# Reactions of $(CF_3)_2BNMe_2$ with ω-Halonitriles – Crystal and Molecular Structure of [*cyclo*-$C_3H_4(CN)](CF_3)_2B\cdot NHMe_2$☆

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Dimethylaminobis(trifluoromethyl)borane, $(CF_3)_2BNMe_2$ (**A**), reacts with $Cl(CH_2)_3CN$ to yield $[Cl(CH_2)_2CH(CN)](CF_3)_2B\cdot NHMe_2$ (**1**) whereas $Br(CH_2)_3CN$ and **A** combine in a 1:2 ratio to form [*cyclo*-$C_3H_4(CN)](CF_3)_2B\cdot NHMe_2$ (**2**) and $Br(CF_3)_2B\cdot NHMe_2$. $Br(CH_2)_nCN$ and **A** yield $[Br(CH_2)_{n-1}CH(CN)](CF_3)_2B\cdot NHMe_2$, $n=4$ (**3**), $n=5$ (**4**) and $n=6$ (**5**). Compound **2** and $(NCCH_2)(CF_3)_2B\cdot NHMe_2$ can be alkylated at nitrogen with $CH_3I$/KOH in ether to yield [*cyclo*-$C_3H_4(CN)](CF_3)_2B\cdot NMe_3$ (**6**) and $(NCCH_2)(CF_3)_2B\cdot NMe_3$ (**7**), respectively. Treatment of **1** and **3** with hydroxide in ether gives the respective five- and six-membered heterocycles $(CF_3)_2B$-$NMe_2$-$(CH_2)_2$-$CH(CN)$ (**8**) and $(CF_3)_2B$-$NMe_2$-$(CH_2)_3$-$CH(CN)$ (**9**). Reduction of the nitrile group with $(i\text{Bu})_2AlH$ in $CH_2Cl_2$ at −50 °C followed by hydrolysis furnishes the corresponding aldehydes $(OCHCH_2)(CF_3)_2B\cdot NMe_3$ (**10**), [*cyclo*-$C_3H_4(CHO)](CF_3)_2B\cdot NMe_3$ (**11**) and $(CF_3)_2B$-$NMe_2$-$(CH_2)_2$-$CH(CHO)$ (**12**). The structure of **2** was determined by an X-ray investigation.

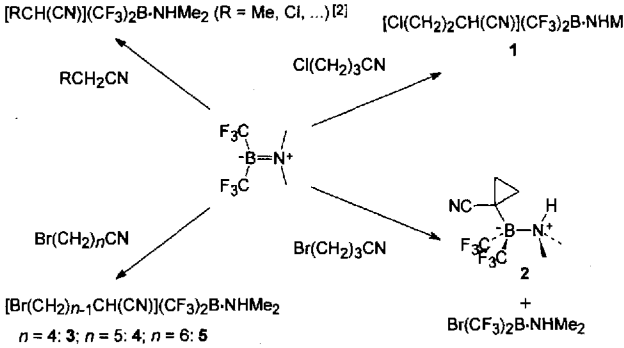
Owing to a synergism of pronounced electrophilic character and steric protection of the boron atom, dimethylaminobis(trifluoromethyl)borane, $(CF_3)_2BNMe_2$ (**A**), possesses chemical properties that are unique in aminoborane chemistry[1]. In a preceding paper we reported on ene-type reactions of **A** with nitriles and carbonyl derivatives[2]. Nitriles $RCH_2CN$ (R = Cl, Me, ...) with at least two hydrogens placed on the α-carbon atom underwent ene-type reactions to yield dimethylamine–bis(trifluoromethyl)boranes with a cyanoalkyl group linked to boron (eq. 1). This reaction is a route for forming new carbon–boron bonds and was shown to be useful for incorporating a bis(trifluoromethyl)boron group into carbon-containing frameworks[1]. In these dimethylamine adducts the cyano group is a functional group that is accessible to further modifications. For example, in addition to its hydrolysis to an amide and a carboxylic acid, a cyano group can be converted into an aldehyde function and thus provide further functionality useful for the synthesis of amino acids. On the other hand if the above-mentioned substituent R carries a halogen atom in the ω-position, an additional reactive site becomes available.

It is however not clear whether the $B(CF_3)_2$ entity would be unaffected by such reactions. Therefore we decided to study the behavior of compound **A** towards nitriles of the general formula $X(CH_2)_nCN$ with X = Cl, Br and $n$ = 2 to 6, and to investigate conceivable substitution reactions.

## Results and Discussion

When compound **A** was allowed to react with $X(CH_2)_2CN$ (X = Cl, Br), only the corresponding amine–boranes $X(CF_3)_2B\cdot NHMe_2$ and $H_2C{=}CHCN$ were obtained; that is, **A** extracted HX from the nitrile.

$Cl(CH_2)_3CN$ underwent an ene-type reaction with compound **A** to yield $[Cl(CH_2)_2CH(CN)](CF_3)_2B\cdot NHMe_2$ (**1**). The analogous molecule $Br(CH_2)_3CN$ however reacted in a different fashion. Even when the nitrile was applied in a fivefold excess, two equivalents of **A** combined with only one of $Br(CH_2)_3CN$ to form the dimethylamine–boranes $Br(CF_3)_2B\cdot NHMe_2$ and [*cyclo*-$C_3H_4(CN)](CF_3)_2B\cdot NHMe_2$ (**2**) (eq. 1).



(1)

The formation of a three-membered ring in **2** was established by NMR spectroscopy and confirmed by an X-ray structure investigation (vide infra). The different behavior of $Cl(CH_2)_3CN$ and $Br(CH_2)_3CN$ towards **A** must be ascribed to the C–Br bond being weaker than the C–Cl bond. In the first step both nitriles presumably undergo an ene-type reaction, but only the bromo derivative can combine with additional **A** to form the three-membered ring by concomitant HBr elimination.

The longer-chain ($n$ = 4–6) homologues $Br(CH_2)_nCN$ all gave products, in ca. 80% yield, typical of ene-type reactions (eq. 1).

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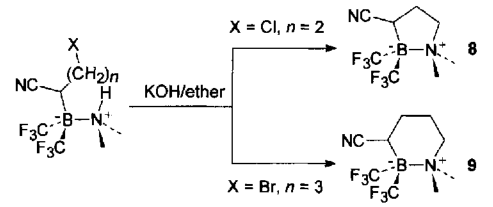
In order to convert the nitrile into an aldehyde it was necessary to methylate the acidic NH function. This was achieved by deprotonation of the nitrogen atom of **2** and $(NCCH_2)(CF_3)_2B \cdot NHMe_2$ (**B**)[2] with KOH in ether and subsequent alkylation of the aminoborates with $CH_3I$. Thus the corresponding trimethylamine–boranes were obtained (eq. 2).

$$\underset{\mathbf{2}}{[\overline{CH_2CH_2C}(CN)](CF_3)_2B \cdot NHMe_2} \xrightarrow{KOH/ether/CH_3I} \underset{\mathbf{6}}{[\overline{CH_2CH_2C}(CN)](CF_3)_2B \cdot NMe_3} \qquad (2)$$

$$\underset{\mathbf{B}}{(NCCH_2)(CF_3)_2B \cdot NHMe_2} \xrightarrow{KOH/ether/CH_3I} \underset{\mathbf{7}}{(NCCH_2)(CF_3)_2B \cdot NMe_3}$$

In contrast the dimethylamine boranes **1** and **3** underwent an intramolecular alkylation reaction on contact with KOH/ether to form the respective five- and six-membered heterocycles **8** and **9** (eq. 3).

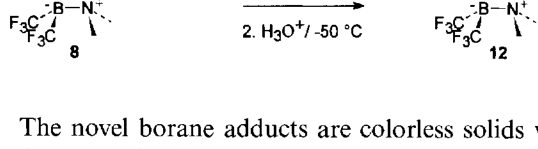


(3)

Reduction of the nitrile group with $(iBu)_2AlH$ in $CH_2Cl_2$ at −50 °C followed by hydrolysis furnished the corresponding aldehydes **10**–**12** (eq. 4–6).

$$\underset{\mathbf{7}}{(NCCH_2)(CF_3)_2B \cdot NMe_3} \xrightarrow[2.\ H_3O^+/-50\ ^\circ C]{1.\ (iBu)_2AlH/CH_2Cl_2/-50\ ^\circ C} \underset{\mathbf{10}}{(OCHCH_2)(CF_3)_2B \cdot NMe_3} \qquad (4)$$

$$\underset{\mathbf{6}}{[\overline{CH_2CH_2C}(CN)](CF_3)_2B \cdot NMe_3} \xrightarrow[2.\ H_3O^+/-50\ ^\circ C]{1.\ (iBu)_2AlH/CH_2Cl_2/-50\ ^\circ C} \underset{\mathbf{11}}{[\overline{CH_2CH_2C}(CHO)](CF_3)_2B \cdot NMe_3} \qquad (5)$$



(6)

The novel borane adducts are colorless solids which are resistant to air, although upon prolonged contact the aldehydes **10**–**12** are slowly oxidized to carboxylic acids.

The $^1H$-, $^{19}F$-, $^{11}B$- and $^{13}C$-NMR data are reported in Table 1. These data confirm the proposed structures and only a few general comments will be made. The fluorine resonances are broadened and the 1:1:1:1 quartets [$^2J(BF)$ = 25–30 Hz] due to the $^{11}B$ nucleus are poorly resolved. The $^{13}C$ signals of the $CF_3$ groups which are expected to be observed at $\delta$ = 130–135 are also broadened by the boron nucleus and hence difficult to detect in routine $^{13}C$-NMR spectra. In most cases, the $^{13}C$-NMR signals of nitrogen-bonded carbon atoms reveal a typical $^4J(CF)$ coupling of ca. 2 Hz.

EI mass-spectrometry data are reported in Table 2. The $[M]^+$ peaks are very weak if detectable at all, but the fragment $[M - C_2F_5]^+$ ($[M - CF_3 - CF_2]^+$) is diagnostic of the molecular mass of the parent molecule. Compounds **1**, **3**, **4** and **5** show an additional common characteristic peak at $m/z$ = 247, which originates from elimination of a $C_nH_{2n}X$ (X = Cl, Br) fragment.

The present investigation shows that the ene-type reaction, which is quite common in the chemistry of **A**, can be successfully extended to suitable ω-halogeno nitriles. The difference in the behaviors of $Br(CH_2)_3CN$ and $Cl(CH_2)_3CN$ towards **A** is, however, striking. Although the 1,3-elimination of HCl or HBr from 3-chloro-1-cyano- or 3-bromo-1-cyano alkanes to form cyanocyclopropanes is well established, it usually requires a base like $NaNH_2$ or triethylamine. However compound **A** cannot be considered to be a base. The driving force for the abstraction of HBr is the tendency of **A** to achieve electronic saturation by increasing its coordination number from 3 to 4, but the mechanism of this reaction is unknown. Ruling out a synchronous elimination of HBr from $[Br(CH_2)_2CH(CN)](CF_3)_2B \cdot NHMe_2$ via a seven-membered ring $\overline{Br \cdots B(CF_3)_2-NMe_2 \cdots H-C(CN)-CH_2-CH_2}$, the elimination of HBr from intermediate $[Br(CH_2)_2CH(CN)](CF_3)_2B \cdot NHMe_2$ is supposedly induced by withdrawal of $Br^-$ by the Lewis acidic boron atom and the formation of an intermediate $\{[CH_2CH_2CH(CN)](CF_3)_2B \cdot NHMe_2\}^+[Br(CF_3)_2BNMe_2]^-$ (eq. 7), rather than the abstraction of a proton. That the subsequent formation of the cyclopropane ring in **2** is not induced by the presence of a base is also suggested by the conditions which favor the formation of compound **8**. This is obtained under the same basic conditions that are usually chosen for the synthesis of cyclopropane derivatives.

The reduction of the nitrile group by $(iBu)_2AlH/CH_2Cl_2$ requires protection of all acidic NH groups, e.g. by alkylation. Then the conversion of the nitrile function to an aldehyde under carefully controlled reaction conditions is selective and not accompanied by significant degradation of $CF_3$ groups. This behavior demonstrates that the $(CF_3)_2B$ moiety is inert towards strong reducing agents such as $(iBu)_2AlH$.

### Description of the Structure of 2

The structure of **2** is depicted in Figure 1, and bond distances and angles are given. Since major structural features of **2** strongly resemble those of the amine boranes $(NCCH_2)(CF_3)_2B \cdot NHMe_2$ (**B**)[2] and $(NCCH_2)(CF_3)(Et)B \cdot NHMe_2$ (**C**)[3], a brief comparison of geometrical details will be presented.

The average $B-CF_3$ bond length in **2** [1.626(3) Å] is identical to those in **B** and **C**: 1.627(3) and 1.628(4) Å, respectively. On the other hand, the B–N(1) distance in **2** [1.607(3) Å] lies between the values for the corresponding

Table 1. NMR-spectral data of **1**–**12**[a]

| | **1** | **2** | **3** | **4** | **5** | **6** | **7** | **8** | **9** | **10** | **11** | **12** |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **$^1H$** | | | | | | | | | | | | |
| δ (BCH) | 2.33 | | ~2.2 | ~2.1 | ~2.0 | | 1.77 | 2.13 | ~2.2 | 2.01 | | 1.92 |
| δ ($BCCH_2$) | ~1.95<br>~2.05 | | ~2.1 | ~2.0 | 1.86 | | | | | | | |
| δ ($CH_2X$) | 3.69<br>3.82 | | 3.53 | 3.48 | 3.46 | | | 3.18<br>3.22 | 3.34<br>3.00 | | | 3.24 |
| δ ($NCH_3$) | 2.65<br>2.73 | 2.80 | 2.65<br>2.74 | 2.61<br>2.71 | 2.62<br>2.72 | 3.00 | 2.92 | 2.84 | 2.77<br>2.90 | 2.85 | 2.83 | 2.71<br>2.83 |
| δ (NH) | 5.7 | 7.2 | 5.5 | 5.8 | 5.6 | | | | | | | |
| δ ($-CH_2-$) | | 1.17<br>1.26 | 1.69 | ~1.55 | 1.46<br>1.52<br>1.69 | ~1.21<br>~1.26 | | 2.43 | 1.8<br>2.0 | | ~0.94<br>~0.99 | 2.62 |
| δ (O=CH) | | | | | | | | | | 9.74 | 8.52 | 9.64 |
| **$^{19}F$** | | | | | | | | | | | | |
| δ ($CF_3$) | –61.5<br>–61.7 | –60.6 | –61.4 | –61.4 | –61.4 | –60.4 | –62.9 | –61.3<br>–64.4 | –57.4<br>–60.9 | –61.2 | –58.6 | –58.8<br>–63.9 |
| **$^{11}B$** | | | | | | | | | | | | |
| δ (B) | –8.4 | –8.7 | –8.5 | –8.1 | –8.0 | –6.1 | –7.1 | –5.2 | –7.9 | –6.1 | –4.6 | –4.9 |
| **$^{13}C$** | | | | | | | | | | | | |
| δ (BC) | ~15.5 | ~–3.3 | ~17.3 | ~18.2 | ~18.2 | ~–3.2 | ~3.0 | ~14 | ~13 | ~36.5 | ~22 | ~44.8 |
| δ ($NCH_3$) | 40.8<br>41.1 | 41.3 | 40.7<br>41.0 | 40.7<br>41.0 | 40.7<br>41.0 | 53.3 | 52.6 | 49.9<br>50.1 | 49.9<br>52.0 | 52.6 | 53.3 | 49.3<br>49.5 |
| δ ($-CH_2X$) | 44.8 | | 34.1 | 34.7 | 35.0 | | | | | | | |
| δ ($-CH_2-$) | 30.9 | 13.5 | 26.3<br>33.2 | 26.9<br>28.8<br>32.7 | 27.5<br>28.0<br>29.4<br>33.2 | 14.3 | | 27.0<br>66.3 | 22.3<br>25.7<br>64.7 | | 12.5 | 20.2<br>66.7 |
| δ (C≡N)/(C=O) | 122.9 | 127.3 | 123.7 | 124.1 | 124.1 | 128.7 | 122.1 | 123.4 | 124.1 | 205.4 | 207.2 | 203.5 |

[a] δ values: **1**–**10** and **12** in $CD_3CN$, **11** in $CD_3OD/CD_3CN$. $^1H$: 250.13 MHz, internal standard, $CHD_2CN$: $\delta = 1.95$. $^{13}C$: 62.9 MHz, internal standard, $CD_3CN$: $\delta = 1.30$/$CD_3OD$: $\delta = 49.0$. $^{19}F$: 84.67 and 235.37 MHz, internal standard, $CFCl_3$. $^{11}B$: 25.52 and 80.25 MHz, external standard $BF_3\cdot OEt_2$.

Table 2. Selected electron-impact mass-spectral data in the order of decreasing intensity {*m/z* (relative intensity [%]) [fragment]$^+$} for compounds **1**–**12**

| | |
|---|---|
| **1** | 94 (100) $[F_2BNH(CH_3)_2]^+$; 247 (12) $[M-CH_2Cl]^+$; 177 (1) $[M-C_2F_5]^+$ |
| **2** | 94 (100) $[F_2BNH(CH_3)_2]^+$; 141 (90) $[M-C_2F_5]^+$; 114 (10) $[M-C_2F_5-HCN]^+$; 191 (4) $[M-CF_3]^+$ |
| **3** | 92 (100) $[CHBr]^+$; 94 (96) $[F_2BNH(CH_3)_2]^+$; 247 (20) $[M-C_2H_4Br]^+$; 235 (4) $[M-C_2F_5]^+$; 275 (1) $[M-Br]^+$ |
| **4** | 94 (100) $[F_2BNH(CH_3)_2]^+$; 96 (11) $[C_6H_{10}N]^+$; 247 (7) $[M-C_3H_6Br]^+$; 289 (6) $[M-Br]^+$; 249 (1) $[M-C_2F_5]^+$; 299 (1) $[M-CF_3]^+$ |
| **5** | 94 (100) $[F_2BNH(CH_3)_2]^+$; 110 (11) $[C_7H_{12}N]^+$; 303 (10) $[M-Br]^+$; 247 (2) $[M-C_4H_8Br]^+$ |
| **6** | 108 (100) $[F_2BN(CH_3)_3]^+$; 58 (91) $[(CH_3)_2N{=}CH_2]^+$; 155 (77) $[M-C_2F_5]^+$; 115 (31) $[M-C_2F_5-CH_2CN]^+$; 92 (14) $[F_2BN{=}CH_2CH_3]^+$; 205 (5) $[M-CF_3]^+$ |
| **7** | 108 (100) $[F_2BN(CH_3)_3]^+$; 129 (72) $[M-C_2F_5]^+$; 58 (62) $[(CH_3)_2N{=}CH_2]^+$; 92 (21) $[F_2BN{=}CH_2CH_3]^+$; 179 (2) $[M-CF_3]^+$; 248 (1) $[M]^+$ |
| **8** | 58 (100) $[(CH_3)_2N{=}CH_2]^+$; 41 (62) $[C_3H_5]^+$; 92 (48) $[F_2BN{=}CH_2CH_3]^+$; 141 (39) $[M-C_2F_5]^+$; 108 (27) $[F_2BN(CH_3)_3]^+$; 260 (7) $[M]^+$; 160 (4) $[M-C_2F_4]^+$; 191 (3) $[M-CF_3]^+$ |
| **9** | 58 (100) $[(CH_3)_2N{=}CH_2]^+$; 55 (83) $[C_4H_7]^+$; 92 (37) $[F_2BN{=}CH_2CH_3]^+$; 155 (36) $[M-C_2F_5]^+$; 174 (11) $[M-C_2F_4]^+$; 274 (4) $[M]^+$; 205 (1) $[M-CF_3]^+$ |
| **10** | 108 (100) $[F_2BN(CH_3)_3]^+$; 132 (69) $[M-C_2F_5]^+$; 58 (38) $[(CH_3)_2N{=}CH_2]^+$; 92 (16) $[F_2BN{=}CH_2CH_3]^+$; 251 (2) $[M]^+$ |
| **11** | 58 (100) $[(CH_3)_2N{=}CH_2]^+$; 108 (80) $[F_2BN(CH_3)_3]^+$; 158 (25) $[M-C_2F_5]^+$; 92 (22) $[F_2BN{=}CH_2CH_3]^+$; 208 (4) $[M-CF_3]^+$; 277 (1) $[M]^+$ |
| **12** | 58 (100) $[(CH_3)_2N{=}CH_2]^+$; 144 (82) $[M-C_2F_5]^+$; 41 (47) $[C_3H_5]^+$; 92 (41) $[F_2BN{=}CH_2CH_3]^+$; 263 (8) $[M]^+$ |

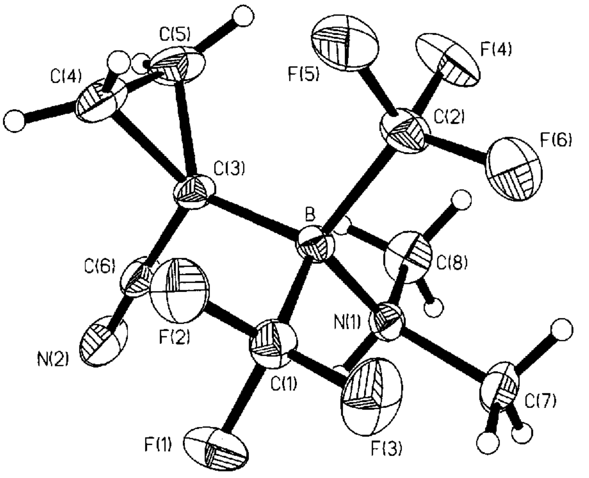
$$\begin{array}{c} [Br(CH_2)_2CH(CN)](CF_3)_2B\cdot NHMe_2 + (CF_3)_2BNMe_2 \\ \downarrow \\ \{[CH_2CH_2CH(CN)](CF_3)_2B\cdot NHMe_2\}^+ [Br(CF_3)_2BNMe_2]^- \\ \downarrow \\ [\overline{CH_2\text{-}CH_2\text{-}C}(CN)](CF_3)_2B\cdot NHMe_2 + Br(CF_3)_2B\cdot NHMe_2 \\ \mathbf{2} \end{array} \qquad (7)$$

linkage in **B** [1.600(3) Å] and **C** [1.616(4) Å]. Interestingly, the B–C(3) bond distance [1.627(3) Å] does not differ from the values for the B–$CH_2CN$ attachments in **B** [1.629(4) Å] and **C** [1.628(4) Å]. The similarity of these distances is retained although in inspection of the bond angles at the C(3) atom reveals that the cyclopropyl ring is pivoted away from the $(CF_3)_2BNHMe_2$ fragment towards the cyano group.

The substituents of the cyclopropyl group have a marked effect on ring geometry. Thus the C(3)–C(4) and C(3)–C(5) bonds are on the average 0.082(8) Å longer than the C(4)–C(5) bond. Systematic evaluation of cyclopropane structures[4,5] has shown that π-acceptor substituents like the cyano group can exert such a weakening of the vicinal and strengthening of the distal C–C bonds. In accord with such an interaction, the C(3)–C(6) bond length in **2** [1.434(3) Å] is significantly shorter than the C–CN bonds of **B** and **C** [1.454(4) and 1.449(4) Å, respectively], although normal for the attachment of a cyano group to a cyclopropane [1.441(4) Å[5]].

As in **C**, molecules of **2** aggregate as centrosymmetric, hydrogen-bonded dimers in the solid state. Both the N(1)···N(2′) separation [2.932(3) Å] and the N(1)–H(N1)–N(2′) angle [146(2)°] compare reasonably well with the respective values in **C**, 2.993(4) Å and 149(3)°.

Figure 1. A perspective drawing of **2** with 20%-probability thermal ellipsoids except for the hydrogen atoms; selected bond lengths [Å] and angles [°]: B–C(1) 1.628(3), C(3)–C(4) 1.537(3), B–C(2) 1.625(3), C(3)–C(5) 1.528(3), B–C(3) 1.627(3), C(3)–C(6) 1.434(3), B–N(1) 1.607(3), C(4)–C(5) 1.450(5), C(1)–F(1) 1.348(3), N(1)–C(7) 1.496(3), C(1)–F(2) 1.349(3), N(1)–C(8) 1.492(3), C(1)–F(3) 1.339(3), N(1)–H(N1) 0.85(2), C(2)–F(4) 1.337(3), N(2)–C(6) 1.133(3), C(2)–F(5) 1.341(3), H(N1)–N(2')[a] 2.19(2), C(2)–F(6) 1.334(3); N(1)–B–C(1) 107.4(2), B–C(3)–C(6) 114.1(2), N(1)–B–C(2) 109.9(2), C(4)–C(3)–C(5) 56.4(2), N(1)–B–C(3) 109.0(2), C(4)–C(3)–C(6) 112.3(2), C(1)–B–C(2) 109.3(2), C(5)–C(3)–C(6) 112.9(2), C(1)–B–C(3) 108.2(2), C(3)–C(4)–C(5) 61.5(2), C(2)–B–C(3) 112.9(2), C(3)–C(5)–C(4) 62.1(2), B–C(3)–C(4) 123.3(2), C(3)–C(6)–N(2) 177.6(2), B–C(3)–C(5) 125.8(2), N(1)–H(N1)–N(2') 146(2)[a]



[a] $x', y', z' = -x, 1-y, 1-z$.

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## Experimental

*X-ray Structural Determination of 2:* A block-shaped crystal of **2** with the dimensions 0.32 × 0.46 × 0.52 mm was sealed in a glass capillary. Counter measurements were made at 26°C with a Siemens AED-1 diffractometer employing Zr-filtered Mo-$K_\alpha$ radiation ($\lambda$ = 0.71073 Å). The compound crystallizes in the monoclinic space group $P2_1/n$ with $a$ = 6.9646(7), $b$ = 14.363(2), $c$ = 11.725(1) Å, $\beta$ = 103.44(1)°, $Z = 4$ and $d_{\text{calcd.}}$ = 1.514 g/cm³. A hemisphere of data ($h \geq 0$, $2\theta \leq 55°$) was collected and corrected for the small (ca. 1%) variation of the three-hourly monitored standard reflections and absorption ($\mu$ = 0.15 mm$^{-1}$; transmission: 0.9293–0.9553). Merging the 5892 data yielded 2603 unique reflections, of which the three with $F_o^2 \leq -3\ \sigma\ (F_o^2)$ were suppressed. The structure was solved by direct methods using the program SHELXS-86[6] and refined on $F^2$ incorporating all nonsuppressed reflections with SHELXTL. The methyl hydrogens were idealized (C–H 0.95 Å) and refined as groups, but the coordinates of the other hydrogens were refined without constraints. Common isotropic thermal parameters were assigned to hydrogens bonded to the same carbon atom. Refinement of the 176 parameters converged with $wR_2 = \sqrt{(\sum w(F_o^2 - F_c^2)^2/\sum wF_o^4)}$ = 0.122 for all data and $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$ = 0.051 for the 1707 data with $F_o > 4\ \sigma\ (F_o)$. The densities in the final $\Delta F$ synthesis (0.22 to –0.17 e/Å³) revealed no misplaced atoms[7].

*Dimethylamine–(3-Chloro-1-cyanopropyl)bis(trifluoromethyl)borane* (**1**), *Dimethylamine–(4-Bromo-1-cyanobutyl)bis(trifluoromethyl)borane* (**3**), *Dimethylamine–(5-Bromo-1-cyanopentyl)bis(trifluoromethyl)borane* (**4**), *Dimethylamine–(6-Bromo-1-cyanohexyl)bis(trifluoromethyl)borane* (**5**): To a stirred solution of 52 mmol of $Cl(CH_2)_3CN$ or $Br(CH_2)_nCN$ ($n$ = 4–6) in 50 ml of dry ether, 52 mmol (10 g) of $(CF_3)_2BNMe_2$ was added dropwise at 0–4°C. Stirring was continued for 1 h at 20°C, the solvent and other volatile by-products were pumped off in vacuo ($10^{-2}$ torr) and the products were crystallized from ether. Yields: ca. 80%. – M.p. [°C]: **1**: 90; **3**: 128; **4**: 89; **5**: 114. – IR [cm$^{-1}$]: $\tilde{\nu}$ (C≡N): **1**: 2239, s; **3**: 2236 s; **4**: 2236 s; **5**: 2233 s.

*Dimethylamine–(1-Cyanocyclopropyl)bis(trifluoromethyl)borane* (**2**): Compound **2** was obtained analogously to **1** except that 52 mmol of $Br(CH_2)_3CN$ was reacted with 105 mmol of $(CF_3)_2BNMe_2$. The $Br(CF_3)_2B{\cdot}NHMe_2$ that was simultaneously formed was separated by sublimation (ca. 45°C/$10^{-2}$ torr) and the remaining crude **2** recrystallized from ether. Yield ca. 40%. – M.p. 177°C. – IR: $\tilde{\nu}$ (C≡N): 2229 cm$^{-1}$, s.

*Trimethylamine–(1-Cyanocyclopropyl)bis(trifluoromethyl)borane* (**6**), *Trimethylamine–(Cyanomethyl)bis(trifluoromethyl)borane* (**7**): A solution of 50 mmol of **2** or $(NCCH_2)(CF_3)_2B$ $NHMe_2$[2] in 300 ml of ether (dried over KOH) was stirred with 2.9 g (52 mmol) of KOH pellets at 20°C for 20 min. Then 74 g (52 mmol) of $CH_3I$ was added slowly and stirring continued for 1 h. The reaction mixture was filtered and all volatile material removed in vacuo. The residue was recrystallized from ether at –40°C. Yields ca. 85%. – M.p. [°C]: **6**: 192; **7**: 122. – IR [cm$^{-1}$]: $\tilde{\nu}$ (C≡N): **6**: 2215, m; **7**: 2247 m.

*3-Cyano-1,1-dimethyl-2,2-bis(trifluoromethyl)-1-azonia-2-borata-cyclopentane* (**8**), *3-Cyano-1,1-dimethyl-2,2-bis(trifluoromethyl)-1-azonia-2-borata-cyclohexane* (**9**): A solution of 100 mmol of **1** or **3** in 100 ml ether was stirred with 5.6 g (100 mmol) KOH pellets for 1 d (**1**) or ca. 1 h (**3**) at 20°C. The solvent was evaporated, the potassium salt dissolved in water and the residue crystallized from ether. Yields ca. 90%. – M.p. [°C]: **8**: 200; **9**: 204. – IR [cm$^{-1}$]: $\tilde{\nu}$ (C≡N): **8**: 2235 s; **9**: 2230 s.

*Trimethylamine–(Formylmethyl)bis(trifluoromethyl)borane* (**10**), *Trimethylamine–(1-Formylcyclopropyl)bis(trifluoromethyl)borane* (**11**), *3-Formyl-1,1-dimethyl-2,2-bis(trifluoromethyl)-1-azonia-2-borata-cyclopentane* (**12**): To a stirred solution of 50 mmol of **6**, **7** or **8** in 50 ml of dry $CH_2Cl_2$, 50 ml of a 1 M solution of $(i\text{Bu})_2AlH$ in $CH_2Cl_2$ (Aldrich) was added dropwise at –50°C. The reaction mixture was allowed to warm to ca. 15°C, then cooled to –50°C again before 155 ml of 1 M aqueous hydrochloric acid was added.

Table 3. Elemental analyses of **1**–**5** and **7**–**12**

| | | | | | | |
|---|---|---|---|---|---|---|
| **1** | $C_8H_{12}BClF_6N_2$ | (296.45) | calcd. | C 32.41 | H 4.08 | N 9.45 |
| | | | found | C 31.9 | H 4.1 | N 9.5 |
| **2** | $C_8H_{11}BF_6N_2$ | (259.99) | calcd. | C 36.96 | H 4.26 | N 10.77 |
| | | | found | C 37.1 | H 4.2 | N 10.2 |
| **3** | $C_9H_{14}BBrF_6N_2$ | (354.93) | calcd. | C 30.46 | H 3.98 | N 7.89 |
| | | | found | C 30.2 | H 4.2 | N 8.2 |
| **4** | $C_{10}H_{16}BBrF_6N_2$ | (368.95) | calcd. | C 32.55 | H 4.37 | N 7.59 |
| | | | found | C 31.8 | H 4.3 | N 7.7 |
| **5** | $C_{11}H_{18}BBrF_6N_2$ | (382.98) | calcd. | C 34.50 | H 4.74 | N 7.31 |
| | | | found | C 33.5 | H 4.7 | N 7.6 |
| **7** | $C_7H_{11}BF_6N_2$ | (247.98) | calcd. | C 33.91 | H 4.47 | N 11.30 |
| | | | found | C 31.3 | H 4.3 | N 10.4 |
| **8** | $C_8H_{11}BF_6N_2$ | (259.99) | calcd. | C 36.96 | H 4.26 | N 10.77 |
| | | | found | C 35.9 | H 4.2 | N 11.0 |
| **9** | $C_9H_{13}BF_6N_2$ | (274.02) | calcd. | C 39.45 | H 4.78 | N 10.22 |
| | | | found | C 39.2 | H 4.8 | N 10.8 |
| **10** | $C_7H_{12}BF_6NO$ | (250.98) | calcd. | C 33.50 | H 4.82 | N 5.58 |
| | | | found | C 32.9 | H 4.7 | N 5.8 |
| **11** | $C_9H_{14}BF_6NO$ | (277.02) | calcd. | C 39.02 | H 5.09 | N 5.06 |
| | | | found | C 38.1 | H 5.2 | N 5.0 |
| **12** | $C_8H_{12}BF_6NO$ | (262.99) | calcd. | C 36.54 | H 4.66 | N 5.33 |
| | | | found | C 36.3 | H 4.5 | N 5.4 |

The organic layer was separated, washed with water, dried and the solvent removed in vacuo. Yields ca. 70%. – M.p. [°C]: **10**: 106; **11**: 133 (dec.); **12**: 162. – IR [$cm^{-1}$]: $\tilde{\nu}$ (C=O): **10**: 1708 s; **11**: 1710 s; **12**: 1697 vs.

For elemental analyses see Table 3.

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☆ Dedicated to Professor *Peter Sartori* on the occasion of his 65th birthday.

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[7] Further details of the crystal structure investigation are available from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen (Germany), on quoting the depository number CSD-405783.

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