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Contributions to the Chemistry of Boron. 121.[1a] Dicoordinate Amidoboron Cations

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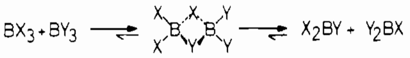
Bromide abstraction from the amidoboron bromides (tmp)B(NR_2)Br (R = CH_3, C_2H_5; tmp = 2,2,6,6-tetramethylpiperidino) and (tmp)B(R)Br (R = CH_3, C_6H_5) in methylene chloride produces tetrabromoaluminates of the dicoordinate diamidoboron cation (tmp=B=NR_2)$^+$ (**5**, **6**) or the amido(organyl)boron cation (tmp=B—R)$^+$ (**7**, **8**). The constitution of these salts has been deduced by NMR spectroscopy (^1H, ^{11}B, ^{13}C, ^{27}Al), infrared spectroscopy, and electrical conductivity. In addition, the crystal structure of [tmp=B=$N(CH_3)_2$]$AlBr_4$ reveals that the C_2NBNC_2 skeleton is of the allene type with a nearly linear NBN atomic arrangement (NBN angle 176°). Both BN distances are rather short (130 and 142 pm), demonstrating in addition to the IR data a fairly high bond order for the BN bonds in **5** and **6**. The thermal stability of the salts decreases in the order **6** ≥ **5** > **7** > **8**, and this is rationalized in terms of better charge delocalization in the diamido- vs. the monoamidoboron cations. This conclusion is substantiated by geometry-optimized MO calculations on model amidoboron cations.

Substituent exchange between two borane species BX_3 and BY_3 provides a common method for preparing mixed species BXY_2 and/or BX_2Y, and it is generally accepted that reactions of this type proceed according to eq 1 via a cyclic four-membered intermediate or transition state.


(1)

In connection with this an observation by Greenwood and Walker[2] is most interesting. They found that the exchange of the halogen atoms between (dimethylamino)dichloroborane and (dimethylamino)dibromoborane occurs at a much slower rate than the scrambling between the analogous (diethylamino)boranes. Two explanations can be offered to rationalize this result. The first one assumes competition among R_2N/R_2N exchange, R_2N/halogen exchange, and halogen/halogen exchange, with only the latter to be observed in this experiment. Since the steric effect of the dimethylamino group is less than that of the diethylamino group, the amino group exchange may compete more favorably with the other two processes for the first pair of boranes, and therefore, the formation of the mixed (dimethylamino)dihaloborane should proceed at a slower rate than in the diethylamino case. As a second explanation we postulate an ionic intermediate, e.g., the formation of an ion pair $(R_2NBX)^+(XY_2BNR_2)^-$. ^{11}B NMR data suggest less π-electron density at the boron atom of the (diethylamino)boranes as compared with that in the (dimethylamido)boron halides. Moreover, the bromides are stronger Lewis acids than the chlorides. Taking into account that the boron–bromine bond is weaker than the boron–chlorine bond, it is difficult to foretell which halogen atom will be more readily transferred. This model will also favor amino group exchange. However, this seems not to be the crucial point in this case because the boron–nitrogen bond is certainly stronger than any of the other two bonds. On the basis of these arguments the more rapid halogen exchange in the diethylamino case can be rationalized. Another example is the transhalogenation of hexachlorotriborylamine with boron tribromide, which proceeds without BN cleavage, e.g., without boron atom exchange.[3]

It therefore appears for these cases—rather unexpectedly—that halogen basicity exceeds the basicity of nitrogen.[4] The questions that emerge from these findings are as follows: Will there be better halogen acceptors than boron halides to favor ion formation, and can experiments be designed to prove or disprove the possible existence of boron cations of low coordination number?

Boron cations are well-known.[5] The first nitrogen-containing boron cation to be firmly established was $[BH_2(NH_3)_2]^+$,[6] and many others of the type $[H_2BL_2]^+$,[7] $[HXBL_2]^+$,[7] and $[X_2BL_2]^+$[8] have since been discovered. Even doubly and triply charged boron cations containing tetracoordinated boron are well characterized. Usually the ligand L is pyridine. The cations are of the types $[HBL_3]^{2+}$,[9] $[XBL_3]^{2+}$,[10] and $[BL_4]^{3+}$.[11] In addition three types of boron cations with tricoordinate boron are described or have been suggested;[12-14] they are, however, not yet well characterized by physical methods.

The existence of dicoordinated diamidoboron cations has been suggested,[15] and the addition product of tris(dimethylamino)borane with phosphorus pentachloride showed features that could be interpreted in this sense.[16] In addition, the formation of a diphenylboron cation was postulated for the interaction of diphenylboron chloride with aluminum chloride in nitrobenzene solution to explain the increased electrical conductivity.[17] However, calculations performed by Perkins et al.[18] show that such cations should become tricoordinate in a donor solvent while a 9-borafluorenium cation might be stable. Such a cation may be present in the blue compound obtained by Köster and Willemsen[19] from 9-chloro-9-borafluorene and aluminum chloride in methylene chloride solution.

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(1) (a) Contribution 120: Nöth, H.; Pommerening, H. *Chem. Ber.*, in press. (b) Institute of Inorganic Chemistry. (c) Institute of Organic Chemistry.

(2) Greenwood, N. N.; Walker, J. *Inorg. Nucl. Chem. Lett.* **1965**, *1*, 65.

(3) Staudigl, R. Ph.D. Thesis, University of Munich, 1981. Exchange of boron isotopes can be observed after about 15 h in contrast to the halogen exchange, which proceeds to the equilibrium state within 5 min.

(4) Basicity and nucleophilicity parallel each other under the conditions of these experiments, which are conducted in nonpolar solvents.

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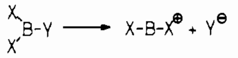
The formation of dicoordinate boron cations may be achieved by a reaction according to eq 2. So that the expected



$$\mathrm{X(X')B{-}Y} \longrightarrow \mathrm{X{-}B{-}X'^{\oplus} + Y^{\ominus}} \qquad (2)$$

equilibrium might be shifted to the right-hand side, e.g. favoring the formation of a boron cation, the following criteria should be met:

(a) The electrophilic nature of the cation must be kept as low as possible. This can possibly be achieved by using proper groups bonded to boron. Such groups should strongly π bond to boron to effect good electronic shielding at the boron atom.

(b) In addition to electronic shielding steric shielding of the boron atom should contribute to stabilize the boron cation.

(c) Since a bond to boron must be broken on cation formation, the atom or group to be removed from boron should be bound as weakly as possible so that little energy is required for heterolytically breaking the bond. Moreover, the leaving group should be a weak nucleophile.

(d) The nucleophilic power of the counterion should be as low as possible; i.e., the charge of the anion is to be spread over a large volume.

(e) The solvent used must have little basicity and must not compete with the anion for a coordination site at boron.

The BN bond with tricoordinate nitrogen optimally fulfills the requirements of (a), and if amino groups with proper substituents are chosen, those of (b) will also be met. Considering (c) the boron–iodine bond would seem to be the most suitable one. However, for practical reasons, we considered boron–bromine bonds as equally feasible. The addition of a strong bromide acceptor is necessary to shift the equilibrium of eq 2 to the ionic side. If an aluminum halide is used as an acceptor, a larger and less nucleophilic anion will be generated, and this corresponds to (d).

For these reasons we investigated the action of aluminum bromide on a number of (2,2,6,6-tetramethylpiperidino)boron bromides,[20] since the tetramethylpiperidino group is very bulky, and we report on the results obtained. In addition some experiments using the corresponding boron chlorides and $AlCl_3$ or $GaCl_3$ will also be discussed. And it should be mentioned at this point that experiments related to the formation of diamidoboron cations have been performed also by Parry at al.[21] using bis(diisopropylamido)- and bis(dimethylamido)boron chlorides and aluminum chloride. Their results are complementary to ours.

Experimental Section

All experiments were performed under rigorously dry conditions in the absence of oxygen using either standard high-vacuum or Schlenk tube techniques. Solvents were carefully purified, dried, and stored under nitrogen. 2,2,6,6-Tetramethylpiperidine (tmp), purity > 98%, was purchased from Fluka and used without further purification. Dimethylamine and diethylamine (BASF-Aktiengesellschaft) were of technical grade. They were used after drying with KOH and BaO. Phenylboron dibromide was obtained from tetraphenyltin and boron bromide and methylboron dibromide from tetramethyltin and boron bromide. Aluminum bromide was synthesized from the elements, and only freshly sublimed material was used. The (dialkylamido)boron bromides were formed by reacting the appropriate amounts of $B(NR_2)_3$ with BBr_3.[22] All compounds were checked for purity by NMR methods.

Instrumentation and Analysis. Nearly all of the reactions were monitored with use of a Bruker WP 200 multinuclei PFT NMR spectrometer. The standards used were C_6D_6, $CDCl_3$, and CD_2Cl_2 as lock and internal ^{13}C standards. $\delta(^{13}C)$ data are however reported with Me_4Si as reference. Boron trifluoride–diethyl ether served as standard for ^{11}B chemical shifts and $Al(OH_2)_6^{3+}$ (1 M aqueous solution) for ^{27}Al NMR data. Me_4Si was the reference for proton NMR. Positive δ values refer to signals at higher frequencies (lower field strength) than the reference frequency. Most of the ^1H NMR spectra were recorded on a Varian A60 instrument. IR spectra were taken on a Perkin-Elmer Model 325 spectrometer. A MTW conductivity meter was used to measure electrical conductivity. Intensity data for the X-ray structure determination were collected with a Syntex $P2_1$ four-circle fully automated diffractometer, and the structure was solved with use of the XTL program package. All elemental analyses were performed at the Institute's analytical laboratory.

1-Lithio-2,2,6,6-tetramethylpiperidine. A solution of 64 mL of 1.57 M LiC_4H_9 in hexane was cooled with stirring to 0 °C followed by addition of 17 mL of tmp (100 mmol) in 20 mL of hexane within 30 min. The mixture was then allowed to warm to ambient temperature and followed by heating to reflux for 2 h. After that time gas evolution ceased. The resulting suspension of the compound (tmp)Li was directly used for further reactions.

Bromo(dialkylamino)(2,2,6,6-tetramethylpiperidino)boranes. A suspension of 100 mmol of (tmp)Li in 80 mL of hexane was added within 30 min to a well-stirred solution of 21.5 g of (dimethylamido)boron dibromide or 24.3 g of (diethylamido)boron dibromide (100 mmol) in 20 mL of hexane with external cooling by ice. A suspension of white to yellowish particles in a reddish brown solution forms under reflux. After the mixture is stirred overnight, the insoluble part is removed by filtration through a sintered-glass disk followed by stripping off the solvent from the filtrate in vacuo. Distillation of the liquid residue yielded 18.9 g (69%) of bromo(dimethylamino)(2,2,6,6-tetramethylpiperidino)borane (**1**), bp 68–70 °C (10^{-1} torr), or 19.2 g (62%) of bromo(diethylamino)(2,2,6,6-tetramethylpiperidino)borane (**2**), bp 80 °C (10^{-1} torr).

Anal. Calcd for $C_{11}H_{24}BBrN_2$ (**1**, M_r 275.0): C, 51.52; H, 9.31; N, 9.24. Found: C, 51.02; H, 9.18; N, 9.29. Calcd for $C_{13}H_{28}BBrN_2$ (**2**, M_r 303.1): C, 48.08; H, 8.80; N, 10.19. Found: C, 48.29; H, 8.69; N, 10.40.

Bromomethyl(2,2,6,6-tetramethylpiperidino)borane. This aminoborane was prepared as the previous ones with use of 100 mmol of (tmp)Li and 18.6 g of CH_3BBr_2. A pure product is obtained only by careful fractional redistillation: bp 95 °C (6 Torr); 9.8 g (40%).

Anal. Calcd for $C_{10}H_{21}BBrN$ (M_r 246.1): C, 48.83; H, 8.60; N, 5.69. Found: C, 50.20; H, 8.63; N, 5.75.

Bromophenyl(2,2,6,6-tetramethylpiperidino)borane. A 100-mmol quantity of (tmp)Li and 100 mmol (24.8 g) of $C_6H_5BBr_2$ in about 100 mL of hexane were kept 2 h under reflux after having reacted at 0 °C. On removal of hexane from the filtrate a brownish precipitate appeared. The solid that was left after completely removing the solvent was purified by sublimation at 100–110 °C (10^{-2} torr). Recrystallization from pentane yielded 17 g (55%) of **3**, mp 113–115 °C, in colorless platelets.

Anal. Calcd for $C_{15}H_{23}BBrN$ (M_r 308.1): C, 58.48; H, 7.53; N, 4.55. Found: C, 58.19; H, 7.64; N, 4.65.

(Dialkylamido)(2,2,6,6-tetramethylpiperidino)boron(1+) Tetrabromoaluminates 5 and 6. A 10-mmol quantity of $R_2N(tmp)BBr$ was dissolved in 8–10 mL of methylene chloride and cooled to −78 °C. Pure anhydrous $AlBr_3$ (10 mmol) was then added in portions within a period of 10 min to the aminoborane solution with continuous stirring to achieve dissolution and good mixing. The mixture was then allowed to warm to ambient temperature. Crystals settled from the clear solution on cooling to −70 °C within 2 days. The mother liquor was then decanted, and the crystals were washed with a few milliliters of cold methylene chloride followed by drying in vacuo (yield approximately 60%). Concentrating the solution to half its volume yielded another crop of the salt. A total yield of about 80% was obtained in several preparations. If the solvent was completely stripped off from the reaction mixture at room temperature, only yellow oils were obtained, which would not crystallize readily.

(Dimethylamido)(2,2,6,6-tetramethylpiperidino)boron(1+) Tetrabromoaluminate (5): mp 112–114 °C dec. Anal. Calcd for $C_{11}H_{24}AlBBr_4N_2$ (M_r 541.7): C, 24.39; H, 4.47; N, 5.17. Found: C, 24.10; H, 4.63; N, 4.97.

(Diethylamido)(2,2,6,6-tetramethylpiperidino)boron(1+)tetrabromoaluminate (6): mp 90–95 °C dec. Anal. Calcd for $C_{13}H_{28}AlBBr_4N_2$ (M_r 569.8): C, 27.40; H, 4.95; N, 4.92; Br, 56.09. Found:

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[20] The interaction of boron trihalides and organylboron halides with these compounds as well as the reaction of various halide acceptors with diamidoboron halides will be reported subsequently.

[21] Higashi, J.; Eastman, A. D.; Parry, R. W. *Inorg. Chem.*, following paper in this issue.

[22] Prepared analogously to $[(CH_3)_2N]_2BBr$.[23]

[23] Kämper, M. Ph.D. Thesis, University of Munich, 1968.

C, 27.22; H, 5.02; N, 4.61; Br, 54.0.

Both compounds are extremely well soluble in CH_2Cl_2 and chlorobenzene. They deliquesce to oils on contact with nonpolar solvents such as benzene or hexane. The crystalline materials hydrolyze only slowly in moist air.

(Dialkylamido)(2,2,6,6-tetramethylpiperidino)boron(1+) Tetrachloroaluminates and Tetrachlorogallates. Only oily products have so far been obtained from (diethylamido)(2,2,6,6-tetramethylpiperidino)boron chloride and $AlCl_3$ or $GaCl_3$ in reactions carried out as described for **5** or **6**. However NMR and IR data for the cationic part of the products obtained are identical with those for **5** and **6**, respectively. Therefore it is safe to assume that salts are being formed in these cases also.

Organyl(2,2,6,6-tetramethylpiperidino)boron(1+) Tetrabromoaluminates 7 and 8. These compounds were obtained in the same manner as described for **5** and **6** with use of 10 mmol of RB(tmp)Br each dissolved in 8 mL of CH_2Cl_2. A 10-mmol quantity of $AlBr_3$ was then added carefully within 15 min at −78 °C. After the solutions were quickly warmed to ambient temperature for 3 min, they were again cooled to −78 °C. Crystals separated within 24 h. The supernatant solution was decanted from the crystals, which were stable for several weeks at dry ice temperature. At −30 °C decomposition was noticeable after about 2 weeks. At ambient temperature they are stable for a few minutes and form red oily and black materials within a few hours. The solutions obtained by reacting the components show the same NMR spectra as the solutions obtained from the crystals.

Phenyl(2,2,6,6-tetramethylpiperidino)boron(1+) Tetrabromoaluminate (7): decomposition at room temperature. Anal. Calcd for $C_{15}H_{23}AlBBr_4N$ (M_r 574.8): N, 2.44. Found: N, 2.60.

Methyl(2,2,6,6-tetramethylpiperidino)boron(1+) Tetrabromoaluminate (8): decomposition at room temperature. Anal. Calcd for $C_{10}H_{21}AlBBr_4N$ (M_r 512.7) C, 23.43; H, 4.13; N, 2.73. Found: C, 24.07; H, 4.40; N, 2.81.

X-ray Data Collection, Structure Solution, and Refinement. A crystal of approximately 0.3 × 0.3 × 0.2 mm grown slowly from methylene chloride solution at −30 °C was mounted in a glass capillary. After optical alignment of the crystal and centering of 10 strong reflections from rotation photographs a monoclinic system could be deduced from the data. Final centering of 13 reflections with 2θ ranging from 5.98 to 30.58° led to the cell dimensions stated in Table IV. Intensity data were collected with use of the ω-scan technique with speeds varying from 29.3°/min for strong to 3°/min for weak reflections. Graphite-monochromated Mo Kα radiation (70.926 pm) was used. The scan range was ±1° from the maximum peak heights. Two standard reflections were measured after every 28 intensity measurements. The intensities of 1456 reflections were obtained. Systematic absences of $0k0$ with $k = 2n$ and $h0l$ with $h + l = 2n$ lead unambiguously to the space group $P2_1/n$. After averaging and removal of data of the check reflections a set of 1224 unique reflections resulted. Applying Lorentz and polarization correction gave 915 reflections with $I > \sigma[1.96(I)]$, which were regarded as observed. The best MULTAN solution led to an E map from which the positions of the bromine atoms and the aluminum atom were recognized. These positions were refined in two cycles of a BLOCK refinement ($R_1 = 0.253$). Ten nonhydrogen atoms could then be detected from a Fourier synthesis (9 carbons and 1 nitrogen). The positions of these atoms were then refined with fixed B values in three cycles ($R_1 = 0.192$). At this stage the rest of the nonhydrogen atoms could be located via a difference Fourier synthesis. The refinement with all bromine atoms anisotropic and the other atoms isotropic converged at $R_1 = 0.133$ and $R_2 = 0.138$ (19 atoms, 152 parameters).

Another set of data was then collected at −40 °C. A total of 3581 reflections led to 3113 unique data. Empirical absorption correction obtained on three hkl values was applied. After data reduction 1851 reflections with $I > \sigma[1.96(I)]$ were regarded as observed. Starting with the atom positions obtained in the previous determination, the refinement converged at $R_1 = 0.12$. With the exception of three H atoms all others were found in a difference map or were calculated. Refinement of all nonhydrogen atoms with anisotropic temperature factors and the hydrogen atoms with fixed B values led to the final R values given in Table IV.

IR data (cm^{-1}) are as follows (abbreviations: v = very, s = strong; m = medium; w = weak; sh = shoulder; br = broad).

1: 3005 m, 1976 s, 2958 s, 2928 vs, 2873 s, 2842 m, 2800 w, 2780 w, 1578 w, 1538 ms, 1520 vs, 1470 sh, 1462 m, 1450 m, 1438 sh, 1412 s, 1398 s, 1380 s, 1365 ms, 1348 ms, 1290 sh, 1268 vs, 1237 s, 1255 w, 1190 s, 1178 s, 1132 s, 1082 s, 1052 m, 1026 s, 1013 ms, 988 w, 968 w, 945 w, 918 w, 907 vw, 883 w, 860 m, 818 m, 805 s, 768 vw, 702 s, 616 vw, 596 w, 579 vw, 548 m, 520 w, 482 w, 463 w, 348 vw, 310 w.

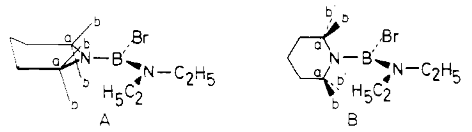


Figure 1. Two conformations of (dialkylamino)(2,2,6,6-tetramethylpiperidino)boron bromides.

2: 3005 m, 2975 vs, 2961 vs, 2930 vs, 2875 s, 2842 m, 1578 vw, 1503 st, sh, 1490 vs, 1470 sh, 1458 s, 1442 s, 1380 s, 1365 s, 1348 s, 1298 s, 1288 s, 1260 s, 1208 ms, 1180 vs, 1132 s, 1105 sh, 1092 s, 1058 m, 1028 s, 1011 ms, 996 m, 988 m, 968 w, 942 w, 918 w, 907 w, 870 w, 855 vw, 825 w, 805 ms, 785 ms, 768 ms, 700 sh, 695 s, 625 s, 610 w, 580 w, 552 m, 528 vw, 300 w, br.

5: 3050 w, 3000 w, 2988 ms, 2966 s, 2930 s, 2865 m, 1925 m, 1908 m, 1872 ms, 1850 vs, 1815 w, 1542 w, 1521 w, br, 1475 m, 1468 ms, 1455 s, 1448 s, 1437 m, 1412 m, 1396 m, 1388 m, 1375 m, 1362 w, 1347 w, 1318 w, 1278 ms, 1265 vs, 1235 m, 1228 m, 1210 w, 1190 w, 1178 w, 1168 m, 1150 w, 1126 m, 1086 m, 1040 m, 1025 m, 1012 w, 970 sh, 958 m, 912 w, 892 w, 858 vw, 828 m, 803 w, 772 w, 738 vs, 703 s, 605 w, 959 w, 548 w, 535 w, 470 w, br, 4335 m, 403 vs, 280 w.

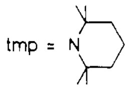
6: 3005 w, 2975 s, 2950 m, 2940 s, 2885 m, 1910 m, 1895 s, 1835 vs, 1810 sh, 1525 vw, 1474 m, 1462 s, 1451 vs, 1405 sh, m, 1495 s, 1388 s, 1382 s, 1373 vs, 1362 w, 1338 w, 1300 w, 12992 w, 1242 vw, 1228 s, 1195 w, 1165 s, 1146 w, 1123 s, 1092 m, 1086 m, 1056 s, 1048 sh, 1003 w, 998 vw, 972 w, 9521 s, 928 w, 910 m, 852 w, 809 m, 770 w, 737 vw, 693 vw, 610 w, 100 m, 658 w, 548 w, 536 w, 475 m, 431 m, 398 vs, 316 vw, 285 w.

Discussion

(2,2,6,6-Tetramethylpiperidino)boron Bromides. The (tetramethylpiperidino)boron bromides **1–4** were prepared from *N*-lithio-2,2,6,6-tetramethylpiperidine and the respective boron bromides according to eq 3. They are colorless liquids or solids (**3**), which slowly hydrolyze in contact with moisture.

$$\text{Litmp} + \text{XBBr}_2 \longrightarrow \text{tmpB(X)Br} + \text{LiBr}$$

tmp =



X	$N(CH_3)_2$	$N(C_2H_5)_2$	C_6H_5	CH_3
	1	2	3	4

(3)

Their ^{11}B NMR data (see Table I) indicate tricoordinate boron in solution. However, the boron atoms in **1–4** are less shielded as compared with those in the corresponding (dimethylamido)boron bromides $R[(CH_3)_2N]BBr$[22–24] (R = $(CH_3)_2N$, $(C_2H_5)_2N$, C_6H_5, CH_3). This would correspond with less π-electron density at the boron atom.[25] ^1H and ^{13}C NMR spectra of **1** and **2** suggest hindered rotation at room temperature at the BN bond of the dimethylamino and diethylamino groups as evidenced by two groups of signals, i.e., magnetic noneqivalence of the two alkyl groups. This is common among mixed monoaminoboranes of the type $R_2NB(X)Hal$[26] but occurs only scarcely for bis(amino)boranes $(R_2N)_2BX$ at room temperature[23] with $C_6H_5B[N(CH_3)_2]_2$[27] and some (diisopropylamino)boranes[28] as exceptions. The ^{13}C resonances of the tmp group in **1** and **2** allow the deduction of the preferred conformation of this group in these molecules:

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(24) The shift differences $\Delta^{11}B$ are 2.8 ppm for **1**, 2.6 ppm for **2**, 3.7 ppm for **3**, and 3.9 ppm for **4**.

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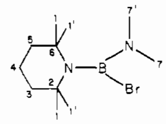
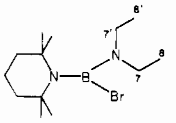
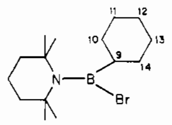
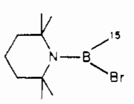
(28) Davis, S. A.; Turchi, I. J.; Maryanoff, B. E.; Hutchins, R. O. *J. Org. Chem.* **1971**, *36*, 1300.

Table I. NMR Data of Some (2,2,6,6-Tetramethylpiperidino)boron Bromides at Ambient Temperature (δ Values, Methylene Chloride Solution at Ambient Temperature)

	atom				
$\delta(^{11}B)$			30.6	40.4	41.7
$\delta(^{13}C)$	1	32.6	33.1	33.1	32.0
	1	25.5	26.0	33.1	32.0
	2, 6	51.9	51.9	57.1	56.2
	3, 5	40.7	40.6	36.0	35.6
	4	18.4	18.6	14.7	14.4
	7	40.2	42.2		
	7′	40.9	43.0		
	8		13.7		
	8′		14.0		
	10, 14			132.0	
	11, 15			127.2	
	12			128.5	
	15				18.3
$\delta(^{1}H)$	1	1.35	1.32	1.45	1.53
	1′	1.08	1.12	1.45	1.53
	3–5	*a*	*a*	*b*	*c*
	7	2.68	3.37		
	7′	2.78	3.45		
	8		0.97		
	8′		1.01		
	10–14			*d*	
	15				1.24

[a] The proton signals resulting from the methylene groups form a broad multiplet centered at 1.37 and 1.42 ppm. [b] The proton signals resulting from the methylene groups form a multiplet centered at 1.78 ppm. [c] A multiplet centered at 1.60 ppm results from the methylene groups. [d] The most intense signal for the phenyl protons was observed at 7.36 ppm.

there are two signals for the CH_3 groups but only a single resonance for the carbon atoms to which these methyl groups are attached. In addition two more ^{13}C NMR signals were observed, which are readily assigned to the methylene carbon atoms of the tmp ring system. These data rule out conformation A (Figure 1) in which both C_2N groups of the two dialkylamino groups would be coplanar (or nearly so) with the N_2BBr plane. This conformation requires four NMR signals to be observable for the carbon atoms 2, 6, 3, and 5, which are not observed. However, the data agree with conformation B for which only three ^{13}C NMR signals for the ring atoms are to be expected, making the carbons 2, 6, 3, and 5 magnetically equivalent while carbon 4 is unique. Furthermore this conformation requires two signals for the tmp's methyl groups. In addition the $\delta(^{11}B)$ data are also in consonance with model B because there is only one nitrogen atom that significantly contributes to BN π bonding and this is expected to result in a reduced π-electron density at boron as compared with sterically less hindered bis(amino)boranes. B allows also a good packing of the methyl groups in this compound.

In contrast to **1** and **2** only single ^{1}H and ^{13}C resonance signals for the methyl groups of tmp and the carbon atoms 2 and 6 of this ring were observed in **3** and **4**. If there was hindered rotation at the BN bond with a conformation of the tmp group analogous to A (replace R_2N by R in Figure 1), two signals, both in the ^{1}H and ^{13}C NMR spectra, should be observable. No splitting of the respective signals was found, however, even at −60 °C. Free rotation of all groups in the temperature range studied must therefore prevail.[29] On the other hand, the ^{13}C NMR signals of the carbon atoms 2 and 6 of the tmp ring are deshielded in **3** and **4** with respect to **1** and **2**. This can be explained by locating more positive charge on the nitrogen atom in **3** and **4**. Indeed, the ^{13}C NMR data for the tmp group in **3** and **4** closely resemble those of $(tmp)BCl_2$ (see Table II).

The IR bands of the new bis(amido)boron bromides are difficult to assign completely. Certainly the N_2BBr skeleton will be planar and therefore possess C_{2v} symmetry. However, when the carbon skeleton is taken into account, the total symmetry will be C_s at best. Nevertheless a partial assignment can be based on the analysis of the IR spectra of bis(dimethylamido)- and bis(diethylamido)boron bromides.[30] $\nu_{as}(BN_2)$ shows typical isotope splitting. It is found at 1520 cm^{-1} for **1** and 1490 cm^{-1} in **2**, both frequencies being somewhat lower than in the model compounds (1532 and 1519 cm^{-1}). $\nu_s(BN_2)$ is observed at 1268 and 1300 cm^{-1}, respectively. NC_2 stretching bands can be assigned at 1082, 1026, and 805 cm^{-1} for **1** and at 1092, 1028, and 802 cm^{-1} in **2**. BNC_2 in-plane deformations are to be associated with bands at 548 and 520 cm^{-1} (**1**) and with 552 and 528 cm^{-1} (**2**), respectively. $\nu(BBr)$ was found at 331 or 361 cm^{-1} for $[(CH_3)_2N]_2BBr$ and $[(C_2H_5)_2N]_2BBr$ according to Davidson and Phillips. We observe only very weak bands in this region for **1** and **2** (300–400 cm^{-1}), which cannot possibly be due to such a vibration. Therefore, we tentatively assign bands of medium intensity at 548 cm^{-1} in **1** and 552 cm^{-1} in **2** to this vibration. These bands disappear on reaction with $AlBr_3$ while the weak bands at 350–400 cm^{-1} persist.

Bis(amido)boron(1+) Tetrabromoaluminates. Addition of $AlBr_3$ to a solution of **1** or **2** in a 1:1 molar ratio produces dramatic changes in the NMR spectra. These are demonstrated in Figure 2, which shows the ^{13}C and ^{11}B NMR spectra of **2** and **2**$\cdot AlBr_3$ (**6**) as well as the ^{27}Al NMR signals of $AlBr_3$

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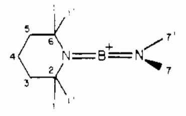
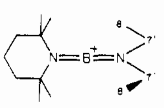
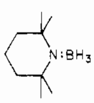
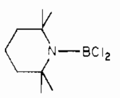
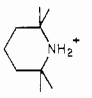
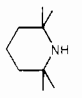
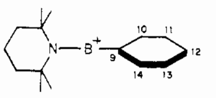
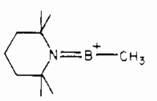
(29) Free rotation of the phenyl group can be envisaged from the fact that only three ^{13}C resonances are observed even at low temperature. The ^{13}C NMR signal due to the boron-bonded carbon atom was not recorded; it is expected to be rather broad since its nuclear spin may relax rapidly. This atom was also not observed in a $^{13}C\{^{11}B\}$ double-resonance experiment.

(30) Davidson, G.; Phillips, S. *J. Chem. Soc., Dalton Trans.* **1981**, 306 and literature cited therein.

Table II. NMR Data of the (2,2,6,6-Tetramethylpiperidino)boron Cations and Some Data for Comparison (δ Values, Methylene Chloride Solution at Ambient Temperature)

	atom								
$\delta(^{11}B)$		36.7 (420)[d]	37.6 (420)[d]	−21.8	33.2			56.0 (550)[d]	59.6
$\delta(^{13}C)$	1	31.1	31.5	20.8	31.3	27.9	32.0	31.6	30.2
	1′	31.1	31.5	33.8	31.3	27.9	32.0	31.6	30.2
	2, 6	58.1	58.3	58.6	56.4	58.5	49.5	60.6	59.9
	3, 5	37.0	37.1	41.0	35.2	35.5	38.6	36.8	36.4
	4	16.7	16.6	16.7	14.3	16.6	18.7	16.5	16.3
	7, 7′	39.5	45.4						
	8, 8′		14.5						
	15								4.2
$\delta(^{1}H)$	1	1.52	1.53	1.33	1.40	1.59	1.05	1.70	1.64
	1′	1.52	1.53	1.37	1.40	1.59	1.05	1.70	1.64
	3-5	1.73[a]	1.73	1.60	1.53	1.77	1.37[b]	1.88	1.72
	7, 7′	3.19	3.46[c]						
	8, 8′		1.43[c]						
	15								2.08

[a] Center of the multiplet. [b] Approximate center of the multiplet. [c] Triplet and quartet, respectively. $^3J_{HH} = 7$ Hz. [d] $h_{1/2}$ value in Hz.

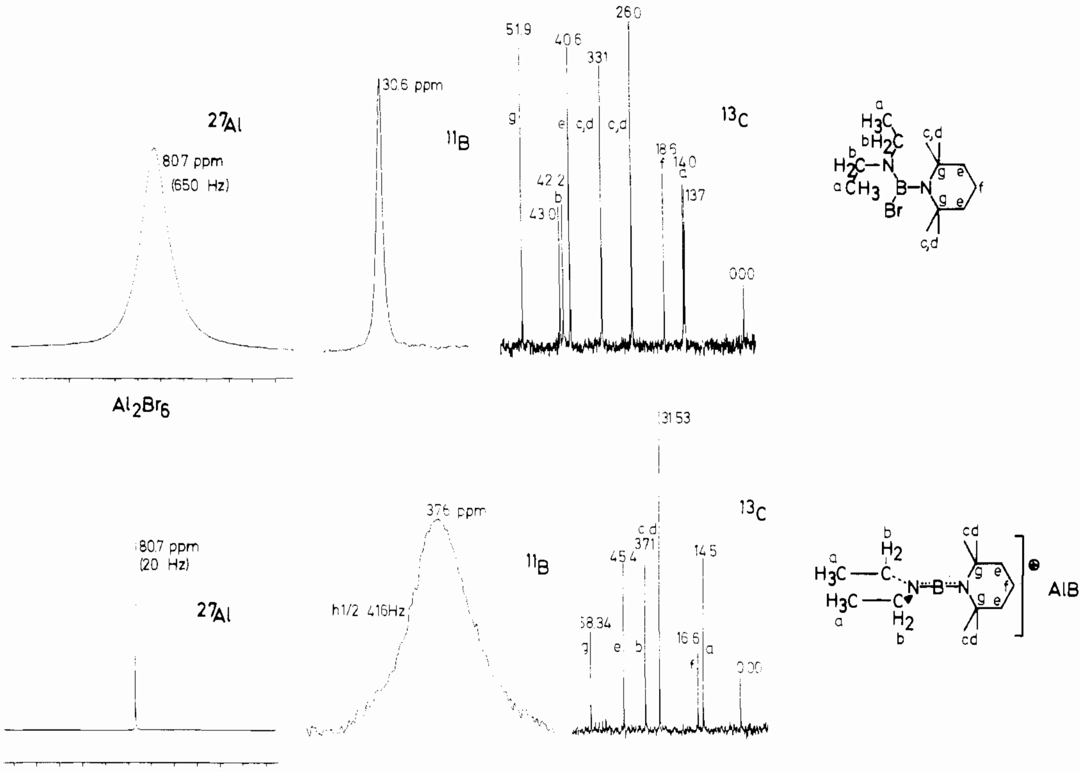
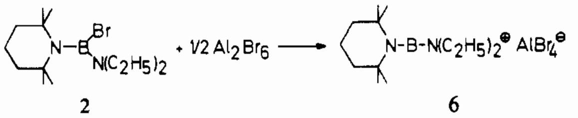


Figure 2. $\delta(^{11}B)$, $\delta(^{13}C)$, and $\delta(^{27}Al)$ NMR spectra of (diethylamido)(2,2,6,6-tetramethylpiperidino)boron bromide, aluminum bromide, and (diethylamido)(2,2,6,6-tetramethylpiperidino)boron(1+) tetrabromoaluminate in methylene chloride solution.

and **6**, all in methylene chloride solution. Additional data as well as those for **1**·$AlBr_3$ (**5**) are summarized in Table II. The results are consistent only with boron cation formation according to eq 4.



(4)

2 6

The prominent feature of the ^1H and the ^{13}C NMR spectra of the reaction product formed on the interaction of **2** with $AlBr_3$ is the loss of the nonequivalence of both the ethyl groups as well as of the methyl groups of tmp. This rules out the addition of the Lewis acid to one of the nitrogen atoms of **2**. The magnetical and chemical equivalence of these groups indicates that a species of higher symmetry is generated from **2**, and this is best explained with the formation of the proposed cation in eq 4 for which a linear NBN skeleton with trigonal-planar-coordinated nitrogen atoms is to be expected. This cation is isoelectronic and should also be isostructural with an allene. The observed shifts of the ^{13}C resonances to higher frequencies, which approach those in the 2,2,6,6-tetramethylpiperidinium ion and the diethylammonium ion (see Table II), allows the conclusion that part of the positive charge associated with the diamidoboron cation in **6** also rests on the nitrogen atoms. This is substantiated by the MO model calculations described in a later section.

The ^{11}B NMR signal of **2** is shifted to low field (high frequency) on addition of $AlBr_3$ by 7 ppm. This is rather little

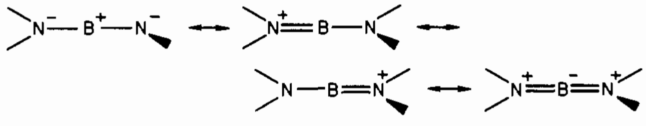
Table III. Equivalence Conductance of (2,2,6,6-Tetramethylpiperidino)boron(1+) Tetrabromoaluminates and of Some Bis(diarylmethylen)imminium Salts

	Λ, cm^2 Ω^{-1} mol^{-1}	solvent
$[\mathrm{tmp{=}B{=}N(CH_3)_2}]\mathrm{AlBr_4}$	31	CH_2Cl_2
$[\mathrm{tmp{=}B{=}N(C_2H_5)_2}]\mathrm{AlBr_4}$	19.4	CH_2Cl_2
$[\mathrm{Ph_2C{=}N{=}CPh_2}]\mathrm{BCl_4}^a$	26	$C_6H_5NO_2$
$[\mathrm{Ph_2C{=}N{=}CPh_2}]\mathrm{AlCl_4}^a$	24	$C_6H_5NO_2$
$[(p\text{-tol})_2\mathrm{C{=}N{=}CPh_2}]\mathrm{SbCl_6}^a$	27	$C_6H_5NO_2$

[a] Samuel, B.; Wade, K. *J. Chem. Soc. A* 1969, 1742.

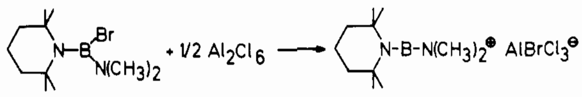
as compared with the shift differences observed on carbocation formation. The reason for this will be discussed in a moment. Another striking feature is the increase of the line width of this signal: it is about 4 times as wide as for the aminoborane **2**, indicating a more rapid relaxation of the boron nuclear spin in **6**. If the cation is linear as expected, a stronger field gradient should result since the electron distribution at the boron atom should deviate even more strongly from a sphere than in **2**.[31] The opposite is observed for the ^{27}Al NMR signals. There is practically no change in the shielding at aluminum as one changes from Al_2Br_6 to **6**, and this is an indication that aluminum remains tetracoordinated by four bromine atoms in both cases. Eye-catching is, however, the dramatic decrease in the line width that is associated with the formation of **6**. Both chemical shift of the ^{27}Al signal and its line width of only 20 Hz are typical for the formation of free tetrahedral $AlBr_4^-$.[32] No additional signals due to AlN coordination or to BN cleavage products were observed.[33] Thus the reaction according to eq 4 proceeds specifically, and the evidence from all NMR data can only be explained by ion formation with no disturbance of the tetrahedral symmetry at the tetrabromoaluminate ion in solution.

The high-frequency shift of the ^{1}H and ^{13}C resonances in **6** as compared with those in **2** can be explained by the canonic formulas



These formulas indicate charge delocalization to the nitrogen atoms in this system (see also Table IX). It also follows that this cation will be strongly stabilized by BN π back-bonding, which increases the electron density at boron. We regard this contribution as one of the reasons for the rather small low-field shift of the ^{11}B NMR signal on cation formation. And although the resonance formulas imply that a large portion of the positive charge resides on the nitrogen atoms, it is to be kept in mind that the bond polarity in the BN π bonds is opposed to that in the σ bond with the latter usually dominating so that boron is positively charged (see also the section on MO calculations).

1 reacts in exactly the same manner with $AlBr_3$ as does **2** although there is a better chance for the acid to attack at the nitrogen atom of the sterically less demanding dimethylamino group. Thus halogen basicity exceeds again that of nitrogen. In order to see whether a less bulky Lewis acid would be able to discriminate between Br and N attack, we treated **1** with $AlCl_3$. In the case of N attack a single ^{27}Al NMR signal should result due to adduct formation and another one at 114.4 ppm[34] might appear if there is BN cleavage with the formation of $Cl_2AlN(CH_3)_2$. On the other hand, attack of $AlCl_3$ at the bromine atom of **1** will produce Cl_3AlBr^- as indicated in eq 5. $AlCl_3Br^-$ is known to disproportionate, producing all members of the series $AlCl_{4-n}Br_n^-$.[35] It is exactly this and only this situation that can be observed in the ^{27}Al NMR spectrum as indicated by five signals at 102.4, 98, 93, 87.2, and 81 ppm representing $AlCl_4^-$, $AlCl_3Br^-$, $AlCl_2Br_2^-$, $AlClBr_3^-$, and $AlBr_4^-$.



(5)

The measurement of the equivalence conductance of **5** and **6** in methylene chloride solution is consistent with the presence of a 1:1 electrolye, and this conclusion is further substantiated by comparing with analogous data obtained for salts of similar constitution. Table III presents pertinent data.

Finally, the IR data obtained are also in accord with an allene type skeleton for the cations present in **5** and **6**. One may expect local D_{2d} symmetry for the C_2NBNC_2 group in these compounds. However, C_s symmetry is a more likely picture since two different amino groups are bound to the boron atom. Free rotation of the methyl and ethyl groups has to be assumed. In this case $\nu_{as}(BN_2)$ and $\nu_s(BN_2)$ are allowed in the infrared. The first can be readily assigned to the very strong bands at 1850 (for **5**) and 1835 cm^{-1} (for **6**) with ^{10}B satellites at 1872 and 1865 cm^{-1}, respectively. Two bands at even higher wavenumbers are present in both IR spectra (1925, 1908 cm^{-1} in **5**; 1895 and 1875 cm^{-1} in **6**). We believe that these result from the Fermi resonance of $\nu_s(BN_2)$. The reliable assignment of the symmetric BN_2 vibration is not unambiguous in the absence of Raman data. A possible candidate is a band of medium intensity at 958 cm^{-1} in **5** and at 952 cm^{-1} in **6**. They could give rise to Fermi bands at 1916 and 1904 cm^{-1}, respectively, and this supports the assignment. While it is also difficult to definitely assign the other skeletal vibrations, the AlBr stretching frequency of F type represents itself by a very strong band at 400 cm^{-1}, typical for tetrahedral $AlBr_4^-$.

The fact that $\nu_{as}(BN_2)$ of **5** and **6** is found at much higher wavenumbers than in most bis(amino)boranes[36] indicates strong BN bonding and a high BN bond order. With use of Siebert's rule[37] a bond order of 1.8 can be estimated from the data. However, this value is only approximate due to the fact that BN vibrations couple strongly with symmetry-related CN vibrations. Therefore, they are not characteristic vibrations and the estimated bond order must be regarded an upper limit. On the other hand, if one compares the BN bands found for monoaminoboranes (1480–1550 cm^{-1}), bis(amino)boranes (1450–1580 cm^{-1}), aldimino- and ketiminoboranes (1600–1790 cm^{-1}),[31a,38] bis(amido)boron cations (1830–1855 cm^{-1}), and

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(31) (a) Rather large line widths for the ^{11}B NMR signals have also been observed for the linear ketiminoboranes,[31b] phosphaniminoboranes,[31b,c] and dicoordinate boron imides.[31d] However, it is only the last type of compound that resembles the boron situation in **6** more closely, i.e., a dicoordinate boron site. (b) Schroen, R. Ph.D. Thesis, University of Marburg, 1969. (c) Marringele, A.; Meller, A.; Nöth, H.; Schroen, R. *Z. Naturforsch., B* **1978**, *33*, 673. (d) Paetzold, P. I.; Richter, A.; Thijssen, T.; Würtenberg, S. *Chem. Ber.* **1979**, *112*, 3811.

(32) In acetonitrile as a solvent $\delta(^{27}Al)$ for $AlBr_4^-$ has been reported to be 80, with line width 35 Hz: Haraguchie, H.; Fujiwara, S. *J. Phys. Chem.* **1969**, *73*, 3467.

(33) The line widths of the ^{27}Al NMR signals of amine adducts of $AlBr_3$ are much broader than those of $AlBr_4^-$ although the latter is also influenced by solvents. For instance $\delta(^{27}Al)$ is 104, line width 78 Hz, for $AlBr_3{\cdot}N(C_2H_5)_3$ in benzene solution or 118.8, line width 210 Hz, for $[(CH_3)_2NAlBr_2]_2$.[34]

(34) Wolfgardt, P. Ph.D. Thesis, University of Munich, 1975.

(35) Kidd, R. G.; Truax, D. R. *J. Am. Chem. Soc.* **1968**, *90*, 6867.

(36) Weinstock, N. "Gmelins Handbuch der Anorganischen Chemie", 8th ed.; Springer-Verlag: West Berlin, 1975; Vol. 23, Supplement, p 57 ff.

(37) Siebert, H. "Infrarotspektren Anorganischer Verbindungen", 2nd ed.; Springer-Verlag: Heidelberg, New York, 1966.

(38) Dorochov, V. A.; Lappert, M. F. *Chem. Commun.* **1968**, 250. Jennings, J. R.; Pattison, J.; Wade, K. *J. Chem. Soc. A* **1969**, 565. Jennings, J. R.; Pattison, J.; Summerford, C.; Wade, K.; Wyatt, B. K. *Chem. Commun.* **1968**, 250.

Table IV. Crystal Data for **5** and Data Concerning Data Collection and Structure Determination

formula	$C_{11}H_{24}AlBBr_4N_2$
M_r	541.7
cryst size	0.2 × 0.3 × 0.3 mm
cryst syst	monoclinic
space group	$P2_1/n$
a, Å	7.678 (4)
b, Å	14.56 (1)
c, Å	17.91 (1)
β, deg	97.25 (4)
formula units	4
d(calcd)	1.81
μ(Mo Kα), cm^{-1}	86.2
2θ range, deg	0–48
unique reflctns	3113
reflctns $I > \sigma[1.96(I)]$	1851
variables in refinement	172
R_1[a]	10.4
R_2[b]	10.2

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $R_2 = (\Sigma w||F_o| - |F_c||^2/\Sigma|F_o|^2)^{1/2}$ with $w = |F_o|^2/\sigma$.

pentafluorophenyl(*tert*-butylimino)borane (2045 cm^{-1}),[31c] this trend indicates an increasing BN bond order along this series of BN compounds.

X-ray Structure of (Dimethylamido)(2,2,6,6-tetramethylpiperidino)boron(1+) Tetrabromoaluminate. Since **5** and **6** form well-defined crystals from CH_2Cl_2 solution, being apparently stable enough at ambient temperature, a single-crystal X-ray structure determination on crystals of **5** was attempted in order to obtain direct information on the structure of the cation and to prove the conclusion drawn from spectrosopic data. However, **5** decomposed significantly during data collection at room temperature and data were then collected at −40 °C. Data for empirical absorption correction were collected at room temperature. The best set of data converged at an R value of 0.104. Therefore, standard deviations on bond lengths and bond angles are fairly large. However, the characteristic features of the structure are well documented. Tables IV–VI contain fractional coordinates, B_{ij}'s of the temperature factors, and atomic distances and angles.

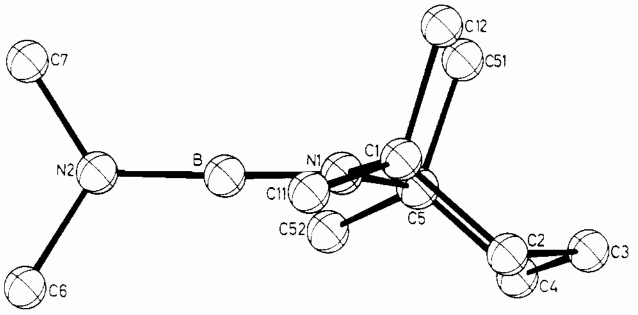


Figure 3. ORTEP plot of the (dimethylamido)(2,2,6,6-tetramethylpiperidino)boron cation using isotropic temperature factors. Hydrogen atoms have been excluded since they could not be reliably recognized for one methyl group.

Figure 3 shows the ORTEP plot of the cationic part of **5**. It clearly demonstrates the nearly linear arrangement of the NBN part (NBN angle 176 (3)°) and the orthogonal conformation of the two different C_2N units. Since the sums of the bond angles at the nitrogen atoms is 360° in each case, the nitrogen atoms can be regarded as sp^2 hydrids and the boron atom as sp hybridized. Thus the essential part of the cation is isostructural with an allene.

The two BN bond lengths are different. This is to be expected since the two nitrogen atoms carry different substituents. One BN bond is considerably shorter than any other known BN bond, and also the mean value of the two BN bonds (136.5 pm) is quite short. The BN bond that can best be compared with those in **5** is the BN bond in (diphenyl-

Table V. Fractional Coordinates of Atomic Positions and Thermal Parameters for **5**[a]

atom	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Al	0.490 45 (112)	0.453 55 (55)	0.217 65 (45)	2.26 (45)	1.70 (38)	2.33 (38)	0.53 (34)	1.28 (34)	0.78 (31)
Br1	0.623 55 (45)	0.586 82 (21)	0.264 73 (17)	4.57 (19)	2.48 (14)	3.70 (15)	−0.91 (15)	−1.75 (14)	−0.79 (13)
Br2	0.687 04 (43)	0.337 05 (17)	0.224 89 (17)	3.59 (18)	3.01 (15)	3.81 (15)	0.91 (15)	0.93 (14)	0.13 (13)
Br3	0.258 48 (48)	0.420 67 (24)	0.281 87 (19)	4.96 (21)	3.34 (17)	5.81 (20)	0.11 (16)	3.65 (17)	0.97 (15)
Br4	0.392 72 (45)	0.477 03 (23)	0.092 15 (17)	3.57 (18)	3.54 (15)	2.91 (14)	−0.28 (16)	0.53 (13)	0.37 (13)
B	0.643 02 (408)	0.203 20 (216)	0.438 31 (181)	0.99 (158)	1.03 (140)	3.45 (160)	0.99 (127)	−0.14 (136)	0.78 (134)
N1	0.717 64 (262)	0.267 10 (148)	0.481 44 (104)	1.12 (112)	2.96 (118)	1.32 (95)	−0.11 (97)	1.09 (87)	−0.82 (89)
N2	0.561 19 (302)	0.137 35 (159)	0.387 37 (123)	2.29 (129)	2.95 (130)	3.47 (122)	−1.10 (108)	1.81 (109)	0.07 (102)
C1	0.622 48 (359)	0.29421 (177)	0.546 40 (134)	3.02 (152)	1.56 (126)	1.56 (118)	−0.07 (121)	1.86 (116)	−1.49 (103)
C11	0.489 62 (367)	0.218 25 (210)	0.558 48 (175)	1.27 (141)	3.60 (162)	6.30 (185)	−2.10 (136)	0.86 (141)	−0.82 (147)
C12	0.521 77 (363)	0.384 86 (184)	0.527 47 (150)	2.47 (159)	2.19 (149)	3.55 (139)	1.65 (128)	1.42 (131)	0.10 (115)
C2	0.759 74 (402)	0.300 34 (219)	0.618 77 (151)	2.93 (168)	4.85 (178)	2.64 (138)	2.43 (154)	0.59 (133)	−0.16 (130)
C3	0.922 23 (402)	0.356 10 (206)	0.605 99 (145)	3.37 (174)	3.71 (171)	2.57 (140)	−1.95 (149)	−1.18 (134)	−0.48 (128)
C4	1.012 79 (340)	0.315 92 (183)	0.542 59 (144)	1.65 (133)	2.50 (142)	2.34 (127)	−0.08 (115)	1.68 (111)	−0.19 (111)
C5	0.889 98 (323)	0.311 75 (160)	0.469 15 (140)	1.53 (133)	0.43 (115)	2.40 (123)	−0.28 (100)	0.86 (112)	0.72 (96)
C51	0.858 37 (440)	0.407 34 (200)	0.434 09 (140)	5.82 (197)	2.41 (146)	2.28 (130)	−2.17 (158)	0.90 (136)	0.41 (118)
C52	0.971 57 (357)	0.250 41 (183)	0.412 09 (161)	1.83 (148)	1.84 (135)	5.95 (168)	−0.94 (117)	1.74 (137)	−0.82 (120)
C6	0.597 04 (378)	0.036 87 (160)	0.399 24 (151)	2.81 (151)	0.12 (112)	3.39 (144)	−0.45 (115)	0.81 (121)	1.45 (104)
C7	0.426 25 (356)	0.159 26 (195)	0.325 56 (132)	2.21 (147)	3.45 (151)	1.77 (116)	−0.08 (136)	−1.05 (117)	2.06 (114)

atom	x	y	z	atom	x	y	z
H61	0.543 20 (0)	−0.018 98 (0)	0.358 96 (0)	H63	0.720 55 (0)	0.029 23 (0)	0.404 88 (0)
H71	0.437 50 (0)	0.109 37 (0)	0.281 25 (0)	H72	0.442 53 (0)	0.220 15 (0)	0.305 86 (0)
H121	0.578 24 (0)	0.422 54 (0)	0.476 11 (0)	H73	0.310 93 (0)	0.157 13 (0)	0.340 00 (0)
H511	0.766 20 (0)	0.407 19 (0)	0.403 98 (0)	H122	0.531 73 (0)	0.426 38 (0)	0.568 83 (0)
H21	0.795 95 (0)	0.239 99 (0)	0.635 46 (0)	H123	0.399 20 (0)	0.373 68 (0)	0.512 19 (0)
H22	0.705 00 (0)	0.327 82 (0)	0.659 95 (0)	H512	0.952 88 (0)	0.426 18 (0)	0.407 65 (0)
H31	1.003 53 (0)	0.361 12 (0)	0.651 11 (0)	H513	0.845 70 (0)	0.453 23 (0)	0.471 84 (0)
H32	0.886 61 (0)	0.419 25 (0)	0.592 31 (0)	H521	0.898 50 (0)	0.253 12 (0)	0.358 95 (0)
H41	1.053 39 (0)	0.255 72 (0)	0.557 00 (0)	H522	0.976 00 (0)	0.187 85 (0)	0.427 85 (0)
H42	1.114 80 (0)	0.352 29 (0)	0.535 54 (0)	H523	1.088 05 (0)	0.270 62 (0)	0.406 45 (0)
H62	0.555 84 (0)	0.020 92 (0)	0.446 03 (0)				

[a] B_{ij} is defined as $\exp[-(h^2B_{11} + ... + hkB_{12} + ...)]$. The g value for all atoms is 1.00. B for all hydrogen atoms is 4.00 Å^2. Estimated standard deviations are given in parentheses.

Table VI. Bond Distances (pm) and Selected Bond Angles (Deg) for 5 with Standard Deviations in Parentheses

Distances			
BN1	130 (4)	C2C3	153 (4)
BN2	142 (4)	C3C4	152 (4)
N2C6	150 (3)	C4C5	152 (4)
N2C7	145 (3)	C5C51	153 (4)
C1C1	150 (3)	C5C52	155 (4)
N1C5	152 (3)	AlBr1	230.3 (9)
C1C2	157 (4)	AlBr2	226.3 (9)
C1C11	154 (4)	AlBr3	228.9 (9)
C1C12	155 (4)	AlBr4	230.3 (9)

Angles			
N1BN2	176 (3)	C2C3C4	111 (2)
BN2C6	121 (2)	C3C4C5	112 (2)
BN2C7	124 (2)	C4C5N1	110 (2)
C6BC7	115 (2)	C11C1C12	109 (2)
BN1C1	115 (2)	N1C1C11	108 (2)
BN1C5	123 (2)	N1C1C12	109 (2)
C1N1C5	121 (2)	N1C5C51	110 (2)
N1C1C2	108 (2)	N1C5C52	106 (2)
C1C2C3	112 (2)	C51C5C52	108 (2)

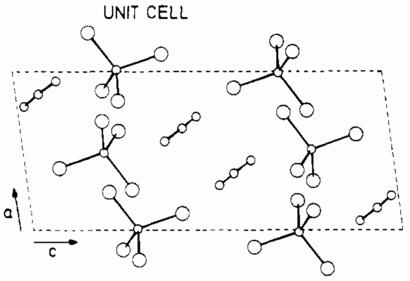


Figure 4. ORTEP plot of 5 projected on the *a*/*c* plane. Carbon and hydrogen atoms have been omitted for the sake of clarity. The shortest B···Br distance is 412 pm excluding B···Br interactions.

methylenimino)dimesitylborane.[39] This molecule possesses a linear BNC skeleton and belongs to the heteroallenes. Its BN bond was found to be 138 (2) pm, and the NBC bond angle was determined as 173 (2)°. However, its boron atom is three-coordinate, and although one may expect that the sum of the covalent radii for trigonal boron and sp type nitrogen should be rather similar to the sum of the covalent radii of trigonal-planar nitrogen and sp boron, the latter seems to be shorter. We believe that this shortening is the result of the positive charge associated with the NBN skeleton in **5**.

It is evident from Figure 4, which shows the projection on the *ac* plane of the unit cell, that there is no direct interaction between the boron atom of the cation in **5** and the tetrabromoaluminate. Actually the boron atom is sterically well shielded against nucleophilic attack by a large anion.

The crystal structure of **5** gives credence to the conclusions drawn from all other data obtained on **5** and **6**. It is the first reported structure in which the boron atom is dicoordinate. The short BN bonds support also the description of the cation by the canonical formulas as discussed, i.e., the high BN bond order.

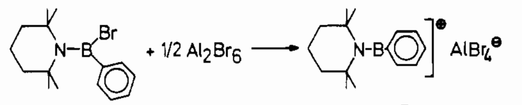
Amido(organyl)boron(1+) Tetrabromoaluminates. The formation of bis(amido)boron cations by halide abstraction from bis(amido)boron bromides having been established, the question arose whether a single amino group attached to boron might sufficiently stabilize a dicoordinate boron cation. For this reason the interaction of **3** and **4** with $AlBr_3$ was studied.

Mixtures of these components gave rise to brown or black solutions at room temperature. At −78 °C, however, colorless 1:1 adducts form, which are fairly stable, though only for a short while, at ambient temperature to allow their analytical characterization. First signs of decomposition in solution are noticeable 15–20 min after mixing **3** with $AlBr_3$ and 5 min for similar solutions of **4** with $AlBr_3$. This, however, is sufficient to allow NMR spectra to be recorded at ambient temperatures. Their data are summarized in Table II and are in accord with boron cation formation according to eq 6.

Table VII. $\delta(^{13}C)$ and $\Delta(^{13}C)$ for the Phenyl Groups of Phenyl(2,2,6,6-tetramethylpiperidino)boron Bromide, Benzoyl Chloride, and Thiobenzoyl Chloride and the Cations Generated from These Halides[40]

	$\delta(^{13}C)$		
	C_{ortho}	C_{meta}	C_{para}
C_6H_5–B(Br)tmp[a]	132.0	127.2	128.5
$[C_6H_5$–B=tmp$]AlBr_4$	141.4	130.7	142.3
$\Delta(^{13}C)$	9.4	3.5	13.8
C_6H_5–C(Cl)=S	132.7	130.5	132.4
$[C_6H_5$–C=S$]SbF_6$	143.3	131.8	145.3
$\Delta(^{13}C)$	10.3	1.3	12.9
C_6H_5–C(Cl)=O	131.3	129.9	136.1
$[C_6H_5$–C=O$]AlCl_4$	141.4	133.0	149.5
$\Delta(^{13}C)$	10.1	3.1	13.4

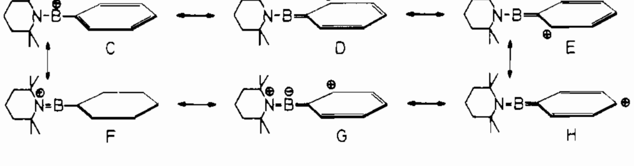
[a] tmp = 2,2,6,6-tetramethylpiperidino group.



3 7 (6)

The ^{27}Al NMR signal found for **7** (**3**·$AlBr_3$) was observed at 81.6 ppm. This corresponds to the $AlBr_4^-$ anion although the line width is larger than for **5** or **6** but definitely narrower than for an aluminum bromide solution. We surmise that the line width indicates some interaction of the cation with the $AlBr_4^-$ moiety thereby disturbing the tetrahedral symmetry of the anion and hence the increase in the line width. Also the line width of the ^{11}B NMR signal at **7** (800 Hz) is considerable. The signal has moved 16 ppm downfield from the aminoborane **3** from which **7** is generated. Thus the shift difference is much larger as compared with the pair **2**/**6**. The large line width may be explained by an even lower symmetry of the electron density at the boron atom in **7**, and the greater deshielding is rationalized by the presence of only a single amino group, which can help in reducing electron deficiency at the dicoordinate boron atom via BN π bonding.

In the ^1H NMR spectrum of **7** all protons have suffered a high-frequency shift as compared with those giving the signals of **3**. Their position does not change on adding $AlBr_3$ beyond the 1:1 ratio. More importantly, the ^{13}C NMR signals for the tmp group in **7** are found at even higher frequencies than in **5** or **6** especially for the carbon atoms 2 and 6. Also the ^{13}C signals of the phenyl group have moved downfield in comparison with **3**. This not only indicates cation formation but also charge delocalization with a considerable contribution of canonical formulas C and F placing the positive charge on



nitrogen. In addition the contributions by D, E, G, and H add to the shielding at boron, though not as effectively as an amino group. That BC π bonding plays this role reflects itself in the ^{13}C NMR data for the phenyl group. Similar deshieldings were observed on the ion formation of phenylacylium cations, and pertinent data are summarized in Table VII.[40] This

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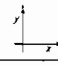
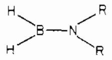
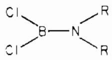
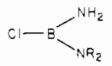
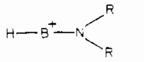
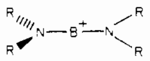
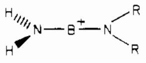
(39) Bullen, G. J. *J. Chem. Soc., Dalton Trans.* **1973**, 858.

Table VIII. Calculated STO-3G Total Energies E (au) for Geometry-Optimized Structures (Abbreviated as R–X) of Dicoordinate Boron Cations Including Reference Structures as well as Substituent Effects ΔE (kcal/mol)

		R				
X		H	CH_3	C_6H_5	NH_2	NMe_2
CH_3	E	−39.726 86	−78.306 18	−266.474 31	−94.016 16	−171.174 04
	ΔE	0	0	0	0	0
CH_2^+	E	−38.779 48	−77.406 22	−265.646 59	−93.234 80	−170.422 84
	ΔE	0	−29	−75	−104	−123
BH^+	E	−25.174 43	−63.816 78	−252.022 81	−79.629 55	−156.807 18
	ΔE	0	−40	−63	−104	−116
BNH_2^+	E	−79.629 55	−118.254 18	−306.448 77	−134.054 74	−211.224 05
	ΔE	0	−28	−45	−85	−92
$BNMe_2^+$	E	−156.807 19	−195.426 54	−383.616 59	−211.224 05	−288.390 77
	ΔE	0	−23	−39	−80	−86
BH_2	E	−26.070 70	−64.667 19	−252.842 19	−80.465 90	−157.622 30
	ΔE	0	−11	−15	−67	−66
$BClNH_2$	E	−534.525 78	−573.119 02	−761.290 00	−588.894 78	−666.046 50
	ΔE	0	−9	−11	−50	−46
	ΔE_{Cl}	0	−20	−35	−35	−46

Table IX. Calculated BN Bond Lengths and Mulliken Electron Populations at the Boron Atom for Some Relevant Boron-Containing Systems[a]

	r_{BN}, pm	s + p_x	p_y	p_z	$\Sigma\sigma + \pi$
	137.6	4.414		0.329	4.744
	137.6	4.008		0.496	4.504
	139.1 (NH_2) 140.1 (NR_2)	3.941		0.509	4.450
	130.6	3.762	0.094	0.531	4.387
	132.5	3.372	0.489	0.489	4.350
	133.0 (NH_2) 132.1 (NR_2)	3.373	0.504	0.430	4.307
$H_3C{-}B^+{-}NH_2$	132.2	3.690	0.137	0.448	4.275
$Ph{-}B^+{-}NH_2$	132.7	3.641	0.310	0.410	4.362

[a] $R = CH_3$; $Ph = C_6H_5$. The horizontal x and the vertical y axes lie in the paper plane; the z axis is defined as orthogonal to it.

relationship shown there supports the conclusion that bromide is removed from **3** by $AlBr_3$ addition.

The salt obtained from **4** and $AlBr_3$ (**8**) is less stable at ambient temperature than **7**. This can be understood because the boron atom in **8** formally possesses only an electron sextet in contrast to the electron octet structure of the boron atom in **5**, **6**, and **7**. Surprisingly the ^{27}Al NMR signal of **8** (48 Hz) is narrower than than in **7**. The shift difference of the ^{11}B NMR signals between **4** and **8** has now increased to 18 ppm, and the boron NMR signal in **8** is again remarkably broad (550 Hz). $\delta(^{11}B)$ depends somewhat on the ratio **4**:$AlBr_3$, which also indicates an interaction of the counterions in solution. Substantial shifts to high frequencies are observed in the ^1H NMR spectrum of **8** as compared with that of **4**, especially for the CH_3B group. Its signal at 2.08 ppm represents the most deshielded protons for this group that we know of. This deshielding is fully in accord with the expected inductive electron withdrawal from the CH_3 group in the cation of **8**.[40] The ^{13}C NMR signal of this group was observed at −60 °C (not at ambient temperature). It is found at a lower frequency than in **4**, similar to the methyl carbons on passing from CH_3COCl to CH_3CO^+.[40] On the other hand, the ^{13}C NMR signals for the tmp group are found at similar δ values as observed for **7**.

Ab Initio MO Calculations on Model Cations. In order to contribute to the conclusions drawn from the spectroscopic and structural data on the cations in **5**–**8**, we calculated energies as well as structural and physical properties on some typical model amidoboron cations related to the present work using the STO-3G method.[41] The total energies listed in Table VIII refer to the geometry-optimized structures.[42] These have been used to calculate the energy differences ΔE for isodesmic reactions[43–45] shown in eq 7 with eq 8 as a specific example.

$$X{-}H + CH_3{-}R \rightleftharpoons X{-}R + CH_4 \qquad (7)$$

$$\begin{gathered} HB^+{-}H + CH_3{-}NH_2 \rightleftharpoons HB^+{-}NH_2 + CH_4 \\ \Delta E = -104 \text{ kcal/mol} \end{gathered} \qquad (8)$$

These allow an estimate of the stabilization of a system X by the substituent R. Negative ΔE values correspond to a stabilization of the system X by the substituent R as compared to the methyl derivatives as the chosen standard.

An inspection of the data for the carbocations $R{-}CH_2^+$ and borocations $R{-}BH^+$ demonstrates that these electron-deficient ions are stabilized to about the same extent by the same substituent R. However, the methyl group will stabilize the borocation more effectively than the carbocation. The reason for this remarkable effect can be found in the double hyperconjugation of the CH_3 group with two vacant p orbitals at the boron atom. Similarly, the cations $H_2N{-}B{-}R^+$ and $(CH_3)_2N{-}B{-}R^+$, which are already stabilized, become even

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(40) Olah, G. A.; Westerman, P. *J. Am. Chem. Soc.* **1973**, *95*, 3706. Olah, G. A.; Prakash, G. K.; Nakajima, T. *Angew. Chem.* **1980**, *92*, 838.

(41) All RHF/STO-3G calculations were carried out with a modified version of the GAUSSIAN 70 series of programs: (a) Hehre, W. J.; Lathan, W. A.; Newton, M. D.; Ditchfield, R.; Pople, J. A. Program No. 236, Quantum Chemistry Program Exchange, Indiana University, Bloomington, Ind.; Program 236. (b) Hehre, W. J.; Stewart, R. F.; Pople, J. A. *J. Chem. Phys.* **1969**, *51*, 2657. (c) Ditchfield, R.; Hehre, W. J.; Pople, J. A. *Ibid.* **1971**, *54*, 724. (d) Hariharan, P. C.; Pople, J. A. *Theor. Chim. Acta* **1973**, *28*, 213.

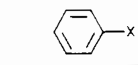
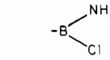
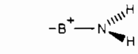
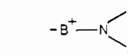
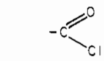
(42) The gradient optimization technique has been used: Poppinger, D. *Chem. Phys. Lett.* **1975**, *34*, 333. STO-3G results for some molecules and cations discussed in this work are already published in the literature. But in the calculation done here, we have recalculated these systems in order to be consistent with the following geometry constraints: planar amino substituents, local C_3 symmetry for the methyl groups, and no optimization for the phenyl groups in standard geometry. The geometry parameters can be ordered from H.-U.W.

(43) Hehre, W. J.; Ditchfield, R. D.; Radom, L.; Pople, J. A. *J. Am. Chem. Soc.* **1970**, *92*, 4796.

(44) MNDO[45] calculations carried out by us on the same molecules and cations produced essentially the analogous results concerning the stability and structures of these systems.

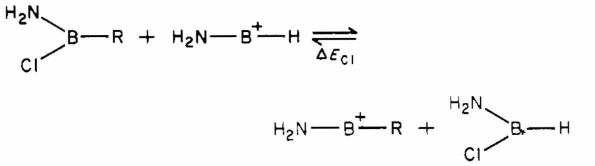
(45) Dewar, M. J. S.; McKee, M. L. *J. Am. Chem. Soc.* **1977**, *99*, 5231.

Table X. Charge Distribution q (e × 10^3) in Phenyl-Substituted Systems

	q_π ortho	q_π meta	q_π para	Σq_π-(C_6H_5)	Σq_{total}-(C_6H_5)
	26	−5	20	61	−80
	108	4	149	373	256
Δq	82	9	129	312	336
	67	15	115	309	260
Δq	41	20	95	248	340
	36	3	36	114	121
$-C^+{=}O$	106	14	167	407	481
Δq	70	11	131	293	360

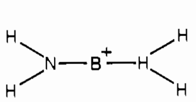
more stable by the substituents R. In accord with experimental data the highest sum of stabilization energies for two substituents is found for two amino groups.

Table VIII also contains ΔE_{Cl} data for some chloroboranes, which relate to isodesmic reactions described in eq 9. These

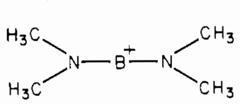

(9)

values provide an estimate for the manner in which a substituent R influences the formation tendency of dicoordinate boron cations. Donor substituents have, as is well-known, the effect of making the starting aminochloroboranes more stable. Therefore, the relative effect of R on the ease of forming dicoordinate boron cations is smaller in comparison with the methyl derivatives.

The energies listed in Table VIII for diamidoboron cations are those calculated for structures with D_{2d} symmetry (allene type with orthogonal amino substituents as found in the crystal structure of **5**). This structure with linear arrangement of the amino substituents at boron was found in all cases to be the energy minimum. Rotation of the amino groups into the totally planar conformation with D_{2h} symmetry destabilizes the systems. The ΔE values given for the formulas I and K refer to the energy difference with the respective D_{2d} conformation. Table IX contains the calculated BN bond length


I

ΔE = +18 kcal/mol


K

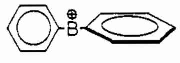
ΔE = +22 kcal/mol

for diamido-substituted boron cations. These are rather short and correspond to the experimentally determined short BN bond in **5**. The relatively high electron population in the originally empty p_y and p_z orbitals at the boron atoms demonstrates π back-bonding from nitrogen to boron, the polarity being opposite to the σ bonding. Also, the fairly high contribution to the electron density by hyperconjugation of the CH_3 group should be noted.

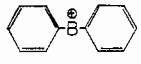
Additional information on the electronic structure of dicoordinate boron cations can be deduced from the phenyl-substituted systems. Relevant data are found in Table X. Inspection of the calculated π-charge changes shows that the carbon atoms of the phenyl substitutent will be deshielded to a similar extent on removing a chloride ion from the amidoboron chloride or benzoyl chloride on boron cation or benzoyl cation formation, respectively. However, this striking analogy holds only for an amidophenylboron cation with the amino and phenyl groups perpendicular to one another and holds much less firmly when these groups are coplanar. These results correspond to the changes in the shielding of the ^{13}C nuclei (see Table VII) on cation formation, and we take this correlation as evidence for the orthogonal conformation of the dicoordinate cation in **7**.

If the phenyl group of the amidophenylboron cation is rotated from this most stable conformation into the planar conformation, a calculated energy difference of +8 kcal/mol results. This energy difference is much smaller than for the corresponding process with the diamidoboron cations.

Obviously the lone p orbitals at the boron atom will be stabilized nearly as much by hyperconjugation with the neighboring CC bond as with the π system of the phenyl group itself. Earlier calculations[18] were unable to contribute to this point because these considered only the π system of the coplanar structure.

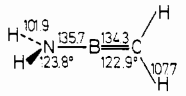

L

$E = -478.83480$ au


M

ΔE = 3.1 kcal/mol

The experimental results of this work led to the consideration of other possible and hitherto unknown heteroallenes containing boron. As will be mentioned in the conclusion an aminomethyleneborane is such a candidate and a challenge for the preparatively oriented chemist. The following theoretical study was conducted under this aspect in order to see whether such a molecule might be sufficiently stabilized. Calculations using again the STO-3G method predict that the most stable configuration of $H_2N{-}B{=}CH_2$ corresponds indeed to the heteroallene type structure containing a linear NBC skeleton. The following bond lengths and bond angles have been calculated:



$E = -117.79539$ au

	$H_2N{-}B{=}CH_2$	$H_2C{=}C{=}CH_2$
LUMO, eV	+9.53	+8.67
HOMO, eV	−6.48	−8.79

There are no significant differences in the energies of the frontier orbitals of the aminomethyleneborane and allene. Also, the dipole moment calculated with the STO-3G basis set is fairly small. A value of 2.55 D was found. This small dipole moment results from a significant contribution of π-electron density from the more electronegative atoms N and C rather than from boron since the bond dipoles of the BN and the BC bond are opposite to one another. In addition, π back-bonding generates fairly high electron densities on the p_y and p_z orbitals at boron (0.314 and 0.804).

Finally, the calculated energy difference of ΔE = +55 kcal/mol for the isodesmic reaction shown in eq 10 is not as

$$\underset{-118.25418\ \text{au}}{H_2N{-}B^+{-}CH_3} + \underset{-114.42172\ \text{au}}{CH_2{=}C{=}CH_2} \rightleftharpoons \underset{117.79539\ \text{au}}{H_2N{-}B{=}CH_2} + \underset{114.79225\ \text{au}}{CH_3{-}C^+{=}CH_2} \quad (10)$$

$$\Delta E = +55\ \text{kcal/mol}$$

unfavorable as to exclude the deprotonation of an alkylamidoboron cation as an energetically possible preparative route. However, the prominent electrophilic character of the boron atom in aminomethyleneborane prompts for steric shielding, i.e., the concept used successfully in this study.

Conclusions

The results described in the Discussion demonstrate convincingly that $AlBr_3$ attacks specifically at the bromine atoms of the amidoboron bromides investigated, removing it as $AlBr_4^-$ with formation of amidoboron(1+) cations of dicoordinate boron. The thermal stability of the salts decreases in the order **6** ≥ **5** > **7** > **8**, i.e., with decreasing electronic and steric shielding of the boron atoms. A similar situation holds for dicoordinate phosphorus cations[46] with bis(amido)phosphorus cations forming the most stable salts. However, attempts to prepare tricoordinate tris(amido)silicon cations have failed so far.[47] This indicates that presently our understanding of the governing factors that will lead to nonmetal cations of low coordination numbers is still incomplete.

The remarkable stability of the diamidoboron(1+) cations is due to the fact that these are isoelectronic with allenes, providing an all-octet situation for the NBN skeleton. π bonding between B and N is certainly stronger than in neutral BN compounds but is still weaker than in allenes in spite of the positive charge. Nevertheless it may be expected that other species isoelectronic with allenes may be prepared with use of the principles outlined in this work, e.g., aminomethyleneboranes $R_2N{-}B{=}CR_2$. This type of compound is a missing link and a challenge, too, because it is a molecule with the still rather rare BC double bond.[48] In contrast, the isomeric ketimino- or aldiminoboranes possessing an allene type structure but tricoordinate boron are well-known.[49,50]

If BX π bonding contributes significantly to the stabilization of dicoordinate boron cations, then one may expect boron cations of this type containing BO and BF bonds. The cations R_2NBOR^+ and R_2NBF^+ should form more readily than $ROBOR^+$. The cation FBF^+ is another possible candidate and should be an extremely strong electrophile. Since its boron atom cannot be sterically shielded, it is quite unlikely that stable salts containing this cation can be made. However, it cannot be excluded from the present experiments that salts of diarylboron cations may be made under certain experimental conditions. On the other hand, dialkylboron cations will possess only an electron quartet and will be most likely too strong an electrophile to be either formed or detected. We are presently engaged in testing these hypotheses and believe that the result of these investigations will be of importance to the understanding of reaction pathways in boron chemistry.

Acknowledgment. A grant by Deutsche Forschungsgemeinschaft for purchasing the Bruker WP 200 instrument is gratefully acknowledged as is the support for this work. In addition we thank Fonds der Chemischen Industrie and BASF-Aktiengesellschaft for financial assistance. Miss H. Wagner and cand. chem. D. Neumeier helped with the experiments, Mrs. G. Hanatschek recorded the IR spectra, and Mrs. L. Moser and Mr. K. Schönauer are responsible for the elemental analysis. We gratefully acknowledge their assistance. Thanks are due also to Dr. U. Schubert and Mr. H. Riedl for permission to use the Syntex $P2_1$ equipment and help in the low-temperature study. This work was carried out at TU Garching. Dr. R. Schell and Dr. P. Konrad conducted similar though less definite experiments as described in this work in the late 1960s; it is due to their observations that our interest in the possibility of finding the dicoordinate boron cation continued.

Registry No. **1**, 78837-58-8; **2**, 78837-59-9; **3**, 78837-60-2; **4**, 78837-61-3; **5**, 78870-24-3; **6**, 78870-26-5; **7**, 78870-28-7; **8**, 78870-30-1; (tmp)Li, 38227-87-1; Me_2NBBr_2, 7360-64-7; Et_2NBBr_2, 868-29-1; CH_3BBr_2, 17933-16-3; $Ph{-}BBr_2$, 4151-77-3; $AlBr_3$, 7727-15-3; $(tmp)BCl_2$, 79855-29-1; $(tmp)H_2^+$, 79855-30-4; (tmp)H, 768-66-1; CH_4, 74-82-8; $H_3C{-}CH_3$, 74-84-0; Me–Ph, 108-88-3; $Me{-}NH_2$, 74-89-5; Me_3N, 75-50-3; CH_3^+, 14531-53-4; $CH_3{-}CH_2^+$, 14936-94-8; $Ph{-}CH_2^+$, 6711-19-9; $H_2N{-}CH_2^+$, 54088-53-8; $Me_2N{-}CH_2^+$, 77267-03-9; BH_2^+, 15194-16-8; $Me{-}BH^+$, 79855-31-5; $Ph{-}BH^+$, 79855-32-6; $H_2N{-}BH^+$, 79855-33-7; $Me_2N{-}BH^+$, 79855-34-8; $H_2N{-}B^+{-}Me$, 79855-35-9; $H_2N{-}B^+{-}Ph$, 79855-36-0; $H_2N{-}B^+{-}NH_2$, 79855-37-1; $Me_2N{-}B^+{-}NH_2$, 79855-38-2; $Me_2N{-}B^+{-}Me$, 79855-39-3; $Me_2N{-}B^+{-}Ph$, 79855-40-6; $Me_2N{-}B{-}NMe_2$, 79840-42-9; BH_3, 13283-31-3; $Me{-}BH_2$, 12538-96-4; $Ph{-}BH_2$, 45481-30-9; $H_2N{-}BH_2$, 14720-35-5; $Me_2N{-}BH_2$, 1838-13-7; $H_2N{-}BH{-}Cl$, 47938-17-0; $H_2N{-}BCl{-}Me$, 79855-41-7; $H_2N{-}BCl{-}Ph$, 79855-42-8; $H_2N{-}BCl{-}NH_2$, 79855-43-9; $H_2N{-}BCl{-}NMe_2$, 79855-44-0; $Me_2N{-}BCl_2$, 1113-31-1; Ph–CO–Cl, 98-88-4; $Ph{-}CO^+$, 19270-10-1; $H_2N{-}B{=}CH_2$, 79855-45-1.

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Synthesis and Characterization of Salts of the Bis(diisopropylamido)boron(III) Cation and Attempted Reactions To Make the Corresponding Bis(dimethylamido)boron(III) Cation[1]

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Bis(diisopropylamino)chloroborane and pure $AlCl_3$ react under rigorously anhydrous conditions in a one to one ratio to give an ionic compound that can be formulated as $[(i\text{-}Pr)_2N{=}B{=}N(i\text{-}Pr)_2]^+[AlCl_4]^-$. This representation is supported by ^{27}Al, ^1H, ^{13}C, and ^{11}B NMR data as well as by IR absorption bands at 1830–1900 cm^{-1} assigned to the B=N double bond. Conductivity data are also given for the related compound made from bis(dimethylamino)chloroborane. The $[Me_2N{=}B{=}NMe_2]^+$ cation was not stable in solution. Evidence is interpreted in favor of either its condensation to bigger units and/or the formation of a molecular compound with the $AlCl_4^-$ anion. Lewis base molecules will add to the tetramethyl cation to give a four-coordinate boron cation.

The bis(dimethylamido)phosphorus cation, $[(Me_2N)_2P]^+$, was described in papers from this laboratory.[2] The existence of that species, a coordinately unsaturated system stabilized by extensive $p\pi{-}p\pi$ bonding, in this case across the N–P–N

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