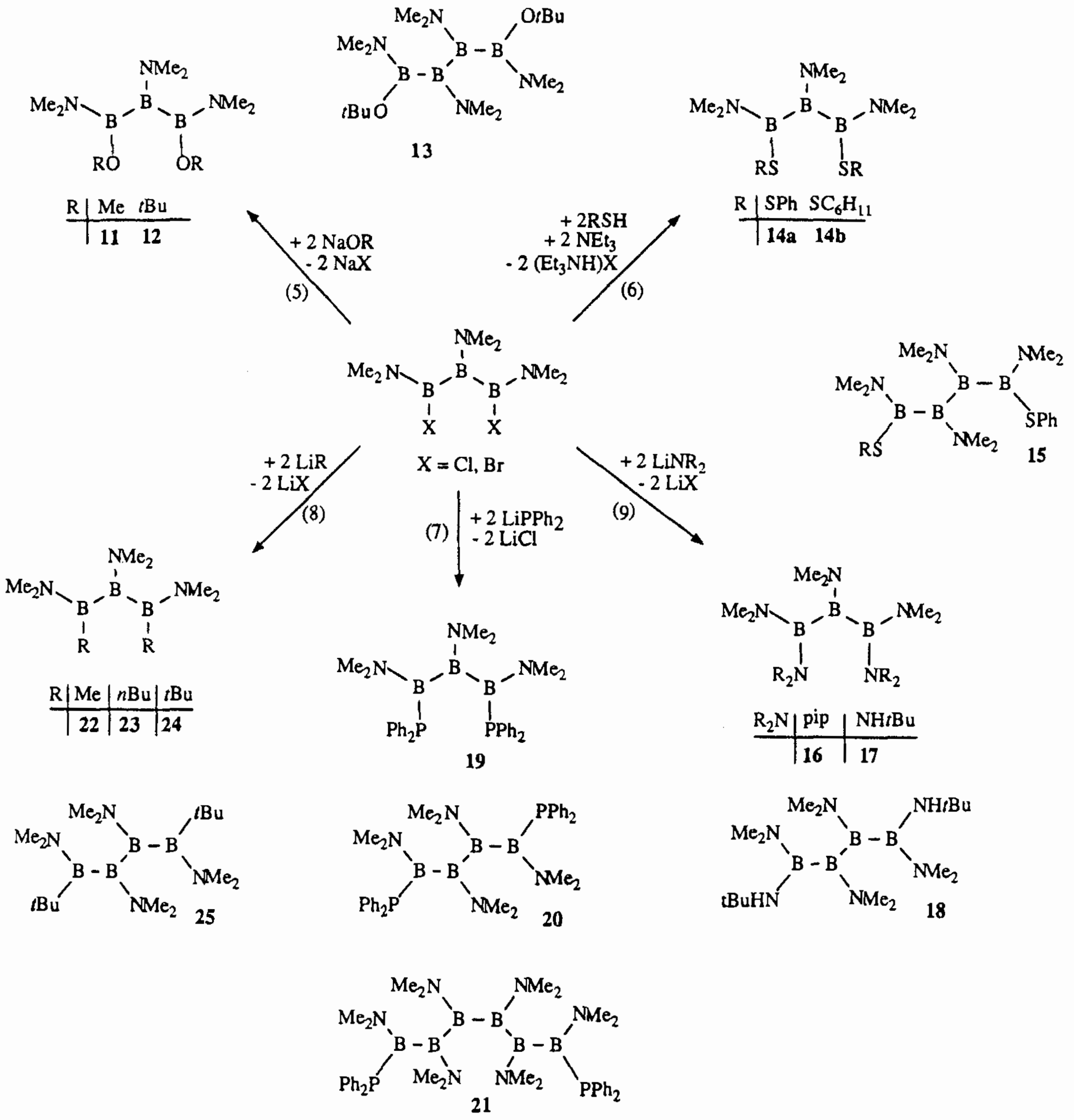
The halogen atoms of **5**, **6**, and **8** can also be readily replaced by alkyl groups by allowing lithium organyls to react with **5** or **6**. Thus, the butyl compounds **23** to **25** are accessible in good yields but the preparation of the tris(dimethylamino)dimethyltriborane **22** from **5** and LiMe is accompanied by the formation of $B_2(NMe_2)_4$ indicating a base-catalyzed decomposition of **5**. This can be prevented by using **6** as the triborane(5) source. $SnMe_4$, which is a powerful methylating agent, did not react with either **5** or **8** to give **22** even under rigorous conditions. This is in accord with the relatively weak Lewis acidity of **5** and **8**.

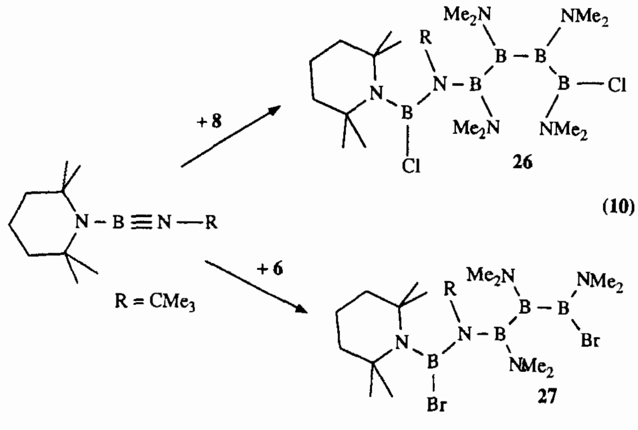
Reactions with the Amino Iminoborane tmp-B≡N−CMe$_3$

We have previously shown that diborane(4) derivatives $B_2(NMe_2)_2X_2$ (X = Cl, Br) add chemospecifically to the aminoiminoborane tmp−B≡N−CMe$_3$ (tmp = 2,2,6,6-tetramethylpiperidino) by haloboration of the BN triple bond. Irrespective of the molar ratio used only a 1:1 reaction occurred[8], and this was explained in terms of steric hindrance. Therefore, it was of interest to see whether this holds also for the higher homologues. Indeed, both **6** and **8** react smothly and quantitatively with tmp−B≡N−CMe$_3$ but only in a 1:1 ratio as depicted in eq. (10). This is rather surprising because the two B−Cl bonds in **6** and even more so in **8** are rather far apart from one another, and there should be no enhancement of the steric shielding at the second B-halogen moiety after the 1:1 addition had occurred. However, we have not tried to use rigorous conditions to stimulate this second B−Cl bond to add to the aminoiminoborane.

NMR Spectra

NMR data of the α,ω-disubstituted(dimethylamino)tri- and -tetraboranes are summarized in Table 2. The most relevant trend in the ^{11}B-NMR data of the triboranes(5) $B_3(NMe_2)_2X_2$ is that the halogen atoms (X = Cl, Br, I) induce only a small deshielding effect (ca. 3 ppm) on the two terminal boron nuclei as compared to **2**. However, the central boron atom becomes considerably better shielded by ca. 10 ppm, but this is not transmitted to the ^{13}C nuclei of the central Me_2N groups. While there is only a single signal for the terminal Me_2N groups in **2**, two are observed for the halides **5** to **7** as well as for the derivatives with X = OMe, SPh, Me, *t*Bu, Ph, and PPh_2 indicating hindered rotation about the respective B−N axis. On the other hand, there is not only a free rotation about the B−B bond but also about the terminal B−N bonds for X = NMe_2 and NH*t*Bu because only a single signal is observed for the terminal Me_2N groups.





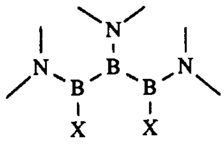
(10)

At least four borderline conformations for compounds of type $B_3(NMe_2)_3X_2$ can be envisaged if there is a hindered rotation about their B–B and B–N axis. These are depicted in formulae **A** to **D**. For **A** and **B** a planar arrangement of the skeletal atoms is assumed while **C** and **D** are representing examples where the trigonal plane of the terminal boron atoms is located perpendicularly to the B_3 plane. Since only two ^{13}C- and ^{1}H-NMR signals are present in the NMR spectra for the terminal Me_2N groups this would be in agreement with the conformer **A**. Conformer **B** requires four signals for these groups and conformer **C** as well as **D** two each. Thus, only the conformer **B** can be excluded. However, there is no reason to believe that only one conformer is present in solution, and, therefore, free rotation about the B–B bonds is indicated.

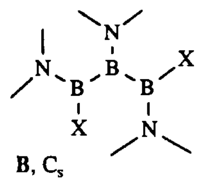
The two ^{13}C-NMR signals for the terminal Me_2N groups of the bis(phosphanyl)triborane **19** are doublets due to $^{31}P^{13}C$ coupling. The coupling constants $^{3}J(^{31}P^{11}B)$ are 7 and 24 Hz, respectively. Since the B–N bond of monoaminoboranes is isoelectronic with an olefinic CC double bond, we assign the doublet with the larger coupling to the C atom *cis* to the P atom, and the signal with the smaller coupling to the C atom *trans* to the phosphanyl group in analogy with similar couplings in olefins.

Table 2. NMR data of the α,ω-disubstituted (dimethylamino)tri-, -tetra- and -hexaboranes recorded in C_6D_6 solution at 28°C. The number of ^1H-NMR signals correspond with the suggested structures and are found in regions typical of the groups present

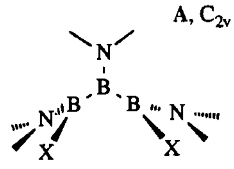
δ ^{11}B													
X =	Cl	Br	I	OMe	O*t*Bu	SPh	SC_6H_{11}	NMe_2	pip	NH*t*Bu	PPh_2	Me	*t*Bu
B(1,3)	40.0	40.3	40.0	35.1	34.0	46.7	47.7	36.9	37.0	34.1	52.8	51.3	53.7
B(2)	50.0	50.1	53.3	56.0	54.6	54.2	54.3	60.2	58.9	58.1	52.8	60.5	60.9
B(1,4)	42.3	42.1	39.4		33.8	44.8		37.6		32.8	57.5		53.7
B(2,3)	55.8	54.5	54.5		54.3	55.1		61.3		60.0	57.5		61.1
δ ^{13}C													
NMe_2(1,3)	42.4 37.6	40.2 43.4	45.4 45.6	35.1 39.4	35.7 39.9	39.8 42.6	40.0 40.5	41.4	41.5 41.6	39.5	42.9$^{*)}$ 45.7$^{+)}$	38.0 45.0	40.9 46.0
NMe_2(2)	47.7	45.3	46.2	46.4	46.4	46.0	45.9	46.1	46.4	46.3	46.4	46.1	46.5
NMe_2(1,4)	37.4 41.6	40.0 42.4	43.9 45.0		35.5 39.5	39.6 42.7				46.4 47.0	41.2$^{**)}$ 45.5$^{++)}$		41.0 46.2
NMe_2(2,3)	45.9 46.2	46.0 46.1	43.9 45.9		42.3 46.4	46.8 46.9				47.2$^{\#)}$	45.9 47.2		46.0



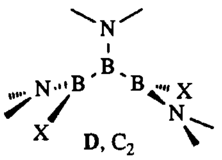
A, C_{2v}



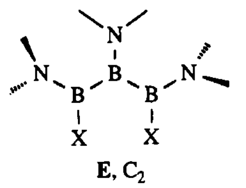
B, C_s



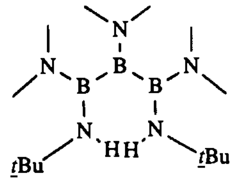
C, C_s



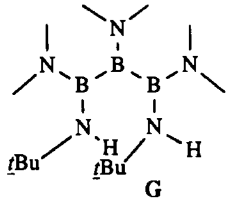
D, C_2



E, C_2



F



G

The shielding of the terminal boron atoms in $B_3(NMe_2)_3X_2$ molecules decreases in the order X = OR ≈ NHR > NR_2 > Hal > SR > PR_2 > R. This is in consonance with a similar order in aminoboranes $(Me_2N)B(R)X$[11] and reflects primarily the π-electron donor potential of the substituent X. The influence of the substituents X on the shielding of the central boron nucleus in this series of compounds varies with X in the order R < R_2N < NHR < OR < SR < I < PR_2 < Br < Cl. This indicates in a first approximation that the central boron nucleus is more strongly shielded as the negative inductive effect of the group X incrases, and this can be correlated with an increase of the strength of the terminal B–N bond.

The same trend can be noted for the tetraborane compounds $B_4(NMe_2)_4X_2$. The most noticeable difference to the NMR data of the triborane series is that the central Me_2N units give rise to two signals in the ^{13}C- and ^1H-NMR spectra. This is in accordance with a hindered rotation about the respective B–N bonds because the four methyl groups are then becoming pairwise chemically nonequivalent. This result is also an argument for hindered rotation about the central B–N bond in the triboranes $B_3(NMe_2)_3X_2$ although only a single signal is observed as expected for symmetry reasons.

To conclude, there is an additional point to be noted. Compound $B_4(NMe_2)_4(NHtBu)_2$ (**18**) shows two sets of signal for the *t*Bu group in the ^{13}C-NMR spectrum and two signals in the proton-NMR spectrum. If we assume free rotation about the B–B bonds then the *t*Bu groups should be magnetically equivalent. The two sets of signals, therefore, require the presence of two nonequivalent NH*t*Bu groups. If there is hindered rotation about the B–N bond of the NH*t*Bu group then two orientations of the *t*Bu group are possible as shown in formulae **F** and **G**. In general, the NMR spectra are in accord with the suggested configuration but they do provide only limited information on the conformation of these molecules at ambient temperature.

X-Ray Structural Investigations

The range of new electron-precise triborane(5) and tetraborane(6) derivatives made it desirable to gain more information on their structure than can be derived from their NMR data. Since many of the new compounds crystallize well we subjected a selected number of these compounds to a crystal structure analysis.

Relevant bonding parameters are summarized in Table 3, and plots of molecular structures are presented in Figures 1 to 8. Inspection reveals that the symmetry of the triborane(5) derivative is precisely or approximately (compound **14a**) that of point group C_2.

Table 3. Selected bond lengths and bond angles of the triboranes **6**, **7**, **12**, **14a**, **17**, and **24**. Estimated standard deviations are given in parenthesis. In the case of compounds **6**, **7**, and **17** data for both independent molecules are presented. [x] These data refer to bonds and angles subtending at atom B3

X	Br	I	O*t*Bu	SPh	NH*t*Bu	*t*Bu
Bond lengths (in Å)						
B1-B2	1.69(1) 1.68(1)	1.703(7) 1.704(7)	1.755(5)	1.719(3)	1.740(3)	1.732(3)
B2-B3[a)]	1.69(1) 1.68(1)	1.703(7) 1.704(7)	1.755(3)	1.715(3)	1.740(3)	1.732(3)
B1-N1	1.38(1) 1.35(2)	1.354(8) 1.332(8)	1.427(5)	1.384(3) 1.394(3)[x]	1.430(3)	1.405(3)
B1-X	1.99(1) 2.00(1)	2.224(6) 2.237(6)	1.396(5)	1.864(2) 1.849(2)[x]	1.424(3)	1.622(4)
B2-N2	1.38(2) 1.40(2)	1.36(1) 1.376(9)	1.408(7)	1.385(3)	1.410(4)	1.401(6)
Bond angles (in °)						
X-B1-N1	117.7(8) 116.4(8)	118.9(4) 117.8(4)	111.2(3)	114.4(2) 114.6(1)[x]	114.8(2)	120.4(2)
X-B1-B2	112.9(5) 112.6(7)	110.6(3) 109.7(3)	129.1(3)	119.6(1) 122.2(1)	126.8(2)	120.4(2)
N1-B1-B2	129.4(8) 130.9(10)	130.5(5) 132.5(4)	119.7(3)	122.8(2)	118.4(2)	119.1(2)
B1-B2-B3[a)]	119.4(11) 119.1(10)	116.8(6) 117.5(6)	126.7(4)	114.2(2)	127.6(3)	121.1(3)
B1-B2-N2	120.5(6) 120.3(6)	121.6(3) 121.3(3)	116.6(2)	123.3(2)	116.2(1)	119.4(1)
B3-B2-N2	120.3(6) 120.3(6)	121.6(3) 121.3(3)	116.6(2)	122.5(2)	116.2(1)	119.4(1)
B-X-C			130.7(4)	105.2(2) 104.9(2)[x]	123.5(2)	

Another general feature displayed by the molecular structures is the orientation of the Me_2N groups to one another. Thus, all $(C_2N)B$ skeletons are not only perfectly or almost planar, providing optimal conditions for strong BN-π bonding, but are oriented in such a manner that they approach orthogonality to one another. The interplanar angles range from 67.8 to 104.6° for compounds in Figures 1 to 5. In the case of the bromide **6** and the iodide **7** there are two independent molecules in the unit cell which differ only marginally in their bonding parameters but considerably by the orientation of their C_2NB places to one another. The interplanar angles are 94.0 and 79.2° in **6** and 104.6 and 95.8° in **7**.

It should also be noted that the B–N bond length of the central $BNMe_2$ unit remains virtually unaffected within the series of compounds $B_3(NMe_2)_3X_2$ where the shortest B–N bond is found for the iodide **7**. In contrast, the B–N bond lengths of the terminal Me_2N groups show a definite dependence on the nature of the substituent X and they increase along the series for X = I < SPh < CMe_3 < $OCMe_3$ ≈ $NHCMe_3$. In the case of the first three members of this series it is the decreasing –I effect that weakens the B–N bond, while for the last two compounds the –I effect of X is overruled by π-bonding effects. Associated with these effects is a change in the B1–B2–B3 bond angle which opens from 112° found for the thio compound **14** to 127° in the *tert*-butoxy derivative **12**. This structural change may be due to the increased electron density at the terminal boron atoms which should lead to an increased repulsion between the adjacent boron atoms the higher the total charge is at the terminal boron atoms.

Steric factors influence the size of the B–X–C bond angle. Thus, the B–O–C bond angle is fairly large (130.7°) for an oxygen atom assumed to be sp^2-hybridized, and this may be taken as evidence for BO-π bonding. That this kind of bonding plays a part becomes apparent by comparing

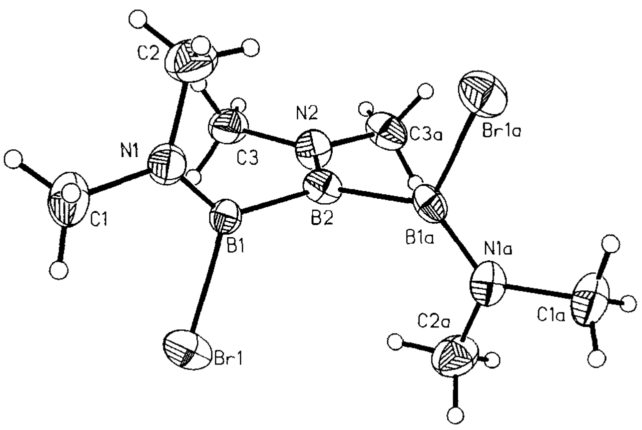


Figure 1. ORTEP-type representation of the molecular structure of $B_3(NMe_3)_3Br_2$ (**6**) in the crystal. Shown is one of the two crystallographically independent molecules. Thermal ellipsoids are represented at a 25% probability level

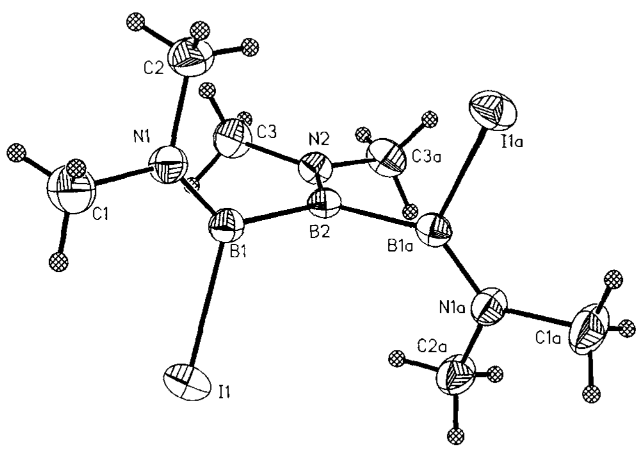


Figure 2. ORTEP-type representation of the molecular structure of $B_3(NMe_3)_3I_2$ (**7**) in the crystal. Shown is one of the two crystallographically independent molecules. Thermal ellipsoids are represented at a 25% probability level

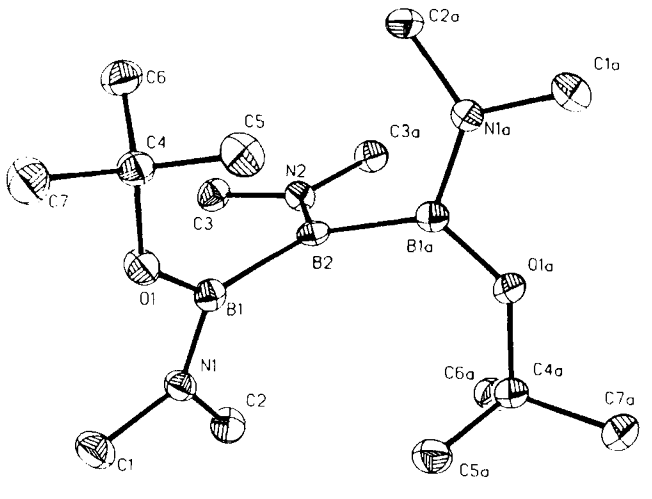


Figure 3. ORTEP-type representation of the molecular structure of $B_3(NMe_2)_3(OtBu)_2$ (**12**). Thermal ellipsoids are represented at a 25% probability level

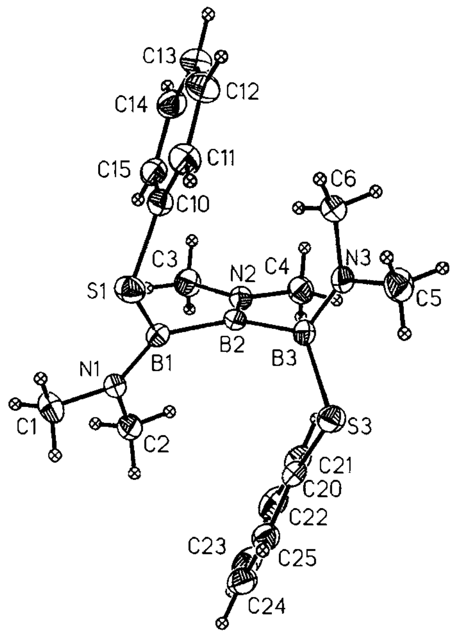


Figure 4. ORTEP-type representation of the molecular structure of $B_3(NMe_2)_3(SPh)_2$ (**14a**). Thermal ellipsoids are represented at a 25% probability level

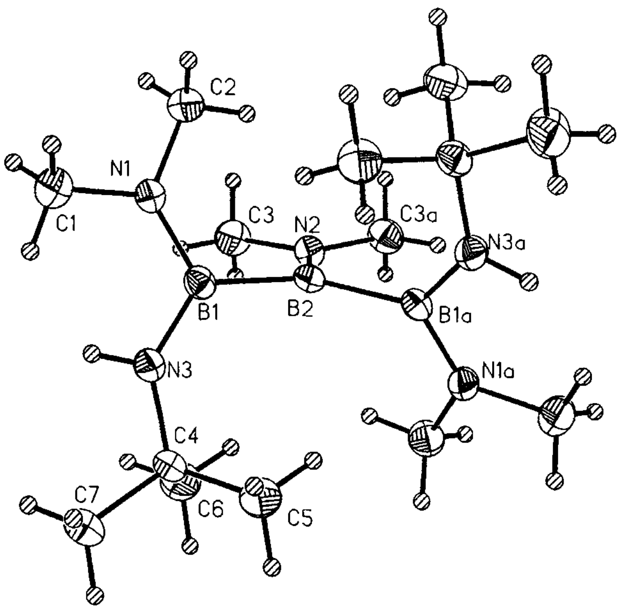


Figure 5. ORTEP-type representation of the molecular structure of $B_3(NMe_2)_3(NHtBu)_2$ (**17**). Thermal ellipsoides are represented at a 25% probability level

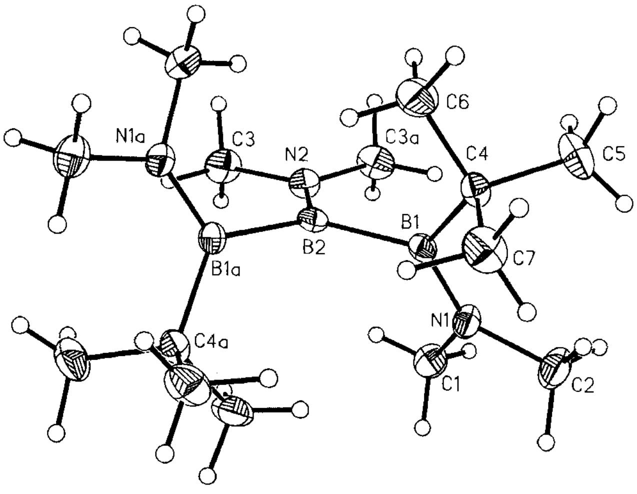


Figure 6. ORTEP-type representation of the molecular structure of $B_3(NMe_2)_3(tBu)_2$ (**24**). Thermal ellipsoids are represented at a 25% probability level

the B–O bond length of **12** (1.396 Å) with the B–O bond lengths in $B(OMe)_3$ (1.38 Å)[12], $(HBO)_3$ [1.376(2) Å][13] or p-$BrC_6H_4B(OH)_2$ (1.36 Å)[14]. Also, the B–S–C bond angles are rather wide (105.2°) but compare well with those found in $N[B(SMe)_2]_3$ (104.8–107.3°)[15].

Finally, a dependence of the B–B bond length on the nature of the group X is evident. The shortest bonds found are those in the iodide **7** (1.68 Å), the longest in the *tert*-butoxide **12** (1.75 Å). The B–B bond length in **7** equals that found for B_2F_4 [1.67(5) Å][16], while the B–B bond length of **12** exceeds those determined in B_2Cl_4 [1.75 Å][17] or or even $B_2(pip)_4$ (1.746 Å)[8]. Taking all known B–B bonds lengths of electron-precise polyborans into account[18], we note a variation of this parameter by 8%. The longest bonds are those determined for peramino-substituted compounds which exhibit obviously the weakest B–B bonds as a consequence of fairly high charge densities at the neighboring boron atoms.

In the tetraborane(6) derivative $B_4(NMe_2)_4(SPh)_2$ (**15**) (see Figure 7) we find two distinctly different B–B bond lengths: two short ones involving the terminal boron atoms (average 1.685 Å) and a longer one between the two central boron atoms (1.724 Å). All B–N bonds are rather short and fall in line with those observed for the triborane(5) derivatives. The dihedral angle B1–B2–B3–B4 is 53.3° and interplanar angles between C_2N planes range from 63.5 to 84.2°.

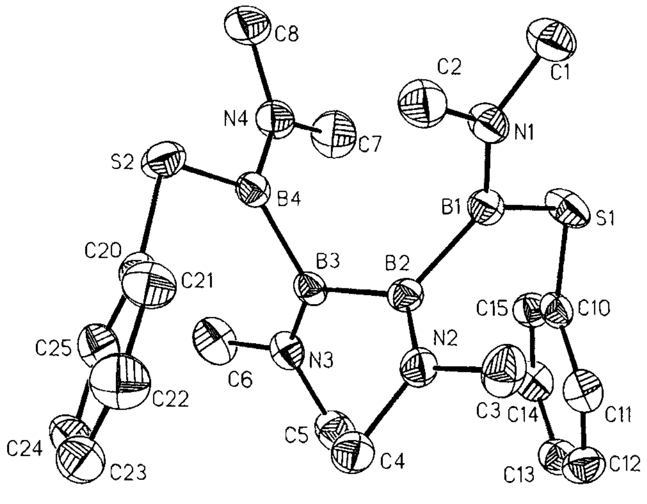


Figure 7. ORTEP-type representation of the molecular structure of $B_4(NMe_2)_4(SPh)_2$ (**15**). Thermal ellipsoids are represented at a 25% probability level. Selected bond angles [Å]: B1−B2 1.684(8), B2−B3 1.710(7), B3−B4 1.709(6), B1−N1 1.386(6), B2−N2 1.371(6), B3−N3 1.395(7), B4−N4 1.376(7), B1−S1 1.846(5), B4−S4 1.845(5). − Selected bond angles [°]: N1−B1−B2 121.6(4), S1−B1−B2 123.1(3), N1−B1−S1 114.7(4), B1−B2−N2 121.1(4), N2−B2−B3 125.6(4), B1−B2−B3 113.0(4), B2−B3−B4 117.7(4), N−B3−N2 123.3(3), B4−B3−N3 118.5(4), N4−B4−N3 124.6(4), S2−B4−B3 121.5(3), S2−B4−N4 113.8(4)

The molecular structure of **26** is presented in Figure 8. It shows a helical tetraboron chain terminated by a tmp(Cl)BN(CMe$_3$) group on one side of the molecule and a (Me$_2$N)ClB group on the other. N−B−B−N torsion angles range from 63.2 to 74.8°, and the dihedral angle comprising the tetraboron chain is 87.3°. The B−B bonds cover distances from 1.706 to 1.737(5) Å, and these lengths are comparable with those found in $B_4(NMe_2)_4(SPh)_2$. B−N bond lengths to Me$_2$N groups in the B$_4$ chain of **26** vary from 1.378 to 1.418(5) Å with the shortest B−N bond found at atom B4, a terminal boron atom which also carries a Cl atom. However, the B−N bond which extends from the tetraborane chain to the *tert*-butylamino group is rather long (1.548 Å). This can be rationalized with the almost perpendicular orientation of the plane B1−N−C9−Cl to the plane B−Cl−N20. Consequently no BN-π bonding is involved in this B−N bond. Also the the bonding parameters for the diaminoboron chloride unit at atom B1 are of interest. We note a short and a long BN bond, the longer one is directed to the tetramethylpiperidino group [1.451(5) Å], the shorter one [1.392(5) Å] to the *tert*-butylamino group. Again, this is a consequence of the different dihedral angles.

Therefore, the tendency of the Me$_2$NB groups to arrange themselves in a more or less perpendicular array is the most significant structural element in (dimethylamino)polyboranes. Consequently, there is no π conjugation along their chain of boron atoms.

MNDO Calculations

In order to find out what kind of conformation is preferred by aminopolyboranes we decided to study

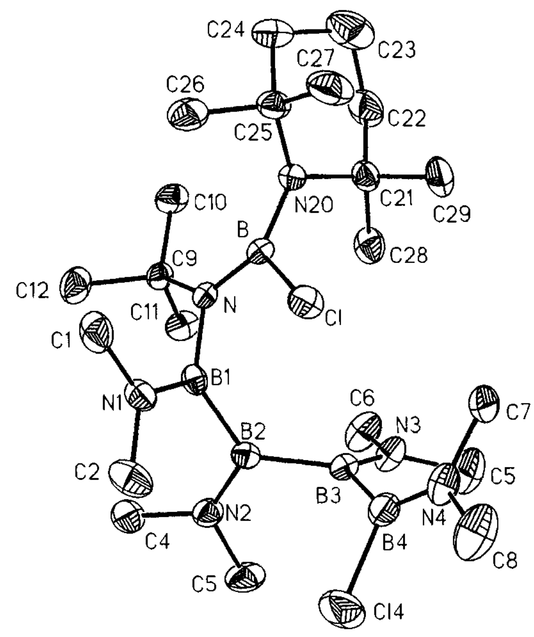


Figure 8. ORTEP representation of the molecular structure of **26** in the crystal. Thermal ellipsoids are represented at a 25% probability. Selected bond lengths [Å]: Cl−B 1.870(4), Cl4−B4 1.809(5), N20−B 1.451(4), N−B 1.392(4), N−B1 1.548(4), B1−B2 1.737(5), B2−B3 1.725(5), B3−B4 1.706(6), B1−N1 1.394(5), B2−N2 1.418(5), B3−N3 1.397(5), B4−N4 1.378(5). − Selected bond angles [°]: Cl−B−N20 115.5(2), Cl−B−N 111.5(2), N−B1−N20 132.9(3), B−N−B1 116.5(2), N1−B1−N 117.9(3), N−B1−B2 122.1(3), B1−B2−B3 123.0(3), B2−B3−B4 118.3(3), B2−B3−N3 122.1(3), N1−B1−B2 120.0(3), N1−B1−N 117.9(3), N2−B2−B1 120.2(3), N2−B2−B3 116.6(3), N3−B3−B4 119.1(3), N4−B4−B3 132.0(4), B3−B4−Cl4 113.2(3), Cl4−B4−N4 114.8(3)

$B_n(NH_2)_nX_2$ compounds as models by MNDO methods[19]. Calculations on a more advanced level of theory will be reported later.

The fist model compound that we looked at was B_2H_4. Irrespective of the starting geometry the minimum on the energy hypersurface is a molecule with D_{2h} symmetry. Closer to the adressed problem is the model compound $B_2(NH_2)_4$. This molecule adopts also D_{2d} symmetry, and both the boron and the nitrogen atoms show a planar coordination sphere which allows optimal conditions for BN-π bonding. Consequently, there is no π bonding between the adjacent boron atoms. The heat of formation is calculated as $\Delta H^f_{25} = -87.7$ kcal/mol. Thus, $B_2(NH_2)_4$ is a stable molecule in contrast to B_2H_4 ($\Delta H^f_{25} = 13.7$ kcal/mol) due to strong B−N bonds. The calculated B−N bond length is 1.411 Å which fits well the experimental values for bis(amino)boranes[18]. Compared to B_2H_4 ($d_{B-B} = 1.57$ Å) we find a comparatively long boron-boron bond of 1.694 Å. This is within the region of B−B bond lengths determined experimentally[18].

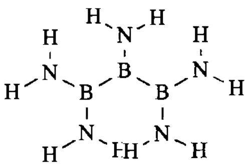
Relevant data obtained for the most stable conformation by MNDO calculations for $B_3(NH_2)_3X_2$ model compounds are listed in Table 4. Data for two other conformers of $B_3(NH_2)_5$ are shown as formulae **28** and **29**. Irrespective of the relative orientation of the amino groups it is evident that once again the dihedral angles N−B−B−N are close to 90°. As expected, the B−N bond length increases by ro-

Table 4. Selected data from MNDO calculation on electron-precise model triboranes

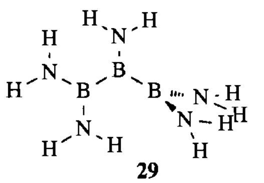
Molecule	Point group symmetry	d(B-B) Å	d(B-N) Å		τ(NBBN) (in °)	ΔH^f_0 kcal/mol
B_2H_4	D_{2d}	1.572			90[+)]	+13.7
$B_2(NH_2)_4$	D_{2d}	1.694	1.411		90.2	-87.7
$B_3(NH_2)_5$	C_{2v}	1.715	1.423[a]	1.386[b]	0	-94.6
	x)	1.700 1.688	1.423[a] 1.428 1.411 1.420	1.380[b]	1	-106.2
	y)	1.683 1.682	1.418 1.412 1.425 1.420	1.377	89.4	-111.0
$B_3(NH_2)_3(OH)_2$	y)	1.690 1.689	1.414 1.416	1.375	71.6	-222.4
$B_3(NH_2)_3Me_2$	y)	1.674 1.679	1.388 1.387	1.381	79.4	-102.4

[a)] Terminal NH_2 groups. – [b)] Internal NH_2 group. – [+)] τ(HBBH). – [x)] Geometry optimized with free rotation about one B–B axis. – [y)] Geometry optimized.

tating the planar H_2N groups into a perpendicular orientation to the N_2BB plane, and this also results in a shortening of the boron-boron bond. In line with experimental data is the result that the central BN bond is shorter than those of the terminal BN bonds, a typical feature of a monoaminoborane unit. In principle, the same result is obtained for $B_4(NH_2)_6$: the N–B–B–N dihedral angle is 90°, the terminal BN bonds are longer than the central ones, and the BB bond lengths are slightly longer for the terminal boron atoms as compared with the central BB bond. Indeed, there is a fair agreement between the calculated bonding parameters and those found for $B_n(NMe_2)_n(SPh)_2$ except for the definitely smaller dihedral angles in the real molecules.



28



29

We also studied the influence of various substituents on the structure of $B_3(NH_2)_3X_2$ compounds (X = F, OH, NH_2, CH_3). According to the MNDO calculations $B_3(NH_2)_3(OH)_2$ shows the longest and $B_3(NH_2)_3(CH_3)_2$ the shortest B–B bond length. In contrast to $B_3(NH_2)_5$ with a calculated N–B–B–N dihedral angle of 89.4° this angle decreases for X = CH_3 (79.4°) to X = OH (71.6°) considerably. Thus, there seems to be no direct correlation between the B–B bond length and the N–B–B–N dihedral angle.

All triaminotriborane(5) molecules described here are thermodynamically stable as demonstrated by negative heats of formation. The excellent stability of $B_3(NH_2)_3F_2$ is of course the consequence of the strong BF bond.

Discussion

As has been shown previously[5,7], amino groups stabilize electron-precise polyboranes due to BN-π bonding which reduces the electron deficiency at the boron atoms. MNDO calculations on some model compounds demonstrate that these molecules are thermodynamically stable, but it is also well-known that the electron-precise diborane(4) compounds tend to disproportionate into BX_3 and (formally) polymeric BX boranes.

The aminotri- and -tetraboranes studied show conformations that are reminiscent of diborane(4) derivatives. B_2Cl_4, for instance, is known to adopt D_{2d} symmetry in the gas phase[21] but is planar in the solid state (D_{2h} point group symmetry)[17]. B_2F_4 is another molecule with D_{2d} symmetry[16]. On the other hand, the structures of tetraaminodiborane(4) derivatives all have or approach C_2 symmetry as described by formula E[8,18]. All molecules exhibit rather long BB bonds. If amino groups are absent as exemplified by tetraorganyldiboranes(4), then we find a dihedral angle C–B–B–C of 85° for B_2mes_3Ph[22] and of 89.8° for $B_2(tBu)_2(fl)_2$ (fl = 9-fluorenyl)[23]. However, the orientation of the two C_2B groups in these molecules very close to orthogonality may result from the steric demand of the rather large organic groups and may not be of electronic origin, but corresponds with the results of calculations by MNDO and ab initio[20] methods for B_2H_4.

It is evident that calculations on the model compounds described here on advanced levels are required in order to get a better understanding of the various electronic and steric effects that determine the structures of electron-precise polyboranes.

The reactions of the (dimethylamino)polyboron dihalides correspond with those of "normal" aminoboron halides as far as nucleophilic substitutions are concerned. Attempts to replace also the central Me_2N groups by halogen atoms, e.g. with electrophilic reagents, have so far met with failure. Obviously, the electrophilic reagents cannot attack at this site due to the strongly reduced basicity of the nitrogen centers at these positions as a consequence of strong BN-π bonding. On the other hand, reactions of $B_4(NMe_2)X_2$ with the aminoiminoborane tmpB≡$NCMe_3$ are similar to aminoboron halides[24]: attack occurs only at the boron-halogen bond in a 1:1 ratio. However, we cannot rationalize the failure of reactions in a 2:1 molar ratio. Nevertheless, the reactions reported in this work indicate that the aminopolyboron halides are versatile reagents, and we have used them in the synthesis of boron-rich heterocycles. This work will be reported shortly.

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Experimental

All experiments required anhydrous and oxygen-free conditions. Therefore, the Schlenk technique was employed. Preparations of the (dimethylamino)polyboranes followed the established procedure[5], but was modified as described later. All other reagents were purified by distillation prior to use. Anhydrous solvents were stored under dry nitrogen. – NMR: Bruker WP 200. – MS: Varian CH7, 70 eV. – IR: Perkin-Elmer model 325.

Preparation of the (Dimethylamino)polyboranes: Pentane (400 ml) was placed in a three-necked flask fitted with a vacuum-tight stirrer, a reflux condensor made of stainless steel, a dropping funnel with a pressure equalizer, and a valve for flushing the flask with argon or nitrogen. The flask itself was put into a metal tub as an additional safety measure. After the flask had been flushed with nitrogen (or argon) a constant flow of approximately two bubbles per second was maintained. Then 56 ml of liquid $Na/K_{2.8}$ alloy was transferred into the flask by means of a syringe. Vigorous stirring was then started, and 10 ml of a mixture of 75.3 g of $B_2(NMe_2)_3Cl$ (398 mmol) and 53.5 g of $B(NMe_2)_2Cl$ (398 mmol) was added. It took 10 to 20 min until the exothermic reaction started as noted by a color change of the alloy to almost black and shortly thereafter by the refluxing pentane. When the boiling seemed to cease the rest of the aminoboron chloride mixture was added in such a manner that refluxing was maintained. The dehalogenation should be finished within approximately 2 h. Stirring was then continued for an additional 4 h. At this stage of the reaction a 1-ml portion of the solution was tested for absence of chloride. If the test was not negative then stirring had to be continued and the suspension had to be kept at reflux until dehalogenation was quantitative. The solid blackblue material was removed by filtration through a dry, nitrogen-filled glass frit (G3) and washed 5 times with 50 ml of pentane. Pentane was removed from the combined solutions in vacuo or distilled off at normal pressure. The remaining viscous brown residue was subjected to fractional distillation by using a 20-cm Vigreux column. The following fractions were obtained: 1) 3.0 g (21 mmol, 5%) of $B(NMe_2)_3$, b.p. 25°C/50 Torr; 2) 6.7 g (33.7 mmol, 8.5%) of $B_2(NMe_2)_4$, b.p. 52–58°C/10 Torr; 3) 22.7 g (89.9 mmol, 23%) of $B_3(NMe_2)_5$ (**2**), b.p. 75–85°C/0.01 Torr. Finally, the residue was distilled by means of a short-path distillation apparatus (Normag), and 3.2 g (10.5 mmol, 3%) of $B_4(NMe_2)_6$ (**1**), b.p. 90–110°C/0.001 Torr, and 0.90 g (2.1 mmol, 0.5%) of $B_6(NMe_2)_8$ (**4**), b.p. 115–125°C/0.001 Torr, were isolated.

It is advisable to collect the residues from various preparations of (dimethylamino)polyboranes and subject them together to a short-path distillation for getting larger quantities of **1** and particularly **4**. Usually, these compounds are pure as demonstrated by their NMR spectra, but they may either be redistilled or crystallized from pentane at −78°C.

Hexakis(dimethylamino)tetraborane(6) (**1**): In analogy to the previous experiment a 2-l flask was charged with 450 ml of pentane and 17 g of liquid Na/K alloy. Stirring was then started, and 10 ml of a solution of 70.1 g of $B_2(NMe_2)_3Br$ (300 mmol) in 70 ml of pentane was added. The reaction set in within 5 min. The rest of the solution was then added in such a manner that refluxing was maintained. After 5 h the solid material was allowed to settle and the yellow solution tested for absence of bromide. In this case workup as described in the previous experiment was started; otherwise, the suspension was heated to reflux with vigorous stirring for 3 h. Fractional distillation gave 5 g of $B(NMe_2)_3$, 7 g of $B_2(NMe_2)_4$ (b.p. 25–30°C/1 Torr), and 35.6 g of **1** (38%), b.p. 90–95°C/10^{-4} Torr. The material solidified within a short time, m.p. 97–100°C (ref.[5] 98–100°C).

Dimethylammonium Tetraphenoxyborate: A solution of phenol in benzene (1.64 g, 17.4 ml) was dropped into a stirred solution of $B_3(NMe_2)_5$ (0.88 g, 3.5 mmol) in 20 ml of benzene. Gas bubbles formed as the reaction proceeded, and a solid precipitated. The solid was separated by filtration after 6 h. Yield: 1.65 g of $(Me_2NH_2)[B(OPh)_4]$ (92% calc. for PhOH). Benzene was evaporated from the filtrate. The off-white residue was dissolved in CH_2Cl_2 and contained $B(OPh)_3$ ($\delta^{11}B$ = 15.7) besides a small amount of $(Me_2NH_2)[B(OPh)_4]$ ($\delta^{11}B$ = 1.4). – $C_{26}H_{28}BNO_4$ (429.3): calcd. C 72.74, H 6.58, N 3.27; found C 71.77, H 6.67, N 3.15.

1,3-Dichloro-1,2,3-tris(dimethylamino)triborane(5) (**5**)

a) $B_3(NMe_2)_5$ (**2**) (8.61 g, 43.1 mmol) was dissolved in 100 ml of benzene, and a solution of $EtBCl_2$ (7.55 g, 68.1 mmol) in 25 ml of benzene was added dropwise with vigorous stirring. After stirring had been continued for 14 h all volatile products were removed in vacuo. The condensate contained benzene and $EtB(Cl)NMe_2$, $\delta^{11}B = -49$[11]. Fractional distillation of the oily amber-colored residue gave **5** as a viscous liquid. Yield: 3.79 g (48%), b.p. 76–80°C/10^{-3} Torr. The nonvolatile material, 1.9 g, was a light brown-colored viscous material which was not further investigated.

b) BCl_3 (2.1 ml, 24.5 mmol) was condensed into a stirred solution of **2** (12.36 g, 48.9 mmol) in 100 ml of hexane at 0°C. An exothermic reaction occurred which was controlled by means of an ice bath. After all BCl_3 had been added the mixture was allowed to attain ambient temp. within 30 min followed by continuous stirring for 1 h. All volatile material was then removed in vacuo [the condensate consisting of hexane and $ClB(NMe_2)_2$] and **5** recovered from the residue at b.p. 73–82°C/10^{-2} Torr, yield 8.62 g (75%). – MS (^{11}B and ^{35}Cl), *m/z* (%): 235 (25) $[M^{+\cdot}]$, 220 (52) $[M - Me]^+$, 145 (84) $[M - (Me_2N)_2BCl)^{+\bullet}]$, 165 (74) $[(M - 2\ Cl)^+]$, 90 (100) $[B(NMe_2)Cl^{+\bullet}]$, correct isotope pattern. – $C_6H_{18}B_3Cl_2N_3$ (235.6): calcd. C 30.59, H 7.70, N 17.84; found C 30.20, H 7.46, N 17.33.

1,3-Dibromo-1,2,3-tris(dimethylamino)triborane(5) (**6**): $B_3(NMe_2)_5$ (**2**) (11.6 g, 46 mmol) was dissolved in 40 ml of *n*-hexane, and a solution of $MeBBr_2$ (8.8 ml, 92 mmol) in 10 ml of *n*-hexane was added with stirring. An exothermic reaction started which was controlled by cooling with a water bath. After stirring had been continued overnight the solvent and $MeBBr(NMe_2)$ ($\delta^{11}B$ = 37.8[11], b.p. 42°C/22 Torr) were condensed into a cold trap in vacuo. Distillation of the yellow viscous residue gave 6.8 g of **6** (21 mmol, 46%), b.p. 80–90°C/10^{-2} Torr. The compound crystallized quickly. Recrystallization of the solid mass from cold pentane afforded crystals of **6**, m.p. 93–95°C. – $C_6H_{18}B_3Br_2N_3$ (324.5): calcd. C 22.12, H 5.59, N 12.95; found C 22.33, H 6.00, N 12.52.

1,2,3-Tris(dimethylamino)-1,3-diiodotriborane(5) (**7**): A solution of $MeBI_2$ (1.09 g, 3.9 mmol) in 10 ml of benzene was dropped slowly into a stirred solution of 0.49 g of $B_3(NMe_2)_5$ (**2**) (1.95 mmol). The solution first turned yellow, then became turbid. Crystals settled from the solution which redissolved after about 10 min. Stirring was continued for 4 h, and the volatile products were condensed at 10^{-1} Torr in a cold trap. The volatile material consisted of solvent and $MeB(NMe_2)I$, $\delta^{11}B = 35$[11]. Most of the remaining residue dissolved in 40 ml of hexane. Insoluble material (0.1 g of a red solid) was removed by filtration and the clear filtrate cooled to −18°C. 0.63 g of **7** (77%) separated within 18 h as cube-shaped crystals, m.p. 126–127°C. – MS (^{11}B), *m/z* (%): 419 (9) $[M^{+\bullet}]$, 404 (5) $[M - Me]^+$, 375 (5) $[M - NMe_2]^+$, 292 (100) $[M - I]^+$, 248 (44) $[M - B(NMe_2)I]^+$, 237 (30) $[B_2(NMe_2)_2I]^+$, 182 (42) $[Me_2BI]^+$. – $C_6H_{18}B_3I_2N_3$ (418.5): calcd. C 17.22, H 4.34, N 14.04; found C 17.32, H 4.43, N 13.76.

1,4-Dichloro-1,2,3,4-tetrakis(dimethylamino)tetraborane(6) (**8**): BCl_3 (3.12 ml, 36 mmol) was condensed into a stirred solution of $B_4(NMe_2)_6$ (**1**) (10.58 g, 36 mmol) in 75 ml of toluene at 0°C. After 1 h the solution was allowed to attain ambient temp. within 30 min. Toluene was then evaporated at 10 Torr from the bright yellow solution and the residue subjected to distilaltion at 10^{-2} Torr. After $(Me_2N)_2BCl$ had been condensed at −78°C the product, 7.35 g of **8** (74%), was distilled at b.p. 98–111°C/0.1 Torr (100–105°C/10^{-2} Torr on redistillation) as a colorless viscous liquid. The liquid was dissolved in 50 ml of pentane and the solution cooled to −78°C. Within 4 weeks 6.87 g of **8** (69%) separated as colorless crystals, m.p. 109–111°C. – $C_8H_{24}B_4Cl_2N_4$ (290.5): calcd. C 33.08, H 8.33, N 19.26; found C 31.79, H 8.71, N 19.02.

1,4-Dibrom-1,2,3,4-tetrakis(dimethylamino)tetraborane(6) (**9**): A solution of 3.64 ml of BBr_3 in 10 ml of benzene was dropped into a solution of 11.8 g of $B_4(NMe_2)_6$ (**1**) (38.4 mmol) in 100 ml of benzene at 0°C with continuous stirring. After 1 h the solution was allowed to attain ambient temp. (30 min), and benzene was removed from the light yellow-colored solution at 10 Torr. A viscous brownish-colored residue remained from which $(Me_2N)_2BBr$ was distilled at ≈25°C/10^{-1} Torr. The nonvolatile material was then dissolved in 50 ml of *n*-hexane. Within 9 d at −78°C crystals separated which were isolated by filtration (G3 frit). Yield: 11.89 g of **9** (82%), m.p. 137–139°C. – Alternatively, **9** can also be isolated from the residue by distillation at b.p. 115–117°C/10^{-2} Torr. – $C_8H_{24}B_4Br_2N_4$ (379.4): calcd. C 25.33, H 6.38, N 14.77; found C 25.06, H 6.57, N 14.70.

1,2,3,4-Tetrakis(dimethylamino)-1,4-diiodotetraborane(6) (**10**): $B_4(NMe_2)_6$ (**1**) (0.44 g, 1.4 mmol) was dissolved in 10 ml of benzene, and a solution of 0.88 g of $MeBI_2$ (2.9 mmol) in 10 ml of benzene was added with stirring. The light brown solution became almost colorless, and a precipitate formed which went into solution as stirring was continued for 30 min. After 2 h all volatile material was condensed at 10^{-3} Torr into a cold trap, and $MeBI(NMe_2)$ was detected in the condensate by ^{11}B−NMR spectroscopy ($\delta^{11}B$ = 35.2)[11]. The off-white residue was then treated with 20 ml of benzene/hexane (1:1). This left an off-white powder, m.p. 160–163°C, yield: 0.35 g of **10** (48%). Compound **10** is sparingly soluble in boiling toluene and insoluble in boiling ether or hexane. – $C_8H_{24}B_2I_2N_4$ (473.4): calcd. C 20.30, H 5.11, N 11.84; found C 19.15, H 4.58, N 11.02.

1,2,3-Tris(dimethylamino)-1,3-dimethoxy-triborane(5) (**11**): Prepared in analogy to **12** from $B_3(NMe_2)_3Br_2$ (**6**) (1.12 g, 4.35 mmol) in 30 ml of toluene and NaOMe (0.37 g, 6.85 mmol) in 10 ml of toluene. Workup after stirring overnight. Evaporation of the solvent left pure **11** as an oily residue, yield 0.73 g (93%). – $C_8H_{24}B_3N_3O_2$ (226.7): calcd. C 42.38, H 10.67, N 18.53; found C 42.27, H 10.54, N 17.63.

1,3-Di-tert-butoxy-1,2,3-tris(dimethylamino)triborane(5) (**12**): A suspension of $NaOCMe_3$ (0.87 g, 9 mmol) in 20 ml of *n*-hexane was added to a stirred solution of $B_3(NMe_2)_3Br_2$ (**6**) (1.62 g, 4.5 mmol) in 20 ml of *n*-hexane at −40°C. Almost no reaction could be detected by ^{11}B-NMR spectoscopy at this as well as at ambient temp. 3 ml of toluene was added at this time and stirring continued for 18 h. Then the insoluble material (1.0 g) was removed by filtration, and solvents were evaporated in vacuo from the filtrate. The residue was crystallized from 10 ml of *n*-hexane at −78°C. Yield: 1.05 g of **12** (75%), colorless needles, m.p. 82–84°C. – MS; *m/z* (%): 311 (4) $[M^{+\bullet}]$, 296 (5) $[M - Me]^+$, 254 (30) $[M - CMe_3]^+$, 238 (6) $[M - OCMe_3]^+$, 197 (100) $[C_7H_{22}B_3N_3O]^+$.

1,4-Di-tert-butoxy-1,2,3,4-tetrakis(dimethylamino)-tetraborane(6) (**13**): Prepared in analogy to **12** from 0.93 g of $B_4(NMe_2)_4Br_2$ (**9**) (2.45 mmol), dissolved in 30 ml of hexane, and 0.47 g of Na*Ot*Bu (4.9 mmol) in 20 ml of hexane. Yield: 0.70 g of **13** (78%); needles, m.p. 139–141°C. MS, *m/z* (%): 366 (5) $[M^{+\bullet}]$, 351 (15) $[M - Me]^+$, 309 (32) $[M - tBu]^+$, 252 (100) $[B_4(NMe_2)_4O_2]^+$, 236 (100) $[B_4(NMe_2)_4O]^+$, 128 (98) $[B(NMe_2)OtBu]^+$. – $C_{16}H_{42}B_4N_4O_2$ (365.8): calcd. C 52.24, H 11.57, N 15.32; found C 51.31, H 11.11, N 15.01.

1,2,3-Tris(dimethylamino)-1,3-bis(phenylthio)triborane(5) (**14a**): A solution of PhSH (1.06 g, 9.6 mmol) and NEt_3 (1.34 ml, 9.62 mmol) in 30 ml of cyclohexane was added to a well-stirred solution of 1.56 g of $B_3(NMe_2)_3Br_2$ (**6**) 4.8 mmol) in 50 ml of cyclohexane. A solid formed which was removed by filtration after 5 h. Cyclohexane was evaporated from the colorless solution in vacuo and the residue crystallized from pentane. Yield: 1.32 g of **14a** (72%), m.p. 70–73°C. – $C_{18}H_{28}B_3N_3S_2$ (383.0): calcd. C 56.45, H 7.37, N 10.97; found C 55.92, H 7.30, N 10.97.

1,3-Bis(cyclohexylthio)-1,2,3-tris(dimethylamino)triborane(5) (**14b**) was prepared as described for **14a** from $B_3(NMe_2)_3Br_2$ (**6**) (1.75 g, 5.4 mmol), cyclohexanethiol (1.25g, 10.8 mmol), and NEt_3 (1.09 g, 10.8 mmol) in 55 ml of hexane at −45°C. Stirring for 14 h at ambient temp. completed the reaction. Yield: 1.47 g of **14b** (69%) as a crystalline material from hexane/toluene (10:1), m.p. 86–88°C. – $C_{18}H_{40}B_3N_3S_2$ (395.0): calcd. C 54.72, H 10.20, N 10.65; found C 50.78, H 9.93, N 10.26.

1,2,3,4-Tetrakis(dimethylamino)-1,4-bis(phenylthio)tetraborane(6) (**15**): PhSH (9.67 g, 0.61 mmol) and NEt_3 (0.62 g, 6.1 mmol) were dissolved in 15 ml of toluene, and the solution was dropped into a stirred solution of $B_4(NMe_2)_4Br_2$ (**9**) (1.16 g, 3.06 mmol) in 45 ml of toluene. An insoluble material formed (1.23 g isolated) which was removed after 3 h of stirring. The solid which remained after the solvent had been evaporated in vacuo was crystallized from pentane/toluene (10:1). Yield: 1.20 g of **15** (89%). – MS, *m/z* (%): 362 (100) $[M - Ph]^+$, 306 (82) $[B_3(NMe_2)_3S_2Ph]^+$, 274 (11) $[B_3(NMe_2)_2SPh]^+$, 219 (32) $[B_2(NMe_2)_2SPh]^+$, 164 (41) $[B(NMe_2)SPh]^+$, 132 (74) $[B(NMe_2)Ph]^+$, 110 (88) $[B_2(NMe_2)_2]^+$. – $C_{20}H_{34}B_4N_4S_2$ (437.9): calcd. C 54.86, H 7.83, N 12.79; found C 53.15, H 7.54, N 12.08.

1,2,3-Tris(dimethylamino)-1,3-dipiperidinotriborane(5) (**16**): A solution of $B_3(NMe_2)_3Br_2$ (**6**) (1.65 g, 5.09 mmol) in 40 ml of cyclohexane was vigorously stirred, and a suspension of $LiNC_5H_{10}$ (0.93 g, 10.2 mmol) in 10 ml of cyclohexane was added within 20 min. Stirring was continued for 6 h. Then the solid material was removed by centrifugation (0.95 g) and the solvent evaporated (10^{-2} Torr). Compound **16** was left as an amber-colored oil. It was dissolved in a minimum amount of hexane. On cooling to −78°C **16** separated as a solid. Yield 1.20 g (71%). – $C_{16}H_{38}B_3N_5$ (332.95): calcd. C 57.72, H 11.50, N 21.03; found C 55.94, H 11.23, N 21.10.

1,3-Bis(tert-butylamino)-1,2,3-tris(dimethylamino)triborane(5) (**17**): A solution of $B_3(NMe_2)_3Br_2$ (**6**) (1.72 g, 5.3 mmol) in 20 ml of toluene was cooled to −78°C, and a solution of $LiNHCMe_3$ (1.84 g, 10.6 mmol) in 15 ml of toluene was added with stirring within 10 min. The mixture was then allowed to attain ambient temp. After 3 h the insoluble material was removed by centrifugation followed by evaporation of the solvent from the solution in vacuo. Crystallisation of the solid residue from pentane/toluene (1:1) by cooling to −78°C yielded 1.38 g of **18** (81%), m.p. 125–128°C. – MS, *m/z* (%): 309 (12) $[M^{+\bullet}]$, 294 (18) $[M - Me]^+$, 265 (18) $[M - NMe_2]^+$, 252 (92) $[M - CMe_3]^+$, 195 (90) $[M - 2CMe_3]^+$, 127 (100) $[Me_2NB(NHCMe_3)]^+$. – $C_{14}H_{38}B_3N_5$ (308.9): calcd. C 54.43, H 12.40, N 22.67; found C 54.57, H 12.58, N 22.51.

1,4-Bis(tert-butylamino)-1,2,3,4-tetrakis(dimethylamino)-tetraborane(6) (**18**): A solution of $B_4(NMe_2)_4Br_2$ (**9**) (1.21 g, 3.19

mmol) in 45 ml of *n*-hexane was cooled to −60°C. A solution of 510 mg of LiNH*t*Bu (6.45 mmol) in 15 ml of hexane was added within 10 min. After the suspension had reached ambient temp., stirring was continued for an additional 5 h. Then the insoluble material was removed by centrifugation and the solvent evaporated from the clear solution in vacuo. Recrystallization of the residue from pentane/toluene (10:1) at −78°C gave 700 mg of **19** (63%), m.p. 142−145°C. − MS, *m/z* (%): 364 (45) [$M^{+\bullet}$], 349 (44) [M − Me]$^+$, 320 (100) [M − NMe$_2$]$^+$, 307 (96) [M − *t*Bu]$^+$, 262 (97) [$B_4(NMe_2)_3NH_2$*t*Bu]$^+$, 257 (93) [$B_3(NMe_2)_3NH$*t*Bu]$^+$, 250 (92) [M − 2*t*Bu]$^+$, 237 (87) [$B_3(NMe_2)_3NH$*t*Bu]$^+$, 207 (93) [$B_3(NMe_2)_2NH$*t*Bu], 165 (64) [$B_3(NMe_2)_3$]$^+$, 127 (100) [$B(NMe_2)NH$*t*Bu]$^+$. − $C_{16}H_{44}B_4N_6$ (363.8): calcd. C 52.82, H 12.19, N 23.10; found C 51.85, H 12.21, N 22.43.

1,2,3-Tris(dimethylamino)-1,3-bis(diphenylphosphanyl)-triborane(5) (**19**): Prepared in analogy to **20** from $B_3(NMe_3)_2Br_2$ (**6**) (1.71 g, 5.27 mmol) and $LiPPh_2$ (2.05 g, 10.7 mmol) in 65 ml of hexane. Addition at −78°C, stirring at ambient temp. for 2 d. Yield: 0.84 g of **19** (30%), m.p. 91−93°C. − $C_{30}H_{38}B_3N_3P_2$ (535.0): calcd. C 67.35, H 7.16; found C 67.25, H 7.05.

1,2,3,4-Tetrakis(dimethylamino)-1,4-bis(diphenylphosphanyl)tetraborane(6) (**20**): At −60°C a suspension of 0.98 g of $LiPPh_2$ (5.12 mmol) in 15 ml of toluene was added to a suspension of $B_4(NMe_2)_4Br_2$ (**9**) (0.97 g, 2.5 mmol) in 30 ml of toluene. After stirring for 2 d at ambient temp. the insoluble material was removed by filtration from a light yellow solution. Then the solvent was evaporated from the filtrate in vacuo and the yellow residue dissolved in 15 ml of pentane. Crystals separated from the solution at −78°C within 14 d. They melted at about 0°C to give a yellow−colored oil. Yield: 0.86 g of **20** (57%). − $C_{32}H_{44}B_4N_4P_2$ (589.9): calcd. C 65.15, H 7.52, N 9.50; found: 61.58, H 7.79, N 9.77.

1,2,3,4,5,6-Hexakis(dimethylamino)-1,6-bis(diphenylphosphanyl)hexaborane(8) (**21**): As described for **20** 2.0 g of (4.1 mmol) in 65 ml of hexane was allowed to react with 1.6 g of $LiPPh_2$ in 50 ml of hexane at −78°C. After 6 d of stirring removal of solvent and crystallization of the residue at −78°C from hexane yielded 2.0 g of **21** (69%), m.p. ca. 20°C; yellow viscous oil. − $C_{36}H_{56}B_6N_6P_2$ (699.7): calcd. C 61.80, H 8.07, N 12.01; found C 59.93, H 7.93, N 11.87.

1,2,3-Tris(dimethylamino)-1,3-dimethyltriborane(5) (**22**): 15 ml of a 0.56 M solution of LiMe (8.4 mmol) in ether was added at −78°C to a stirred solution of $B_3(NMe_2)_3Cl_2$ (**5**) (0.99 g, 4.2 mmol) in hexane. On warming a solid separated at about −20°C from the solution. After stirring for 1 h at ambient temp. the solid material was separated by filtration (G3 frit) and the solvent removed in vacuo (final presure 0.01 Torr) from the solution). 0.70 g of **22** (86%) remained which was not subjected to distillation as its quantity was too small. The product proved to be pure **22** by NMR spectroscopy. − $C_8H_{24}B_3N_3$ (194.7): calcd. C 49.34, H 12.42, N 21.58; found C 48.70, H 11.93, N 21.04.

1,3-Dibutyl-1,2,3-tris(dimethylamino)triborane(5) (**23**): A solution of LiBu (15 ml of a 0.57 M solution, 8.4 mmol) in hexane was added to a well stirred suspension of $B_3(NMe_2)_3Br_2$ (**6**) (1.4 g, 4.2 mmol) in 50 ml of *n*-hexane. The mixture turned yellow on warming to ambient temp. After stirring overnight an ochre-colored material was separated by filtration (1.1 g). Then the solvent was removed from the filtrate in vacuo and the oily residue kept at 10^{-2} Torr for 3 h. The yellow oil (0.4 g, 36%), which could not be distilled undecomposed, was pure **23**. − $C_{14}H_{36}B_3N_3$ (278.9): calcd. C 60.29, H 13.01, N 15.07; found C 60.27, H 12.85, N 14.90.

1,3-Di-tert-butyl-1,2,3-tris(dimethylamino)triborane(5) (**24**): As described for **23** 15 ml of a 0.55 M hexane solution of Li*t*Bu was treated with **6** (1.35 g, 4.16 mmol) in 20 ml of hexane at −78°C. Stirring was continued at ambient temp. for 7 d, solid material removed by filtration and the filtrate reduced in volume to 1/3. At −78°C 0.53 g of **26** (46%) separated as well-formed crystals, m.p. 85−86°C. − MS, *m/z* (%): 279 (100) [$M^{+\bullet}$], 264 (100) [M − Me]$^+$, 222 (100) [M − *t*Bu]$^+$, 208 (14) [$C_9H_{25}B_3N_3$]$^+$, 194 (26) [$C_8H_{23}B_3N_3$]$^+$, 179 (94) [$C_8H_{22}B_3N_2$]$^+$, 165 (85) [$C_6H_{18}B_3N_3$]$^+$ 151 (100) [$C_5H_{16}B_3N_3$]$^+$. − $C_{14}H_{36}B_3N_3$ (278.9): calcd. C 60.29, H 13.01, N 15.07; found C 57.28, H 12.74, N 14.79.

1,4-Di-tert-butyl-1,2,3,4-tetrakis(dimethylamino)tetraborane(6) (**25**): A suspension of $B_4(NMe_2)_4Br_2$ (**9**) (1.07 g, 2.8 mmol) in 35 ml of low-boiling petroleumether was cooled to −78°C, and 10 ml of a solution of *t*BuLi (5.6 mmol) in hexane was added with stirring. The suspension became a clear solution on warming to ambient temp., and after some time a solid separated from the solution. After 7 d of stirring 0.61 g of solid was recovered by filtration (G3 frit). The solution was then reduced in volume by about 2/3. At −78°C 0.38 g of **25** (40%) settled as a microcrystalline powder, m.p. 129−131°C. − MS, *m/z* (%): 334 (91) [$M^{+\bullet}$], 319 (4) [M − Me]$^+$, 278 (36) [M − *t*Bu]$^+$, 262 (61) [$B_4(NMe_2)_4CMe_2$]$^+$, 221 (64) [$B_4(NMe_2)_4H$]$^+$, 179 (24) [$C_8H_{22}B_3N_2$]$^+$, 151 (67) [$C_5H_{16}B_3N_3$]$^+$, 69 (100) [BH*t*Bu]$^+$.

1-{tert-Butyl[chloro(2,2,6,6-tetramethylpiperidino)-boryl]amino}-4-chloro-1,2,3,4-tetrakis(dimethylamino)tetraborane(6) (**26**): A solution of $B_4(NMe_2)_4Cl_2$ (**8**) (3.0 g, 10.1 mmol) in 10 ml of hexane was added to 20.9 ml of a 0.5 M solution of tmp-B≡NCMe$_3$ (10.2 mmol)[25]. After stirring for 1 d at ambient temp. the solvent was removed in vacuo and the residue crystallized from a minimum amount of hot hexane to give well-formed prisms and needles. Yield: 4.2 g of **26** (78%), m.p. 118−121°C. − $C_{21}H_{51}B_5Cl_2N_6$ (512.6): calcd. C 49.20, H 10.03, N 16.39; found C 49.62, H 10.04, N 15.90. − Mol. mass (MS, ^{11}B, ^{35}Cl): found : 513.

1-Bromo-3-{[2,2,6,6-tetramethylpiperidino)boryl]-tert-butylamino}-1,2,3-tris(dimethylamino)triborane(5) (**27**): A suspension of $B_3(NMe_2)_3Br_2$ (**6**) (1.80 g, 5.5 mmol) in 50 ml of *n*-hexane was cooled to −78°C, and 6.63 ml of a 0.83 M solution of tmp-B≡NCMe$_3$[26] (5.5 mmol) was added with stirring. The mixture was then allowed to attain a temperature of about −10°C when the solid material started to dissolve. At ambient temp. a clear solution was obtained. After stirring had been continued overnight small amounts of a solid were removed by filtration, the solution was reduced in volume by about 2/3 and cooled to −78°C. 1.39 g of **27** (48%) separated within 4 d, m.p. 68−70°C. − MS, *m/z* (%): no $M^{+\bullet}$; 372 (6) [M − (2Br − Me)]$^+$, 302 (30) [BBr(NH*t*Bu)tmp]$^+$, 287 (100) [BBr(CHCMe$_3$)tmp − Me]$^+$, 245 (90) [BBr(NH)tmp]$^+$?, 244 (68) [$B_3Br(NMe_2)_3$]$^+$, 223 (94) [B(NH*t*Bu)tmp]$^+$, 188 (20) [$B_2Br(NMe_2)$]$^+$, 126 (100) [B(NH*t*Bu)NMe$_2$]$^+$. − $C_{19}H_{45}B_4Br_2N_5$ (546.7): calcd. C 41.57, H 8.30, N 12.81; found C 41.48, H 8.96, N 12.28.

X-Ray Structure Determinations: Single crystals were sealed in glass capillaries under argon. Determination of the unit cells and data collections were performed at ambient temperature with an Enraf-Nonius CAD diffractometer (compounds **7**, **14a**, **24**) or a Siemens R3m diffractometer by using Mo-K_α radiation and a graphite monochromator. The axes of the unit cells were controlled by axial photograpy. The structures were solved either by Patterson or Direct methods using the program packages MULTAN, SHELXL Plus, and SHELX93[26]. A semiempirical absorption correction was applied to the data set of **7**. For technical reasons this could not be done for compound **6**, and structural data have there-

Table 5. Crystallographic data and data for the X-ray structure determination of (dimethylamino)triboranes and -tetraboranes

Compound	**6**	**7**	**12**	**14a**	**17**	**24**	**15**	**26**
Formula	$C_6H_{18}B_3Br_2N_3$	$C_6H_{18}B_3I_2N_3$	$C_{14}H_{36}B_3N_3O_2$	$C_{18}H_{28}B_3N_3S_2$	$C_{14}H_{38}B_3N_5$	$C_{14}H_{36}B_3N_3$	$C_{20}H_{34}B_4N_4S_2$	$C_{21}H_{51}B_5Cl_2N_6$
Mol.-mass	324.5	418.5	310.6	383.0	308.9	278.9	437.9	512.6
Size of cryst. (mm)	.32x.25x.41	.15x.30x.33	.28x.6x.6	.2x.27x.35	.33x.36x.4	.4x.29x.6	.3x.35x.52	.3x.4x.65
a (Å)	13.975(3)	14.161(2)	14.406(	14.301(2)	14.608(3)	17.011(1)	17.214(3)	8.269(2)
b (Å)	7.048(1)	7.235(1)	11.664	9.272(2)	11.880(3)	8.391(1)	8.771(2)	10.998(4)
c (Å)	14.290(3)	14.418(2)	12.019	16.631(4)	11.721(2)	12.943(2)	18.518(4)	18.103(6)
ß (°)	93.30(3)	92.59(2)	90.97	100.40(2)	90.55(2)	90	111.70(3)	82.01(3)[a]
V (Å^3)	1405.2(7)	1475.7(4)	2019.3	2169.0(8)	2034.1(7)	1966.4(5)	2598(2)	1565.5(9)
Space group	P2/n	P2/n	C2/c	P2$_1$/n	C2/c	Pbcn	P2$_1$/c	P-1
Z	4	4	4	4	4	4	4	2
d (Mg/m^3)	1.534	1.884		1.173	1.009	0.942	1.120	0.227
µ (mm$^{-1)}$	5.738	4.234	0.600	0.252	0.059	0.053	0.219	1.088
F(000)	640	784		816	688	624	936	556
Data Collection								
2Θ-Range (°)	3 - 51	4 - 50	2 - 45	4 - 50	4 - 48	4.8 - 45	2 - 48	2.3 - 48
Scans type	ω	ω	ω	ω	2Θ-Θ	ω	ω	ω
Scan speed (°/min)	2 - 29.3	1.5	2.0 - 29.3	1.5	1.0-3.0	2.3-29.3	1.8-29.3	3.5-29.3
Scan Range (°)	1.2	0.9	1.2	0.9	1.0	0.7	0.8	0.8
Refl. collect.	1625		1390			2719	4507	4219
Refl. indep.	1534	2446	1255	3401	1457	1280	4039	
Refl. observ.	1151	2193	981	2885	1270	982	2854	3931
F>nσ(F) n =	3	3	4	3	3	3	3	4
max./min.transmiss.	-	0.999/0.668	-	-				
Solution and Refinement								
Method	Patterson	Patterson	Direct Meth.	Dir Meth.	Dir. Meth.	Dir. Meth.	Dir. Meth.	Dir. Meth.
No. of param. refined	121	130	155	235	101	146	373	445
R	0.0658	0.0341	0.0601	0.0347	0.0549	0.0523	0.0421	0.0525
R_w	0.0954	0.0729	0.0646	0.0484	0.0804	0.0674	0.0657	0.0734
g[a)]	0.0072	0.0075	0.00059	0.0005	0.0003	0.0128	x	x
GOOF	1.02	0.78		1.61	3.25	1.024	0.927	1.111
Larg. resid. e/Å^3	0.51	0.44		0.23	0.24	0.134	0.168	0.328

[a)] Additional angles of the unit cell: α = 76.13(3)°, γ = 79.91(3). – x The parameters for the weighting scheme are given in ref.[27].

fore to be considered as preliminary. – All nonhydrogen atoms were refined anisotropically. Hydrogen atoms were included in the final refinement in calculated positions and refined as riding on the respective C atom with fixed isotropic *U*. However, H positions of compounds **14a**, **15**, and **26** were freely refined. Refinement of these compounds was on F^2, but the conventional *R* values are given in Table 5[27].

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