A Diazenidoborate: Formation and Structure of Cs[(CF₃)₃BN=NCF₃]

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Dedicated to Professor Othmar Stelzer on the occasion of his 60th birthday

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 $Cs[(CF_3)_3BNH_2]$ reacts with CF_3NO to form cesium *trans*-trifluoromethyldiazenido-tris(trifluoromethyl)borate $Cs[(CF_3)_3BN=NCF_3]$ (2), the structure of which has been investigated by single-crystal X-ray diffraction. The diazene nature of the anion is confirmed by the length of the N=N bond, 1.231(6) Å, and the size of the N-N-B angle, 115.5(4)° – the B-N bond length being 1.559(7) Å. Compound 2 is hitherto the first diazenidoborate which has been fully characterized.

Introduction

In a preceding paper we have reported on the electrochemical and ozone oxidation of (CF₃)₃B·NH₃ (1) [1]. In alkaline solution, first the nitrogen atom of 1 is deprotonated to form the aminoborate anion $[(CF_3)_3BNH_2]^-$, which behaves like a primary amine. It can be oxidized to yield the nitroborate $[(CF_3)_3BNO_2]^-$, the azodioxy-bis-tris(trifluoromethyl)borate $[(CF_3)_3BN(O)=N(O)B(CF_3)_3]^{2-}$, and the azoxy-bis-tris(trifluoromethyl)borate $[(CF_3)_3 BN=N(O)B(CF_3)_3]^{2-}$. The species most closely related to this series of compounds, the azo-bis-tris-(trifluoromethyl)borate $[(CF_3)_3BN=NB(CF_3)_3]^{2-}$, was not obtained, and we have been speculating about the stability of such an anion. In order to test the accessibility of the related azoborate unit, we have attempted to prepare such a species by a reaction which is well established in organic chemistry for the synthesis of azo derivatives $F_3 CN = NR^1$. Such compounds are generally formed by the condensation reaction of CF₃NO with a primary amine H_2NR^1 , e. g., $CF_3NO + H_2NCH_3 \rightarrow F_3CN=NCH_3$ + H₂O [2]. We wished to test whether we could perform the above reaction with $[(CF_3)_3BNH_2]^-$. Here we report on our observations.

Results and Discussion

Ammine tris(trifluoromethyl)borane (1), which is very soluble in water, is a weak acid which, upon treatment with CsOH, forms the stable salt $Cs[(CF_3)_3BNH_2]$ [1, 3]. A solution of this salt in methanol was reacted with a tenfold excess of CF₃NO at room temperature. According to ¹⁹F NMR measurements made on the reaction mixture, 28 % of the aminoborate was converted to Cs[(CF₃)₃BN=NCF₃] (2) according to eq. (1).

$$Cs[(CF_3)_3BNH_2] + CF_3NO$$

$$\rightarrow Cs[(CF_3)_3BN=NCF_3] + H_2O$$
(1)

Still 16% of the Cs[(CF₃)₃BNH₂] had not reacted, and two further signals at -62.3 and -64.2 ppm with relative intensities of 38 and 16% were present. These arise from hitherto unidentified tris-trifluoromethylboron species. Traces of $C_{s}[(CF_{3})_{3}BF] [3] \text{ and } C_{s}[(CF_{3})_{3}BOH] [1] (ca. 1\%)$ show that the condensation reaction was accompanied by some decomposition. We conclude that the two latter products are formed from intermediates because the azoborate 2 is unexpectedly stable. Our attempts to increase the yield of 2 by varying the pH, the solvent, and the stoichiometry of the reactants failed, more by- and decomposition products rather than 2 being formed. After removal of the methanol solvent, 2 was isolated by repeated crystallization from water as an orange-vellow solid. It is soluble in polar organic solvents like acetone, acetonitrile and ether.

A thermogravimetric study of compound 2 reveals that it decomposes in two distinct steps. First a loss of weight of 18% is observed between 146 °C and 250 °C. Second, further loss of weight of 29% occurs between 300 °C and 400 °C. This degradation can be interpreted by an idealized equation:

K

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$$Cs[(CF_3)_3BN=NCF_3] \xrightarrow{-N_2, -CF_2} Cs[(CF_3)_3BF]$$

$$\xrightarrow{-3CF_2} Cs[BF_4]$$

Compound 2 is stable to hydrolysis. When an aqueous solution of 2 is irradiated with the 254 nm line of a mercury lamp, the BN bond is cleaved, $Cs[(CF_3)_3BOH]$ [1] being the major reaction product.

$$Cs[(CF_3)_3BN=NCF_3] \xrightarrow{h \cdot \nu / H_2O} Cs[(CF_3)_3BOH] + N_2 + HCF_3$$

The UV/Vis spectrum of **2** in water shows a broad absorption at $\lambda_{max} = 440$ nm ($\varepsilon = 10 \text{ cm}^{-1} \text{ mol}^{-1}$) with a width at half height of *ca*. 60 nm. The formal replacement of a methyl group in F₃CN=NCH₃, which has $\lambda_{max} = 353$ nm ($\varepsilon = 3.58 \text{ cm}^{-1} \text{ mol}^{-1}$) [2], by the [B(CF₃)₃]⁻ moiety causes a significant red shift of 87 nm and an increase of ε .

The ¹⁹F, ¹³C, and ¹¹B NMR chemical shifts and coupling constants of **2** (see Experimental) are consistent with the proposed structure. The relatively large ³J(BC) coupling constant of 12.5 Hz should be mentioned.

According to the infrared and Raman spectra of **2** this novel borate contains a $(CF_3)_3B$ group, the typical vibrations of which have been discussed [1]. Of particular interest is the N=N stretching vibration which gives rise to a medium intensity Raman line and an IR band at 1595 cm⁻¹. This is close to the value reported for $F_3CN=NCH_3$ (1592 cm⁻¹) [2]. A further strong Raman line observed at 235 cm⁻¹ is tentatively ascribed to the bending mode δ (B-N=N).

The anion of **2** is isoelectronic with the neutral species $(CF_3)_3CN=NCF_3$, which has been obtained in 2.5% yield by irradiation of CF_3CN

Fig. 1. A perspective drawing of 2 employing 20% probability thermal ellipsoids. The location of the low-occupancy fluorine atoms attached to the C(4) atom are illustrated with unfilled circles.

Table 1. Selected bond lengths [Å] and angles [°] for $Cs[(CF_3)_3BN=NCF_3]$.

B-C(1)	1.602(8)	B-N(1)	1.559(7)
B-C(2)	1.612(8)	C(4)-N(2)	1.472(8)
B-C(3)	1.617(8)	N(1)-N(2)	1.231(6)
N(1)-B-C(1)	116.4(4)	C(1)-B-C(3)	110.3(5)
N(1)-B-C(2)	104.7(4)	C(2)-B-C(3)	108.0(5)
N(1)-B-C(3)	106.0(4)	N(2)-N(1)-B	115.5(4)
C(1)-B- $C(2)$	111.0(5)	N(1)-N(2)-C(4)	110.3(4)

and $(CF_3)_2C=O$ [4]. While numerous azobenzeneborane complexes have been reported [5], reports on borylated diazenes (azoboranes or azoborates) are scarce. $(C_6H_5)_2B-N=N-C(=O)-C_6H_5$ has been obtained by oxidation of the corresponding hydrazino derivative [6], and polymeric (C₆H₅)₂B- $N=N-B(C_6H_5)_2$ was prepared from $(CH_3)_3Si-N=N-$ Si(CH₃)₃ and (C₆H₅)₂BCl [7]. However, these compounds have not been structurally characterized. A formally related species is the dianion $[B_6H_5(NN)B_6H_5]^{2-}$ which, however, reveals an NN stretching vibration at 2065 cm^{-1} and possesses a linear BNNB unit. This anion is therefore deemed a dinitrogen complex [8] rather than an azo derivative. Thus we can conclude that 2 is the first boron-substituted diazene derivative which has been unambiguously characterized.

Description of the Crystal Structure

A drawing of the anion of **2** is displayed in Fig. 1, and selected bond lengths and angles are listed in Table 1. The structure is flawed by the 84:16 disorder of the trifluoromethyl group bonded to the N(2) atom. The minor conformation has its C(4)-F(10A) bond roughly eclipsing the nitrogen-nitrogen dou-



ble bond, and this is the rotamer found by gas phase electron diffraction for the trifluoromethyl groups in *trans*-CF₃N=NCF₃ (**3**) [9]. However, this conformation is destabilized by packing forces in the solid state because the F(11A)…F(7)(-x, 2 - y, 1 - z) and F(12A)…F(3)(0.5 - x, 0.5 + y, 1.5 - z) separations of 2.68(3) and 2.85(3) Å, respectively, are shorter than the sum of the corresponding van der Waals radii of fluorine (2.94 Å) [10].

The N(1)-N(2) and N(2)-C(4) bond lengths of 1.231(6) and 1.472(8) Å, respectively, do not differ significantly from the values 1.235(10) and 1.460(6) Å reported for these bonds in **3**. The N(1)-N(2)-C(4) bond angle (110.3(4)°) in **2** is slightly smaller than the 113.4(16)° value found in the gas phase perhaps because of the above-mentioned difference in the major conformation of the nitrogenbonded trifluoromethyl group in **2** and **3**.

It is interesting to compare the B-N(1) bond length in **2**, 1.559(7) Å, with the bonds of tetracoordinate boron to nitrogen in other multiply-bonded systems. The bond in **2** is slightly but not significantly longer than that determined for the formamidine adduct (CF₃)₃BNHCHNMe₂ (**4**), 1.541(4) Å [11], marginally shorter than the bonds to the azodioxy groups in Cs₂[(CF₃)₃BN(O)N(O)B(CF₃)₃] (**5**), 1.59(2) Å [1], and significantly shorter than the linkage to the nitro group in Cs[(CF₃)₃BNO₂], 1.606(4) Å [1]. The B-N(1)-N(2) bond angle in **2**, 115.5(4)°, is markedly smaller than the B-N-C angle in **4**, 127.3(3)°, and the B-N-O angle in 5, $123(1)^{\circ}$. Perhaps these angular differences reflect not only the structural importance of the nitrogen lone pair in 2 but also the steric demands of the formamidine and azodioxy groups. The structure of the azoborate 2 deviates markedly from that found for the bridging of two pentahydrocloso-hexaborate groups by a dinitrogen unit in [AsPh₄]₂[B₆H₅NNB₆H₅] [8] for which shorter B-N (1.42(1) Å) and N-N (1.129(8) Å) bond lengths and B-N-N bond angles of 180° were reported.

Nonbonded repulsions are probably responsible for the large spread in the N(1)-B-C bond angles in **2**. The largest angle $(116.4(4)^{\circ})$ involves the C(1) atom, the B-C(1) bond of which roughly eclipses the diazene linkage (torsion angle $-13.9(7)^{\circ}$), and the other two N(1)-B-C angles are on the average $11(1)^{\circ}$ smaller.

Contacts have been detected between cesium and fluorine atoms in a variety of cesium salts of trifluoromethylborates, and these interactions generally appear to be weaker than contacts involving cesium and other nucleophilic sites of the anions [1, 3]. In 2 the trifluoromethyl groups compete with the diazene group for cesium coordination. Excluding the fluorine positions of low occupancy, the cation in 2 enters ten Cs \cdots F approaches in the 3.194(4) to 3.450(13) Å range and forms two Cs…N contacts of 3.405(5) and 3.421(4) Å. The relative importance of Cs ... F interactions in 2 probably reflects the fact that the fluorine atoms are located on the surface of the anion whereas the nitrogen atoms occupy less exposed sites. While the nucleophilicity of the trifluoromethyl group should be affected by the element to which it is bonded, we note that no sharp distinction is found between the eight Cs…F approaches involving the B-CF₃ entities and the two associated with the N-CF₃ fragment. The anion of 2 makes contacts with five distinct cations. Only those to the cesium cation in the asymmetric unit are shown in Fig. 1.

Experimental

NMR: Bruker ARX 400 (100.6 MHz and 376.5 MHz for ¹³C and ¹⁹F respectively), Bruker AC 250 (79.8 MHz for ¹¹B). [D₆]acetone as solvent and internal standard ¹³C: $\delta_{\rm C} = 30.5$, ¹⁹F: external standard CFCl₃, ¹¹B: external standard BF₃·OEt₂. – IR: Bruker IFS 25; – Raman: Cary 82, Kr⁺ 647.1 nm. – Thermogravimetry: Netzsch STA 409 – UV/Vis: Shimadzu UV-2102PC.

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Empirical formula	$C_4BC_8F_{12}N_2$
Formula weight	447.78
Crystal system	Monoclinic
Space group	P2(1)/n
a (Å)	7.6764(11)
$b(\mathbf{A})$	11.543(2)
c(Å)	13.386(2)
$\beta(^{\circ})$	99.169(12)
$V(Å^3)$	1170.9(3)
Z	4
D_{calc} (g cm ⁻³)	2.540
Radiation	MoK_{α}
Wavelength (Å)	0.71073
T (K)	294(2)
Diffractometer	Siemens P3
Scan mode	Profile data from $\theta/2\theta$ scans
θ Range (°)	2.34 to 25.05
Limiting indices	-9 < h < 9, -13 < k < 13,
	-15 < l < 15
Reflections collected	6366
Unique	2070
R(int)	0.0495
Observed (I > 2σ)	1587
Crystal size (mm)	$0.44 \times 0.10 \times 0.05$
$\mu (\mathrm{mm}^{-1})$	3.310
Transmission	0.8499 to 0.7175
R1 (all data)	0.0449
wR2 (all data)	0.0867
Goodness-of-fit on F^2	0.997
Parameters	194
ΔF map (e Å ⁻³)	0.802 to -0.891

Table 2. Crystallographic data for Cs[(CF₃)₃BN=NCF₃].

Cesium trans-trifluoromethyldiazenido-tris(trifluoromethyl)borate $Cs[(CF_3)_3BN=NCF_3]$ (2): Onto a solution of 2 g (5.5 mmol) of $Cs[(CF_3)_3BNH_2]$ in 5 ml of abs. methanol 50 mmol of CF_3NO were condensed at –196 °C and stirred for 48 h at 20 °C. Unreacted CF_3NO and methanol were removed in vacuo, and the residue was crystallized from water. Yield 0.3 g (12%). – ¹⁹F NMR: δ

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(BC*F*₃) –63.5 ppm, ²*J*(BF) 25.2 Hz; δ (NC*F*₃) –78.2. ¹¹B NMR: δ (*B*) –9.5, ²*J*(BF) 25.2 Hz. ¹³C NMR: δ (BCF₃) 133.2, ¹*J*(BC) 77 Hz, ¹*J*(CF) 307 Hz; δ (NCF₃) 119.8, ¹*J*(CF) 276.7 Hz, ³*J*(BC) 12.5 Hz. – UV/Vis H₂O: $\lambda_{max} =$ 440 nm, $\varepsilon = 10 \text{ cm}^{-1} \text{ mol}^{-1}$ – IR (film) / Raman cm⁻¹: 1595 m/1591 m ν (N=N); 1278 vs/1275 m, 1194 vs/-, 1116 vs/1112 m, 1005 s/1005 w ν (CF₃); 693 s/-, -/722 vs δs(CF₃); -/309 s, -/282 s ρ (CF₃); -/235 s δ (B-N=N).

A crystal of 2 was glued to a glass fiber and transferred to a Siemens P3 diffractometer which employed graphite-monochromated MoK_{α} radiation. Intensities were derived from the profiles of the $\theta/2\theta$ scans and were corrected for Lorentz and polarization effects, the drift of the three periodically-monitored standard reflections and absorption by integration. The structure was solved by direct methods. Following anisotropic refinement, maxima in a difference Fourier map indicated an alternative conformation of the trifluoromethyl group of the C(4)atom. The anisotropically refined atoms F(10), F(11) and F(12) were assigned an occupancy α , and the atoms of the alternative conformation were given occupancies of $1 - \alpha$ and were refined isotropically. The value of α converged to 0.84(1), and the C(4)-F bond lengths of the conformation of higher occupancy were determined more precisely (1.27(1) Å) than those of the other rotamer (1.28(15) Å). Crystal data are summarized in Table 2. Structural solution, refinement and graphical display were all made with a SHELXTL program package [12]. Crystallographic data for 2 have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-137707. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: int. code +44(1223)336-033, E-mail: deposit@ccdc.cam.ac.uk].

Acknowledgements

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