The Molecular Structure of 1,3,5,7-Tetra(*tert*-butyl)-2,4,6,8-tetraazido-borazocine [1]

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The tetra(*tert*-butyl)-tetraazido-borazocine, **1**, has the expected tub shape as determined for (SCNB=N*t*Bu)$_4$. However, it crystallizes in the triclinic system and shows no symmetry element in contrast to the isothiocyanato derivate which has C_2 symmetry. There are two kinds of BN bonds which alter from long to short (average 1.491 and 1.388 Å). The BN bond lengths to the azido groups are, on average, 1.486 Å. All B and N atoms of the ring reside in a trigonal planar environment. The B–N–N bond angles are close to 120° showing that the central nitrogen atom can be considered as sp^2-hybridized. The N–N–N bond angles are on average 173.6°. The two sets of the opposite B_2N_2 planes include an angle of 114.8°. The atoms of the azido groups are almost coplanar with the respective NBN planes. This together with the short BN(N_2) bond lengths indicates that these azido groups are π-bonded to their corresponding boron atom.

Key words: Tetra(*tert*-butyl)tetraazidoborazocine, Crystal Structure

Introduction

Amongst the BN heterocycles (XB=NR)$_n$ those of the eight-membered borazocines (XB=NR)$_4$, which are isoelectronic with cyclooctatetraene, have not been extensively studied in comparison to the six-membered borazines (XB=NR)$_3$ [2 – 4]. Actually, the latest report dates back to the year 1979 [5]. The formation of borazocines requires bulky substituents at the nitrogen atoms such as *t*Bu [6 – 12], CMe$_2$Et, Me(cyhex)$_2$C [7 – 9], Me$_2$CHCH$_2$CMe$_2$, or Me$_3$CCH$_2$CMe$_2$ [8, 9]. Boron substituents are either Cl and Br, or SCN, OCN, SeCN, and N$_3$, and (PhB=N*t*Bu)$_4$ is the only B-organyl derivative as yet [13]. A single ^{11}B NMR signal has been observed for the borazocines (XB=N*t*Bu)$_4$ (X = Cl, Br) with δ^{11}B ranging from 28.8 to 28.2, *i. e.* the substituents show little influence on the shielding of the boron nuclei [14]. These data are typical for tricoordinated boron atoms. In addition, IR data [14], and Cl nuclear quadrupole resonance data [15] indicate the tub conformation of the eight-membered B$_4$N$_4$ ring. This has been veryfied by the X-ray structure determination of the molecules (SCNB=N*t*Bu)$_4$ [6] and (ClB=NCMe$_2$CH$_2$CMe$_3$)$_4$ [6]. Here, the molecular structure of (N$_3$B=N*t*Bu)$_4$ is reported.

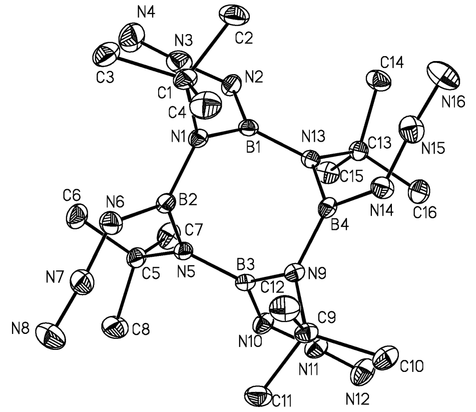

Fig. 1. View on top of molecule **1**.

The Molecular Structure of (N$_3$B=N*t*Bu)$_4$ (1)

In contrast to the tetragonal crystals of (SCNB=N*t*Bu)$_4$, **2**, the azido compound **1** crystallizes in the triclinic system, space group $P\bar{1}$, with Z = 2. While the molecules of **2** exhibit C_2 symmetry, compound **1** has no crystallographic symmetry (Fig. 1). However, both compounds show tub conformation and resemble in this respect the isoelectronic cyclooctatetraenes.

The ring boron and nitrogen atoms of **1** reside in a trigonal planar environment. The sums of the bond angles are 360(±0.2)°. The largest deviation from the 120° NBN angle is observed for the N2–B1–N13 bond angle with 118.8(2)°, and 121.0(2)° for N1–B1–N13. In contrast, the B–N–B bond angles are all smaller than 120° and deviate up to 115.7(1)° for B1–N1–B2. The B–N–N bond angles to the azido groups are larger than 120°, ranging from 120.2(2) to 122.5(2)°, but it is clear that the boron-bonded N atoms are of the sp^2 type allowing B–N π bond-

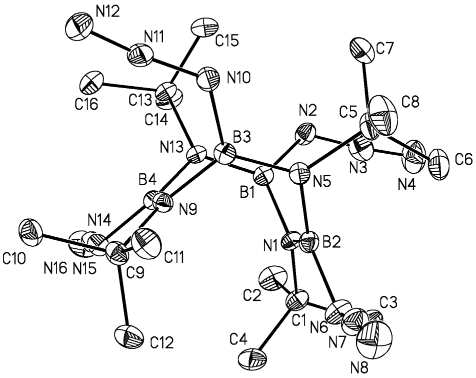

Fig. 2. Side-on view of molecule **1** (H atoms omitted for clarity; displacement ellipsoids at the 25 % probability level). Bond lengths (Å): B1–N1 1.484(3), N1–B2 1.399(2), B2–N5 1.494(3), N5–B3 1.348(3), B3–N9 1.487(3), N9–B4 1.402(2), B4–N13 1.500(2), N13–B1 1.402(3), B1–N2 1.497(3), N2–N3 1.198(3), N3–N4 1.146(3), B2–N6 1.480(3), N6–N7 1.213(2), N7–N8 1.139(3), B3–N10 1.478(3), N10–N11 1.223(3), N11–N12 1.133(2), B4–N14 1.505(3), N14–N15 1.202(2), N15–N16 1.143(2). – Bond angles (deg): N1–B1–N13 121.0(2), N1–B1–N2 120.2(2), N2–B1–N13 118.8(2), N1–B2–N5 120.6(2), N1–B2–N5 120.6(2), N1–B2–N6 119.2(2), N5–B2–N6 120.3(2), N5–B3–N9 120.7(2), N5–B3–N10 120.2(2), N9–B3–N10 120.2(2), N9–B4–N13 120.2(2), N9–B4–N14 119.6(2), N13–B4–N14 120.2(2), B1–N1–B2 115.6(2), B2–N1–C1 124.9(2), B1–N1–C1 119.4(2), B1–N2–N3 120.5(2), N2–N3–N4 174.0(2), B3–N5–C5 124.9(2), B2–N5–B3 116.1(2), B2–N5–C5 119.0(2), B2–N6–N7 122.5(2), N6–N7–N8 173.3(2), B3–N9–B4 115.7(1), B4–N9–C9 125.1(1), B3–N9–C9 119.2(1), B3–N10–N11 121.5(2), N10–N11–N12 173.7(2), B1–N13–B4 116.0(2), B1–N13–C13 124.9(2), B4–N13–C13 119.1(2), B4–N14–N15 120.2(2), N14–N15–N16 173.5(2), N–C–C and C–C–C bond angles vary from 107.3(2) to 110.7(2) Å.

ing. The N–N–N bond angles span the small range from 173.2(2) to 174.0(2)°. In analogy to the borazocine **2**, the ring B–N bonds show alternating short and long B–N bonds. The average length of the longer B–N bonds is 1.491 Å, while the average of the shorter bonds is 1.388 Å. This latter bond length corresponds to a B(sp^2)N(sp^2) double bond, the former to a B(sp^2)N(sp^2) single bond. On the other hand, the B–N bond lengths to the azido groups are on average 1.490 Å. They are, therefore, identical with the longer B–N bonds of the ring system and have to be considered as single bonds. However, the atoms of each azido group are almost coplanar with the BN_2 group to which they are coordinated. This is an argument that the azido groups may be in π-bonding interaction with the boron atom in spite of the fact that the BN bond to the azido groups are rather long.

Table 1. Crystallographic data and data related to data collection and structure refinement of compound **1**.

Formula	$C_{16}H_{36}N_{16}B_4$
M_r	495.85
Cryst. size, mm^3	$0.4 \times 0.4 \times 0.45$
Crystal system	triclinic
Space group	$P\bar{1}$
a, Å	9.590(1)
b, Å	10.215(1)
c, Å	15.672(2)
α, deg	75.251(2)
β, deg	80.399(2)
γ, deg	66.475(2)
V, Å^3	1357.6(3)
Z	2
T, K	193
D_{calcd}, g cm^{-3}	1.213
$\mu(\text{Mo}K_\alpha)$, cm^{-1}	0.81
$F(000)$, e	528
hkl range	$-9 \le h \le 12$, $-13 \le k \le 13$, $-20 \le l \le 20$
2 $\theta_{\max}$, deg	59.32
Transmission (max/min)	0.968/0.771
Refl. measured/unique/R_{int}	8047/4223/0.0209
Refl. observed [$4\sigma(F)$]	2923
Param. refined	325
$R(F)$ $(4\sigma)/wR(F^2)^{\text{a}}$ (all refl.)$^{\text{a}}$	0.0473/0.1271
GoF $(F^2)^{\text{b}}$	1.014
$\Delta\rho_{\text{fin}}$ (max), e Å^{-3}	0.168

[a] $R1 = \|F_o| - |F_c\|/\Sigma|F_o|$, $wR2 = [\Sigma w(F_o{}^2 - F_c{}^2)^2/\Sigma w(F_o{}^2)^2]^{1/2}$, $w = [\sigma^2(F_o{}^2) + (0.0844P)^2]^{-1}$, where $P = (\text{Max}(F_o{}^2, 0) + 2F_c{}^2)/3$; [b] $\text{GoF} = [\Sigma w(F_o{}^2 - F_c{}^2)^2/(n_{\text{obs}} - n_{\text{param}})]^{1/2}$.

In the azido groups of **1** the N_α–N_β bonds are on average 1.248 Å and thus slightly longer than the N_β–N_γ bonds (1.140 Å). This corresponds with data observed in azido-borates or in dimeric azido(pentafluorophenyl)boranes (1.234 and 1.131 Å) [16].

The tub conformation of the eight-membered ring demonstrated in Fig. 2 has an dihedral angle of 62.1° between the opposite four-membered ring planes N1B1N3B4 and B2N5B3N9.

Conclusion

The eight-membered ring of the borazocines **1** and **2** are tub-shaped, but molecule **1** is less symmetrical than compound **2**. The main difference between the two molecules are the lengths of the B–N bonds which are 1.456, 1.402 and 1.431 Å for **2** and 1.491, 1.388 and 1.490 Å for **1**. Obviously, the BN bonds to the azido groups are weaker bonds than those to the BN bond to the NCS groups. This obviously has the consequence that the ring BN bonds in **1** differ more strongly in their charge distribution than in **2**.

Experimental Section

The X-ray diffraction data of compound **1** were collected with a Siemens P4 instrument equipped with an area detector and an LT2 low-temperature device using MoK_α radiation and a graphite monochromator. Compound **1** was prepared according to the literature [9]. A single crystal was selected from a suspension of **1** in a polyfluorether oil and fixed on the tip of a glass fiber. It was cooled on the diffractometer head to 193 K. The unit cell was determined from the reflections collected on three sets of 20 frames taken at different settings in ω and χ. Data were collected in the hemisphere mode. The data were reduced with the program SAINT [17] after absorption correction had been applied [18]. The structure was solved with Direct Methods as implemented in SHELX-97 [19]. Table 1 shows relevant crystallographic data and information about the structure determination.

CCDC 716054 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

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