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Highly Energetic Tetraazidoborate Anion and Boron Triazide Adducts[†]

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The first crystal structures of the highly energetic tetraazidoborate anion and boron triazide adducts with quinoline and pyrazine as well as of tetramethylpiperidinium azide have been determined. Synthesis procedures and thorough characterization by spectroscopic methods of these hazardous materials are given. Quantum chemical calculations were carried out for $B(N_3)_4^-$, $B(N_3)_3$, $C_5H_5N{\cdot}B(N_3)_3$, $(N_3)_3B{\cdot}NC_4H_4N{\cdot}B(N_3)_3$, and the hypothetical $C_3H_3N_3{\cdot}[B(N_3)_3]_3$ at HF, MP2, and B3-LYP levels of theory. The structure of tetraazidoborate was optimized to S_4 symmetry and confirmed the results obtained from the X-ray diffraction analysis. The dissociation enthalpies for the pyridine (model for quinoline) as well as for the pyrazine adduct were calculated. For pyridine−boron triazide a value of 10.0 kcal mol^{-1} (for pyrazine−bis(boron triazide) an average of 2.35 kcal mol^{-1} per BN unit) was obtained.

Introduction

The chemistry of boron azides, first reported by E. Wiberg et al. in 1954,[1] was further investigated by P. I. Paetzold,[2−4] and the field has been reviewed.[5,6] Although the tetraazidoborate anion is known for more than 40 years, no spectroscopic data exist.[1] Structural and spectroscopic data for boron dichloride azide (trimeric)[7,8] and dimethylboron azide have, however, been reported in the literature.[9] Quite recently, additional boron azides have been reported and structurally characterized.[10−12] Calculated structures and gas-phase syntheses of boron triazide, boron chloride diazide, and boron dichloride azide are known; however, $B(N_3)_3$ has not been characterized in the condensed phase.[13−15] An isoelectronic analogue of boron triazide, the triazidocarbenium cation, has lately been reexamined with experimental and theoretical studies.[16]

In this work we present synthetic, spectroscopic, structural, and computational aspects of new sensitive boron triazide adducts and tetraazidoborate anion. The explosive properties of these materials were mentioned on the basis of qualitative observations. Detailed investigations of this field on related boron azides are reported.[4,5,13]

Results and Discussion

Syntheses and Properties of Boron Azides. The highly explosive lithium tetraazidoborate (**1**) was prepared according to a slightly modified procedure (cf. ref 1) by the reaction of lithium tetrahydridoborate with etheral hydrazoic acid. Hydrazoic acid was conveniently prepared by treatment of sodium azide with etheral tetrafluoroboric acid.

Compound **1** can be isolated as a solid but detonates when exposed to heat, electrostatic discharge, and/or mechanical shock. According to ref 1, lithium tetraazidoborate is also friction-sensitive. Traces of moisture immediately result in formation of hydrazoic acid, identified in the IR and ^{14}N NMR spectra.

Three coordinated boron azides (R_2BN_3) and diazides [$RB(N_3)_2$] are well-known; however, structural data previously reported are limited. Our interest in boron azides[11,12] prompted us to examine the reactivity of boron halides containing bulky substituents toward azides. Such a bulky, electron-donating substituent is the 2,2,6,6-tetramethylpiperidino (tmp) group. Attempts to convert bis(2,2,6,6-tetramethylpiperidino)boron fluoride into the corresponding azide failed, which is in contrast to the reported synthesis of bis(2,6-dimethylpiperidino)boron azide containing a less bulky substituent.[17] This is likely due to the fact that two tmp groups attached to boron prevent further nucleophilic attack. Prolonging the reaction time in addition to refluxing in dichloromethane led to the isolation of crystals suitable for X-ray crystallography. It was shown that hydrolysis (formation of HN_3) under BN bond cleavage took place and that 2,2,6,6-tetramethylpiperidinium azide (**2**) was formed. This observation was applied in the following reaction for the synthesis of an ammonium tetraazidoborate, displaying an alternative route for creating $B(N_3)_4^-$.

The reaction of tmpBCl$_2$ with trimethylsilyl azide has been reported to result in the formation of 2,2,6,6-tetramethylpiperidinoboron diazide (**3**).[18] Compound **3** is stable at ambient

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[†] Dedicated to Professor P. I. Paetzold on the occasion of his 65th birthday.

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(1) Wiberg, E.; Michaud, H. *Z. Naturforsch.* **1954**, *96*, 497, 499.
(2) Paetzold, P. I. *Z. Anorg. Allg. Chem.* **1963**, *326*, 47.
(3) Paetzold, P. I.; Hansen, H. J. *Z. Anorg. Allg. Chem.* **1966**, *345*, 79.
(4) Paetzold, P. I. *Fortschr. Chem. Forsch.* **1967**, *8*, 437.
(5) Paetzold, P. I. *Adv. Inorg. Chem.* **1987**, *31*, 123.
(6) Müller, J.; Paetzold, P. I. *Heteroat. Chem.* **1990**, *1*, 461.
(7) Müller, U. *Z. Anorg. Allg. Chem.* **1971**, *382*, 110.
(8) Wiberg, N.; Joo, W. C.; Schmid, K. H. *Z. Anorg. Allg. Chem.* **1972**, *394*, 197.
(9) Hausser-Wallis, R.; Oberhammer, H.; Einholz, W.; Paetzold, P. I. *Inorg. Chem.* **1990**, *29*, 3286.
(10) Paine, R. T.; Koestle, W.; Borek, T. T.; Duesler, E. N.; Hiskey, M. A. *Inorg. Chem.* **1999**, *38*, 3738.
(11) Fraenk, W.; Habereder, T.; Klapötke, T. M.; Nöth, H.; Polborn, K. *J. Chem. Soc., Dalton Trans.* **1999**, 4283.
(12) Fraenk, W.; Klapötke, T. M.; Krumm, B.; Mayer, P. *J. Chem. Soc., Chem. Commun.* **2000**, 667.
(13) Mulinax, R. L.; Okin, G. S.; Coombe, R. D. *J. Phys. Chem.* **1995**, *99*, 6294.
(14) Johnson, L. A.; Sturgis, S. A.; Al-Jihad, I. A.; Liu, B.; Gilbert, J. V. *J. Phys. Chem. A* **1999**, *103*, 686.
(15) Travers, M. J.; Eldenburg, E. L.; Gilbert, J. V. *J. Phys. Chem. A* **1999**, *103*, 9961.
(16) Petrie, M. A.; Sheehy, J. A.; Boatz, J. A.; Rasul, G.; Surya Prakash, G. K.; Olah, G. A.; Christe, K. O. *J. Am. Chem. Soc.* **1997**, *119*, 8802.
(17) Pieper, W.; Schmitz, D.; Paetzold, P. I. *Chem. Ber.* **1981**, *114*, 3801.

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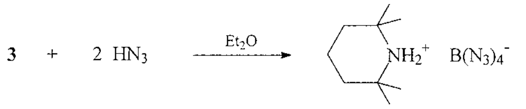
Table 1. NMR Data of **1**−**6** (δ in ppm, $\Delta\nu_{1/2}$ in Hz)

	$LiB(N_3)_4$,[a] **1**, THF-d_8	$[tmpH_2]N_3$,[b] **2**, $CDCl_3$	$tmpB(N_3)_2$, **3**, C_6D_6	$[tmpH_2][B(N_3)_4]$, **4**, CD_2Cl_2	qui·$B(N_3)_3$,[c] **5**, $CDCl_3$	pyr·$[B(N_3)_3]I_2$,[d] **6**, $CDCl_3$
CHN					9.37 (m, 1H)[e]	9.01 (s)
NH_2	8.7 (br)			6.5 (br)		
CH_2	1.72−1.61 (m)	1.39−1.25 (m)	1.81−1.69 (m)			
CH_3	1.45	1.20 (s)	1.50 (s)			
$^{13}C\{^1H\}$						
CN					148.0/145.0[f]	142.6
C-2,6		55.9	54.4	59.0		
C-3,5		35.2	36.6	35.6		
C-4		16.4	15.0	16.3		
CH_3		27.4	31.9	28.0		
^{11}B	−0.2		23.0	0.5	2.0	14.6
^{14}N ($\Delta\nu_{1/2}$)						
N_α	−312(400)	−303(300)	−298(700)	−308(870)	−311(660)	−307(800)
N_β	−141(40)	−133(100)	−149(70)	−141(110)	−144(70)	−147(70)
N_γ	−206(35)	−303(300)	−183(130)	−200(150)	−199(140)	−186(130)
NC		−276(350)	−261(680)	−296(120)	−154(290)	−70(∼1500)

[a] ^7Li NMR, $\delta = -0.9$. [b] tmp = 2,2,6,6-tetramethylpiperidino. [c] qui = quinoline. [d] pyr = pyrazine. [e] Additional ^1H NMR resonances: δ 8.71 (m, 2H), 8.08 (m, 1H), 7.84 (m, 1H), 7.76 (m, 2H). [f] Additional ^{13}C NMR resonances: δ 141.1, 133.4, 130.1, 129.5, 129.0, 124.1, 120.7.

temperature and reacts readily with HN_3 via BN bond cleavage to the tetramethylpiperidinium salt of tetraazidoborate (**4**):



(**4**) (1)

Both the lithium (**1**) and tetramethylpiperidinium salts (**4**) are highly moisture-sensitive (HN_3 formation); however, **4** is less explosive than **1**.

From earlier reports,[1] it was shown that it is extremely difficult to obtain the free boron triazide in the solid state. The adduct with pyridine, $C_5H_5N{\cdot}B(N_3)_3$, is a distillable liquid but explodes violently above certain temperatures or when traces of HN_3 are present (hydrolysis).[4] To obtain information with regard to the solid-state structure of a boron triazide adduct, we selected quinoline as a promising pyridine analogue. The quinoline and also the pyrazine adduct of boron triazide were synthesized according to

$$L[BCl_3]_n + 3n\,Me_3SiN_3 \xrightarrow{CH_2Cl_2} L[B(N_3)_3]_n \qquad (2)$$

$$L = \text{quinoline},\ n = 1\ (\mathbf{5}) \quad = \text{pyrazine},\ n = 2\ (\mathbf{6})$$

modified to ref 4, by addition of trimethylsilyl azide to a mixture consisting of the Lewis base and boron trichloride. Both adducts, in particular the diadduct pyrazine−bis(boron triazide) (**6**), are explosive crystalline solids, which detonate violently on impact, rapid heating, and/or electrostatic discharge.

The reaction of trimethylsilyl azide with a 3:1 mixture consisting of boron trichloride and 1,3,5-triazine resulted in a violent explosion during the workup procedures. Therefore, studies on this system were not further pursued. It remains unclear whether the triazine−tris(boron triazide) adduct and/or partially substituted boron azides had been formed. All compounds are expected, and $(BCl_2N_3)_3$[2,19] was proved to be extremely explosive.

All of the boron azides discussed here show in the vibrational spectra (IR, Raman) the characteristic antisymmetric stretching vibrations ($\nu_{N=N}$) in the regions 2183−2113 cm^{-1} (IR) and 2192−2102 cm^{-1} (Raman). The symmetric stretching vibration (ν_{N-N}) is not as useful for characterizing boron azides because it occurs in the same frequency range as ν_{BN}.

NMR Spectroscopy. The multinuclear NMR data of compounds **1**−**6** are listed in Table 1. A solvent effect on the line shape of the azide resonances in the ^{14}N NMR spectrum is observed for **1**. Changing from diethyl ether to THF-d_8 causes a decrease of the line width of all three resonances, the largest observed for N_γ ($\Delta\nu_{1/2} = 250$ Hz, Et_2O). This is presumably due to the better coordination ability of THF to lithium, causing a tetraazidoborate with smaller interactions with the cation, therefore leading to sharper resonances in the ^{14}N NMR spectrum.[20] The ^{11}B NMR shifts of $B(N_3)_4^-$ in **1** (δ −0.2) and **4** (δ 0.5) are comparable to that of BF_4^- (δ −1.4) and are low-field-shifted compared to other tetrapseudohalogen borates (δ $B(NCO)_4^-$, −11.5; $B(NCS)_4^-$, −16.7; $B(CN)_4^-$, −38.6).[21]

Keeping in mind the typical range of amine−borane adducts in the region around zero,[22] the resonance of **6** (^{11}B NMR, δ 14.6) is exceptionally low-field-shifted. Compared with the expected value of the quinoline adduct in **5** (^{11}B NMR, δ 2.0), this shift indicates a weaker interaction between boron and donor nitrogen in **6** and suggests more a dissociated form of boron triazide in the presence of pyrazine. The ^1H resonances of the hydrogen atoms in α-position to the nitrogen of the donor base in **5** and **6** are deshielded by 0.55 ppm relative to that of the free base because of the electron-withdrawing borane. The ^{14}N resonances of quinoline and pyrazine in **5** (δ −154) and **6** (δ −70) are high-field shifted, displaying quinolinium and pyrazinium character, respectively, relative to the shifts of the free bases (^{14}N NMR, δ −73 for quinoline and δ −50 for pyrazine in $CDCl_3$).

Description of the Crystal Structures. Tetramethylpiperidinium azide (**2**) crystallizes in the space group $Cmc2_1$ with four formula units in the unit cell. The cation takes up a chair conformation as shown in Figure 1. The N−N−N angle of the azide group is close to linearity (178.8(2)°), as expected, and the N−N distances are 1.174(3) Å for N(1)−N(2) and 1.177(2) Å for N(2)−N(3), typical for ionic azides. The cation and anion are linked by $NH_2{\cdots}N_3$ hydrogen bridges as displayed

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(18) Mennekes, T.; Paetzold, P. I. *Z. Anorg. Allg. Chem.* **1995**, *621*, 1175.

(19) Paetzold, P. I.; Gayoso, M.; Dehnicke, K. *Chem. Ber.* **1965**, *98*, 1173.

(20) Witanowski, M.; Stefaniak, L.; Webb, G. A. *Annu. Rep. NMR Spectrosc.* **1986**, *18*, 486.

(21) Bernhardt, E.; Henkel, G.; Willner, H. *Z. Anorg. Allg. Chem.* **2000**, *626*, 560 and references therein.

(22) Nöth, H.; Wrackmeyer, B. *Nuclear Magnetic Resonance, Spectroscopy of Boron Compounds*; Springer-Verlag: Berlin, 1978; Vol. 14.

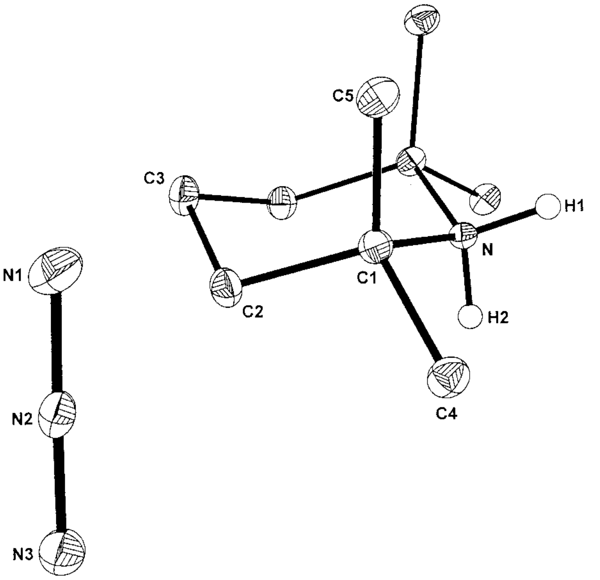


Figure 1. ORTEP plot of the molecular structure of 2,2,6,6-tetramethylpiperidinium azide (**2**) with thermal ellipsoids drawn at the 25% probability level. Hydrogen atoms bound to carbon are omitted for clarity. Selected bond lengths (Å) and angles (deg) are the following: N(1)−N(2) 1.174(3), N(2)−N(3) 1.177(2), N−C(1) 1.527(2), N−H(1) 0.89(2), N−H(2) 0.87(3), N(1)−N(2)−N(3) 178.8(2), C(1)−N−C(1A) 120.2(2).

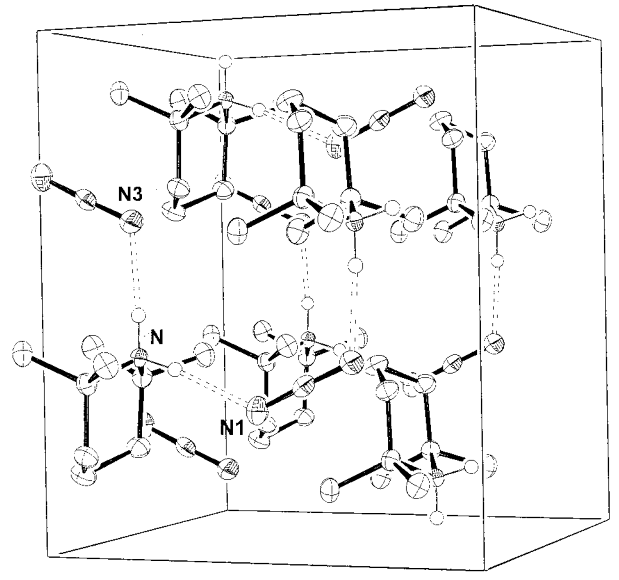


Figure 2. View of the unit cell of **2** showing N−H···N interactions. Bond lengths (Å) and angles (deg) are the following: N−H(1)···N(3) 2.864(2), 176(2); N−H(2)···N(1) 2.945(2), 173(2).

in Figure 2. The N···N(3) and the N···N(1) contacts are 2.864(2) and 2.945(2) Å, and the N−H(1)···N(3) and the N−H(2)···N(1) angles are almost linear (176(2)° and 173(2)°).

The tetraazidoborate **4** crystallizes in the space group $P2_1/n$ with $Z = 8$. Therefore, there are two independent [tmpH_2][$B(N_3)_4$] units in the asymmetric unit (Figure 3). This is due to the fact that one tmpH_2 cation is present in a chair conformation while the second cation is disordered. The fact that there are two independent units results from the different arrangement of N−H···N bridges between the tmpH_2 cations and the azido groups of the borate (Figure 4). One type of tmpH_2^+ coordinates via two single NH hydrogen atoms adjacent to α-nitrogen atoms of the two different $B(N_3)_4^-$ units, while the second tmpH_2^+ makes single N−H···N bridges to one α-nitrogen and one

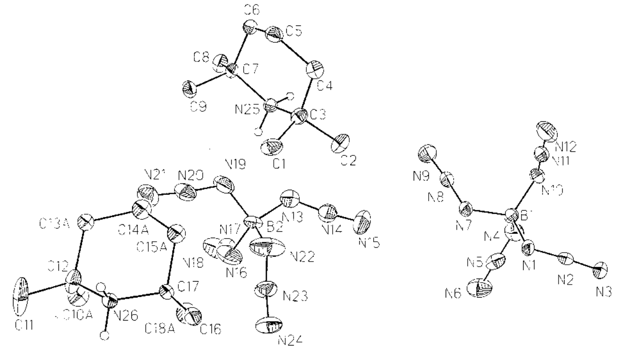


Figure 3. ORTEP plot of the molecular structure of the two 2,2,6,6-tetramethylpiperidinium tetraazidoborate (**4**) units with thermal ellipsoids drawn at the 25% probability level. Selected bond lengths (Å) and angles (deg) are the following: B(1)−N(1) 1.549(6), N(1)−N(2) 1.219(5), N(2)−N(3) 1.135(5), N(1)−N(2)−N(3) 176.8(5), B(1)−N(1)−N(2) 117.6(4), N(1)−B(1)−N(4) 113.2(4), N(1)−B(1)−N(10) 113.7(5), N(7)−B(1)−N(10) 114.6(4), N(4)−B(1)−N(7) 113.6(5), N(4)−B(1)−N(10) 101.5(4), N(7)−B(1)−N(1) 100.9(3).

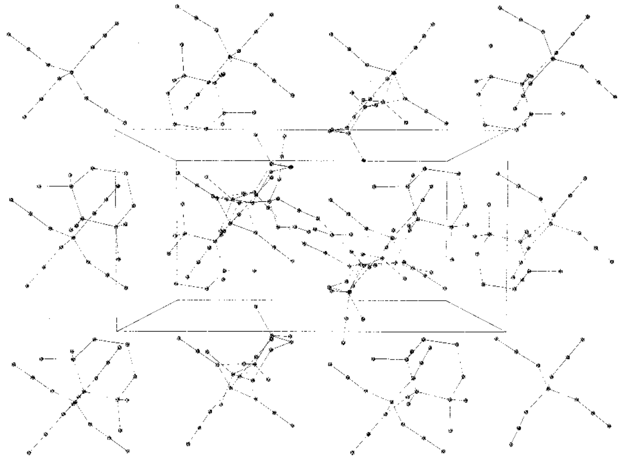
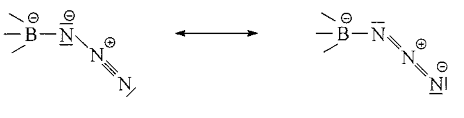


Figure 4. View of the unit cell of **4** showing N−H···N interactions. Bond lengths (Å) and angles (deg) are the following: N(25)−H(25A)···N(19) 3.047(6), 169.7; N(25)−H(25B)···N(10) 3.116(5), 172.3; N(26)−H(26A)···N(1) 3.076(5), 175.4; N(26)−H(26B)···N(15) 3.209(6), 167.6.

Scheme 1



A **B**

γ-nitrogen atom of two adjacent $B(N_3)_4^-$ groups; e.g., all NH hydrogens are involved in hydrogen bridges.

In the two $B(N_3)_4^-$ units the B−N bond lengths ranges from 1.529(7) to 1.549(6) Å and from 1.509(8) to 1.535(8) Å. The shorter bonds are those in which the γ-nitrogen atom is involved in N−H···N bonding. The $N_\alpha-N_\beta$ bond lengths are on average equal for both $B(N_3)_4^-$ anions (1.22/1.24 Å), while the terminal $N_\beta-N_\gamma$ bonds are significantly shorter, the ranges spanning values of 1.046(6)−1.142(7) Å. Thus, the bonding contribution of **A** dominates over **B** (Scheme 1). These data agree very well with calculated values as do the bond angles. Here for B(1) the B(1)−N−N bond angles range from 116.8(4)° to 120.6(4)°, while they are much more uniform for B(2) (119.0(6)−120.3(5)°).

The reverse is found for the N−N−N bond angles, which are 175.0(6)−176.8(5)° for B(1) and 162.8(6)−174.8(6)° for

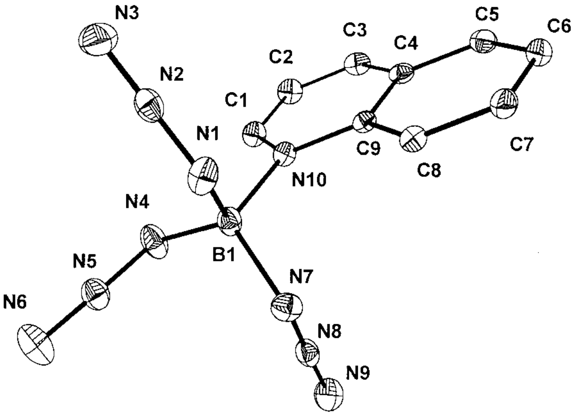


Figure 5. ORTEP plot of the molecular structure of quinoline−boron triazide (**5**) with thermal ellipsoids drawn at the 25% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg) are the following: B(1)−N(1) 1.527(3), N(1)−N(2) 1.226(2), N(2)−N(3) 1.137(2), B(1)−N(10) 1.619(2), N(1)−N(2)−N(3) 175.2(2), B(1)−N(1)−N(2) 118.8(2), N(1)−B(1)−N(4) 114.0(1), N(1)−B(1)−N(10) 109.9(1), N(7)−B(1)−N(10) 110.9(1), N(4)−B(1)−N(7) 113.6(2), N(4)−B(1)−N(10) 104.6(1), N(7)−B(1)−N(1) 104.0(1).

B(2). In any case, $B(2)(N_3)_4^-$ is much less symmetric than $B(1)(N_3)_4^-$. Therefore, the ideal S_4 symmetry for the $B(1)(N_3)_4^-$ anion is almost realized while the $B(2)(N_3)_4^-$ anion is less symmetric. Obviously, N−H···N bonding and packing effects play a role.

Quinoline−boron triazide (**5**) crystallizes in the space group $P\bar{1}$ with two formula units in the unit cell. The boron atom is surrounded by the three azide groups and the quinoline in a tetrahedral fashion (Figure 5). The $B-N_\alpha$ distance is 1.523(3)−1.527(3) Å, which is comparable with the distance found for **4**. While the $N_\alpha-N_\beta$ bond lengths range from 1.216(2) to 1.226(2) Å, the $N_\beta-N_\gamma$ bond distances range from 1.129(2) to 1.137(2) Å, showing considerable N≡N triple bond character.[23,24] The $B-N_{qui}$ distance is as for a coordinative bond, 1.619(2) Å, longer than the $B-N_\alpha$ bond lengths. The three azide groups are, as for a typical covalently bound azide group, slightly bent (N−N−N, 173.7(2)−175.2(2)°); the B−N−N angles range from 118.8(2)° to 119.4(2)°.

The 1:2 adduct pyrazine−bis(boron triazide) (**6**) crystallizes in the space group $P\bar{1}$ with one molecule in the unit cell (Figure 6). The $B-N_\alpha$ (1.511(3)−1.520(3) Å), $N_\alpha-N_\beta$ (1.217(2)−1.225(2) Å), and the $N_\beta-N_\gamma$ (1.128(2)−1.133(2) Å) distances are almost identical with those found for **5**. A significant difference is found for the $B-N_{pyr}$ bond length. The latter is 1.657(2) Å, significantly longer than the corresponding distance found for **5**, assuming only a weak $B-N_{pyr}$ interaction. However, a boron atom on the way to planarity in **6** is not unambiguously observed. The N−N−N (175.4(2)−175.4(2)°) and the B−N−N (118.6(2)−121.1(2)°) angles are similar to the corresponding values found for **5**.

Recently, the crystal structures of group13 tetraazido anions of the heavier homologues (Al, Ga, In) as well as amine adducts of gallium/indium triazides have been reported.[25]

Quantum Chemical Calculations. The calculations were performed with the program package Gaussian 98.[26] The structure of $B(N_3)_4^-$, its total energy (E) and zero-point energy (zpe), and the vibrational data were calculated at the electron-correlated MP2 and B3-LYP levels of theory,[27,28] using a polarized 6-31+G(d,p) double-ζ basis set with a diffuse function added.[29]

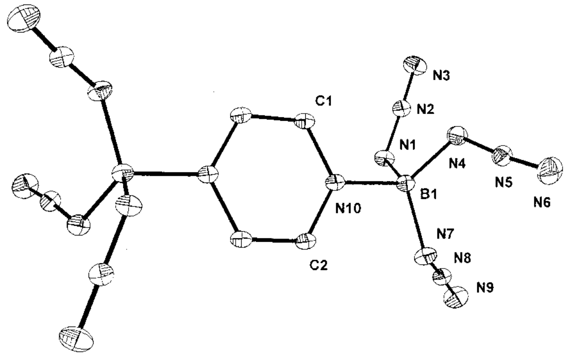


Figure 6. ORTEP plot of the molecular structure of pyrazine−bis(boron triazide) (**6**) with thermal ellipsoids drawn at the 25% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg) are the following: B(1)−N(1) 1.511(3), N(1)−N(2) 1.225(2), N(2)−N(3) 1.132(2), B(1)−N(10) 1.657(2), N(1)−N(2)−N(3) 175.4(2), B(1)−N(1)−N(2) 118.6(2), N(1)−B(1)−N(4) 111.2(1), N(1)−B(1)−N(10) 106.4(1), N(7)−B(1)−N(10) 103.7(1), N(4)−B(1)−N(7) 115.2(2), N(4)−B(1)−N(10) 105.5(1), N(7)−B(1)−N(1) 113.9(2).

The structures and frequencies of $B(N_3)_3$ and the adducts $C_5H_5N{\cdot}B(N_3)_3$ (as a model for $C_9H_7N{\cdot}B(N_3)_3$ (**5**)) and $C_4H_4N_2{\cdot}[B(N_3)_3]_2$ (**6**) were computed at SCF (HF) and density functional levels of theory (B3-LYP).[28]

Whereas the CCSD(T) method has generally been shown to be reliable for covalently bound nonmetal compounds,[30,31] often the less expensive MP2 and B3-LYP methods in combination with a double-ζ basis set give very good structural results and vibrational frequencies.[30,31]

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(23) Klapötke, T. M. *Chem. Ber.* **1997**, *130*, 443 and references therein.

(24) Tornieporth-Oetting, I. C.; Klapötke, T. M. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 511.

(25) Sussek, H.; Stowasser, F.; Pritzkow, H.; Fischer, R. A. *Eur. J. Inorg. Chem.* **2000**, 455 and references therein.

(26) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B. G.; Chen, W.; Wong, M. W.; Andres, J. L.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. Gaussian 98, revision A.3; Gaussian, Inc.: Pittsburgh, PA, 1998.

(27) (a) Møller, C.; Plesset, M. S. *Phys. Rev.* **1934**, *46*, 618. (b) Bartlett, R. J.; Silver, D. M. *J. Chem. Phys.* **1975**, *62*, 3258. (c) Pople, J. A.; Binkley, J. S.; Seeger, R. *Int. J. Quantum Chem., Quantum Chem. Symp.* **1976**, *10*, 1. (d) Pople, J. A.; Seeger, R.; Krishnan, R. *Int. J. Quantum Chem., Quantum Chem. Symp.* **1977**, *11*, 1. (e) Saebo, S.; Almlof, J. *Chem. Phys. Lett.* **1989**, *154*, 83. (f) Head-Gordon, M.; Pople, J. A.; Frisch, M. J. *Chem. Phys. Lett.* **1988**, *153*, 503. (g) Frisch, M. J.; Head-Gordon, M.; Pople, J. A. *Chem. Phys. Lett.* **1990**, *166*, 275, 281. (h) Head-Gordon, M.; Head-Gordon, T. *Chem. Phys. Lett.* **1994**, *220*, 122.

(28) (a) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev.* **1988**, *B37*, 785. (b) Becke, A. D. *Phys. Rev.* **1988**, *A38*, 3098. (c) Miehlich, B.; Savin, A.; Stoll, H.; Preuss, H. *Chem. Phys. Lett.* **1989**, *157*, 200. (d) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648.

(29) (a) Ditchfield, R.; Hehre, W. J.; Pople, J. A. *J. Chem. Phys.* **1971**, *54*, 724. (b) Hehre, W. J.; Ditchfield, R.; Pople, J. A. *J. Chem. Phys.* **1972**, *56*, 2257. (c) Hariharan, P. C.; Pople, J. A. *Mol. Phys.* **1974**, *27*, 209. (d) Gordon, M. S. *Chem. Phys. Lett.* **1980**, *76*, 163. (e) Hariharan, P. C.; Pople, J. A. *Theor. Chim. Acta* **1973**, *28*, 213.

(30) Dixon, D. A.; Feller, D. *Computational Thermochemistry of Fluorinated Compounds*; 14th ACS Winter Fluorine Conference, St. Petersburg, FL, January 17−22, 1999; Abstract 29.

(31) Klapötke, T. M.; Schulz, A.; Harcourt, R. D. *Quantum Chemical Methods in Main-Group Chemistry*; Wiley: Chichester, New York, 1998; p 89.

Table 2. Crystal Data and Structure Refinements for **2** and **4**−**6**

	2	**4**	**5**	**6**
empirical formula	$C_9H_{20}N_4$	$C_9H_{20}BN_{13}$	$C_9H_7BN_{10}$	$C_4H_4B_2N_{20}$
fw	184.28	321.15	266.06	353.86
temp [K]	200(3)	200(3)	193(2)	193(2)
cryst size [mm]	0.30 × 0.05 × 0.03	0.36 × 0.10 × 0.07	0.40 × 0.30 × 0.30	0.20 × 0.10 × 0.10
cryst syst	orthorhombic	monoclinic	triclinic	triclinic
space group	$Cmc2_1{}^a$	$P2_1/n$	$P\bar{1}$	$P\bar{1}$
a [Å]	9.581(1)	7.7179(3)	7.2035(7)	6.7658(7)
b [Å]	11.325(1)	14.8750(8)	8.2093(8)	7.1468(8)
c [Å]	9.945(1)	29.553(2)	11.642(1)	8.2400(9)
α [deg]			104.729(2)	66.586(2)
β [deg]		95.438(6)	96.014(2)	83.475(2)
γ [deg]			112.423(1)	84.455(2)
V [Å^3]	1079.0(2)	3377.5(3)	599.6(1)	362.68(7)
Z	4	8	2	1
D_{calcd} [g/cm^3]	1.134	1.263	1.474	1.620
abs coeff [mm^{-1}]	0.072	0.089	0.104	0.125
F(000)	408	1360	272	178
θ range [deg]	2.78−27.98	1.95−24.03	3.72−57.74	5.40−58.46
index range	$-12 \leq h \leq 12$	$-8 \leq h \leq 8$	$-9 \leq h \leq 9$	$-7 \leq h \leq 8$
	$-14 \leq k \leq 14$	$-17 \leq k \leq 17$	$-10 \leq k \leq 10$	$-8 \leq k \leq 9$
	$-12 \leq l \leq 11$	$-33 \leq l \leq 25$	$-14 \leq l \leq 14$	$-10 \leq l \leq 10$
reflns collected	4361	10 762	3530	2120
independent reflns	1305 (R_{int} = 0.0416)	4970 (R_{int} = 0.0464)	1854 (R_{int} = 0.0176)	1107 (R_{int} = 0.0213)
obsd reflns	1047	2334	1492	972
max, min transm		0.9956, 0.9915	1.000, 0.706	1.000, 0.5810
data/restraints/params	1305/1/111	4970/5/411	1854/0/181	1107/0/126
goodness-of-fit F^2	0.954	0.867	1.054	1.062
R1, wR2 [$I > 4\sigma(I)$]	0.0295, 0.0585^b	0.0684, 0.1690^b	0.0400, 0.1085	0.0391, 0.1092
R1, wR2 (all data)	0.0446, 0.0622	0.1366, 0.1968	0.0520, 0.1176	0.0439, 0.1131
largest diff peak/hole [e/Å^3]	0.168/−0.185	0.619/−0.293	0.233/−0.177	0.185/−0.197

[a] Flack parameter 0(2). [b] [$I > 2\sigma(I)$].

Table 3. Computed Structural Parameters and Energies for $B(N_3)_4^-$

	HF/6-31+G(d,p)	B3-LYP/6-31+G(d,p)	MP2(FC)/6-31+G(d,p)	MP2(FULL)/6-31+G(d,p)
symmetry	S_4	S_4	S_4	S_4
$-E$/au	677.964 094	681.873 491	680.129 841	680.182 260
NIMAG	0	0		
zpe/kcal mol^{-1}	39.6	36.2		
d(B−N1)/Å	1.552	1.552	1.544	1.542
d(N1−N2)/Å	1.206	1.217	1.229	1.227
d(N2−N3)/Å	1.109	1.149	1.177	1.176
×c1∠(N1′−B−N1)/deg	107.9	108.1	107.7	107.8
∠(B−N1−N2)/deg	118.0	121.1	120.2	120.2
∠(N1−N2−N3)/deg	175.9	174.8	173.9	174.0

Tetraazidoborate Anion, $B(N_3)_4^-$. At the HF/6-31+G(d,p) level of theory the structure of the $B(N_3)_4^-$ anion was fully optimized in C_1 symmetry, resulting in an S_4 structure with no imaginary frequencies (NIMAG = 0). Consequently, the MP2 and B3-LYP computations were performed within S_4 symmetry (Table 3). The computed B3-LYP frequencies (Table 4) are in excellent accord with the experimental IR and Raman data. Table 4 shows a comparison of the experimentally observed and computed frequencies, which have been scaled with appropriate scaling factors (HF, 0.89; B3-LYP, 0.96).[32]

Compounds $B(N_3)_3$, $C_5H_5N{\cdot}B(N_3)_3$ (As a Model for $C_9H_7N{\cdot}B(N_3)_3$ (5)), $C_4H_4N_2{\cdot}[B(N_3)_3]_2$ (6), and $C_3H_3N_3{\cdot}[B(N_3)_3]_3$. The structures, energies and vibrational data of $B(N_3)_3$, $C_5H_5N{\cdot}B(N_3)_3$, and $C_4H_4N_2{\cdot}[B(N_3)_3]_2$ (**6**) were computed at HF/6-31G-(d) and B3-LYP/6-31G(d) levels of theory. Whereas at the noncorrelated HF level the 1:1 adduct $C_5H_5N{\cdot}B(N_3)_3$ was found to represent a true minimum; the 1:2 adduct $C_4H_4N_2{\cdot}[B(N_3)_3]_2$ (**6**) was found not to be stable but to dissociate and form a very weakly bound van der Waals type complex with B···N bond lengths of 3.63 Å. However, when electron correlation was taken into account at the hybride B3-LYP level of theory both experimentally observed adducts, $C_5H_5N{\cdot}B(N_3)_3$ and $C_4H_4N_2{\cdot}[B(N_3)_3]_2$ (**6**) were found to represent true minima (NIMAG = 0) with very good agreement between the observed and computed structural parameters. It is important to stress that for the 1:1 adduct the computed B···N ($C_5H_5N{\cdot}B(N_3)_3$) bond length of 1.663 Å is considerably shorter than the computed B···N bond length of 1.735 Å for the 1:2 adduct $C_4H_4N_2{\cdot}[B(N_3)_3]_2$ (**6**). This trend is in good agreement with the experimental values of 1.619(2) Å for $C_9H_7N{\cdot}B(N_3)_3$ (**5**) and 1.657(2) Å for $C_4H_4N_2{\cdot}[B(N_3)_3]_2$ (**6**).

The dissociation energies according to

$$C_5H_5N{\cdot}B(N_3)_3 \rightarrow B(N_3)_3 + C_5H_5N \tag{3}$$

and

$$C_4H_4N_2{\cdot}[B(N_3)_3]_2\ (\mathbf{6}) \rightarrow 2B(N_3)_3 + C_4H_4N_2 \tag{4}$$

can be used to obtain an appreciation for the B···N bond strengths in both adducts. The calculated total energies (Table 5) can be used to predict theoretically the reaction enthalpy

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[32] Foresman, J. B.; Frisch, A. *Exploring Chemistry with Electronic Structure Methods*, 2nd ed.; Gaussian, Inc.: Pittsburgh, PA, 1993; p 64.

Table 4. Computed and Vibrational Results for $B(N_3)_4^-$

	HF/6-31+G(d,p),[a,b] $F = 0.89$	B3-LYP/6-31+G(d,p),[a] $F = 0.96$	IR (intens) (1)	Raman (intens) (1)
ν_1 (A)	2200 (0/154)	2175 (0)		2192 (2)
ν_2 (B)	2178 (1387/112)	2158 (955)	2183 (s)	2172 (1)
ν_3 (E)	2160 (2167/85)	2143 (1399)	2131 (vs)	2140 (2)
ν_4 (A)	1317 (0/47)	1344 (0)		1373 (4)
ν_5 (B)	1289 (561/2)	1332 (259)	1361 (s)	1352 (6)
ν_6 (E)	1284 (724/2)	1331 (266)	1326 (s)	1319 (3)
ν_7 (E)	900 (540/6)	875 (443)	885 (s)	917 (1)
ν_8 (B)	846 (529/7)	845 (480)	826 (m)	
ν_9 (A)	743 (0/1)	708 (0)		
ν_{10} (B)	700 (135/8)	663 (63)	701 (m)	
ν_{11} (E)	649 (72/3)	623 (48)	645 (m)	
ν_{12} (B)	629 (43/0)	583 (26)	584 (m)	
ν_{13} (A)	626 (0/0.1)	580 (0)		
ν_{14} (E)	622 (5/0.2)	576 (4)		
ν_{15} (A)	490 (0/6)	483 (0)		507 (4)
ν_{16} (B)	402 (13/10)	396 (8)	424 (w)	
ν_{17} (E)	385 (3/1)	380 (3)		
ν_{18} (A)	291 (0/6)	288 (0)		303 (6)
ν_{19} (B)	285 (2/2)	281 (3)		
ν_{20} (A)	160 (0/5)	154 (0)		180 (8)
ν_{21} (E)	130 (2/1)	122 (2)		
ν_{22} (B)	81 (0/9)	73 (0)		108 (10)
ν_{23} (E)	45 (0.2/7)	41 (0.3)		
ν_{24} (B)	36 (0.2/9)	36 (0.1)		
ν_{25} (A)	30 (0/10)	29 (0)		

[a] IR intensities in km mol^{-1}. [b] Raman intensities in Å^4 amu^{-1}.

Table 5. Computed Structural Parameters and Energies for $B(N_3)_3$, $C_5H_5N{\cdot}B(N_3)_3$, and $C_4H_4N_2{\cdot}[B(N_3)_3]_2$ (**6**)

compound	$-E$, au	zpe, kcal mol^{-1}	NIMAG	d(B···N), Å
	HF/6-31G(d)			
$B(N_3)_3$	514.615732	31.1	0	
$C_5H_5N{\cdot}B(N_3)_3$	761.310530	92.7	0	1.679
$C_4H_4N_2{\cdot}[B(N_3)_3]_2$ (**6**)	1291.920907	114.9	0	3.630
C_5H_5N	246.695820	59.9	0	
$C_4H_4N_2$	262.683005	52.1	0	
	B3LYP/6-31G(d)			
$B(N_3)_3$	517.542046	28.6	0	
$C_5H_5N{\cdot}B(N_3)_3$	765.841636	86.0	0	1.663
$C_4H_4N_2{\cdot}[B(N_3)_3]_2$ (**6**)	1299.404581	107.6	0	1.735
C_5H_5N	248.284973	55.9	0	
$C_4H_4N_2$	264.317234	48.4	0	

values for reactions 3 and 4. The dissociation energies of reactions 3 and 4 were calculated, which, after correction[31] for zero-point energies (Table 5), differences in rotational ($\Delta U(1)^{\rm rot} = (^3/_2)RT$; $\Delta U(2)^{\rm rot} = 3RT$) and translational ($\Delta U(1)^{\rm tr} = (^3/_2)RT$; $\Delta U(2)^{\rm tr} = 3RT$) degrees of freedom, and the work term ($p\Delta V(1) = 1RT$; $p\Delta V(2) = 2RT$), were converted into the gas-phase dissociation enthalpies at room temperature:

$$\Delta H^\circ_{298} = +10.0 \text{ kcal mol}^{-1} \qquad \text{for reaction 3}$$

$$\Delta H^\circ_{298} = +4.7 \text{ kcal mol}^{-1} \qquad \text{for reaction 4}$$

Therefore, the bond dissociation enthalpy value (BDE) for the 1:1 adduct (dissociation into $B(N_3)_3$ and C_5H_5N) is 10.0 kcal mol^{-1} and corresponds to a “normal” Lewis acid−Lewis base B···N bond strength.[31,33] However, for the 1:2 adduct the average BDE is only 2.35 kcal mol^{-1}, which accounts for a very weak and only loosely bound adduct (cf. ^{11}B NMR chemical shifts in solution). This value, however, reflects only the average BDE; the elimination of the *first* $B(N_3)_3$ unit from **6** is thermodynamically even more feasible than the value of 2.35 kcal mol^{-1} suggests.

The adduct of 1,3,5-triazine, $C_3H_3N_3$, and $B(N_3)_3$, i.e., the compound $C_3H_3N_3{\cdot}[B(N_3)_3]_3$, was found to be unstable at both HF and B3-LYP levels of theory. At the density functional B3-LYP/6-31G(d) level this species was found to represent a very weakly bound van der Waals type adduct with B···N distances of 3.5 Å ($E = -1\,833.001\,393$ au, NIMAG = 0, zpe = 127.9 kcal mol^{-1}).

Conclusion

The highly explosive lithium tetraazidoborate, in agreement with its first report by E. Wiberg, was shown to be $LiBN_{12}$, is the third highest nitrogen-containing solid material (90.45%) following hydrazinium azide and ammonium azide (93.29%). As the last member in the series of the group13 tetraazido anions, tetraazidoborate is finally structurally and spectroscopically characterized. Moreover, in addition to this, structurally characterized explosive adducts of boron triazide are reported. NMR shifts and quantum chemical calculations have been used to predict and/or confirm the BN_3 bonding situation obtained from the results of X-ray crystallography.

Experimental Section

CAUTION. All of the materials described here are explosive and toxic, in particular hydrazoic acid, **1**, and **6**. They may violently explode under various conditions and should be handled only in small amounts with extreme caution. The use of safety equipment like leather gloves, leather coat, and face shield is strongly advised.

General. All manipulations of air- and moisture-sensitive materials were performed under an inert atmosphere of dry nitrogen using standard Schlenk techniques. Solvents were dried and degassed by standard methods. Raman spectra were recorded on a Perkin-Elmer 2000 NIR FT-Raman spectrometer fitted with a Nd:YAG laser (1064 nm), and infrared spectra were recorded on a Nicolet 520 FT-IR spectrometer between KBr plates or as a pellet as described. The elemental analyses were performed with a C, H, N Analysator Elementar Vario EL. NMR spectra were recorded on a JEOL EX400 instrument. Chemical shifts are recorded with respect to $(CH_3)_4Si$ (^{1}H, ^{13}C), $BF_3{\cdot}OEt_2$ (^{11}B), CH_3NO_2 (^{14}N), and LiCl (^{7}Li). For the determination of the melting points, samples were heated in capillaries in a Büchi B540 instrument. Bis(2,2,6,6-tetramethylpiperidino)boron fluoride and 2,2,6,6-tetramethylpiperidinoboron dichloride were prepared according to refs 34 and 35. Other chemicals were used as received (Aldrich, Fluka).

Recordings of mass spectra and NMR spectra of the triazine reaction were not done because of possible damage to the instruments. Elemental analyses were performed for all compounds except for **1** and **6**, but only useful results are reported.

Crystallography. The data for **2** and **4** (Table 2) were collected on a STOE IPDS area detector. The structures were solved and refined by direct methods using the SHELX-97 package. The data for **5** and **6** (Table 2) were collected on a SIEMENS SMART area detector. The structures were solved by direct methods (SHELXS-97) and refined by means of full-matrix least-squares procedures using SHELXL-97.

For **4**, all non-hydrogen atoms were refined anisotropically except for the disordered carbon atoms of one of the tmp cations. Their refinement leads to SOF values of 0.48 and 0.52. All hydrogen atoms were put in calculated positions.

Syntheses and Characterization of Compounds. Improved Preparation of Etheral Hydrazoic Acid. A solution of HBF_4 in diethyl ether (2 M) was added dropwise to a suspension of NaN_3 in diethyl ether at −78 °C. The mixture was warmed slowly and stirred for an additional 12 h at ambient temperature. The volatile components of this mixture

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(33) Klapötke, T. M.; Tornieporth-Oetting, I. C. *Nichtmetallchemie*; VCH: Weinheim, 1994.

(34) Nöth, H.; Weber, S. *Z. Naturforsch.* **1983**, *38b*, 1460.

(35) Nöth, H.; Rasthofer, B.; Weber, S. *Z. Naturforsch.* **1984**, *39b*, 1058.

were condensed under reduced pressure into a glass vessel containing dry ether to give a solution of HN_3 in diethyl ether.

Lithium Tetraazidoborate (1). A solution of 1.3 M HN_3 in diethyl ether (5.2 mmol, 4 mL) was added to a solution of $LiBH_4$ (1.0 mmol) in diethyl ether (10 mL) at −78 °C. A colorless solid immediately precipitated. The suspension was allowed to warm slowly, and the formation of hydrogen was observed. After the solution was additionally stirred (12 h) at ambient temperature, all volatile products were removed in vacuo and the remaining oil was extracted twice with diethyl ether. After vacuum evaporation of the ether, the remaining solid was washed with hexane and dried again in vacuo. **1** was isolated as a colorless solid; yield, 0.11 g; mp, 75−78 °C (dec). IR (Nujol, selected absorptions): 2183/2131 (s−vs) ($\nu_{as}(N_3)$), 1361 (s), 1326 (s), 1263 (vs), 1146 (m), 1099 (m), 1043 (s), 885 (s), 826 (m), 701 (m), 645 (m), 584 (m), 424 (w) cm^{-1}. Raman (50 mW): 2192/2172/2140 (1−2) ($\nu_{as}(N_3)$), 1373 (4), 1352 (6), 1319 (3), 1033 (1), 917 (1), 599 (1), 583 (1), 507 (4), 303 (6), 180 (8), 108 (10) cm^{-1}.

Reaction of Bis(2,2,6,6-tetramethylpiperidino)boron Fluoride with Trimethylsilyl Azide. A solution of tmp$_2$BF (0.31 g, 1.0 mmol) in dichloromethane (5 mL) was treated with trimethylsilyl azide (0.23 g, 2.0 mmol) at −78 °C. The solution was allowed to warm slowly and was stirred for 2 weeks at ambient temperature. Monitoring of this mixture by ^{11}B NMR spectroscopy showed no change of the starting material. After it was additionally refluxed for 48 h, crystals were slowly obtained. By use of X-ray analyses, these crystals were found to be 2,2,6,6-tetramethylpiperidinium azide (**2**). The remaining solution gave no evidence of the formation of a boron azide and was discarded. Data for **2**: mp 143−146 °C. IR (pellet, selected absorptions): 3443 (s, br) (νNH), 3011/2952/2857/2821/2770 (m) (ν(CH)), 2037/2024/2010 (vs) ($\nu_{as}(N_3)$), 1634 (m), 1579 (m), 1474 (w), 1387 (m), 1335 (vw) ($\nu_s(N_3)$), 1231 (m), 1119 (m), 980 (w), 910 (w), 710 (w), 641 (m) cm^{-1}. Raman (200 mW): 3024/2978/2963/2934/2917 (6−9) (ν(CH)), 1747 (1), 1452 (2), 1335 (10) ($\nu_s(N_3)$), 1270 (2), 1228 (2), 1055 (2), 915 (2), 886 (2), 788 (2), 574 (4), 473 (6), 325 (5), 178 (6), 119 (7) cm^{-1}.

2,2,6,6-Tetramethylpiperidinoboron Diazide (3). A solution of 2,2,6,6-tetramethylpiperidinoboron dichloride (0.44 g, 2.0 mmol) in toluene (10 mL) was treated with trimethylsilyl azide (0.23 g, 2.0 mmol) at −78 °C. The solution was allowed to warm slowly and was stirred for 12 h at ambient temperature. The solvent and all volatile products were removed by vacuum evaporation at 25 °C, leaving a liquid. The product was distilled under reduced pressure to give 0.38 g of colorless liquid **3** (80%); bp, 70−72 °C/0.01 Torr. Anal. Calcd for $C_9H_{18}BN_7$: C, 45.98; H, 7.71; N, 41.70. Found C, 45.68; H, 7.70; N, 40.07. IR (neat): 3018/2945/2865 (m−s) (ν(CH)), 2157/2114 (m−vs) ($\nu_{as}(N_3)$), 1458 (m), 1384 (vs), 1354 (vs), 1318 (s), 1286 (s), 1173 (m), 1131 (m), 1064 (m), 975 (w), 876 (w), 707 (w), 649 (w), 574 (w), 476 (w) cm^{-1}. Raman (50 mW): 3022 (2), 2988 (4), 2962 (6), 2934 (7), 2152/2133/2113/2102 (1−2) ($\nu_{as}(N_3)$), 1476 (3), 1441 (3), 1404 (3), 1356 (2), 1321 (2), 1115 (1), 974 (1), 883 (1), 786 (1), 549 (3), 304 (2), 121 (10) cm^{-1}.

2,2,6,6-Tetramethylpiperidinium Tetraazidoborate (4). A solution of HN_3 in diethyl ether (1.0 mL, 1.3 mmol) was added to a solution of **3** (0.12 g, 0.5 mmol) in diethyl ether (5 mL) at −20 °C and was allowed to warm slowly. After it was additionally stirred for 12 h at 25 °C the solvent and all volatile compounds were removed by vacuum evaporation, leaving a colorless solid. The crude product was purified by recrystallization from a cooled concentrated solution in dichloromethane, resulting in 0.22 g (70%) of pure **4**; mp, 81−84 °C (dec). IR (Nujol): 3407 (m) (ν(NH)), 3019/2982/2857 (m−s) (ν(CH)), 2146/2113 (vs) ($\nu_{as}(N_3)$), 1607 (s), 1592 (s), 1474 (vs), 1458 (vs), 1440 (vs), 1369 (vs), 1303 (vs), 1275 (vs), 1178 (s), 1154 (s), 1116 (m), 1040 (m), 975 (vs), 879 (vs), 863 (vs), 797 (m), 588 (w), 466 (w) cm^{-1}. Raman (100 mW): 3022/2988/2962/2934/(3−9) (ν(CH)), 2152/2113/2103 (2−3) ($\nu_{as}(N_3)$), 1475 (2), 1459 (2), 1437 (2), 1398 (1), 1334 (4), 1319 (4), 1267 (1), 1229 (2), 1059 (1), 883 (1), 707 (4), 571 (2), 352 (4), 287 (4), 164 (6), 95 (10) cm^{-1}.

Quinoline−Boron Triazide (5). Trimethylsilyl azide (0.35 g, 3.0 mmol) was added to a mixture of quinoline (0.13 g, 1.0 mmol) and boron trichloride (1.0 mmol, 1 M in hexane) in dichloromethane (5 mL) at −78 °C. After it was additionally stirred for 4 h at ambient temperature all volatile materials were removed in vacuo, leaving a colorless solid. The product was recrystallized from dichloromethane, resulting in colorless crystals of **5**; yield, 0.24 g (90%); mp, 100−105 °C (dec). Anal. Calcd for $C_9H_7BN_{10}$: C, 40.63; H, 2.65; N, 52.65. Found C, 40.58; H, 2.98; N, 51.22. IR (Nujol, selected values): 3125/3111/3053 (m) (ν(CH)), 2162/2155/2122 (m−vs) ($\nu_{as}(N_3)$), 1593 (vs), 1518 (vs), 1404 (s), 1373 (vs), 1236 (vs), 1149 (vs), 981 (vs), 922 (vs), 878 (vs), 776 (vs), 643 (vs), 586 (vs), 479 (s) cm^{-1}. Raman (50 mW): 3102/3067/2987 (2−4) (ν(CH)), 2154/2115 (1) ($\nu_{as}(N_3)$), 1623 (2), 1595 (4), 1446 (1), 1375 (10), 1331 (3), 1311 (3), 1151 (1), 1085 (2), 1030 (1), 834 (2), 807 (1), 704 (3), 536 (4), 298 (4), 287 (3), 250 (2), 218 (3), 188 (3), 127 (9) cm^{-1}.

Pyrazine−Bis(boron triazide) (6). **6** was prepared from trimethylsilyl azide (0.17 g, 1.5 mmol), pyrazine (0.02 g, 0.25 mmol), and boron trichloride (0.25 mmol) in dichloromethane solution (5 mL) following the method described for **5**. Yield, 0.07 g (75%); mp, 85−88 °C (explosion). IR (Nujol, selected values): 3125/3102 (m) (ν(CH)), 2151/2131 (vs) ($\nu_{as}(N_3)$), 1489 (s), 1434 (vs), 1382 (vs), 1190 (s), 1124 (s), 1099 (vs), 991 (vs), 972 (vs), 959 (vs), 831 (vs), 746 (vs), 667 (vs), 634 (vs) 578 (s), 541 (s), 488 (s) cm^{-1}. Raman (50 mW): 3114/3105 (2−3) (ν(CH)), 2167/2139/2124 (1−3) ($\nu_{as}(N_3)$), 1643 (6), 1541 (1), 1348 (3), 1340 (2), 1328 (2), 1305 (2), 1088 (1), 1054 (5), 1003 (1), 957 (1), 785 (1), 696 (1), 634 (1), 486 (2), 420 (2), 321 (4), 189 (4), 170 (5), 128 (10), 106 (8), 90 (9) cm^{-1}.

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Supporting Information Available: Tables of crystal data, structure solutions and refinement, atomic coordinates, bond lengths and angles, and anisotropic thermal parameters for **2** and **4−6** in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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