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[2 + 2] Cycloaddition reactions of dialkylaminobis(trifluoromethyl)boranes with isocyanates and isothiocyanates. Crystal structures of $(CF_3)_2\overline{BNMe_2CON}{}^tBu$, $(CF_3)_2\overline{BNMe_2CSN}{}^tBu$, $(CF_3)_2\overline{BNPhC(NMe_2)S}$ and $(CF_3)_2\overline{BNMeC(NEt_2)OCON}Me$ *

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Abstract

The reactions of $(CF_3)_2BNMe_2$ (**D1**) and $(CF_3)_2BNEt_2$ (**D2**) with isocyanates and isothiocyanates have been studied. At or near room temperature the C=N bonds of RN=C=O and RN=C=S enter into [2+2] cycloadditions with the B–N bond of **D1** to yield the four-membered rings $(CF_3)_2\overline{BNMe_2CON}R$; R = Me (I), ${}^tBu$ (II), Ph (III), CF_3 (IV), and $(CF_3)_2\overline{BNMe_2CSN}R$; R = Me (V), Et (VI), ${}^tBu$ (VII), Ph (VIII) and p-FC_6H_4 (IX) respectively. I, V, VI, VIII and IX rearrange at ~ 60 °C to form the isomers $(CF_3)_2\overline{BNMeC(NMe_2)O}$ (XI) and $(CF_3)_2\overline{BNRC(NMe_2)S}$; R = Me (XII), Et (XIII), Ph (XIV) and p-FC_6H_4 (XV), respectively. At room temperature **D2** reacts with MeN=C=O to yield $(CF_3)_2\overline{BNMeC(NEt_2)O}$ (X) directly. X and XI reversibly incorporate MeN=C=O to form the six-membered heterocycles $(CF_3)_2\overline{BNMeC(NR_2)OCON}Me$; R = Me (XVI) and Et (XVII). The structures of II, VII, XIV and XVII have been established by single-crystal X-ray diffraction studies. The bond distances indicate that the π-bonding is delocalized over OCN (sp^2), SCN (sp^2) and SCN_2 (sp^2) fragments in II, VII and XIV, respectively. Furthermore, the π-character of the exocyclic C–N bonds in XIV and XVII, while considerable, is lower than that of the exocyclic C–O(S) bonds in II, VII and XVII. The other structural assignments were based on mass spectrometry and vibrational and multinuclear NMR spectra.

Introduction

Aminoboranes $X_2B{=}NR_2$, X = H or halogen, are known to form cyclic dimers such as **A** readily provided that the substituents R are not too bulky [1,2]. While they do not undergo [2 + 2] cycloaddition reactions with double bonds their reactions with organic isocyanates $R^3N{=}C{=}O$ were reported to yield the *N*-boronated

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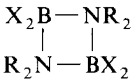
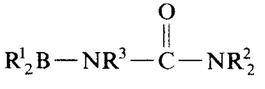
* Dedicated to Professor Kurt Dehnicke on the occasion of his 60th birthday.

ureido derivatives **B** [3]. Similarly ketene adds bis(dialkylamino)halogenoboranes $(R_2N)_2BX$ across the C=C bond to give dimer **C** [4].

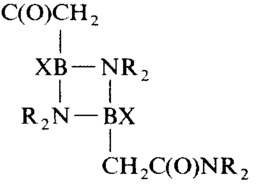


(A)



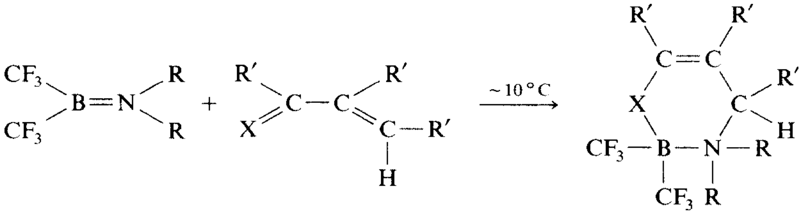
$R^1_2B-NR^3-C(=O)-NR^2_2$

(B)



(C)

On the other hand bis(trifluoromethyl)aminoboranes $(CF_3)_2B{=}NR_2$, R = Me (**D1**) [5] and Et (**D2**) [6], show no tendency to dimerize, although the considerable $B^{\delta+}-^{\delta-}N$ polarity might have been expected to favour a structure of type **A**. On the other hand, the CF_3 derivatives undergo a variety of [2 + 4] cycloaddition reactions with 1,3-dienes and enones, and novel six-membered heterocycles containing the $-B(CF_3)_2NR_2-$ fragment have been prepared under mild conditions, generally in high yields, eq. 1 [7].



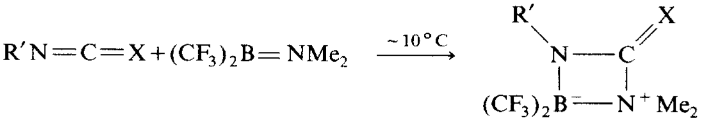
(1)

($X = CH_2$, O; R = Me; Et; R′ = H, Me, OMe)

We describe here the reaction of the aminoboranes **D1** and **D2** with organic isocyanates R′N=C=O and isothiocyanates R′N=C=S. These cumulenes were chosen as representative examples of systems containing two reactive polar double bonds.

[2 + 2] Cycloaddition reactions

At or slightly below room temperature **D1** reacts with organic isocyanates and isothiocyanates to yield almost quantitatively the 1 : 1 adducts **E** (eq. 2).

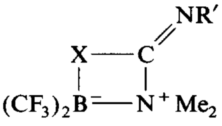


(2)

(**E**: I–IX)

X	R		Yield (%)
O	Me	I	96
	${}^tBu$	II	97
	Ph	III	77
	CF_3	IV	65
S	Me	V	95
	Et	VI	88
	${}^tBu$	VII	96
	Ph	VIII	93
	p-FC_6H_4	IX	97

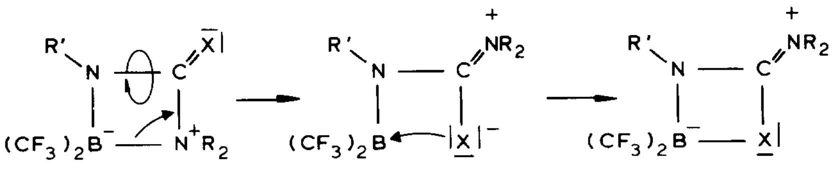
The unambiguous assignment of the 1-borata-2-azonia-4-azacyclobutane structure **E** rather than the alternative structure **F** followed from the vibrational and



(F)

multinuclear NMR spectra of I–IX and the results of the X-ray diffraction studies described later.

Upon gentle heating, e.g. at 60 °C, for a few hours some compounds of type **E** isomerize quantitatively, as shown in eq. 3.



(3)

(E; I,V,VI,VIII,IX) (G; XI–XV)

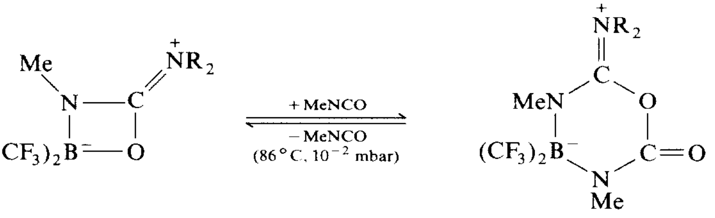
X	R	R′	
O	Et	Me	X
	Me	Me	XI
S	Me	Me	XII
	Me	Et	XIII
	Me	Ph	XIV
	Me	p-FC_6H_4	XV

The irreversible rearrangement **E** → **G** can be monitored by observing changes in the physical properties and the NMR spectra. The structure of XIV was established by an X-ray investigation. The consistency of diagnostic spectroscopic parameters of the compounds X–XV indicates that they have a common structural framework.

The diethylamino derivative X was obtained directly from the reaction of **D2** with MeNCO; it is likely that X also has a precursor of type **E**, but this could not be isolated. Presumably the conditions necessary to bring about reaction of the diethylamino derivative **D2** are so vigorous that only the thermodynamically favoured rearranged product X was obtained, not the intermediate.

The sterically more demanding tert-butyl group R′ effectively inhibits a rearrangement of II and VII in the sense of eq. 3. Unlike its thio analogue VIII, the PhNCO adduct III did not isomerize at temperatures up to 100 °C, and IV was also resistant to thermal rearrangement. A *para*-fluorine substituent did not influence the rearrangement of the phenylisothiocyanate adduct significantly.

The rearranged cycloadducts from MeNCO (X and XI) react with additional MeNCO in a [2 + 2] cycloaddition fashion to form six-membered rings (eq. 4).



(4)

(XVI: R = Me; XVII: R = Et)

Compounds XVI and XVII were isolated and characterized by elemental analyses and vibrational, NMR and mass spectra. Furthermore, the structure of XVII was established by a single crystal X-ray diffraction study. Both compounds are thermally unstable towards loss of MeNCO. Thus reaction 4 represents a true equilibrium, which can be reversed by pumping off the isocyanate, the six-membered rings being stable only at room temperature.

Properties and spectra

The physical properties and the ^{1}H, ^{19}F, ^{11}B and ^{13}C NMR spectroscopic data for I–XVII are outlined in Table 1. All the compounds form colourless crystals. They are very soluble in polar solvents ($HCCl_3$, CH_2Cl_2, $(CH_3)_2CO$, CH_3CN), but poorly soluble in aliphatic and aromatic hydrocarbons. The oxo derivatives are insensitive to moisture while the thio compounds are slowly hydrolyzed.

The ^{11}B and ^{13}C (ring), but also ^{19}F chemical shifts are particularly sensitive to the constitution of the ring framework. Apparently each of the groups comprising the compounds I–IV, V–IX, X/XI, XII–XV and XVI/XVII shares specific structural elements. For example, the strong infrared absorption near 1820 cm^{-1} revealed by I–IV is characteristic of a C=O stretching vibration expected for a type **E** framework. That I–IV and, analogously, V–IX have a cyclic rather than the noncyclic structure **B** is suggested by the ^4J(CF) coupling of the C atoms of the NMe_2 group of ca. 2 Hz. No ν(C=O) band is observed for compounds V–XV. In XVI and XVII ν(C=O) is shifted to 1768 cm^{-1}.

On the other hand, the ν(C=S) band for V–IX is not characteristic, and could not be identified unambiguously among the numerous vibrations of these molecules. The structural assignment of V–IX is therefore mainly based on the consistency of the NMR spectra, which suggests a framework corresponding to that determined for VII by X-ray diffraction.

The rearrangement **E** → **G** can be monitored by ^{1}H and ^{13}C NMR spectroscopy. At low temperature the C atoms of the $N(CH_3)_2$ group are magnetically nonequivalent because of hindered rotation about the C=N bond.

The EI mass spectra of I–XVII are set out in Table 2. Isomers give rise to different and specific fragmentation patterns, that support the assignments shown in structures **E** and **G**. Relationships within different groups of molecules justify the unified presentation of the spectra in Table 2. Peaks for the M^+ ion were detected in all cases, their intensities ranging from $< 1\%$ (IV, X, XVI, XVII) to 87% (VI). The fragmentation patterns for the t-butyl derivatives II and VII reflect the high stability of the $(CH_3)_3C^+$ ion, and are therefore somewhat different from those of related molecules.

Comparison of the fragmentation of the isomers I/XI, V/XII, VI/XIII, VIII/XIV and IX/XV proves the diagnostic value of the mass spectra. While the $R'NCS^+$ ion is the base peak for the type **E** species, that for the **G** type isomers corresponds to the $R'NCNMe_2^+$ ion. Analogously, the $MeNCNEt_2^+$ ion has a high intensity in the spectra of X and XVII. The patterns of XVI and XVII are analogous.

Discussion

While organic isocyanates react with aminoboranes to form ureido derivatives of type **B**, they all undergo [2 + 2] cycloaddition reactions with bis(trifluoromethyl)boron derivatives to yield four-membered rings **E**. The strong electron-withdrawing effect of the two CF_3 groups at boron stabilizes four-coordinate over three-coordinate boron, which is present in an acyclic species **B**, and thus favours the ring systems **E** or **G** that contain tetracoordinate boron. In the **E** → **G** rearrangement a strong C=X double bond and a weak B–N single bond are replaced by a B–X single bond and a $C-NR_2$ bond with partial double bond character. However, multiple bonding in the latter linkage requires the NR_2 group to lie in the plane of the four-membered ring. Such coplanarity is apparently precluded for R' = t-butyl, while for R' = phenyl isomerization was observed for X = S (VIII → XIV) but not for III. The thio derivatives V–IX generally rearrange more readily than their oxo homologues. This difference is consistent with the greater strength of the C=O than of the C=S π-bond, the π bonding being lost upon rearrangement. Since C=N bonds are generally weaker than C=O bonds, the reaction of RNCO with **D1** to give **E** and not **F** appears to be thermodynamically controlled. The observed mode of addition of MeNCO to X and XI also appears to be the thermodynamically favoured pathway, the C=O linkage of the MeNCO moiety being retained.

Crystallographic studies of II, VII, XIV and XVII

Crystals of $(CF_3)_2\overline{BN(^tBu)C(O)N}Me_2$ (II), $(CF_3)_2\overline{BN(^tBu)C(S)N}Me_2$ (VII) and $(CF_3)_2\underline{BSC(NMe_2)N}Ph$ (XIV) were grown by sublimation, and those of $(CF_3)_2\overline{BN(Me)C(NEt_2)OC(O)N}Me$ (XVII) were obtained by crystallization from ether. They were mounted in glass capillaries under argon. A Siemens AED 1 diffractometer employing Zr-filtered Mo-K_α radiation (λ = 0.71073 Å) was used to determine the lattice constants (Table 3) and intensity data. Intensities were measured by the θ–2θ technique and were corrected for absorption and the change in the intensities of the standard reflections examined every 3 h. The structures were solved by direct methods and refined by full-matrix least-squares techniques. Dispersion-corrected Hartree–Fock scattering factors were used for all atoms except hydrogen (SDS) [18]. Hydrogen coordinates were placed in calculated positions (C–H 0.95 Å) and these atoms were assigned group isotropic temperature factors. Disorder involving the C(5) and C(6) atoms was detected in XVII, and the model for this structure was augmented with the alternative atoms C(5A) and C(6A) and appropriately constrained occupancies. These refined to 0.71(1) and 0.72(1) for C(5) and C(6) respectively, and since the hydrogen atoms were only introduced for the

Table 1

Physical properties and NMR data for I–XVII (δ in ppm, J in Hz) [a]

	I	II	III	IV	V	VI	VII	VIII	IX	X	XI	XII	XIII	XIV	XV	XVI	XVII
M.p. (°C)	52	97	71	79	43	22	69	35	72	33	77	83	49	115	122	96	89
^1H																	
$\delta(N(CH_3)_2)$	2.88	2.86	3.04	3.03	2.91	2.92	2.88	3.04	3.05		3.09	3.21	3.19	2.17 3.13	2.73 3.14	3.12	
$\delta(NCH_3)$	2.81				3.05					3.00	3.00	3.10				2.97 3.14	2.98 3.12
$\delta(CH_2CH_3)$						1.27				1.28			1.24				1.29
$\delta(CH_2CH_3)$						3.49				3.44			3.42				3.45
$\delta(CCH_3)$		1.35					1.48										
$\delta(H_{phenyl})$			7.22 7.55					7.42 7.96	7.12 7.93					7.33 7.37	7.07 7.18		
^{19}F																	
$\delta(BCF_3)$	−65.9	−64.4	−63.7	−66.5	−65.6	−65.4	−63.9	−64.4	−65.8	−73.0	−73.1	−68.0	−68.2	−66.9	−68.2	−67.1	−67.4
^2J (BF)	31	30.6					31					26.7				27	33.9
$\delta(CF)$				−58.4					−115.0						−114.8		
^5J (FF)				1.8													

^{11}B																	
$\delta(B)$	−6.2	−5.0	−5.1	−5.7	−1.5	−2.2	−1.9	−1.6	−2.0	−2.1	−3.0	−11.5	−10.3	−8.1	−8.5	−8.4	−8.4
^{13}C																	
$\delta(N(CH_3)_2)$	42.6	42.6	43.2	43.3	44.9	45.0	45.2	45.6	45.7		35.7	39.8	39.9	39.8 40.9	39.6 40.9	39.9	
$\delta(NCH_3)$	26.4				30.0					29.3	29.3	34.1				32.4 36.9	32.5 37.0
$\delta(NCF_3)$				116.4													
$\delta(CH_2CH_3)$						11.7				13.8			14.4				13.0
$\delta(CH_2CH_3)$						39.5				41.6			42.0				44.6
$\delta(CCH_3)$		27.7					26.3										
$\delta(CCH_3)$		52.7					55.8										
$\delta(C_{phenyl})$			119.6 125.8 129.3 135.6					120.5 127.5 129.1 136.6	116.0 122.4 132.8 160.9					125.9 127.9 129.3 139.1	116.2 127.7 135.6 161.6		
$\delta(C_{ring})$	154.1	152.6	150.6	149.5	189.2	188.7	186.6	182.6	182.6	162.9	163.0	171.9	172.2	171.2	171.4	147.9 161.0	148.1 161.0

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[a] In $CDCl_3$. ^1H: 250.13 MHz, internal standard $CHCl_3 = 7.27$ ppm. ^{19}F: 84.67 MHz, internal standard $CFCl_3$. ^{13}C: 62.90 MHz, internal standard $CDCl_3 = 77.0$ ppm. ^{11}B: 25.52 MHz, external standard $F_3B \cdot OEt_2$.

Table 2

Selected peaks (^{11}B only) and their relative intensities in the mass spectra of I–XVII

m/e	II	III	IV	VII	I	XI	V	XII	VI	XIII	VIII	XIV	IX	XV	X	XVI	XVII
$[M]^+$		18		17	1	1	70	2	87	6	39	25	23	18			
$[M-CF_3]^+$			8	3	20	22	30	30	43	50	3	8	1	4	12	20	12
$[M-C_2F_5]^+$		5	27		40	100	80	48	100	83	21	25	12	22	6	21	9
$[M-CH_3]^+$	23			1													
$[M-CH_3-C_2F_4]^+$	38			3													
$[M-C_2F_4]^+$		10															
$[M-CH_3NCO-C_2F_5]^+$																100	100
183 $[M-CF_3-(CH_3)_2CCH_2]^+$				13													
165 $[(CH_3)_2NCNC_6H_4F]^+$													39	100			
153 $[FC_6H_4NCS]^+$													100	13			
150 $[FC_6H_4NCNCH_3]^+$													9	33			
147 $[(CH_3)_2NCNC_6H_5]^+$		9									57	100					
135 $[C_6H_5NCS]^+$											100	10					
124 $[F_2BSCH_2NCH_3]^+$							22		42	1	12						
122 $[F_2BOCNH_2NCH_3]^+$															47		
119 $[C_6H_5NCO]^+$		100															
119 $[NCBF_2N(CH_3)_2]^+$				10						10	36	30	24	27			
113 $[CH_3NCN(C_2H_5)_2]^+$															8		40
106 $[(CH_3)_2NBFS]^+$							39				7						
100 $[(C_2H_5)_2NCO]^+$																	35
99 $[(CH_3)_2NCNC_2H_5]^+$									92	100							
95 $[FC_6H_4]^+$													18	10			
94 $[BF_3CN]^+$			52														
92 $[F_2BNCH_2CH_3]^+$	14		30		100	18	80	5	82	6						35	
88 $[(CH_3)_2NCS]^+$				21			40	12	62	40	13	28	12	21			
87 $[C_2H_5NCS]^+$									72	7							
85 $[(CH_3)_2NCNCH_3]^+$						70	80	100							21	40	
84 $[(CH_3)_2CNCO]^+$	32																
77 $[C_6H_5]^+$											27	18					
73 $[CH_3NCS]^+$							100	5									
72 $[(CH_3)_2NCO]^+$	61	56	100		97	60										40	
57 $[(CH_3)_3C]^+$	100			100													
57 $[CH_3NCO]^+$					24	4									100	30	30

Table 3

Crystallographic data for II, VII, XIV and XVII

	II	VII	XIV	XVII
Formula	$C_9H_{15}BF_6N_2O$	$C_9H_{15}BF_6N_2S$	$C_{11}H_{11}BF_6N_2S$	$C_{10}H_{16}BF_6N_3O_2$
Mr	292.03	308.10	328.09	335.06
Space group	*Pnma*	*Pnma*	*C2/c*	$P2_1/c$
a(Å)	11.191(2)	8.536(2)	25.566(6)	10.160(3)
b(Å)	10.694(3)	11.209(2)	8.336(2)	8.002(3)
c(Å)	11.384(2)	15.011(3)	16.673(4)	19.712(7)
β(°)	90	90	123.28(1)	111.23(2)
V(Å^3)	1362.3(5)	1436.1(5)	2971(1)	1493.8(9)
Z	4	4	8	4
D_c(g cm^{-3})	1.424	1.425	1.467	1.490
t(°C)	25	24	25	24
2θ limits(°)	4–50	5–50	5–50	4–55
Reflections				
measured	6904	1557	5809	7400
unique	1270	1331	2609	3448
with $F \geqslant 4\sigma(F)$	977	641	1400	1967
μ(Mo-K_α)cm^{-1}	1.4	2.7	2.6	1.4
Transmission	0.9825–0.9667	0.9093–0.8873	0.9628–0.9382	0.9706–0.9152
$R(F_o)$	0.108	0.072	0.089	0.100
$R_w(F_o)$	0.106	0.093	0.090	0.122
Parameters	110	110	199	221
$\Delta\rho$(e/Å^3) [a]	0.39/−0.40	0.23/−0.26	0.35/−0.36	0.42/−0.26

[a] Densities in final difference Fourier syntheses.

primary conformation their occupancies were constrained accordingly. Except for C(5A) and C(6A), nonhydrogen atoms were refined anisotropically, the coordinates obtained at convergence being given in Tables 4–7. The numbering schemes are

Table 4

Positional and equivalent isotropic temperature factors [a] for II

Atom	x	y	z	U
C(1)	0.4179(6)	0.2500	0.3968(6)	0.050(2)
C(2)	0.1589(5)	0.1255(7)	0.4772(4)	0.065(2)
C(3)	0.2955(5)	0.1382(5)	0.2476(5)	0.068(2)
C(4)	0.4286(6)	0.2500	0.6153(6)	0.051(2)
C(5)	0.3358(9)	0.2500	0.7126(6)	0.121(5)
C(6)	0.4990(8)	0.1334(8)	0.6261(6)	0.126(4)
B	0.2375(6)	0.2500	0.4530(6)	0.043(3)
F(1)	0.0727(3)	0.1067(4)	0.3976(3)	0.100(1)
F(2)	0.2230(4)	0.0189(3)	0.4767(3)	0.105(2)
F(3)	0.1054(4)	0.1248(4)	0.5809(3)	0.126(2)
N(1)	0.3659(4)	0.2500	0.5003(4)	0.040(2)
N(2)	0.3031(4)	0.2500	0.3247(4)	0.040(2)
O	0.5161(4)	0.2500	0.3577(4)	0.088(3)

[a] $\frac{1}{3}\sum_i\sum_j U_{ij}a_i^*a_j^*(\mathbf{a}_i\cdot\mathbf{a}_j)$.

Table 5

Positional and equivalent isotropic temperature factors [a] for VII

Atom	*x*	*y*	*z*	*U*
C(1)	0.072(1)	0.2500	0.5239(6)	0.066(3)
C(2)	0.342(1)	0.131(1)	0.3921(6)	0.119(4)
C(3)	−0.013(1)	0.141(1)	0.3907(6)	0.156(5)
C(4)	0.320(1)	0.2500	0.6167(5)	0.072(4)
C(5)	0.488(1)	0.2500	0.5925(7)	0.108(5)
C(6)	0.2754(9)	0.1377(7)	0.6692(5)	0.098(3)
B	0.258(1)	0.2500	0.4321(7)	0.075(4)
F(1)	0.3037(8)	0.1146(5)	0.3059(3)	0.180(3)
F(2)	0.3046(9)	0.0336(5)	0.4332(4)	0.169(3)
F(3)	0.4992(9)	0.1367(8)	0.3935(5)	0.205(4)
N(1)	0.2265(7)	0.2500	0.5318(4)	0.053(2)
N(2)	0.070(1)	0.2500	0.4235(5)	0.080(3)
S	−0.0789(3)	0.2500	0.5874(2)	0.127(2)

[a] See footnote *a* of Table 4.

Table 6

Positional and equivalent isotropic temperature factors [a] for XIV

Atom	*x*	*y*	*z*	*U*
C(1)	0.3748(3)	0.5670(9)	0.3776(5)	0.054(4)
C(2)	0.4311(4)	0.268(1)	0.3186(7)	0.078(5)
C(3)	0.3064(4)	0.285(1)	0.2049(6)	0.081(5)
C(4)	0.3699(4)	0.3112(8)	0.4537(5)	0.057(4)
C(5)	0.3158(5)	0.242(1)	0.4355(7)	0.084(6)
C(6)	0.3196(7)	0.147(1)	0.507(1)	0.13(1)
C(7)	0.374(1)	0.127(2)	0.591(1)	0.16(2)
C(8)	0.4266(8)	0.194(2)	0.6057(9)	0.15(1)
C(9)	0.4253(4)	0.289(1)	0.5370(5)	0.094(5)
C(10)	0.3660(4)	0.663(1)	0.5080(6)	0.082(6)
C(11)	0.3923(4)	0.8498(9)	0.4168(7)	0.091(6)
B	0.3692(4)	0.361(1)	0.2912(6)	0.060(5)
F(1)	0.4333(3)	0.1154(7)	0.3455(5)	0.130(5)
F(2)	0.4406(2)	0.2599(7)	0.2479(4)	0.132(4)
F(3)	0.4837(2)	0.3301(7)	0.3933(4)	0.121(3)
F(4)	0.3019(3)	0.2839(9)	0.1227(3)	0.143(4)
F(5)	0.2980(3)	0.1326(8)	0.2207(4)	0.132(4)
F(6)	0.2550(2)	0.3596(7)	0.1875(4)	0.128(3)
N(1)	0.3671(2)	0.4102(7)	0.3795(3)	0.053(3)
N(2)	0.3775(2)	0.6835(7)	0.4322(4)	0.063(4)
S	0.3774(1)	0.5911(3)	0.2758(1)	0.078(1)

[a] See footnote *a* of Table 4.

defined in Figs. 1–4. The program SHELX-76 [9] was used for structure solution and refinement. No extinction correction was necessary [10*]. Important bond distances and angles are listed in Table 8 for II and VII, Table 9 for XIV, and Table 10 for XVII.

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* A reference number with an asterisk indicates a note in the list of references.

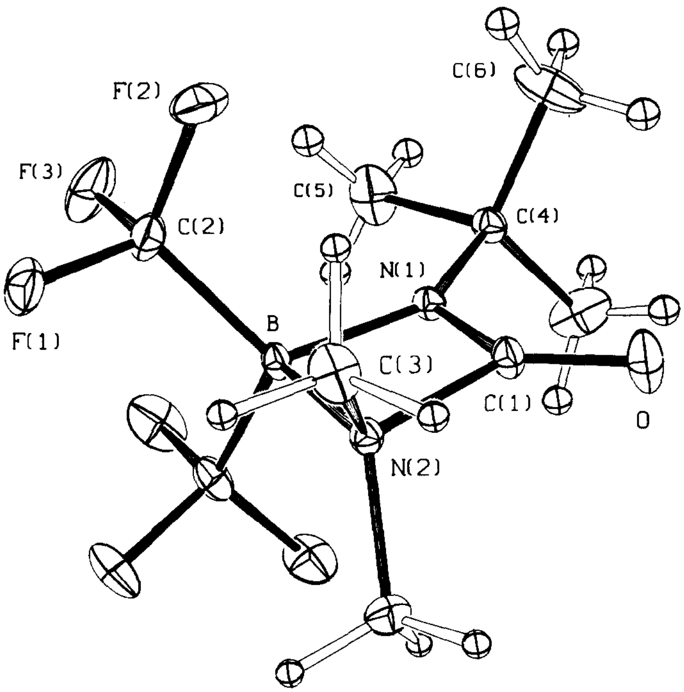

Fig. 1. A perspective drawing of II with 10% probability thermal ellipsoids and arbitrary radii for the hydrogens.

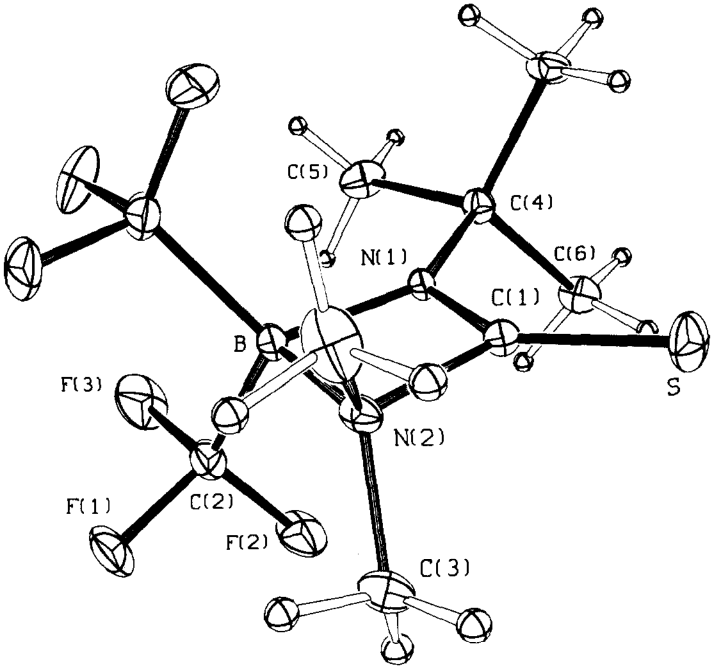

Fig. 2. A perspective drawing of VII with 5% probability thermal ellipsoids and arbitrary radii for the hydrogens.

Table 7

Positional and equivalent isotropic temperature factors [a] for XVII

Atom	*x*	*y*	*z*	*U*
B	0.2547(5)	0.6437(6)	0.5889(2)	0.063(2)
N(1)	0.2272(5)	0.7246(4)	0.5139(2)	0.082(2)
N(2)	0.2824(4)	0.4569(4)	0.5828(2)	0.069(2)
N(3)	0.2811(4)	0.7348(4)	0.4097(2)	0.073(2)
O(1)	0.3224(3)	0.5037(4)	0.4769(2)	0.078(1)
O(2)	0.3395(5)	0.2489(4)	0.5206(2)	0.112(2)
C(1)	0.3874(6)	0.7311(7)	0.6487(3)	0.088(2)
C(2)	0.1160(6)	0.6680(8)	0.6123(3)	0.098(3)
C(3)	0.2759(4)	0.6601(5)	0.4685(2)	0.055(2)
C(4)	0.3143(5)	0.3920(6)	0.5295(2)	0.074(2)
C(5)	0.1145(8)	0.8598(8)	0.4859(4)	0.076(3)
C(5A)	0.311(2)	0.920(3)	0.532(1)	0.101(7)
C(6)	0.3233(7)	0.9198(7)	0.4144(3)	0.068(3)
C(6A)	0.156(2)	0.859(2)	0.367(1)	0.086(7)
C(7)	0.2247(7)	1.0162(7)	0.3519(3)	0.098(3)
C(8)	0.3121(7)	0.6350(7)	0.3544(3)	0.090(3)
C(9)	0.1916(7)	0.5341(8)	0.3079(3)	0.106(3)
C(10)	0.2817(9)	0.3350(7)	0.6384(3)	0.118(3)
F(1)	0.3717(4)	0.8924(5)	0.6614(3)	0.167(3)
F(2)	0.5014(4)	0.7290(5)	0.6291(3)	0.147(2)
F(3)	0.4310(5)	0.6611(7)	0.7135(2)	0.169(2)
F(4)	0.0020(4)	0.5937(6)	0.5679(2)	0.155(2)
F(5)	0.0839(4)	0.8320(6)	0.6167(2)	0.153(2)
F(6)	0.1347(5)	0.6134(7)	0.6781(2)	0.160(3)

[a] See footnote *a* of Table 4.

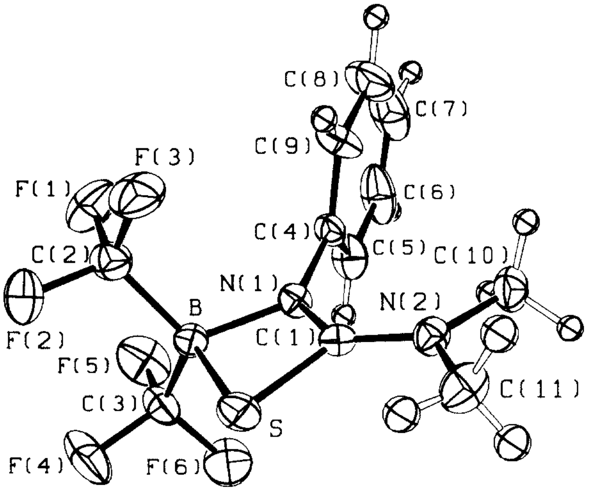

Fig. 3. A perspective drawing of XIV with 13% probability thermal ellipsoids and arbitrary radii for the hydrogens.

Table 8

Selected bond distances (Å) and angles (°) in II and VII

	II	VII
B–N(1)	1.535(8)	1.52(1)
B–N(2)	1.635(8)	1.61(1)
B–C(2)	1.619(7)	1.63(1)
C(1)–N(1)	1.314(8)	1.328(9)
C(1)–N(2)	1.525(8)	1.51(1)
C(1)–X [a]	1.186(8)	1.600(9)
N(1)–C(4)	1.485(7)	1.50(1)
N(2)–C(3)	1.485(5)	1.50(1)
N(1)–B–N(2)	83.8(4)	84.5(6)
N(1)–B–C(2)	116.7(3)	116.1(6)
N(2)–B–C(2)	113.3(3)	114.1(6)
C(2)–B–C(2′) [b]	110.6(5)	110.0(8)
B–N(1)–C(1)	95.8(4)	95.0(7)
B–N(1)–C(4)	138.8(5)	137.9(7)
C(1)–N(1)–C(4)	125.5(5)	127.1(7)
N(1)–C(1)–N(2)	96.3(5)	95.7(7)
N(1)–C(1)–X	138.3(6)	138.3(7)
N(2)–C(1)–X	125.4(6)	126.0(7)
B–N(2)–C(1)	84.1(4)	84.8(6)
B–N(2)–C(3)	120.2(3)	119.7(6)
C(1)–N(2)–C(3)	111.5(3)	109.5(6)
C(3)–N(2)–C(3′)	107.2(5)	110(1)

[a] X is O in II and S in VII. [b] $x, y', z' = x, 0.5 - y, z$.

Description and discussion of the crystal structures

The molecular structures of II and VII (Figs. 1 and 2) are very similar. Each $\overline{\text{BN(1)C(1)N(2)}}$ ring lies on a crystallographic mirror plane, and each ^{t}Bu group is so oriented that its in-plane C(4)–C(5) bond eclipses the B–N(1) bond. The resulting Pitzer strain as well as F(3) · · · Me repulsions are relieved by tilting of the N(1)–C(4)

Table 9

Selected bond distances (Å) and angles (°) in XIV

B–N(1)	1.557(9)	N(1)–C(1)	1.325(8)
B–S	1.963(8)	N(1)–C(4)	1.456(8)
B–C(2)	1.59(1)	C(1)–N(2)	1.306(8)
B–C(3)	1.59(1)	N(2)–C(10)	1.457(9)
S–C(1)	1.747(7)	N(2)–C(11)	1.494(9)
N(1)–B–S	85.8(4)	B–N(1)–C(4)	130.0(6)
N(1)–B–C(2)	113.7(6)	C(1)–N(1)–C(4)	129.8(6)
N(1)–B–C(3)	115.0(6)	N(1)–C(1)–S	102.8(5)
S–B–C(2)	110.7(6)	N(1)–C(1)–N(2)	132.0(6)
S–B–C(3)	113.7(6)	S–C(1)–N(2)	125.1(6)
C(2)–B–C(3)	114.6(7)	C(1)–N(2)–C(10)	124.1(6)
B–S–C(1)	72.3(4)	C(1)–N(2)–C(11)	119.5(7)
B–N(1)–C(1)	99.0(5)	C(10)–N(2)–C(11)	116.4(6)

Table 10

Selected bond distances (Å) and angles (°) in XVII

B-N(1)	1.544(6)	N(2)-C(10)	1.470(6)
B-N(2)	1.534(6)	N(3)-C(3)	1.322(5)
B-C(1)	1.595(7)	N(3)-C(6)	1.534(7)
B-C(2)	1.645(8)	N(3)-C(8)	1.474(6)
N(1)-C(3)	1.278(5)	O(1)-C(3)	1.327(5)
N(1)-C(5)	1.526(7)	O(1)-C(4)	1.394(5)
N(2)-C(4)	1.312(5)	O(2)-C(4)	1.201(5)
N(1)-B-N(2)	107.9(3)	C(4)-N(2)-C(10)	113.8(4)
N(1)-B-C(1)	109.6(4)	C(3)-N(3)-C(6)	118.8(4)
N(1)-B-C(2)	110.0(4)	C(3)-N(3)-C(8)	119.4(4)
N(2)-B-C(1)	110.8(4)	C(6)-N(3)-C(8)	115.9(4)
N(2)-B-C(2)	109.7(4)	C(3)-O(1)-C(4)	125.7(3)
C(1)-B-C(2)	108.8(4)	N(1)-C(3)-O(1)	120.2(4)
B-N(1)-C(3)	121.4(4)	N(1)-C(3)-N(3)	125.5(4)
B-N(1)-C(5)	119.7(4)	O(1)-C(3)-N(3)	114.3(4)
C(3)-N(1)-C(5)	117.5(4)	N(2)-C(4)-O(1)	116.1(4)
B-N(2)-C(4)	123.7(4)	N(2)-C(4)-O(2)	128.5(5)
B-N(2)-C(10)	122.5(4)	O(1)-C(4)-O(2)	115.4(4)

bonds away from the $B(CF_3)_2$ moieties towards the C(1)-O or C(1)-S bonds, so that the B-N(1)-C(4) angles are about 12° larger than the C(1)-N(1)-C(4) angles.

The B-N(1) bonds, which involve trigonal nitrogen atoms, are on the average 0.09(1) Å shorter than the B-N(2) bonds of the quaternary nitrogen atoms. The latter distances are essentially equal to the average B-N distances (1.63(1) Å) in the three [2 + 4] cycloaddition adducts $(CF_3)_2\overline{BNR_2CH_2CR'CMeX}$ (R = Me, Et; R' = H, Me; X = CH_2, O) [7]. This is surprising, since the conformation of the B-N bonds in these adducts [7] is staggered whereas those of B-N(2) in II and VII are

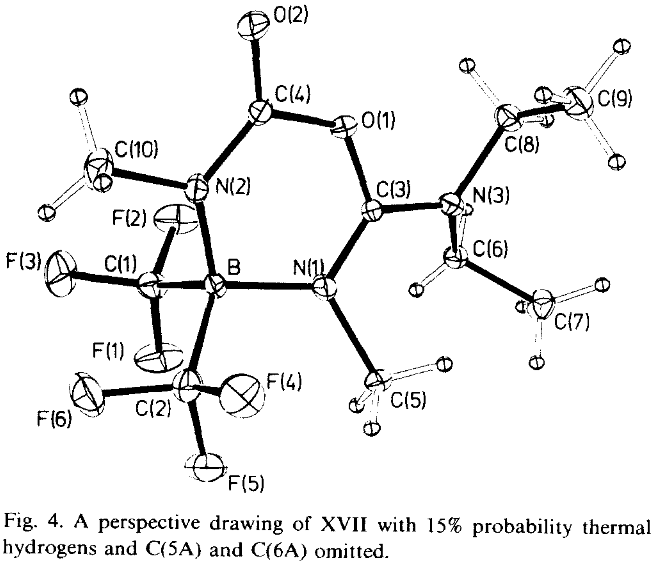

Fig. 4. A perspective drawing of XVII with 15% probability thermal ellipsoids, arbitrary radii for the hydrogens and C(5A) and C(6A) omitted.

eclipsed. Repulsions along the B–N(2) bonds are relieved by pivoting of the NMe_2 groups away from the boron atom, the B–N(2)–C(3) angles being on the average 10(2)° larger than the C(1)–N(2)–C(3) angles. While the $B(CF_3)_2$ entities do not bend away from the N(2) atom, CF_3 groups are rotated about the B–C(2) bonds by 12(2)°, the rotation opening the F(2)–C(2)–B–N(2) torsion angle and thus lengthening the F(2) ··· H(C(3)) contacts.

Both the C(1)–O distance in II and the C(1)–S distance in VII are consistent with high proportion of double bond character. In addition, the C(1)–N(1) bond lengths, which average 1.321(9) Å, are indicative of about 40% [11] double bond character in these linkages. On the other hand, the C(1)–N(2) distances have single bond values, and the C(1)–O(S) bonds are tilted away from N(1) towards N(2).

The $\overline{\mathrm{BN(1)C(1)S}}$ ring (Fig. 3) is planar to within 0.02 Å, and forms an interplanar angle of 8(1)° with the planar C(1), N(2), C(10), C(11) fragment. The C(1)–N(1) and C(1)–N(2) bond distances are indicative of about 40% double bond character.

The B–N(1) bond in XIV is probably longer (0.03(1) Å) than the average (1.53(1) Å) of the B–N(1) distances in II and VII. The B–S bond distance in XIV (1.963(8) Å) appears somewhat long compared with the values of 1.86(1)–1.93(1) Å reported for other B(cn4)–S(cn2) bonds [12] or with the sum of the Pauling tetrahedral covalent radii, 1.92 Å [11]. These two marginally weaker bonds in XIV appear to be compensated by B–C bonds that are probably shorter (0.04(2) Å) than those of II and VII. The short B–C bonds in XIV are consistent with the fact that its C–B–C angles (114.6(7)°) are the largest for the three structures.

The six-membered ring of XVII (Fig. 4) is slightly puckered (rms deviation 0.093 Å). A Cremer–Pople analysis of the ring puckering [13] indicates that the ring conformation lies between the half-chair and the twist-boat form.

Disorder of the C(5) and C(6) atoms necessarily obscures some structural features of the compound. The displacement of the atoms C(5) (−0.878(8) Å), C(5A) (1.05(2) Å), C(6) (0.828(7) Å) and C(6A) (−0.86(2) Å) from the ring plane shows that disorder here involves an inversion of positions of out of plane atoms. The atoms C(8) and C(10) are not susceptible to such disorder since they lie within 0.17 Å of the ring plane. Since N(1) lies 0.133(5) Å to the C(5) side of the ring and since N(1)–C(5A) (1.75(2) Å) is unrealistically long, the nitrogen atom bonded to C(5A) probably lies on the C(5A) side of the ring. Similarly, the disorder of C(6) may also affect the N(3) position. In view of these disorder problems only a discussion of the gross structural features of XVII is appropriate.

While the π-characters of the three bonds formed by C(3) are roughly equal, the delocalization exhibited by C(4) is less symmetric, being highest for C(4)–O(2), moderate for C(4)–N(2), and negligible for C(4)–O(1). The ease of elimination of MeNCO from XVII is consistent with the C(4)–O(1) being 0.067(7) Å longer than C(3)–O(1) bond. The B–N bond lengths in XVII, average 1.539(7) Å, agree well with the values for the B–N(1) bonds in II, VII and XIV. The CF_3 groups are mutually staggered, and the B–C bond distances are normal. The other structural parameters of the three compounds investigated appear normal.

Experimental

IR spectra were recorded with KBr pellets, Raman spectra were recorded for crystalline solids, excitation Kr 647.1 nm. Mass spectra were obtained by EI at 70 eV.

1,1-Bis(trifluoromethyl)-2,2,4-trimethyl-borata-2-azonia-4-azacyclobutan-3-one (I). Methylisocyanate (40 mmol) was added dropwise to a stirred ice-cold solution of 5.3 g (20 mmol) of $(CF_3)_2BNMe_2$ (**D1**) in 10 ml of dry pentane. After 10 min the mixture was warmed to room temperature, the solvent and the excess of methylisocyanate were removed *in vacuo*, and the solid residue was sublimed (bath temperature ~ 20 °C, 1×10^{-2} torr). Yield 96%. Elemental analyses are set out in Table 11, mass spectral data are shown in Table 2. IR/Raman (cm^{-1}): 1836 vs/w, ν(C=O); 1103 vsb/vw, $\nu(CF_3)$; 713 m/s, 684 m/-, δ_s (CF_3).

Compounds II–IX. These were obtained analogously, and had properties as follows.

1,1-Bis(trifluoromethyl)-2,2-dimethyl-4-t-butyl-borata-2-azonia-4-azacyclobutan-3-one (II). IR/Raman (cm^{-1}): 1818 vs/w, ν(C=O); 1110 vsb/-, $\nu(CF_3)$; 712 m/vs, 682 m/-, δ_s (CF_3).

1,1-Bis(trifluoromethyl)-2,2-dimethyl-4-phenyl-borata-2-azonia-4-azacyclobutan-3-one (III). IR/Raman (cm^{-1}): 1825 vs/w, ν(C=O); 1100 vsb/-, $\nu(CF_3)$; 1002 -/vs, ν(C-C, C_6H_5); 715 m/s, 682 m/m, δ_s (CF_3).

1,1-Bis(trifluoromethyl)-2,2-dimethyl-4-trifluoromethyl-borata-2-azonia-4-azacyclobutan-3-one (IV). IR/Raman (cm^{-1}): 1865 vs/w, ν(C=O); 1255 vs/-, 1107 vsb/-, $\nu(CF_3)$; 720 w/s, 709 m/s, 683 m/-, δ_s (CF_3).

Table 11

Elemental analyses

Compound	Formula	Analyses (Found (calc.) (%))		
		C	H	F
I	$C_6H_9BF_6N_2O$	28.9	3.69	45.2
		(28.84)	(3.63)	(45.62)
II	$C_9H_{15}BF_6N_2O$	37.0	4.9	39.3
		(37.02)	(5.18)	(39.04)
III	$C_{11}H_{11}BF_6N_2O$	42.8	3.7	36.2
		(42.34)	(3.55)	(36.53)
IV	$C_6H_6BF_9N_2O$	24.6	2.0	53.0
		(23.71)	(1.99)	(56.26)
V	$C_6H_9BF_6N_2S$	27.3	3.4	42.7
		(27.09)	(3.41)	(42.85)
VI	$C_7H_{11}BF_6N_2S$	27.7	3.8	41.6
		(30.02)	(3.96)	(40.71)
VII	$C_9H_{15}BF_6N_2S$	35.29	4.96	36.6
		(35.09)	(4.91)	(37.00)
VIII	$C_{11}H_{11}BF_6N_2S$	41.1	3.7	34.7
		(40.27)	(3.38)	(34.74)
IX	$C_{11}H_{10}BF_7N_2S$	38.5	3.0	38.4
		(38.63)	(2.91)	(38.43)
X	$C_8H_{13}BF_6N_2O$	34.8	4.8	40.4
		(34.56)	(4.71)	(41.00)
XVI	$C_8H_{12}BF_6N_3O_2$	31.4	4.2	36.8
		(31.31)	(3.94)	(37.15)
XVII	$C_{10}H_{16}BF_6N_3O_2$	36.4	5.0	33.5
		(35.85)	(4.81)	(33.02)

1,1-Bis(trifluoromethyl)-2,2,4-trimethyl-borata-2-azonia-4-azacyclobutan-3-thione (V). IR/Raman (cm^{-1}); 1552 bd/-, ν("ring"); 1093 vsb/-, $\nu(CF_3)$; 718 m/s, 676 -/s, δ_s (CF_3); 622 m/vs, ν("ring").

1,1-Bis(trifluoromethyl)-2,2-dimethyl-4-ethyl-borata-2-azonia-4-azacyclobutan-3-thione (VI). IR/Raman (cm^{-1}): 1535 vs/-, ν("ring"); 1103 vsb/-, $\nu(CF_3)$; 717 m/s, 690 w/m, δ_s (CF_3); 654 m/m, ν("ring").

1,1-Bis(trifluoromethyl)-2,2-dimethyl-4-t-butyl-borata-2-azonia-4-azacyclobutan-3-thione (VII). IR/Raman (cm^{-1}): 1510 vs/w, ν("ring"); 1090 vsb/-, $\nu(CF_3)$; 703 m/vs, 660 m/-, δ_s (CF_3); 625 -/s, ν("ring").

1,1-Bis(trifluoromethyl)-2,2-dimethyl-4-phenyl-borata-2-azonia-4-azacyclobutan-3-thione (VIII). IR/Raman (cm^{-1}): 1510 vs/w, ν("ring"); 1105 vsb/-, $\nu(CF_3)$; 1005 -/vs, $\nu(C{-}C,\ C_6H_5)$; 709 m/m, 680 m/-, δ_s (CF_3); 622 w/m, ν("ring").

*1,1-Bis(trifluoromethyl)-2,2-dimethyl-4-*p*-fluorophenyl-borata-2-azonia-4-azacyclobutan-3-thione (IX).* IR/Raman (cm^{-1}): 1520 vs/s, ν("ring"); 1093 vsb/-, $\nu(CF_3)$; 1244 vs/s, $\nu(C{-}C,\ p\text{-}FC_6H_4)$; 709 s/s, δ_s (CF_3); 628 w/m, ν("ring").

2,2-Bis(trifluoromethyl)-4-dimethyliminium-3-methyloxa-3-aza-2-boratacyclobutane (XI). Compound XI was obtained in quantitative yield by heating a solution of I in $CHCl_3$ in a sealed tube to 60 °C for 6 h. IR/Raman (cm^{-1}): 1650 vs/-, $\nu(C{=}N)$; 1095 vs/-, 1055 s/-, $\nu(CF_3)$; 728 m/s, 688 m/-, δ_s (CF_3). Compounds XII–XV were obtained analogously from V, VI, VIII and IX, respectively.

2,2-Bis(trifluoromethyl)-4-dimethyliminium-3-methylthia-3-aza-2-boratacyclobutane (XII). IR/Raman (cm^{-1}): 1645 vs/-, $\nu(C{=}N)$; 1110 vs/-, 1085 vs/w, $\nu(CF_3)$; 720 m/m, 695 w/vs, 677 s/0, δ_s $(CF_3) + \nu(CS)$.

2,2-Bis(trifluoromethyl)-4-dimethyliminium-3-ethylthia-3-aza-2-boratacyclobutane (XIII). IR/Raman (cm^{-1}): 1630 vs/-, $\nu(C{=}N)$; 1115 vs/-, 1081 vs/w, $\nu(CF_3)$; 718 m/m, 694 w/vs, 680 s/-, δ_s $(CF_3) + \nu(CS)$.

2,2-Bis(trifluoromethyl)-4-dimethyliminium-3-phenylthia-3-aza-2-boratacyclobutane (XIV). IR/Raman (cm^{-1}): 1640 vs/- $\nu(C{=}N)$; 1090 vsb/-, $\nu(CF_3)$; 1005 -/vs, $\nu(C{-}C,\ C_6H_5)$; 708 m/m, 680 m/-, δ_s (CF_3).

*2,2-Bis(trifluoromethyl)-4-dimethyliminium-3-*p*-fluorophenylthia-3-aza-2-boratacyclobutane (XV).* IR/Raman (cm^{-1}): 1638 vs/-, $\nu(C{=}N)$; 1080 vsb/-, $\nu(CF_3)$; 1244 s/s, $\nu(C{-}C,\ p\text{-}FC_6H_4)$; 710 m/m, 681 m/-, δ_s (CF_3).

2,2-Bis(trifluoromethyl)-4-dimethyliminium-3-methyloxa-3-aza-2-boratacyclobutane (X) and 4,4-Bis(trifluoromethyl)-2-diethylamino-3,5-dimethyloxa-5-aza-3-azonia-4-boratacyclohex-2-en-6-one (XVII). Compounds X and XVII were obtained analogously by the reaction at room temperature of $(CF_3)_2BNEt_2$ (**D2**) and MeNCO in a 1 : 1 and 1 : > 2 molar ratio, respectively. X was purified by distillation *in vacuo*, b.p. 86 °C/10^{-2} torr, whereas XVII was recrystallized from Et_2O/hexane.

X: IR/Raman (cm^{-1}): 1679 vs/-, $\nu(C{=}N)$; 1100 vsb/vw, 1035 s/vw, $\nu(CF_3)$; 723 m/vs, 673 m/-, δ_s (CF_3).

XVII: IR/Raman (cm^{-1}): 1767 vs/m, $\nu(C{=}O)$; 1636 vs/-, $\nu(C{=}N)$; 1102 vs/-, 1065 m/-, $\nu(CF_3)$; 710 m/s, 702 w/vs, δ_s (CF_3).

4,4-Bis(trifluoromethyl)-2-dimethylamino-3,5-dimethyloxa-5-aza-3-azonia-4-boratacyclohex-2-en-6-one (XVI). Compound XVI was obtained by stirring XI with an excess of MeNCO at room temperature for 3 d, and purified by sublimation. IR/Raman (cm^{-1}): 1768 vs/m, $\nu(C{=}O)$; 1655 s/-, $\nu(C{=}N)$; 1100 vs/-, 1092 vsb/-, $\nu(CF_3)$; 711 m/s, 701 w/vs, δ_s (CF_3).

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References

1 K. Niedenzu and J.W. Dawson, Boron–Nitrogen Compounds, Springer, Berlin, 1965.
2 W. Maringgele, in I. Haiduc and D.B. Sowerby (Eds.), The Chemistry of Inorganic Homo- and Heterocycles, Vol. I, Academic Press, New York, 1987.
3 H. Beyer, J.W. Dawson, H. Jenne and K. Niedenzu, J. Chem. Soc., (1964) 2115.
4 P. Paetzold and S. Kosma, Chem. Ber., 112 (1979) 654.
5 H. Bürger, M. Grunwald and G. Pawelke, J. Fluorine Chem., 31 (1986) 89.
6 D.J. Brauer, H. Bürger, F. Dörrenbach, G. Pawelke and W. Weuter, J. Organomet. Chem., 378 (1989) 125.
7 A. Ansorge, D.J. Brauer, H. Bürger, F. Dörrenbach, T. Hagen, G. Pawelke and W. Weuter, J. Organomet. Chem., 396 (1990) 253.
8 International Tables for X-ray Crystallography, Vol. IV, The Kynoch Press, Birmingham, 1974, Tab. 2.2B and 2.3.1.
9 G.M. Sheldrick, SHELX-76; Program for crystal structure determination, University of Cambridge, England, 1976.
10 Additional crystallographic data may be obtained from Fachinformationszentrum Karlsruhe, W-7514 Eggenstein-Leopoldshafen 2, by quoting the deposit number CSD 55157, the names of the authors and the literature reference.
11 L. Pauling, The Nature of the Chemical Bond, Cornell, Univ. Press, Ithaca, NY, 1960.
12 H. Nöth and R. Staudigl, Chem. Ber., 115 (1982) 813.
13 D. Cremer and J.A. Pople, J. Am. Chem. Soc., 97 (1975) 1354.