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

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The borazocine $(\mathrm{ClB{=}NCMe_3})_4$ crystallizes in the monoclinic system, space group $C2/c$ with $Z = 6$, *i. e.* there are two independent molecules in the unit cell. The first molecule has no crystallographic symmetry, while the second molecule is characterized by a twofold axis which generates the $(\mathrm{ClB{=}NCMe_3})_4$ molecule from the fragment $(\mathrm{ClB{=}NCMe_3})_2$. The molecules are tub-shaped showing alternating longer and shorter B–N bonds. Compared with the borazocine $(\mathrm{N_3B{=}NCM_3})_4$ the BN bonds of $(\mathrm{ClB{=}NCMe_3})_4$ are on average shorter than those of the azide derivative. Although B–N bond lengths and N–B–N and B–N–B bond angles in both molecules of $(\mathrm{ClB{=}NCMe_3})_4$ are identical within the limits of the standard deviation, the opposite $\mathrm{B_2N_2}$ planes differ significantly for the two independent molecules.

Key words: Tetrachloro-tetra(*tert*-butyl)borazocine, Crystal Structure

Introduction

We have recently shown that the eight-membered borazocine molecule $(\mathrm{N_3B{=}N}t\mathrm{Bu})_4$, **1** [1], has only C_1 symmetry, crystallizing in the triclinic system, space group $P\bar{1}$. We, therefore, expected that the corresponding chloro derivative $(\mathrm{ClB{=}N}t\mathrm{Bu})_4$, **2**, has a molecular structure of higher symmetry than **1**, or $(\mathrm{SCNB{=}N}t\mathrm{Bu})_4$, **3** [2]. Previous attempts to determine the crystal and molecular structure of **2** apparently failed [4] because its structure has not been published to date. Moreover, the crystal structure of $(\mathrm{ClB{=}NCMe_2CH_2CMe_3})_3$ could also not be determined reliably [2] in contrast to those of **3** and **1**. We have now been able to determine the molecular structure of **2** with single-crystal diffraction methods which allows a comparison of three structures of borazocines of type $(\mathrm{XB{=}NCMe_3})_4$.

The Molecular Structure of Tetrachloro-tetra(*tert*-butyl)borazocine (2)

The borazocine **2** was prepared from $\mathrm{BCl_3}$ and $\mathrm{Me_3CNH_2}$ [3, 4]. Single crystals were obtained from toluene/hexane mixtures at −20 °C. The colorless crystals are monoclinic, space group $C2/c$ [5]. It is interest-

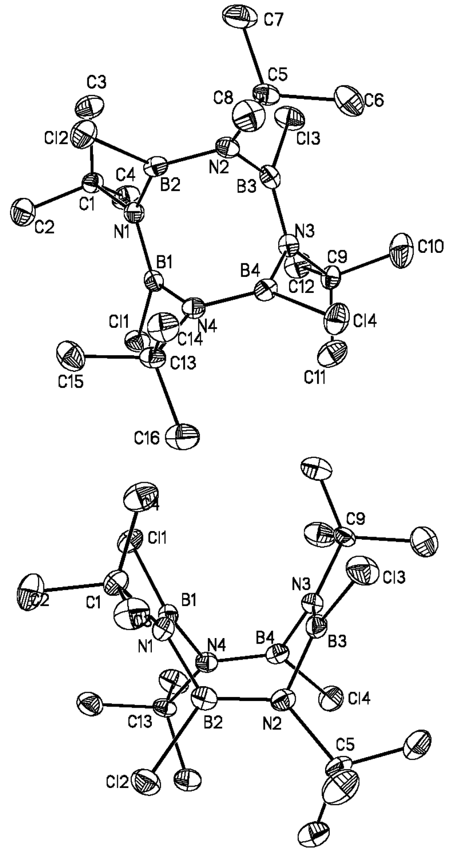

Fig. 1. Side view (top) and top view (bottom) of one of the two cyrstallographically independent molecules of **2** (**2a**). Displacement ellipsoids represent 25 % probability, H atoms omitted for clarity. Selected bond lengths (Å) and angles (deg): B1–N1 1.389(3), B2–N1 1.481(4), B2–N2 1.397(4), B3–N2 1.490(4), B3–N3 1.390(4), B4–N3 1.492(4), B4–N4 1.397(3), B1–N4 1.486(3), B1–Cl1 1.802(3), B2–Cl2 1.810(3), B3–Cl3 1.805(3), B4–Cl4 1.747(3), N1–C1 1.543(3), N2–C5 1.543(3), N3–C9 1.545(3), N4–C13 1.548(3); N1–B1–N4 120.8(2), N1–B2–N2 120.7(2), N2–B3–N3 121.1(3), N3–B4–N4 119.9(4), B1–N1–B2 114.0(4), B2–N2–B3 113.5(2), B3–N3–B4 113.7(3), B4–N4–B1 113.0(2), N1–B1–Cl1 124.1(3), N4–B1–Cl1 115.1(2), N2–B2–Cl2 123.8(2), N1–B2–Cl2 116.5(2), N2–B3–Cl3 116.5(2), N3–B3–Cl3 124.1(2), N4–B4–Cl4 123.5(2), N3–B4–Cl4 116.7(2).

X	B1–N1	N1–B2	B2–N2	N2–B3	B3–N3	N3–B4	B4–N4	N4–B1
Cl, **2**	1.389(3)	1.481(4)	1.397(4)	1.490(4)	1.390(4)	1.492(4)	1.397(3)	1.486(4)
NCS, **3**	1.40(1)	1.46(1)	1.40(1)	1.46(1)	1.40(1)	1.46(1)	1.40(1)	1.46(1)
N_3, **1**	1.402(3)	1.484(3)	1.399(2)	1.494(3)	1.348(3)	1.487(3)	1.402(2)	1.500(2)

Table 1. Comparison of B–N bond lengths of borazocines of type $(XB{=}N\mathit{t}Bu)_4$ (in Å).

Table 2. Crystallographic data and information related to data collection and structure refinement of compound **2**.

Chem. formula	$C_{16}H_{36}N_4B_4Cl_4$
M_r	469.53
Cryst. size, mm^3	$0.3 \times 0.3 \times 0.2$
Cryst. system	monoclinic
Space group	*C*2/*c*
a, Å	29.570(6)
b, Å	16.160(3)
c, Å	17.854(4)
β, deg	115.09(3)
V, Å^3	7726(1)
Z	6
ρ_{calcd}, Mg m^{-3}	1.211
μ, mm^{-1}	0.470
F(000), e	2976
Index range	$-38 \le h \le 38$, $-20 \le k \le 17$, $-23 \le l \le 23$
2θ range, deg	2.94 – 57.34
Temp, K	193(2)
Refl. coll. / unique / R_{int}	21994 / 7533 / 0.0324
Refl. observed (4σ)	4899
No. ref. variables	380
Final $R1^a$ (4σ)	0.0446
Final $wR2^a$	0.1244
Weight. scheme^a A	0.0775
GoF^b (F^2)	1.016
$\Delta\rho_{\mathrm{fin}}$ (max/min), e Å^{-3}	0.82 / −0.28

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

ing to note that there is one complete molecule (**2a**) in the asymmetric unit of the cell in addition to half a molecule **2b** which by means of a crystallographic C_2 axis is transformed into a full eight-membered tub-shaped ring of molecule **2**. Figs. 1 and 2 show these two molecules, and Fig. 3 gives a view down the *b* axis of the cell.

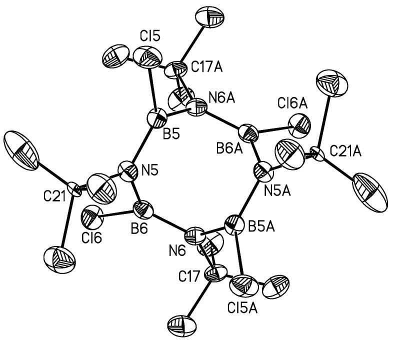

Fig. 2. Top view of the second independent molecule of **2** (**2b**) displaying crystallographical C_2 symmetry. Displacement ellipsoids represent 25 % probability. Selected bond lengths (Å) and angles (deg): B5–N5 1.318(4), B6–N5 1.420(4), B6–N6 1.392(4), B5–N6A 1.486(4), N6–B5A 1.4856(4), B5–Cl5 1.799(3), B6–Cl6 1.806(3), N5–C21 1.631(3), N6–C17 1.546(3); N5–B5–N6A 121.0(3), N5–B6–N6 120.6(2), N6–B5A–N5A 121.9(3), B5–N5–N6 114.0(3), B6–N6–N5A 120.6(2), N5–B5–Cl5 123.2(2), N6A–B5–Cl5 115.9(3), N6–B6–Cl6 123.5(2), N5–B6–Cl6 115.9(2).

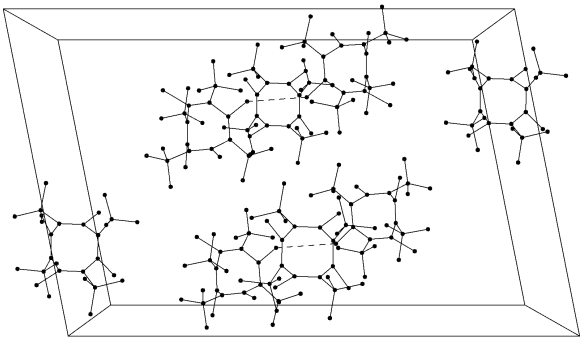

Fig. 3. View of the unit cell of $(ClB{=}NCMe_3)_4$, **2**, down the crystallographic *b* axis. There are intermolecular Cl···Cl contacts of 3.567 Å.

As expected, the B–N bond lengths are alternating, a short bond is always followed by a longer one. The average of the short bonds for both independent molecules is 1.395 Å, the longer ones are on average 1.487 and 1.481 Å, respectively. These differences are just outside the 3σ limit for equal bond lengths. The B–Cl bonds are on average 1.802 Å long which corresponds with the upper range for B–Cl bonds involving tricoordinated boron atoms. Another typical feature is that the N–B–N bond angles are close to 120° while the B–N–B bond angles are more acute by about 7°. Nevertheless, the sum of the three bond angles at the boron as well as at the nitrogen atoms are 360°.

Figs. 1 and 2 show the molecular structures of the two crystallographically independent molecules. Although bond angles and bond lengths are practically equal for both molecules **2a** and **2b**, the interplanar angles are different. The plane N4–B1–N1–B2 forms an angle with the plane B1–N3–B3–N3 of molecule **2a** of 61.1°, and the angle between the planes B1–N4–B4–N3 and B3–N2–B2–N1 is 62.9° while for molecule **2b** the plane N6–B5A–N5A–B6A forms an angle of 91.9° with the opposite plane N6A–B5–N6–B6, and an angle of 62.5° between the planes B3A–N6–B6–N5A and N5A–B5A–N6A–B5. Also, the respective BNC bond angles are not equal, for example the angle B3–N3–C9 is 125.9(2)° while the angle B4–N4–C13 is 128.8(2)°, and the B3–N2–C5 bond angle is 117.4(2).

Discussion

Today, the crystal and molecular structures of three borazocines, **1** to **3**, are available. All of them show the tub conformation in analogy to the isoelectronic cyclooctatetraene systems. Table 1 lists B–N bond lengths for these three compounds. The averages of the longer B–N bond lengths are 1.481 Å for compound **1**, 1.487 Å for compound **2** and 1.46 Å for compound **3**. The averages of the shorter B–N bonds are 1.388, 1.393 and 1.40 Å, respectively. Therefore, the difference in B–N bonds lengths is largest for the chloroborazocine **2**. This reflects the inductive effect of the Cl atom. The (crystallographic) symmetry for the three molecules is highest for the SCN derivative **3** (S_4), followed by **2** (C_2 and C_1) and **1** (C_1). It would be of interest to study the influence of electron-donating B substituents such as RO and R_2N groups. Attempts to isolate these types of compounds have failed as yet. But also organyl-substituted borazocines are rare. Still, it would be worthwhile to determine their structures.

Experimental Section

A suitable crystal was selected from a suspension of **2** in polyperfluoroether oil. It was mounted on a glass fibre on the goniometer head which was cooled to −80 °C by a stream of cold dinitrogen gas (Bruker LT2 device). A Siemens P4 diffractometer was used for data collection using an area detector, MoK_α radiation and a graphite monochromator. The unit cell was determined from the reflections on 3 sets of 15 frames each at three different settings of ω and 2θ angles. The program SAINT was used to determine the unit cell dimensions, followed later with all collected reflections. Data collection was performed in the hemisphere mode, and data reduction was performed with the program SMART. Absorption correction was applied to the data by SADABS leading to max/min transmission of 1.000 and 0.873. The structure was solved with Direct Methods with SHELXS-97. For crystallographic data, data collection and structure refinement parameters see Table 2.

CCDC 734835 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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[1] Contributions to the Chemistry of Boron, 273. For contribution 272 see: H. Nöth, *Z. Naturforsch.* **2009**, *64b*, 581 – 583.

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[4] H. S. Turner, R. J. Warne, *J. Chem. Soc. A* **1965**, 6521 – 6450.

[5] The structure was solved first in the space group *I*2*a*1 but converged more rapidly in the equivalent space group *C*2/*c*.

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