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Bis(pentafluorophenyl)boron azide: synthesis and structural characterization of the first dimeric boron azide

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The reaction of $(C_6F_5)_2BCl$ with trimethylsilyl azide results in the formation of $(C_6F_5)_2BN_3$ 1; evaporation of the stabilizing solvent results in irreversible dimerization yielding $[(C_6F_5)_2BN_3]_2$ 1a as the first example of a dimeric boron azide; in the presence of pyridine a stable adduct $(C_6F_5)_2BN_3{\cdot}py$ 2 is isolated.

Extending the first report in boron azide chemistry by Wiberg and Michaud in 1954, Paetzold *et al.* has made remarkable contributions on this field.[1,2a–e] To our knowledge all of the liquid or solid boron azides reported in the literature are monomeric except for the trimeric boron dihalide azides $(BX_2N_3)_3$ (X = F, Cl, Br) and dimethylboron azide which shows a temperature dependent oligomerization.[3a,b] The structure of boron dichloride azide was determined by Müller in 1971, confirming the six-membered boron nitrogen heterocycle with diazo groups bound to nitrogen.[4] Here, we report on the synthesis and structural characterization of a novel dimeric boron azide, which can be considered as a *N,N′*-diazodiazadiboratacyclobutane.

Bis(pentafluorophenyl)boron chloride was reacted with trimethylsilyl azide in a toluene solution and the resulting mixture was monitored by NMR spectroscopy.† A single resonance was observed in the ^{11}B NMR spectrum at δ 43.9, in the region typical for three-coordinate boron. The ^{19}F NMR spectrum shows three signals for the pentafluorophenyl substituents at δ −131.4 (*o*-F), −146.4 (t, *p*-F, $^3J_{FF}$ 20.8 Hz) and −161.0 (*m*-F). In the ^{14}N NMR spectrum three resonances for covalent azide nitrogens are observed δ −144 (N_β), −160 (N_γ) and −322 (N_α).[5] The NMR data clearly indicate the formation of monomeric bis(pentafluorophenyl)boron azide **1**. After removal of the solvent, **1a** was obtained as a colorless solid which is insoluble in common organic solvents. For the NMR study of **1**, the reaction had to be performed in toluene or benzene as a solvent. In other solvents such as hexane, dichloromethane or chloroform, **1a** precipitated immediately.

The IR spectrum of solid **1a** shows a strong absorption at 2202 cm^{-1} which is the typical region for the asymmetric stretching vibration of azides.[6] However, in comparison to the corresponding asymmetric stretching vibration found for diphenylboron azide (2120 cm^{-1}), this vibration is significantly shifted to a higher wavenumber and is almost identical with that found for trimeric boron dichloride azide $(BCl_2N_3)_3$ (2210 cm^{-1}) which has bridging azides.[2e,7] In the Raman spectrum, $\nu_{as}(N_3)$ was found at 2209 cm^{-1} as a peak of medium intensity (Fig. 1).

A mass spectrum of **1a** recorded in the EI mode did not show a molecular ion peak M^+ and is therefore not expressive regarding a dimeric structure. The monomer **1** is visible, *m/z* = 387 (^{11}B), but N_2-abstraction of this fragment (**1** − N_2), typical for azides, is not observed.

The findings of the vibrational data indicate that **1a** is not monomeric in the solid state, which is in contrast to the structure of the starting material $(C_6F_5)_2BCl$ as determined by single X-ray diffraction techniques.[8] The solid state structure of **1a** (dimeric) has been determined by single crystal X-ray diffraction and confirmed the oligomeric skeleton proposed on the basis of vibrational (IR, Raman) spectroscopy (Fig. 2).‡

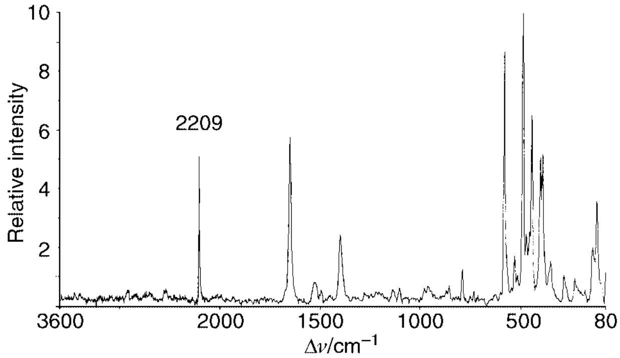


Fig. 1 Raman spectrum of **1a**.

Single crystals suitable for X-ray diffraction studies were obtained by cooling a concentrated solution of **1** in toluene. **1a** crystallized in the space group *C2/c* with four formula units in the unit cell. The B_2N_2 ring is planar with a B–N–B angle of 97.2(1)° and a N–B–N angle of 82.8(1)°. The B–N distances of 1.59/1.60 Å have typical B–N single bond character. The azide group is slightly bent with a N–N–N angle of 177.5(2)° which is in accord with the structures of other covalent boron azides previously determined.[2b,4,9a,b] The N1–N2 bond distance is 1.241(2) Å and comparable with the corresponding N–N distance found in $(BCl_2N_3)_3$ (1.25 Å); the N2–N3 distance is 1.113(3) Å indicating considerable triple bond character (N≡N 1.098 Å).[4,10a–c]

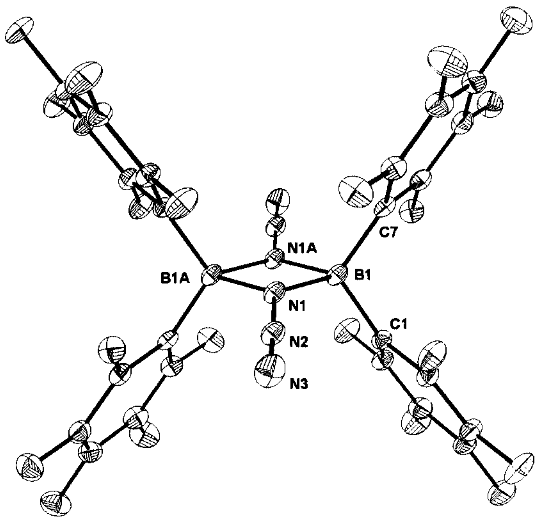
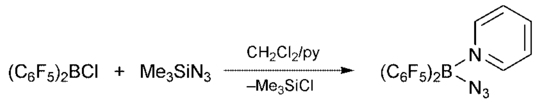


Fig. 2 ORTEP plot of the molecular structure of **1a** with thermal ellipsoids drawn at the 25% probability level. Selected bond lengths (Å) and angles (°): B(1)–N(1) 1.591(3), B(1A)–N(1) 1.601(2), N(1)–N(2) 1.241(2), N(2)–N(3) 1.113(3), B(1)–C(1) 1.607(3), C–F 1.33–1.35; N(1)–N(2)–N(3) 177.5(2), N(2)–N(1)–B(1) 130.3(2), N(1)–B(1)–N(1A) 82.8(1), B(1)–N(1)–B(1A) 97.2(1), C(7)–B(1)–C(1) 113.5(2), C(7)–B(1)–N(1) 115.2(2), C(1)–B(1)–N(1) 114.3(2), C(7)–B(1)–N(1A) 113.4(2).

The results of the X-ray analysis, Raman and IR spectroscopy prove **1a** as the first example of a *N,N′*-diazodiazadiboratacyclobutane. The dimerization can be explained by the electronic character of the boron atom in **1**. The electron-withdrawing pentafluorophenyl substituents create a highly electron deficient boron atom which stabilizes itself to a borate **1a** with the formation of a σ-bond to the α-nitrogen atom of another molecule **1**.

The reaction was also carried out in the presence of pyridine yielding the new adduct $(C_6F_5)_2BN_3{\cdot}py$ **2** as a colorless solid [eqn. (1)].†



2

(1)

This adduct **2** is soluble in toluene, dichloromethane, diethyl ether and chloroform but insoluble in hexane. The IR spectrum shows a very strong absorption at 2137 cm^{-1} and the Raman spectrum shows a weak peak at 2138 cm^{-1} which can be assigned to the asymmetric stretching vibration of the azide group, and is comparable with those found in other reported adducts of this type [$Ph_2BN_3{\cdot}py$ $\nu_{as}(N_3)$ = 2110 cm^{-1}].[2e] The NMR data and elemental analysis are consistent with the product proposed in eqn. (1). The chemical shift for **2** [$\delta(^{11}B)$ −0.5] is in the region of four-coordinate boron, the ^{14}N NMR shows four resonances at δ −144 (N_β), −159 (N-py), −204 (N_γ) and −308 (N_α).

Further investigations of the chemistry of pentafluorophenyl substituted boron azides are in progress and will be reported in a full paper.

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Notes and references

† *Experimental procedures*: **CAUTION** covalent azides are potentially explosive and safety precautions should be taken during work with azides. All manipulations were performed under an inert atmosphere of dry nitrogen using standard Schlenk techniques. All solvents were dried prior to use. Higher deviations from the theoretical values of the elemental analyses are common for boron azides [see refs. 9(*a*) and (*b*)].

1, **1a**: trimethylsilyl azide (1.0 mmol) was added to a solution of $(C_6F_5)_2BCl$ (1.0 mmol) in toluene (10 mL) at −78 °C. After stirring for 12 h at ambient temperature the solution was concentrated and cooled to −25 °C. The crystals of **1a** which formed, were found to be suitable for X-ray diffraction studies, were isolated and dried *in vacuo*. Yield 0.25 g, 65%, mp 73–76 °C (decomp.). Found: C, 38.6; N, 9.9. Calc. for $C_{24}B_2F_{20}N_6$: C, 37.3; N, 10.9%. IR/Raman: 2202vs/2209m [$\nu_{as}(N_3)$] cm^{-1}. ^{19}F NMR (376 MHz, toluene) δ −131.4 (m, *o*-F, 2F), −146.4 (t, *p*-F, 1F, $^3J_{FF}$ 20.8 Hz), −161.0 (m, *m*-F, 2F). ^{11}B NMR (128 MHz, toluene) δ 43.9. ^{14}N NMR (29 MHz, toluene, $\Delta\nu_{1/2}$/Hz) δ −144 (N_β, 220), −160 (N_γ, 300), −322 (N_α, 600).

2: compound **2** was prepared from $(C_6F_5)_2BCl$ (1.0 mmol), trimethylsilyl azide (1.0 mmol) and pyridine (1.0 mmol) in CH_2Cl_2 (10 mL) solution following the method described for **1**. Yield 0.37 g, 80%, mp 76–80 °C. Found: C, 43.2; H, 1.4; N, 11.3. Calc. for $C_{17}H_5BF_{10}N_4$: C, 43.8; H, 1.1; N, 12.0%. IR/Raman 2137vs/2138w [$\nu_{as}(N_3)$] cm^{-1}. ^{19}F NMR (376 MHz, $CDCl_3$) δ −134.1 (m, *o*-F, 2F), −154.7 (t, *p*-F, 1F, $^3J_{FF}$ 20.8 Hz), −162.3 (m, *m*-F, 2F). ^{11}B NMR (128 MHz, $CDCl_3$) δ −0.5. ^{14}N NMR (29 MHz, $CDCl_3$, $\Delta\nu_{1/2}$/Hz) δ −144 (N_β, 200), −159 (N-py, 350), −204 (N_γ, 300) −308 (N_α, 800).

‡ *Crystal data*: $C_{24}B_2F_{20}N_6$ **1a** M = 773.89, monoclinic, space group $C2/c$, a = 15.222(1), b = 10.6024(8), c = 16.895(2) Å, β = 99.73(1)°, V = 2687.4 (4) Å^3, Z = 4, μ(Mo-Kα) = 0.214 mm^{-1}, λ = 0.71073 Å, T = 200 K, 9071 reflections measured, 2545 unique (R_{int} = 0.107) which were used in all calculations. Final R indices [$I > 2\sigma(I)$], $R1$ = 0.055, $wR2$ = 0.135. The structure was solved using direct methods and refined by full-matrix least-squares on F^2. CCDC 182/1568. See http://www.rsc.org/suppdata/cc/b0/b001103g/ for crystallographic files in .cif format.

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