

# BN cleavage of the azoniaboratacyclopropane ring by H<sub>2</sub>O and by carbonyl and nitrile derivatives: crystal structure of (CF<sub>3</sub>)<sub>2</sub>B(OH)CH(SiMe<sub>3</sub>)NHMe<sub>2</sub>, (CF<sub>3</sub>)<sub>2</sub>BCH(SiMe<sub>3</sub>)NMe<sub>2</sub>CMe<sub>2</sub>O and (MeC(O)NH)(CF<sub>3</sub>)<sub>2</sub>BCH(SiMe<sub>3</sub>)NHMe<sub>2</sub> \*

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(Received May 12, 1993)

## Abstract

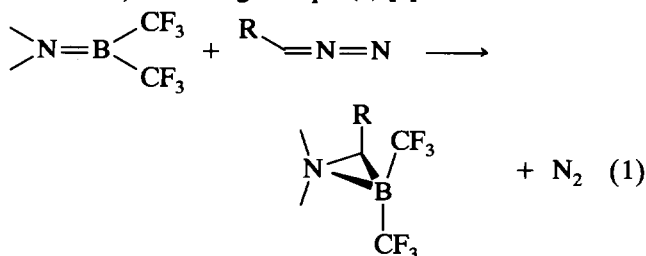
1,1-Dimethyl-2,2-bis(trifluoromethyl)azoniaboratacyclopropane derivatives (CF<sub>3</sub>)<sub>2</sub>BCHRNMe<sub>2</sub> (R = H (I), SiMe<sub>3</sub> (II)) react with H<sub>2</sub>O with cleavage of the NB bond to form (CF<sub>3</sub>)<sub>2</sub>B(OH)CHRNHMe<sub>2</sub> (R = H (III), SiMe<sub>3</sub> (IV)). Carbonyl compounds R<sup>1</sup>R<sup>2</sup>C=O are inserted into the NB bond of I and II to yield the five-membered heterocycles (CF<sub>3</sub>)<sub>2</sub>BCHRNMe<sub>2</sub>CR<sup>1</sup>R<sup>2</sup>O (R = H, R<sup>1</sup> = R<sup>2</sup> = Et (V); R = SiMe<sub>3</sub>, R<sup>1</sup> = H, R<sup>2</sup> = Me (VI), R<sup>1</sup> = R<sup>2</sup> = Me (VII), Et (VIII), R<sup>1</sup> = Me, R<sup>2</sup> = CH=CMe<sub>2</sub> (IX), C=CMe(CH<sub>2</sub>)<sub>2</sub>CH<sub>2</sub> (X)). Similarly nitriles insert to form (CF<sub>3</sub>)<sub>2</sub>BCHRNMe<sub>2</sub>CR<sup>1</sup>=N (R = H, R<sup>1</sup> = CHClMe (XI); R = SiMe<sub>3</sub>, R<sup>1</sup> = Me (XII), CHClMe (XIII), Ph (XIV)). The reaction of H<sub>2</sub>C=CHCH<sub>2</sub>CN with II is accompanied by a shift in the C=C bond whereby the substituent R<sup>1</sup> = *trans*-CH=CHMe (XV) is formed. Hydrogen cyanide combines with II to yield (CF<sub>3</sub>)<sub>2</sub>B(CN)CH(SiMe<sub>3</sub>)NHMe<sub>2</sub> (XVI). The nitrile derivatives XI–XIV are hydrolysed with formation of (R<sup>1</sup>C(O)NH)(CF<sub>3</sub>)<sub>2</sub>BCHRNHMe<sub>2</sub> (R = H, R<sup>1</sup> = CHClMe (XVII); R = SiMe<sub>3</sub>, R<sup>1</sup> = Me (XVIII), CHClMe (XIX), Ph (XX)). The novel boranes have been characterized by elemental analyses, multinuclear NMR, IR and mass spectra. The structures of IV and VII in a mixed crystal and of XVIII have been investigated crystallographically. In the solid state, IV and XVIII show intramolecular N–H···O hydrogen bondings which leads to formation of five- and seven-membered rings respectively. Steric repulsion between the CF<sub>3</sub> and SiMe<sub>3</sub> groups leads to large B–C–Si bond angles (average, 124.1(8)°) and variable B–CHSiN bond distances (1.648(4) Å in VII to 1.690(4) Å in IV).

**Key words:** Boron; Small ring; Trifluoromethyl; Crystal structure

## 1. Introduction

Because of the angular strain in small ring compounds, cyclopropanes are considerably more reactive than unstrained saturated hydrocarbons. For example, a C–C bond of cyclopropane can even be cleaved by strong acids, whereas such bonds in larger essentially strain-free cycloalkanes are relatively inert. A saturated C–C bond is related isosterically to the B–N bonds in amine adducts of boranes, and such bonds are surprisingly inert if the boron atom carries trifluoromethyl substituents [1,2]. Recently the first B–N analogues of cyclopropane were prepared by reaction

of dimethylamino-bis(trifluoromethyl)borane with diazoalkanes, according to eqn. (1) [3].



R = H (I), SiMe<sub>3</sub> (II)

In the light of the C–C and B–N analogy, we were interested in examining the reactivity of the B–N bonds in these new cyclic derivatives. We report below the reactions of I and II with water, carbonyl compounds and nitrile compounds.

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\* Dedicated to Professor Heinrich Nöth on the occasion of his 65th birthday.





## 2. Results

Attempts to recrystallize **II** from moist acetone yielded a crystalline material which was shown by an X-ray diffraction investigation to be a 1:2 mixture of  $(\text{CF}_3)_2\text{B}(\text{OH})\text{CH}(\text{SiMe}_3)\text{NHMe}_2$  (**IV**) and the five-membered heterocyclic species  $(\text{CF}_3)_2\text{BCH}(\text{SiMe}_3)\text{NMe}_2\text{CMe}_2\text{O}$  (**VII**). While cleavage of the B–N bond in **I** and **II** was also observed in other moist solvents such as  $\text{CH}_2\text{Cl}_2$  or  $\text{CHCl}_3$  (Scheme 1), the ring expansion reaction involving incorporation of acetone was an unexpected feature. Analogous experiments employing different carbonyl derivatives, however, revealed that this ring expansion occurred generally with ketones and aldehydes, while esters and amides did not un-

dergo similar reactions. Thus the novel heterocyclic 1,4,2-oxaazoniaboratacyclopentanes  $(\text{CF}_3)_2\text{BCHR-NMe}_2\text{CR}^1\text{R}^2\text{O}$  ( $\text{R} = \text{H}$ ,  $\text{R}^1 = \text{R}^2 = \text{Et}$  (**V**);  $\text{R} = \text{SiMe}_3$ ,  $\text{R}^1 = \text{H}$ ,  $\text{R}^2 = \text{Me}$  (**VI**),  $\text{R}^1 = \text{R}^2 = \text{Me}$  (**VII**), (**VIII**),  $\text{R}^1 = \text{Me}$ ,  $\text{R}^2 = \text{CH}=\text{CMe}_2$  (**IX**),  $\text{R}^2 = \text{C}=\text{CMe}(\text{CH}_2)_2\text{CH}_2$  (**X**)) were obtained with almost quantitative yields. Of these, **VI**, **IX** and **X** can in principle exist in two diastereomeric forms, but their NMR spectra (Table 1) show no evidence for the presence of more than one isomer.

An analogous ring expansion reaction was observed when **I** and **II** were treated with nitriles  $\text{R}^1\text{CN}$  (Scheme 1). Thus 1,4,2-azaazoniaboratacyclopentenes  $(\text{CF}_3)_2\text{BCHR-NMe}_2\text{CR}^1=\text{N}$  ( $\text{R} = \text{H}$ ,  $\text{R}^1 = \text{CHClMe}$  (**XI**);  $\text{R} = \text{SiMe}_3$ ,  $\text{R}^1 = \text{Me}$  (**XII**),  $\text{CHClMe}$  (**XIII**),  $\text{Ph}$  (**XIV**)) were formed readily and isolated with high yields. Compound **XIII**, which contains two asymmetric carbon atoms, was obtained as a mixture of all stereoisomers. In the course of the reaction of **II** with  $\text{H}_2\text{C}=\text{CH}-\text{CH}_2-\text{CN}$  the C=C double bond must have migrated because the  $\text{R}^1$  substituent in the isolated product (**XV**) is *trans*- $\text{CH}=\text{CHMe}$ . Rather than behaving like a nitrile,  $\text{HCN}$  reacts like a protic acid to yield  $(\text{CF}_3)_2\text{B}(\text{CN})\text{CH}(\text{SiMe}_3)\text{NHMe}_2$  (**XVI**).

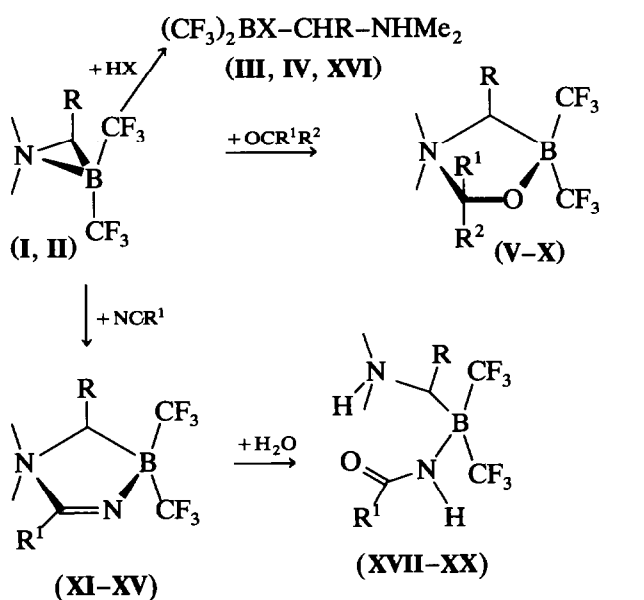
The  $\text{R}^1\text{C}-\text{NMe}_2$  bonds of **XI–XV** are rapidly cleaved by water, and the acetamides **XVII–XX** are obtained almost quantitatively (Scheme 1).

## 3. Properties and spectra

Compounds **III–XX** are colourless solids. Their melting points are given in Section 8. Except for the nitrile derivatives **XI–XV**, they are not sensitive towards air and moisture and are soluble in polar organic solvents such as  $\text{CH}_2\text{Cl}_2$  and  $\text{CH}_3\text{CN}$ .

The  $^1\text{H}$ ,  $^{19}\text{F}$ ,  $^{11}\text{B}$  and  $^{13}\text{C}$  NMR spectra of **III–XX** were recorded. The shift data, which are set out in Table 1, are consistent with the proposed structures, and only a few comments are necessary. Although **VI**, **IX** and **X** have two asymmetric ring carbon atoms only two  $^{13}\text{C}$  and two  $^{19}\text{F}$  signals are observed for the  $\text{NCH}_3$  and  $\text{BCF}_3$  groups respectively. Obviously only one stereoisomer is formed, presumably that with the  $\text{SiMe}_3$  group and the relatively bulky  $\text{R}^2$  substituent in equatorial positions of the five-membered rings.

The nitrile derivative **XIII** has two asymmetric carbon atoms, and in this case the presence of two diastereomers is clearly revealed by its NMR spectra. Thus the  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra both show four signals for the  $\text{NCH}_3$  groups and two resonances for the  $\text{BCH}$  fragments. The *trans* configuration at the C=C bond in **XV** is revealed by the typical  $^3J(\text{H},\text{H})$  coupling constant of 15.0 Hz. Diagnostic resonances for the ring carbon atoms of the heterocycles **V–X** are



	R	X	R <sup>1</sup>	R <sup>2</sup>	Yield %
<b>III</b>	H	OH			95
<b>IV</b>	SiMe <sub>3</sub>	OH			97
<b>V</b>	H		Et	Et	99
<b>VI</b>	SiMe <sub>3</sub>		H	Me	92
<b>VII</b>	SiMe <sub>3</sub>		Me	Me	98
<b>VIII</b>	SiMe <sub>3</sub>		Et	Et	96
<b>IX</b>	SiMe <sub>3</sub>		Me	CH=CMe <sub>2</sub>	88
<b>X</b>	SiMe <sub>3</sub>		Me	C=CMe(CH <sub>2</sub> ) <sub>2</sub> CH <sub>2</sub>	65
<b>XI</b>	H		CHClMe		88
<b>XII</b>	SiMe <sub>3</sub>		Me		98
<b>XIII</b>	SiMe <sub>3</sub>		CHClMe		94
<b>XIV</b>	SiMe <sub>3</sub>		Ph		93
<b>XV</b>	SiMe <sub>3</sub>		CH=CHMe		63
<b>XVI</b>	SiMe <sub>3</sub>	CN			73
<b>XVII</b>	H		CHClMe		82
<b>XVIII</b>	SiMe <sub>3</sub>		Me		97
<b>XIX</b>	SiMe <sub>3</sub>		CHClMe		93
<b>XX</b>	SiMe <sub>3</sub>		Ph		89

Scheme 1.

observed between 102 and 114 ppm (B–O–C–N), and for XI–XV between 145 and 158 ppm (B–N=C–N), whereas the carbonyl groups in XVII–XX give rise to signals near 176 ppm. The  $^{11}\text{B}$  resonance of XVI at  $-21$  ppm is significantly different from that of all other species mentioned here, but typical for that of a boron atom bonded to four carbon atoms.

The EI mass spectral data for IV–X and XII–XX are set out in Table 2. The  $\text{M}^+$  peaks are generally weak, but the fragments  $[\text{M} - \text{CF}_3]^+$  and  $[\text{M} - \text{C}_2\text{F}_5]^+$  are indicative of the molecular weight. Two intense ions, often the base peaks in derivatives bearing the trimethylsilyl group, are  $m/e$  106  $[\text{F}_2\text{BCHN}(\text{CH}_3)_2]^+$ , and  $m/e$  130  $[(\text{CH}_3)_2\text{NCHSi}(\text{CH}_3)_3]^+$ . The latter corresponds to the fragment  $m/e$  58  $[(\text{CH}_3)_2\text{NCH}_2]^+$ , in non-silylated species V and XVII.

#### 4. X-ray structure determination

Crystals were sealed in glass capillaries. The cell constants and intensity data (Table 3) were measured

with a Siemens AED-1 diffractometer. The structures were solved by direct methods using the program SHELXS-86 [4] and were refined with the program SHELX-76 [5], anisotropic temperature factors being used only for the non-hydrogen atoms. While refinement of the hydrogen atoms which are bonded to the oxygen, nitrogen and methine carbon atoms was not constrained, the methyl hydrogen atoms, which were assigned group isotropic temperature factors, were placed in calculated positions (C–H, 0.95 Å) in IV and VII and refined as rigid groups in XVIII. The refinements converged to yield the coordinates given in Tables 4–6.

#### 5. Description of the crystal structure of IV:2VII

The structural analysis shows that IV and VII co-crystallized serendipitously in a 1:2 ratio during an attempt to recrystallize II. As mentioned above, IV and VII are formed by insertion of water and acetone respectively into the B–N bond of II. In order to distinguish between the three molecules in the asym-

TABLE 2. EI-mass spectral data for IV–X and XII–XX

Compound	$m/e$ (relative intensity (%)) [fragment] $^+$
IV	45(100) $[(\text{CH}_3)_2\text{NH}]^+$ , 117(96) $[\text{CH}_3\text{NH}_2\text{CHSi}(\text{CH}_3)_3]^+$ , 180(78) $[\text{M} - \text{C}_2\text{F}_4 - \text{OH}]^+$ , 179(68) $[\text{M} - \text{C}_2\text{F}_4 - \text{H}_2\text{O}]^+$ , 184(71) $[\text{M} - \text{CF}_3 - (\text{CH}_3)_2\text{N}]^+$ , 183(58) $[\text{M} - \text{CF}_3 - (\text{CH}_3)_2\text{NH}]^+$ , 89(58) $[\text{OSi}(\text{CH}_3)_3]^+$ , 59(46) $[(\text{CH}_3)_3\text{N}]^+$ , 106(45) $[\text{F}_2\text{BCHN}(\text{CH}_3)_2]^+$ , 132(34) $[\text{OFBCHSi}(\text{CH}_3)_3]^+$ , 230(15) $[\text{M} - \text{CF}_2 - \text{H}_2\text{O}]^+$ , 229(14) $[\text{M} - \text{CF}_2 - \text{OH}]^+$
V	58(100) $[(\text{CH}_3)_2\text{NCH}_2]^+$ , 174(56) $[\text{M} - \text{C}_2\text{F}_5]^+$ , 88(30) $[\text{FBCH}_2\text{N}(\text{CH}_3)_2]^+$ , 106(10) $[\text{F}_2\text{BCHN}(\text{CH}_3)_2]^+$ , 224(5) $[\text{M} - \text{CF}_3]^+$
VI	130(100) $[(\text{CH}_3)_2\text{NCHSi}(\text{CH}_3)_3]^+$ , 204(98) $[\text{M} - \text{C}_2\text{F}_5]^+$ , 208(55) $[\text{M} - \text{CH}_3 - \text{C}_2\text{F}_4]^+$ , 106(33) $[\text{F}_2\text{BCHN}(\text{CH}_3)_2]^+$ , 73(20) $[\text{Si}(\text{CH}_3)_3]^+$ , 254(11) $[\text{M} - \text{CF}_3]^+$ , 250(2) $[\text{M} - \text{Si}(\text{CH}_3)_3]^+$
VII	130(100) $[(\text{CH}_3)_2\text{NCHSi}(\text{CH}_3)_3]^+$ , 106(97) $[\text{F}_2\text{BCHN}(\text{CH}_3)_2]^+$ , 218(79) $[\text{M} - \text{C}_2\text{F}_5]^+$ , 222(46) $[\text{M} - \text{CH}_3 - \text{C}_2\text{F}_4]^+$ , 73(38) $[\text{Si}(\text{CH}_3)_3]^+$ , 137(18) $[\text{CF}_3\text{BCHN}(\text{CH}_3)_2]^+$ , 268(12) $[\text{M} - \text{CF}_3]^+$ , 264(6) $[\text{M} - \text{Si}(\text{CH}_3)_3]^+$
VIII	106(100) $[\text{F}_2\text{BCHN}(\text{CH}_3)_2]^+$ , 130(77) $[(\text{CH}_3)_2\text{NCHSi}(\text{CH}_3)_3]^+$ , 246(51) $[\text{M} - \text{C}_2\text{F}_5]^+$ , 73(31) $[\text{Si}(\text{CH}_3)_3]^+$ , 250(22) $[\text{M} - \text{CH}_3 - \text{C}_2\text{F}_4]^+$ , 137(16) $[\text{CF}_3\text{BCHN}(\text{CH}_3)_2]^+$ , 296(9) $[\text{M} - \text{CF}_3]^+$ , 292(7) $[\text{M} - \text{Si}(\text{CH}_3)_3]^+$
IX	106(100) $[\text{F}_2\text{BCHN}(\text{CH}_3)_2]^+$ , 130(90) $[(\text{CH}_3)_2\text{NCHSi}(\text{CH}_3)_3]^+$ , 258(60) $[\text{M} - \text{C}_2\text{F}_5]^+$ , 73(32) $[\text{Si}(\text{CH}_3)_3]^+$ , 304(18) $[\text{M} - \text{Si}(\text{CH}_3)_3]^+$ , 178(17) $[\text{F}_2\text{BCSi}(\text{CH}_3)_3\text{N}(\text{CH}_3)_2]^+$ , 262(15) $[\text{M} - \text{CH}_3 - \text{C}_2\text{F}_4]^+$ , 308(14) $[\text{M} - \text{CF}_3]^+$ , 137(7) $[\text{CF}_3\text{BCHN}(\text{CH}_3)_2]^+$
X	106(100) $[\text{F}_2\text{BCHN}(\text{CH}_3)_2]^+$ , 130(94) $[(\text{CH}_3)_2\text{NCHSi}(\text{CH}_3)_3]^+$ , 330(44) $[\text{M} - \text{Si}(\text{CH}_3)_3]^+$ , 284(35) $[\text{M} - \text{C}_2\text{F}_5]^+$ , 73(27) $[\text{Si}(\text{CH}_3)_3]^+$ , 109(19) $[\text{C}_7\text{H}_9\text{O}]^+$ , 137(14) $[\text{CF}_3\text{BCHN}(\text{CH}_3)_2]^+$ , 334(11) $[\text{M} - \text{CF}_3]^+$ , 288(6) $[\text{M} - \text{CH}_3 - \text{C}_2\text{F}_4]^+$
XII	106(100) $[\text{F}_2\text{BCHN}(\text{CH}_3)_2]^+$ , 130(53) $[(\text{CH}_3)_2\text{NCHSi}(\text{CH}_3)_3]^+$ , 137(20) $[\text{CF}_3\text{BCHN}(\text{CH}_3)_2]^+$ , 73(31) $[\text{Si}(\text{CH}_3)_3]^+$ , 201(7) $[\text{M} - \text{C}_2\text{F}_5]^+$ , 247(5) $[\text{M} - \text{Si}(\text{CH}_3)_3]^+$
XIII	130(100) $[(\text{CH}_3)_2\text{NCHSi}(\text{CH}_3)_3]^+$ , 106(86) $[\text{F}_2\text{BCHN}(\text{CH}_3)_2]^+$ , 73(31) $[\text{Si}(\text{CH}_3)_3]^+$ , 137(13) $[\text{CF}_3\text{BCHN}(\text{CH}_3)_2]^+$ , 249(6) $[\text{M} - \text{C}_2\text{F}_5]^+$ , 295(3) $[\text{M} - \text{Si}(\text{CH}_3)_3]^+$
XIV	103(100) $[\text{C}_6\text{H}_5\text{CN}]^+$ , 106(85) $[\text{F}_2\text{BCHN}(\text{CH}_3)_2]^+$ , 137(29) $[\text{CF}_3\text{BCHN}(\text{CH}_3)_2]^+$ , 73(27) $[\text{Si}(\text{CH}_3)_3]^+$ , 77(23) $[\text{C}_6\text{H}_5]^+$
XV	106(100) $[\text{F}_2\text{BCHN}(\text{CH}_3)_2]^+$ , 227(48) $[\text{M} - \text{C}_2\text{F}_5]^+$ , 73(47) $[\text{Si}(\text{CH}_3)_3]^+$ , 130(44) $[(\text{CH}_3)_2\text{NCHSi}(\text{CH}_3)_3]^+$ , 96(31) $[\text{C}_6\text{H}_{10}\text{N}]^+$ , 277(22) $[\text{M} - \text{CF}_3]^+$ , 137(22) $[\text{CF}_3\text{BCHN}(\text{CH}_3)_2]^+$ , 346(19) $[\text{M}]^+$ , 273(8) $[\text{M} - \text{Si}(\text{CH}_3)_3]^+$
XVI	44(100) $[\text{C}_2\text{H}_6\text{N}]^+$ , 116(97) $[\text{CH}_3\text{NHCHSi}(\text{CH}_3)_3]^+$ , 45(96) $[\text{FCN}]^+$ , 187(91) $[\text{M} - \text{C}_2\text{F}_5]^+$ , 73(83) $[\text{Si}(\text{CH}_3)_3]^+$ , 191(65) $[\text{M} - \text{CH}_3 - \text{C}_2\text{F}_4]^+$ , 131(35) $[(\text{CH}_3)_2\text{NHCHSi}(\text{CH}_3)_3]^+$ , 291(19) $[\text{M} - \text{CH}_3]^+$
XVII	58(100) $[(\text{CH}_3)_2\text{NCH}_2]^+$ , 106(40) $[\text{F}_2\text{BCHN}(\text{CH}_3)_2]^+$ , 195(23) $[\text{M} - \text{C}_2\text{F}_5]^+$ , 245(7) $[\text{M} - \text{CF}_3]^+$
XVIII	130(100) $[(\text{CH}_3)_2\text{NCHSi}(\text{CH}_3)_3]^+$ , 245(58) $[\text{M} - \text{Si}(\text{CH}_3)_3 - \text{HF}]^+$ , 116(56) $[\text{CH}_3\text{NHCHSi}(\text{CH}_3)_3]^+$ , 106(42) $[\text{F}_2\text{BCHN}(\text{CH}_3)_2]^+$ , 265(41) $[\text{M} - \text{Si}(\text{CH}_3)_3]^+$ , 73(27) $[\text{Si}(\text{CH}_3)_3]^+$ , 145(25) $[\text{FBCHSi}(\text{CH}_3)_3\text{NCH}_3]^+$ , 184(23) $[\text{HN}(\text{CH}_3)_2\text{CHSi}(\text{CH}_3)_3\text{BNCO}]^+$ , 178(20) $[\text{F}_2\text{BCSi}(\text{CH}_3)_3\text{N}(\text{CH}_3)_2]^+$ , 219(16) $[\text{M} - \text{C}_2\text{F}_5]^+$ , 323(12) $[\text{M} - \text{CH}_3]^+$
XIX	130(100) $[(\text{CH}_3)_2\text{NCHSi}(\text{CH}_3)_3]^+$ , 116(64) $[\text{CH}_3\text{NHCHSi}(\text{CH}_3)_3]^+$ , 106(52) $[\text{F}_2\text{BCHN}(\text{CH}_3)_2]^+$ , 73(27) $[\text{Si}(\text{CH}_3)_3]^+$ , 180(30) $[\text{F}_2\text{BCHSi}(\text{CH}_3)_3\text{NH}(\text{CH}_3)_2]^+$ , 293(29) $[\text{M} - \text{Si}(\text{CH}_3)_3 - \text{HF}]^+$ , 184(24) $[\text{HN}(\text{CH}_3)_2\text{CHSi}(\text{CH}_3)_3\text{BNCO}]^+$ , 313(20) $[\text{M} - \text{Si}(\text{CH}_3)_3]^+$ , 267(15) $[\text{M} - \text{C}_2\text{F}_5]^+$ , 178(12) $[\text{F}_2\text{BCSi}(\text{CH}_3)_3\text{N}(\text{CH}_3)_2]^+$ , 371(7) $[\text{M} - \text{CH}_3]^+$
XX	130(100) $[(\text{CH}_3)_2\text{NCHSi}(\text{CH}_3)_3]^+$ , 106(46) $[\text{F}_2\text{BCHN}(\text{CH}_3)_2]^+$ , 116(31) $[\text{CH}_3\text{NHCHSi}(\text{CH}_3)_3]^+$ , 307(28) $[\text{M} - \text{Si}(\text{CH}_3)_3 - \text{HF}]^+$ , 77(18) $[\text{C}_6\text{H}_5]^+$ , 327(18) $[\text{M} - \text{Si}(\text{CH}_3)_3]^+$ , 73(13) $[\text{Si}(\text{CH}_3)_3]^+$ , 385(8) $[\text{M} - \text{CH}_3]^+$ , 178(7) $[\text{F}_2\text{BCSi}(\text{CH}_3)_3\text{N}(\text{CH}_3)_2]^+$ , 184(24) $[\text{HN}(\text{CH}_3)_2\text{CHSi}(\text{CH}_3)_3\text{BNCO}]^+$

metric unit, the atom numbering carries a 1, 2 or 3 as leading digit, which is occasionally abbreviated with I in the following. Relevant molecular dimensions are given in Tables 7 and 8. The shortest intermolecular contact, namely H(O1)⋯O(3) with (*x*, *y*, *z* − 1), 2.21(3) Å, shows that a weak hydrogen bond is formed between IV and the second molecule of VII.

Insertion of water into the B–N bond of II places a hydroxy group on boron and protonates the nitrogen (Fig. 1). The B–OH linkage, 1.458(5) Å, does not differ significantly from that in (CF<sub>3</sub>)<sub>2</sub>B(OH)CH(Ph)NH(Bz)-<sup>t</sup>Bu (A), 1.465(3) Å [6], but is significantly longer than that in (CF<sub>3</sub>)<sub>2</sub>B(OH)NHMe<sub>2</sub> (B), 1.432(3) Å [7]. Apparently the lengthening of the B–OH bond in IV and A compared with that in B is associated with the separation by a carbon atom of the centres of formal positive and negative charge in IV and A. The greater separation allows the formation of a five-membered ring by N(1)–H(N1)⋯O(1) hydrogen bonding. As in A the hydrogen bond is strongly bent but is ~ 0.2 Å

TABLE 4. Positional and isotropic or equivalent isotropic<sup>a</sup> thermal parameters for IV

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i>
Si(1)	0.1170(1)	0.26715(7)	0.06993(6)	0.0747(4)
F(11)	−0.1166(3)	0.1547(1)	−0.2073(1)	0.118(1)
F(12)	−0.0529(3)	0.1274(1)	−0.1112(1)	0.110(1)
F(13)	0.1286(3)	0.1887(1)	−0.1561(1)	0.118(1)
F(14)	−0.2780(2)	0.3556(1)	−0.0087(1)	0.114(1)
F(15)	−0.3391(2)	0.2667(2)	−0.1292(1)	0.116(1)
F(16)	−0.3141(3)	0.2179(2)	−0.0445(2)	0.126(2)
O(1)	−0.0096(3)	0.3489(1)	−0.1079(1)	0.069(1)
N(1)	0.1988(3)	0.3977(2)	0.0099(2)	0.063(1)
C(11)	−0.0246(4)	0.1902(2)	−0.1361(2)	0.076(2)
C(12)	−0.2437(4)	0.2806(2)	−0.0634(2)	0.075(2)
C(13)	0.0611(3)	0.3305(2)	0.0138(2)	0.057(1)
C(14)	0.3556(4)	0.3682(2)	−0.0089(2)	0.087(2)
C(15)	0.2221(4)	0.4855(2)	0.0792(2)	0.091(2)
C(16)	0.2494(5)	0.1851(3)	0.0212(2)	0.111(3)
C(17)	−0.0771(5)	0.2102(3)	0.0852(2)	0.113(3)
C(18)	0.2211(5)	0.3453(3)	0.1717(2)	0.106(2)
B(1)	−0.0520(4)	0.2861(2)	−0.0754(2)	0.060(1)
H(O1)	−0.006(4)	0.338(2)	−0.147(2)	0.07(1)
H(N1)	0.159(4)	0.403(2)	−0.030(2)	0.063(9)
H(13)	0.000(3)	0.367(2)	0.052(1)	0.055(7)

<sup>a</sup>  $U = \frac{1}{3} \sum_i \sum_j a_i \cdot a_j \cdot a_i^* a_j^* U_{ij}$  for the non-hydrogen atoms.

TABLE 3. Crystallographic data<sup>a</sup> for IV:2VII and XVIII

	IV:2VII	XVIII
Formula	C <sub>8</sub> H <sub>18</sub> BF <sub>6</sub> NOSi + 2C <sub>11</sub> H <sub>22</sub> BF <sub>6</sub> NOSi	C <sub>10</sub> H <sub>21</sub> BF <sub>6</sub> N <sub>2</sub> OSi
<i>M<sub>r</sub></i>	297.12 + 337.19	338.18
Space group	<i>P</i> $\bar{1}$	<i>P</i> 2 <sub>1</sub> / <i>n</i>
<i>a</i> (Å)	8.3884(8)	6.574(2)
<i>b</i> (Å)	17.213(2)	15.826(2)
<i>c</i> (Å)	18.749(2)	16.217(2)
$\alpha$ (°)	115.328(5)	90
$\beta$ (°)	91.759(7)	100.77(2)
$\gamma$ (°)	99.122(6)	90
<i>V</i> (Å <sup>3</sup> )	2401.2	1657.4
<i>Z</i>	2	4
<i>D<sub>c</sub></i> (g cm <sup>−3</sup> )	1.344	1.355
<i>T</i> (°C)	23	24
Radiation	Cu K $\alpha$	Mo K $\alpha$
$\lambda$ (Å)	1.54184	0.71073
2 $\theta$ limits (°)	5–130	3–50
Reflections		
Measured	9221	6711
Unique	8138	2979
With <i>F</i> ≥ 4 $\sigma$ ( <i>F</i> )	5863	2041
Crystal size (mm)	0.18 × 0.30 × 0.75	0.23 × 0.23 × 0.43
$\mu_{\lambda}$ (cm <sup>−1</sup> )	18.53	1.92
Transmission	0.7408–0.4741	0.9735–0.9490
<i>R</i> ( <i>F<sub>o</sub></i> )	0.054	0.051
<i>R<sub>w</sub></i> ( <i>F<sub>o</sub></i> )	0.074	0.050
Parameters	580	226
$\Delta\rho$ (e Å <sup>−3</sup> )	0.30 to −0.22	0.33 to −0.22

<sup>a</sup> Additional crystallographic data may be obtained from Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen 2, by quoting the authors, the literature reference and the deposit number CSD-57456.

shorter than the nearly linear (173(2)°) intermolecular hydrogen bond formed by B.

Hydrolysis of II appears to cause a marked lengthening of the B(1)–C(13) bond in view of the fact that the endocyclic B–C distance in (CF<sub>3</sub>)<sub>2</sub>BC(SiMe<sub>3</sub>)(Bz)-NMe<sub>2</sub> (C) is 0.095(6) Å shorter [3]. Steric interactions may contribute to the lengthening of the B(1)–C(13) bond in IV, since the B(1)–C(13)–Si(1) angle is very large, 125.2(2)°. Analogous arguments were invoked to account for the length, 1.673(4) Å, of the corresponding distance in A. On the contrary, the C(13)–N(1) bond in IV is 0.033(5) and 0.041(5) Å shorter respectively than the analogous linkages in A and C; so relatively enhanced C(13)–N(1) bonding may be compensating for the long B(1)–C(13) bond.

Excellent agreement is found between the molecular dimensions of the two crystallographically independent molecules of VII except for the fact that an enantiomorphic pair was chosen for the asymmetric unit. Thus the twist conformation found for the five-membered ring of VII (Figs. 2 and 3) appears to be quite rigid.

This ring is somewhat smaller and, because of the two additional methyl substituents, sterically more obstructed than that of IV. Nevertheless the B(*I*)–C(*I*3) bonds are significantly shorter (0.042(6) Å average shortening) in VII than in IV. The other bonds formed by boron tend to be longer in VII than in IV, the difference being significant for the B–O distances (0.024(6) Å). While the C(*I*4)–O(*I*) distances (average,

TABLE 5. Positional and thermal <sup>a</sup> parameters for VII

Atom	x	y	z	U
Si(2)	0.4207(1)	0.09423(7)	0.20493(6)	0.0824(5)
F(21)	0.4179(3)	0.2631(1)	0.3860(1)	0.121(1)
F(22)	0.6654(3)	0.2515(1)	0.4003(1)	0.105(1)
F(23)	0.5191(4)	0.2670(1)	0.4941(1)	0.132(1)
F(24)	0.1955(3)	0.0193(2)	0.3715(2)	0.148(2)
F(25)	0.1788(3)	0.1505(2)	0.4044(2)	0.153(2)
F(26)	0.2887(4)	0.1157(2)	0.4853(2)	0.168(2)
O(2)	0.5860(2)	0.0932(1)	0.4191(1)	0.0706(9)
N(2)	0.6130(3)	0.0159(2)	0.2854(2)	0.075(1)
C(21)	0.5135(5)	0.2242(2)	0.4145(2)	0.085(2)
C(22)	0.2828(5)	0.1006(3)	0.4099(2)	0.088(2)
C(23)	0.4644(3)	0.0575(2)	0.2852(2)	0.057(1)
C(24)	0.6237(4)	0.0140(2)	0.3689(2)	0.073(2)
C(25)	0.5950(6)	-0.0741(3)	0.2183(2)	0.122(2)
C(26)	0.7613(4)	0.0726(3)	0.2789(3)	0.113(3)
C(27)	0.7954(4)	0.0109(3)	0.3964(3)	0.109(2)
C(28)	0.5034(5)	-0.0637(2)	0.3668(3)	0.102(2)
C(29)	0.4361(7)	0.0089(3)	0.1036(2)	0.138(3)
C(210)	0.2048(5)	0.1079(3)	0.2125(2)	0.107(2)
C(211)	0.5488(6)	0.1980(3)	0.2153(3)	0.127(3)
B(2)	0.4605(4)	0.1190(2)	0.3807(2)	0.060(1)
H(23)	0.379(3)	0.009(2)	0.270(1)	0.053(7)
Si(3)	0.2433(1)	0.47127(7)	0.61042(6)	0.0798(5)
F(31)	0.1029(2)	0.5188(1)	0.8144(1)	0.099(1)
F(32)	0.3569(2)	0.5427(1)	0.8051(1)	0.098(1)
F(33)	0.2673(3)	0.4776(1)	0.8749(1)	0.105(1)
F(34)	0.4010(3)	0.2797(2)	0.6680(1)	0.117(1)
F(35)	0.5130(2)	0.4020(2)	0.7553(2)	0.139(2)
F(36)	0.3721(3)	0.3128(2)	0.7867(2)	0.158(2)
O(3)	0.0636(2)	0.3337(1)	0.7390(1)	0.0589(8)
N(3)	-0.0115(3)	0.3350(1)	0.6192(1)	0.059(1)
C(31)	0.2356(4)	0.4812(2)	0.8050(2)	0.073(1)
C(32)	0.3724(4)	0.3445(2)	0.7346(2)	0.077(2)
C(33)	0.1695(3)	0.3793(2)	0.6394(2)	0.056(1)
C(34)	-0.0341(3)	0.2795(2)	0.6683(2)	0.060(1)
C(35)	-0.0579(4)	0.2777(2)	0.5318(2)	0.088(2)
C(36)	-0.1175(4)	0.4019(2)	0.6453(2)	0.079(2)
C(37)	-0.2075(4)	0.2635(2)	0.6855(2)	0.084(2)
C(38)	0.0233(4)	0.1930(2)	0.6248(2)	0.080(2)
C(39)	0.1855(6)	0.4369(3)	0.5027(2)	0.133(3)
C(310)	0.4702(5)	0.4875(3)	0.6256(2)	0.114(3)
C(311)	0.1737(6)	0.5774(2)	0.6668(3)	0.109(2)
B(3)	0.2111(4)	0.3860(2)	0.7285(2)	0.057(1)
H(33)	0.219(3)	0.337(2)	0.607(1)	0.050(7)

<sup>a</sup> See Table 4.

1.385(7) Å) are short for an ether-like bond, the C(I4)–N(I) bond lengths (average, 1.582(4) Å) are markedly long. The length of the C(I4)–N(I) interaction may reflect in part the ability of the C–O linkage to stabilize a positive charge on the C(I4) atom via O(pπ) → C(pπ) bonding—the tendency for a hesitant approach of a carbonyl to an amine group being well documented [8]. The short contacts between the F(I4) atoms and the hydrogen atoms bonded to C(I3) and C(I8) should be noted. They cause a ~24° rotation of the trifluoromethyl groups about the B(I)–C(I2) bonds away from the staggered conformation, whereas the

TABLE 6. Positional and thermal <sup>a</sup> parameters for XVIII

Atom	x	y	z	U
Si	0.0247(1)	0.05151(5)	0.83677(5)	0.0536(3)
F(1)	0.1887(3)	0.2657(1)	0.7938(1)	0.0766(8)
F(2)	-0.0619(4)	0.3367(1)	0.7245(1)	0.0864(9)
F(3)	-0.1192(4)	0.2509(1)	0.8196(1)	0.093(1)
F(4)	-0.4204(3)	0.1542(2)	0.7010(2)	0.120(1)
F(5)	-0.3562(3)	0.1290(1)	0.5819(2)	0.105(1)
F(6)	-0.3795(3)	0.2560(1)	0.6201(2)	0.110(1)
O	0.0395(4)	0.1119(1)	0.5236(1)	0.073(1)
N(1)	0.0547(4)	0.2183(2)	0.6156(1)	0.048(1)
N(2)	0.0202(4)	0.0244(1)	0.6587(1)	0.0414(8)
C(1)	-0.0112(6)	0.2582(2)	0.7565(2)	0.063(1)
C(2)	-0.2998(5)	0.1813(2)	0.6484(2)	0.069(1)
C(3)	0.0495(5)	0.0932(2)	0.7272(2)	0.040(1)
C(4)	0.0814(5)	0.1859(2)	0.5436(2)	0.049(1)
C(5)	0.1698(6)	0.2414(2)	0.4840(2)	0.066(1)
C(6)	-0.1577(5)	-0.0336(2)	0.6579(2)	0.061(1)
C(7)	0.2125(5)	-0.0249(2)	0.6562(2)	0.062(1)
C(8)	-0.2460(6)	0.0453(2)	0.8555(2)	0.079(2)
C(9)	0.1435(7)	-0.0560(2)	0.8580(2)	0.078(2)
C(10)	0.1835(7)	0.1184(2)	0.9191(2)	0.084(2)
B	-0.0530(5)	0.1835(2)	0.6865(2)	0.045(1)
H(1)	0.085(4)	0.267(2)	0.620(2)	0.044(9)
H(2)	-0.005(5)	0.054(2)	0.604(2)	0.07(1)
H(3)	0.195(4)	0.104(1)	0.738(1)	0.028(6)

<sup>a</sup> See Table 4.

conformation of the B(I)–C(I1) bonds lies within 4° of being exactly staggered.

## 6. Description of the crystal structure of XVIII

A view of XVIII is given in Fig. 4, and important dimensions are listed in Table 9. The structure of XVIII is closely related to that of IV, the hydroxy group of IV being replaced by an acetamido fragment. The carbonyl function of the latter accepts a proton from the ammonium centre to form an O···H(2)–N(2) hydrogen bond that completes a seven-membered ring. This hydrogen bond is not nearly as bent (160(3)°) and

TABLE 7. Selected bond distances and angles in IV

B(1)–C(11)	1.612(5)	C(13)–H(13)	0.95(3)
B(1)–C(12)	1.624(5)	N(1)–C(14)	1.483(4)
B(1)–C(13)	1.690(4)	N(1)–C(15)	1.490(5)
B(1)–O(1)	1.458(5)	N(1)–H(N1)	0.85(3)
C(13)–Si(1)	1.906(4)	O(1)–H(O1)	0.68(3)
C(13)–N(1)	1.526(4)	O(1)–H(N1)	1.82(3)
O(1)–B(1)–C(13)	104.9(2)	B(1)–C(13)–N(1)	105.4(3)
C(11)–B(1)–C(13)	115.0(3)	B(1)–C(13)–Si(1)	125.2(2)
C(12)–B(1)–C(13)	110.1(2)	B(1)–C(13)–H(13)	107(2)
C(13)–N(1)–C(14)	115.8(3)	N(1)–C(13)–Si(1)	115.9(2)
C(13)–N(1)–C(15)	114.0(3)	N(1)–C(13)–H(13)	102(2)
C(13)–N(1)–H(N1)	99(2)	Si(1)–C(13)–H(13)	98(2)
B(1)–O(1)–H(N1)	88(1)	N(1)–H(N1)–O(1)	139(3)

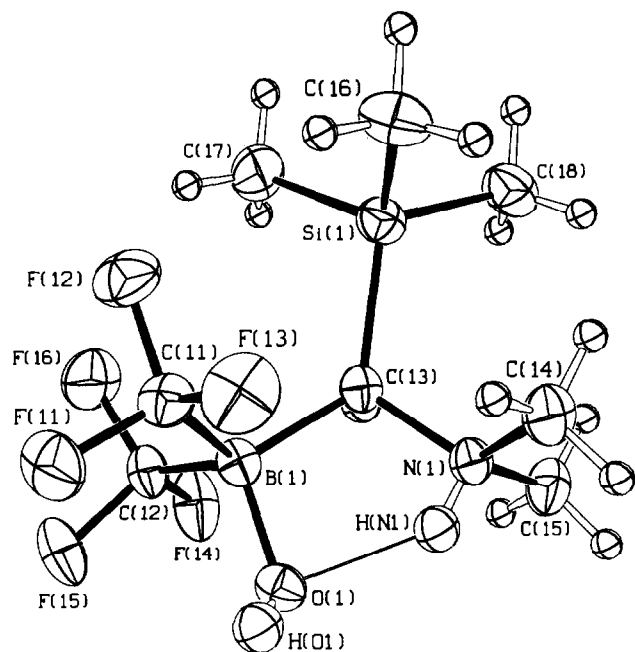


Fig. 1. A perspective drawing of **IV** with ellipsoids of the methyl hydrogen atoms reduced for clarity.

is significantly shorter (0.16(4) Å) than that found in the five-membered ring of **IV**. On the contrary, the hydrogen atom bonded to N(1) forms no hydrogen bond in the solid state.

The H(1), N(1), C(4), C(5), O fragment is planar to within the limits of experimental error, and the boron atom is displaced by 0.158(3) Å from this plane. The B–N(sp<sup>2</sup>) distance does not differ significantly from those reported in other bis(trifluoromethyl)borate structures [9]. The C(3)–B bond length lies between

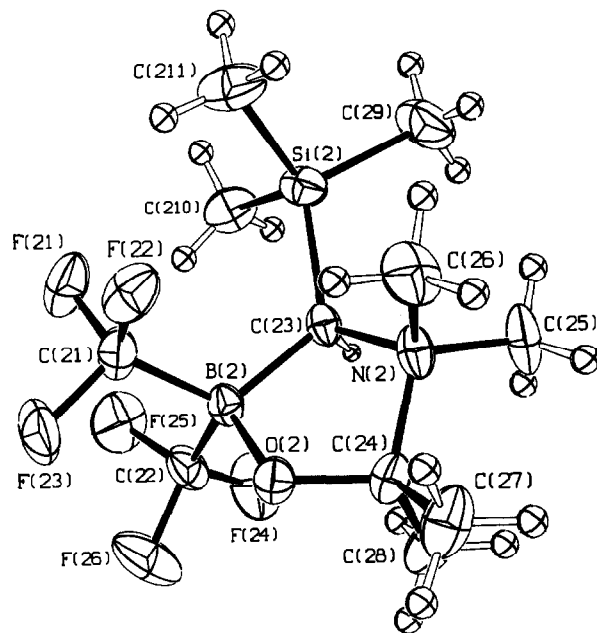


Fig. 2. A view of the first molecule of **VII** from above the ring.

those found in **IV** and **VII** whereas the C(3)–N(2) distance is similar to those of **VII**.

## 7. Discussion

Reactions of the azoniaboratacyclopropanes **I** and **II** result in fission of the B–N bond. This reactivity is significantly higher than that of the less-strained bis(trifluoromethyl)alkylborane-amines. The latter are generally stable to water, their B–N bonds being remarkably inert, since the trifluoromethyl substituents

TABLE 8. Selected bond distances and angles in **VII**

	<i>I</i> = 2	<i>I</i> = 3		<i>I</i> = 2	<i>I</i> = 3
B( <i>I</i> )–C( <i>I</i> 1)	1.620(6)	1.628(5)	C( <i>I</i> 4)–O( <i>I</i> )	1.380(4)	1.390(3)
B( <i>I</i> )–C( <i>I</i> 2)	1.634(5)	1.650(5)	C( <i>I</i> 4)–N( <i>I</i> )	1.581(4)	1.583(4)
B( <i>I</i> )–C( <i>I</i> 3)	1.649(4)	1.647(4)	C( <i>I</i> 4)–C( <i>I</i> 7)	1.531(5)	1.508(4)
B( <i>I</i> )–O( <i>I</i> )	1.483(4)	1.481(4)	C( <i>I</i> 4)–C( <i>I</i> 8)	1.528(6)	1.525(5)
C( <i>I</i> 3)–Si( <i>I</i> )	1.912(3)	1.906(4)	N( <i>I</i> )–C( <i>I</i> 5)	1.500(5)	1.506(4)
C( <i>I</i> 3)–N( <i>I</i> )	1.534(4)	1.543(4)	N( <i>I</i> )–C( <i>I</i> 6)	1.496(6)	1.492(4)
C( <i>I</i> 3)–H( <i>I</i> 3)	0.94(2)	0.90(2)			
O( <i>I</i> )–B( <i>I</i> )–C( <i>I</i> 3)	103.3(3)	103.3(2)	B( <i>I</i> )–C( <i>I</i> 3)–N( <i>I</i> )	102.1(2)	102.1(2)
C( <i>I</i> 1)–B( <i>I</i> )–C( <i>I</i> 3)	118.5(3)	118.9(3)	B( <i>I</i> )–C( <i>I</i> 3)–Si( <i>I</i> )	123.3(2)	123.7(2)
C( <i>I</i> 2)–B( <i>I</i> )–C( <i>I</i> 3)	112.2(2)	112.3(2)	B( <i>I</i> )–C( <i>I</i> 3)–H( <i>I</i> 3)	107(2)	104(2)
C( <i>I</i> 3)–N( <i>I</i> )–C( <i>I</i> 4)	103.8(2)	104.2(2)	N( <i>I</i> )–C( <i>I</i> 3)–Si( <i>I</i> )	120.4(2)	118.9(2)
C( <i>I</i> 3)–N( <i>I</i> )–C( <i>I</i> 5)	112.3(3)	112.9(2)	N( <i>I</i> )–C( <i>I</i> 3)–H( <i>I</i> 3)	101(2)	103(2)
C( <i>I</i> 3)–N( <i>I</i> )–C( <i>I</i> 6)	109.5(3)	110.8(2)	Si( <i>I</i> )–C( <i>I</i> 3)–H( <i>I</i> 3)	100(2)	102(2)
B( <i>I</i> )–O( <i>I</i> )–C( <i>I</i> 4)	112.3(2)	113.3(2)	N( <i>I</i> )–C( <i>I</i> 4)–O( <i>I</i> )	103.0(3)	102.7(2)



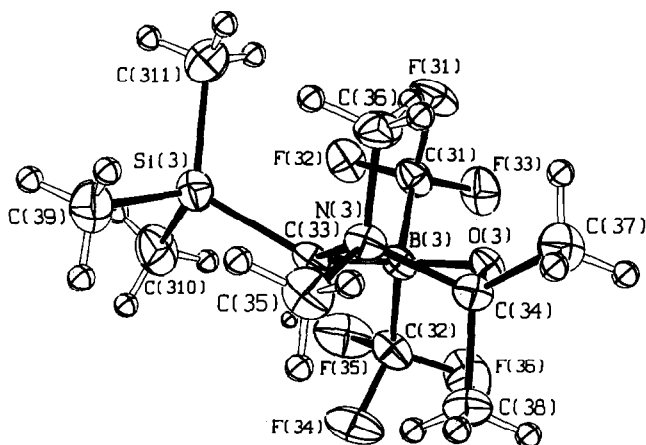


Fig. 3. A side-on view of the ring of the second molecule of VII.

effectively limit adduct dissociation via their inductive-withdrawing effect. Thus a B–N charge distribution is to be expected in these molecules despite fourfold coordination of both the boron and nitrogen atoms. Thus the reactions of I and II may have been initiated by a nucleophilic attack at the boron atoms. This might explain why only carbonyl and nitrile compounds undergo a ring expansion reaction while the formally related but less nucleophilic 1-alkenes such as  $\text{H}_2\text{C}=\text{CHC}_4\text{H}_9$  and 1-alkynes such as  $\text{HC}\equiv\text{CC}_6\text{H}_5$  do not. An analogous insertion of aldehydes into the phosphorus–boron bond has been observed in 1-boryl-2-phosphinoethylenes [10]. In this connection the ten-

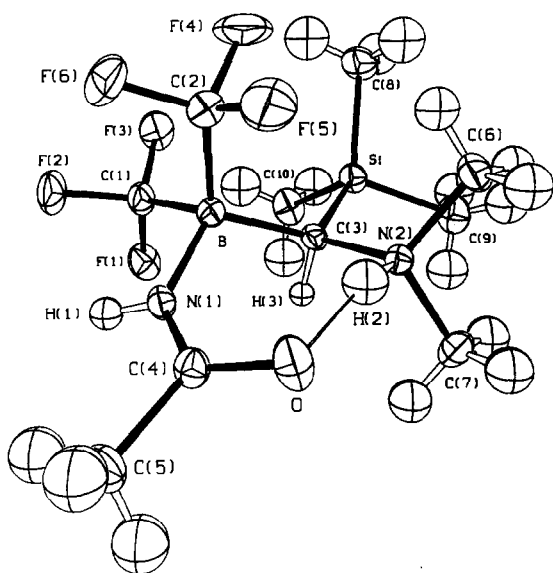
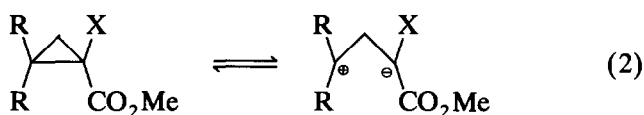


Fig. 4. A perspective drawing of XVIII.

TABLE 9. Selected bond distances and angles in XVIII

B–C(1)	1.627(4)	C(4)–N(1)	1.317(4)
B–C(2)	1.626(5)	C(4)–C(5)	1.501(4)
B–C(3)	1.663(4)	N(1)–H(1)	0.80(3)
B–N(1)	1.558(4)	N(2)–C(6)	1.485(4)
C(3)–Si	1.930(3)	N(2)–C(7)	1.493(4)
C(3)–N(2)	1.541(3)	N(2)–H(2)	0.99(3)
C(3)–H(3)	0.95(2)	O–H(2)	1.66(3)
C(4)–O	1.233(3)		
N(1)–B–C(3)	113.0(2)	B–C(3)–N(2)	109.5(2)
C(1)–B–C(3)	110.1(2)	B–C(3)–Si	124.2(2)
C(2)–B–C(3)	115.7(2)	B–C(3)–H(3)	103(1)
B–N(1)–C(4)	132.0(3)	N(2)–C(3)–Si	113.7(2)
B–N(1)–H(1)	114(2)	N(2)–C(3)–H(3)	104(1)
C(4)–N(1)–H(1)	113(2)	Si–C(3)–H(3)	99(1)
C(3)–N(2)–C(6)	115.8(2)	N(1)–C(4)–O	123.0(3)
C(3)–N(2)–C(7)	113.3(2)	N(1)–C(4)–C(5)	118.3(3)
C(3)–N(2)–H(2)	107(2)	O–C(4)–C(5)	118.7(3)
C(4)–O–H(2)	112(1)	N(2)–H(2)–O	160(3)

dency for cyclopropanes to open heterolytically as in eqn. (2)



should be noted. The importance of such zwitterionic transition states is enhanced by placing electron donors at the cationic site (*e.g.*, R = Me, Ph) and electron acceptors at the anionic site (*e.g.*, X = CN) [11]. Whether a ring-strain-promoted heterolytic cleavage of the NB bonds in I and II must occur before nucleophilic attack can proceed awaits to be seen. Until now no stable three-coordinated trifluoromethylborane had ever been observed without an amino group bonded directly to boron. Since these B–N bonds were usually retained in subsequently formed borate derivatives, the cleavage of the B–N bond in I and II reported here makes these three-membered rings versatile building blocks in bis(trifluoromethyl)boron chemistry.

## 8. Experimental details

### 8.1. 4-Hydroxy-2-methyl-5,5,5-trifluoro-4-trifluoromethyl-2-azonia-4-boratapentane (III) and 4-hydroxy-2-methyl-5,5,5-trifluoro-4-trifluoromethyl-3-trimethylsilyl-2-azonia-4-boratapentane (IV)

A solution of 0.52 g (2.5 mmol) of I or 0.56 g (2 mmol) of II in 10 ml of  $\text{CH}_2\text{Cl}_2$  was stirred with 3 mmol of  $\text{H}_2\text{O}$  for 4 h at ambient temperature. After removal of the solvent and the water *in vacuo*, pure III and IV respectively were obtained.

**III:** Mp. 92°C. IR:  $\nu(\text{OH})$  3660w,  $\nu(\text{NH})$  3280w,  $\nu(\text{CF})$  1080vs, br  $\text{cm}^{-1}$ .

**IV:** Mp. 80°C. IR:  $\nu(\text{OH})$  3668w,  $\nu(\text{NH})$  3080w, br,  $\nu(\text{CF})$  1080vs, br  $\text{cm}^{-1}$ .

8.2. 2,2-Bis(trifluoromethyl)-5,5-diethyl-4,4-dimethyl-1-oxa-4-azonia-2-boratacyclopentane (V), 2,2-bis(trifluoromethyl)-4,4,5-trimethyl-3-trimethylsilyl-1-oxa-4-azonia-2-boratacyclopentane (VI), 2,2-bis(trifluoromethyl)-4,4,5,5-tetramethyl-3-trimethylsilyl-1-oxa-4-azonia-2-boratacyclopentane (VII), 2,2-bis(trifluoromethyl)-5,5-diethyl-4,4-dimethyl-3-trimethylsilyl-1-oxa-4-azonia-2-boratacyclopentane (VIII), 2,2-bis(trifluoromethyl)-4,4,5-trimethyl-3-trimethylsilyl-5-(2-methyl-propenyl)-1-oxa-4-azonia-2-boratacyclopentane (VIII) and 2,2-bis(trifluoromethyl)-4,4,5-trimethyl-3-trimethylsilyl-5-(2-methylcyclopentenyl)-1-oxa-4-azonia-2-boratacyclopentane (X)

A solution of 0.52 g (2.5 mmol) of I or 0.56 g (2 mmol) of II in 10 ml of  $\text{CHCl}_3$  was stirred with one equivalent of the respective anhydrous carbonyl reactant for 12 h at ambient temperature. After removal of the solvent *in vacuo*, compounds V–X were obtained.

**V:** Mp. 132°C. IR:  $\delta(\text{CH})$  1270m,  $\nu(\text{CF})$  1098vs, 1080vs, br  $\text{cm}^{-1}$ .

**VI:** Mp. 119°C. IR:  $\delta(\text{CH})$  1258m,  $\nu(\text{CF})$  1080vs, br,  $\rho(\text{Si}(\text{CH}_3)_3)$  845vs  $\text{cm}^{-1}$ .

**VII:** Mp. 168°C (decomposition). IR:  $\delta(\text{CH})$  1255s,  $\nu(\text{CF})$  1075vs, br,  $\rho(\text{Si}(\text{CH}_3)_3)$  835s  $\text{cm}^{-1}$ .

**VIII:** Mp. 144°C. IR:  $\delta(\text{CH})$  1260m,  $\nu(\text{CF})$  1080vs, br,  $\rho(\text{Si}(\text{CH}_3)_3)$  855s  $\text{cm}^{-1}$ .

**IX:** Mp. 133°C. IR:  $\nu(\text{C}=\text{C})$  1668w,  $\delta(\text{CH})$  1257s,  $\nu(\text{CF})$  1095vs, 1075vs,  $\rho(\text{Si}(\text{CH}_3)_3)$  855s  $\text{cm}^{-1}$ .

**X:** Mp. 150°C (decomposition). IR:  $\nu(\text{C}=\text{C})$  1645vw,  $\delta(\text{CH})$  1260s,  $\nu(\text{CF})$  1075vs, br,  $\rho(\text{Si}(\text{CH}_3)_3)$  852s  $\text{cm}^{-1}$ .

8.3. 2,2-Bis(trifluoromethyl)-5-(1-chloroethyl)-4,4-dimethyl-1-aza-4-azonia-2-boratacyclopentene (XI), 2,2-bis(trifluoromethyl)-4,4-dimethyl-5-methyl-3-trimethylsilyl-1-aza-4-azonia-2-boratacyclopentene (XII), 2,2-bis(trifluoromethyl)-5-(1-chloroethyl)-4,4-dimethyl-3-trimethylsilyl-1-aza-4-azonia-2-boratacyclopentene (XIII), 2,2-bis(trifluoromethyl)-4,4-dimethyl-5-phenyl-3-trimethylsilyl-1-aza-4-azonia-2-boratacyclopentene (XIV) and 2,2-bis(trifluoromethyl)-4,4-dimethyl-5-propenyl-3-trimethylsilyl-1-aza-4-azonia-2-boratacyclopentene (XV)

A solution of 0.52 g (2.5 mmol) of I or 0.56 g (2 mmol) of II in 10 ml of  $\text{CHCl}_3$  was stirred with one equivalent of the respective anhydrous nitrile reactant for 5 h at ambient temperature. After removal of the solvent *in vacuo* the pure compounds XI–XV were obtained.

**XI:** Mp. 111°C. IR:  $\nu(\text{C}=\text{N})$  1730m,  $\delta(\text{CH})$  1275s,  $\nu(\text{CF})$  1085vs, br  $\text{cm}^{-1}$ .

**XII:** Mp. 168°C. IR:  $\nu(\text{C}=\text{N})$  1745m,  $\delta(\text{CH})$  1270s,  $\nu(\text{CF})$  1085vs, br,  $\rho(\text{Si}(\text{CH}_3)_3)$  845s  $\text{cm}^{-1}$ .

**XIII:** Mp. 123°C. IR:  $\nu(\text{C}=\text{N})$  1738s,  $\delta(\text{CH})$  1265s,  $\nu(\text{CF})$  1090vs, br,  $\rho(\text{Si}(\text{CH}_3)_3)$  845s  $\text{cm}^{-1}$ .

**XIV:** Mp. 97°C. IR:  $\nu(\text{C}=\text{N})$  1745m,  $\delta(\text{CH})$  1275s,  $\nu(\text{CF})$  1090vs, 1080vs,  $\rho(\text{Si}(\text{CH}_3)_3)$  845s  $\text{cm}^{-1}$ .

**XV:** Mp. 113°C. IR:  $\nu(\text{C}=\text{N})$  1720w,  $\nu(\text{C}=\text{C})$  1625vw,  $\delta(\text{CH})$  1260s,  $\nu(\text{CF})$  1090vs, 1080vs,  $\rho(\text{Si}(\text{CH}_3)_3)$  845s  $\text{cm}^{-1}$ .

TABLE 10. Elemental analyses for III–XX

Compound	Formula	Found (%) (calc. (%))		
		C	H	N
III	$\text{C}_5\text{H}_{10}\text{BF}_6\text{NO}$	26.79 (26.70)	4.42 (4.48)	6.20 (6.23)
IV	$\text{C}_8\text{H}_{18}\text{BF}_6\text{NOSi}$	32.40 (32.34)	6.07 (6.11)	4.59 (4.71)
V	$\text{C}_{10}\text{H}_{18}\text{BF}_6\text{NO}$	41.22 (40.98)	6.37 (6.19)	4.73 (4.78)
VI	$\text{C}_{10}\text{H}_{20}\text{BF}_6\text{NOSi}$	36.68 (37.17)	5.99 (6.24)	4.20 (4.33)
VII	$\text{C}_{11}\text{H}_{22}\text{BF}_6\text{NOSi}$	39.09 (39.18)	6.51 (6.58)	4.19 (4.15)
VIII	$\text{C}_{13}\text{H}_{26}\text{BF}_6\text{NOSi}$	42.84 (42.75)	7.02 (7.17)	3.92 (3.83)
IX	$\text{C}_{14}\text{H}_{26}\text{BF}_6\text{NOSi}$	44.21 (44.57)	6.78 (6.95)	3.98 (3.71)
X	$\text{C}_{15}\text{H}_{28}\text{BF}_6\text{NOSi}$	47.09 (47.65)	6.73 (7.00)	3.91 (3.47)
XI	$\text{C}_8\text{H}_{12}\text{BClF}_6\text{N}_2$	32.64 (32.41)	4.28 (4.08)	9.22 (9.45)
XII	$\text{C}_{10}\text{H}_{19}\text{BF}_6\text{N}_2\text{Si}$	37.48 (37.52)	6.05 (5.98)	8.93 (8.75)
XIII	$\text{C}_{11}\text{H}_{20}\text{BClF}_6\text{N}_2\text{Si}$	35.49 (35.84)	5.35 (5.47)	7.38 (7.60)
XIV	$\text{C}_{15}\text{H}_{21}\text{BF}_6\text{N}_2\text{Si}$	47.00 (47.14)	5.67 (5.54)	7.50 (7.33)
XV	$\text{C}_{12}\text{H}_{21}\text{BF}_6\text{N}_2\text{Si}$	42.32 (41.63)	6.50 (6.11)	8.48 (8.09)
XVI	$\text{C}_9\text{H}_{17}\text{BF}_6\text{N}_2$	35.67 (35.31)	5.73 (5.60)	9.00 (9.15)
XVII	$\text{C}_8\text{H}_{14}\text{BClF}_6\text{N}_2\text{O}$	35.33 (35.52)	6.38 (6.26)	8.45 (8.28)
XVIII	$\text{C}_{10}\text{H}_{21}\text{BF}_6\text{N}_2\text{OSi}$	30.19 (30.56)	4.28 (4.49)	9.14 (8.91)
XIX	$\text{C}_{11}\text{H}_{22}\text{BClF}_6\text{N}_2\text{OSi}$	34.33 (34.17)	5.55 (5.73)	7.39 (7.25)
XX	$\text{C}_{15}\text{H}_{23}\text{BF}_6\text{N}_2\text{OSi}$	44.92 (45.01)	5.69 (5.79)	6.18 (7.00)

#### 8.4. 4-Cyano-2-methyl-5,5,5-trifluoro-4-trifluoromethyl-3-trimethylsilyl-2-azonia-4-boratapentane (XVI)

A solution of 0.56 g (2 mmol) of II in 10 ml CH<sub>2</sub>Cl<sub>2</sub> was stirred under an atmosphere of HCN for 12 h at ambient temperature. After removal of the solvent *in vacuo*, XVI was obtained as analytically pure crystals.

XVI: Mp. 178°C (decomposition). IR/Raman:  $\nu(\text{NH})$  3165m/—,  $\nu(\text{CH})$  2960m/w,  $\nu(\text{C}\equiv\text{N})$  2220vw/s,  $\nu(\text{CF})$  1090vs, br/vvw,  $\rho(\text{Si}(\text{CH}_3)_3)$  845s/m,  $\delta_s(\text{CF}_3)$  690m/s cm<sup>-1</sup>.

#### 8.5. 4,4-Bis(trifluoromethyl)-7-chloro-2-methyl-5-aza-2-azonia-4-borata-octane-6-one (XVII), 4,4-bis(trifluoromethyl)-2-methyl-3-trimethylsilyl-5-aza-2-azonia-4-borataheptan-6-one (XVIII), 4,4-bis(trifluoromethyl)-7-chloro-2-methyl-3-trimethylsilyl-5-aza-2-azonia-4-borata-octan-6-one (XIX) and 4,4-bis(trifluoromethyl)-2-methyl-6-phenyl-3-trimethylsilyl-5-aza-2-azonia-4-borata-hexan-6-one (XX)

At ambient temperature, XI–XIV were dissolved in (CH<sub>3</sub>)<sub>2</sub>CO–H<sub>2</sub>O. Removal of the solvents yielded pure XVII–XX.

XVII: Mp. 74°C. IR:  $\nu(\text{NH})$  3445w, 3100w,  $\nu(\text{C}=\text{O})$  1635m,  $\nu(\text{CF})$  1095vs cm<sup>-1</sup>.

XVIII: Mp. 100°C. IR:  $\nu(\text{NH})$  3420m, 3100w,  $\nu(\text{C}=\text{O})$  1615m,  $\nu(\text{CF})$  1090vs cm<sup>-1</sup>.

XIX: Mp. 92°C. IR:  $\nu(\text{NH})$  3430w, 3090w,  $\nu(\text{C}=\text{O})$  1620 m,  $\nu(\text{CF})$  1090vs, 1085vs cm<sup>-1</sup>.

XX: Mp. 87°C. IR:  $\nu(\text{NH})$  3420w, 3080w,  $\nu(\text{C}=\text{O})$  1625s,  $\nu(\text{CF})$  1095vs, 1085vs cm<sup>-1</sup>.

For elemental analyses see Table 10.

#### Acknowledgments

We thank Dr. D. Henneberg, Mülheim/Ruhr, for recording the mass spectra. Financial support by the Fonds der Chemie and the Ministerium für Wissenschaft und Forschung NW is gratefully acknowledged.

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