Communication

Synthesis and Crystal Structure of 9,12-Dibromo-ortho-Carborane

Olga B. Zhidkova 1, Anna A. Druzina 1, Sergey A. Anufriev 1, Kyrill Yu. Suponitsky 1, Igor B. Sivaev 1,2,* 1 and Vladimir I. Bregadze 1

1 A.N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, 28 Vavilov Str., 119991 Moscow, Russia; zolga57@mail.ru (O.B.Z.); ilinova_anna@mail.ru (A.A.D.); trueman476@mail.ru (S.A.A.); kirshik@yahoo.com (K.Y.S.); bre@ineos.ac.ru (V.I.B.)
2 Basic Department of Chemistry of Innovative Materials and Technologies, G.V. Plekhanov Russian University of Economics, 36 Stromyanny Line, 117997 Moscow, Russia
* Correspondence: sivaev@ineos.ac.ru

Abstract: Synthesis, NMR spectral data and crystal structure of 9,12-dibromo derivative of ortho-carborane are reported.

Keywords: carboranes; bromo derivatives; synthesis; NMR spectra; single crystal X-ray diffraction

1. Introduction

Icosahedral carboranes C2B10H12 are of interest for a wide variety of applications, from medicinal chemistry [1–8] to design of new materials [9–18]. Although the carborane cage contains ten boron atoms and only two carbon atoms, the CH groups of carboranes exhibit the properties of weak acids, which makes them accessible for functionalization using a rich arsenal of organic chemistry. Therefore, most of the ways of modification of carboranes involve substitution at carbon atoms [19]. The most studied substitution reactions at boron atoms are halogenation reactions. It should be noted that to date, a large number of various iodo derivatives of carboranes have been synthesized, differing in the position of the substituents and their number [20–30]. The increased interest in iodine derivatives of carborane is mainly caused by their use in various cross-coupling reactions [21–23,31–40], as well as in study of intermolecular hydrogen and halogen bonding [41,42] and medicinal chemistry [43]. Despite the fact that the bromination of carboranes was first described as early as the mid-1960s [44], the chemistry of bromo derivatives of carboranes has been studied to a much lesser extent compared to the iodo derivatives. Nevertheless, recently there has been an increase in interest in bromo derivatives of carboranes due to their use in cross-coupling reactions [45–48] and the study of intermolecular interactions with the formation of hydrogen and halogen bonds [49].

In this contribution we describe the synthesis of 9,12-dibromo-ortho-carborane and its characterization by NMR spectroscopy and single crystal X-ray diffraction.

2. Results and Discussion

Despite the fact that the bromination of ortho- and meta-carboranes was first described back in the mid-1960s [44], neither the yield of bromination products nor their characterization (with the exception of X-ray diffraction data for crystals from the same syntheses [50–53]) have been described until recently. For the sake of fairness, it is worth noting an attempt to characterize the obtained bromo derivatives of ortho-carborane using 11B NMR spectroscopy, however, due to the very limited instrumental capabilities of that time, at the present it is rather of historical interest [54]. Synthesis and NMR spectra of 9-bromo- and 9,12-dibromo-meta-carboranes were recently reported by Spokoyny et al. [45]. The NMR spectral data of 9-bromo-ortho-carborane, as well as its crystal and gas phase structures, were recently reported by Hnyk et al. [49,55]. As for 9,12-dibromo-ortho-carborane, its
preparation was also mentioned relatively recently [56]; however, only numerical characteristics of the NMR spectra were reported without their assignment.

The main problem of the 9,12-dibromo-ortho-carborane synthesis is the purification of the target product. It was demonstrated that bromination of ortho-carborane, regardless of the Lewis acid and solvent used, gives, together with the desired 9-bromo-ortho-carborane, approx. 10 mol.% of 8-bromo-ortho-carborane. At the second stage, this leads to the crude product containing approx. 80% of 9,12-dibromo-ortho-carborane, together with significant amount of the 8,9-dibromo and traces of the 8,10-dibromo derivatives [57]. Impurities of 9-bromo- and 8,9,12-tribromo derivatives may also be present in the reaction mixture, which greatly complicates the purification of the target product [58]. Unfortunately, all our attempts to purify the target compound using chromatography methods failed. Therefore, we purified 9,12-dibromo-ortho-carborane by fraction crystallization from chloroform that produced a rather low (22%) yield of pure product (Scheme 1).

Scheme 1. Synthesis of 9,12-Br$_2$-ortho-C$_2$B$_{10}$H$_{10}$.

The $^1$H NMR spectrum of 9,12-Br$_2$-ortho-C$_2$B$_{10}$H$_{10}$ in CDCl$_3$ contains signals of the CH groups at 3.72 ppm and the signals of BH groups in the region of 1.5–3.5 ppm. The $^{13}$C NMR spectrum contains signal of the carborane carbons at 46.8 ppm. The $^{11}$B NMR spectrum consists of one singlet at 0.1 ppm and three doublets at −7.5, −14.4, and 16.9 ppm with the integral intensity ratio of 2: 2: 4: 2 (See Supplementary Information).

It should be noted that the structure of 9,12-dibromo-ortho-carborane was determined in 1966 [50] at room temperature. The quality of that experiment was evidently low and was mostly concentrated on the description of molecular geometry. Therefore, in the present study, we redetermined its structure at low temperature (110 K) focusing on both molecular structure (Figure 1) and, especially, the crystal packing.

Figure 1. General view of 9,12-Br$_2$-ortho-C$_2$B$_{10}$H$_{10}$ showing atomic numbering. Thermal ellipsoids are drawn at 50% probability level.

The presence of two bromine atoms might imply a formation of the Br . . . Br halogen bond in the crystal structure of 9,12-dibromo-ortho-carborane. At the same time, in our
recent study [42] we showed that halogen substituent at the B9 and B12 positions of the ortho-carborane cage can act as a good donor of the lone pair (LP), however, its acceptor ability is low, and therefore, a formation of any strong halogen bond in the crystal is hardly expected. Moreover, in recently studied 1,12-Br$_2$-ortho-C$_2$B$_{10}$H$_{10}$, the C-H…Br interactions were found to be structure-forming while no halogen bonds were observed [49]. It means that it is difficult to predict a priori what type of intermolecular interactions will be predominant in the crystal structure stabilization of dihalogen carboranes. The X-ray study of 9,12-Br$_2$-ortho-C$_2$B$_{10}$H$_{10}$ has revealed that both Br…Br halogen bond of type II and C-H…Br hydrogen bonds are formed in the crystal (Figure 2). The halogen bond is rather weak and strongly distorted (the Br(1)…Br(2) distance is 3.796(2) Å, the B(9)-Br(1)…Br(2) and B(12)-Br(2)…Br(1) angles are 92.5(3)$^\circ$ and 148.4$^\circ$, respectively); the Br(1) atom acts as LP donor while the Br(2) atom is LP acceptor.

Figure 2. Crystal packing fragment of 9,12-Br$_2$-ortho-C$_2$B$_{10}$H$_{10}$. Numbers at the green arrows correspond to pair interaction energies.

Each molecule has two halogen-bonded neighbors and four C-H…Br bonded ones which leads to a formation of layers parallel to the bc plane. In order to understand which interactions play a predominant role in the crystal structure formation, we carried out energetic analysis of the crystal packing by estimation of the dimeric interaction energies [42, 59–61]. Such dimers are formed by the central molecule and the molecule
Molecular features taken from the closest environment of the central molecule. Here, we considered only those molecular pairs which are linked by the C-H . . . Br and Br . . . Br interactions because all the other intermolecular interactions are of van der Waals type. Calculations were carried out with the GAUSSIAN program [62] using PBE0 functional and triple-zeta basis set which were found to be reliable for analysis of halogen and hydrogen bonds [63–65].

As it is seen in Figure 2, the C-H . . . Br interactions are much stronger than Br . . . Br halogen bonds and can be viewed as structure-forming interactions in the crystal of 9,12-Br$_2$-ortho-C$_2$B$_{10}$H$_{10}$. The weakness of the observed halogen bond is also confirmed by near equivalence of the B(9)-Br(1) (1.955(5) Å) and B(9)-Br(2) (1.963(5) Å) bond lengths. In the case of a strong halogen bond, the latter must be significantly longer because the Br(2) atom acts as LP acceptor.

3. Materials and Methods

All reactions were carried out under argon atmosphere. Dichloromethane was dried using standard procedures [66]. The reaction progress was monitored by thin layer chromatography (Merck F254 silica gel on aluminum plates; n-hexane: chloroform 4: 1 (v/v)) and visualized using 0.5 % PdCl$_2$ in 1% HCl in aq. MeOH (1:10). The NMR spectra at 400 MHz (1H), 128 MHz (13B), and 100 MHz (13C) were recorded with Varian Inova 400 spectrometer. The residual signal of the NMR solvent relative to Me$_4$Si was taken as the internal reference for $^1$H and $^{13}$C NMR spectra. $^{11}$B NMR spectra were referenced using BF$_3$-Et$_2$O as external standard. Mass spectra (MS) were measured using Shimadzu LCMS-2020 instrument with DUIS ionization (ESI—Electrospray ionization and APCI—Atmospheric pressure chemical ionization). The measurements were performed in a negative ion mode with mass range from m/z 50 to m/z 2000. Isotope distribution was calculated using Isotope Distribution Calculator and Mass Spec Plotter [67].

Anhydrous AlCl$_3$ (0.80 g, 6.0 mmol) was added to solution of ortho-carborane (5.0 g, 34.7 mmol) in dichloromethane (200 mL) and stirred for 15 min. A solution of Br$_2$ (1.78 mL, 5.55 g, 34.7 mmol) in dichloromethane (50 mL) was added dropwise and the reaction mixture was stirred until it became colorless. Then, a solution of Br$_2$ (1.78 mL, 5.55 g, 34.7 mmol) in dichloromethane (50 mL) was added dropwise and the reaction mixture was stirred under reflux for 16 h. The reaction mixture was cooled and treated with a solution of Na$_2$S$_2$O$_3$ (30.00 g) in water (100 mL). The organic phase was separated, the aqueous fraction was extracted with dichloromethane (3 × 50 mL). The organic fractions were combined, dried with anhydrous Na$_2$SO$_4$, filtered, and evaporated to dryness to give 9.75 g (93%) of crude product. Fraction crystallization from chloroform gave 2.30 g (22% yield) of pure of 9,12-Br$_2$-ortho-C$_2$B$_{10}$H$_{10}$ as colorless crystals.

$^1$H NMR (400 MHz, CDCl$_3$), $\delta$: 3.72 (2H, br.s, CH$_{\text{carb}}$), 3.5–1.5 (8H, br.m, B$_{9,10}$-Br), 1.5–0.5 (2B, d, B(12), $J = 158$ Hz), –14.4 (4B, d, B(4,5,7,11), $J = 171$ Hz), –16.9 (2B, d, B(3,6), $J = 183$ Hz). $^{13}$C[$^1$H] NMR (100 MHz, CDCl$_3$), $\delta$: 46.8 (C$_{\text{carb}}$). MS (DUIS), m/z: found: 301.0 (M–H)$^-$; calculated for C$_2$H$_8$B$_{10}$Br$_2$ (M–H)$^-$ 301.0.

The single crystals of 9,12-Br$_2$-ortho-C$_2$B$_{10}$H$_{10}$ were grown by slow evaporation of a solution of the title compound in chloroform at room temperature. Single crystal X-ray diffraction experiment was carried out using SMART APEX2 CCD diffractometer (\(\lambda\)(Mo-K$_\alpha$) = 0.71073 Å, graphite monochromator, $\omega$-scans) at 110 K. Collected data were processed by the SAINT and SADABS programs incorporated into the APEX2 program package [68]. The structure was solved by the direct methods and refined by the full-matrix least-squares procedure against $I^2$ in anisotropic approximation. The refinement was carried out with the SHELXTL program [69]. The CCDC number 2132434 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif (accessed on 15 February 2022).

Crystallographic data for 9,12-Br$_2$-ortho-C$_2$B$_{10}$H$_{10}$: C$_2$H$_{10}$B$_{10}$Br$_2$ are orthorhombic, space group Pnma; $a = 12.8889(5)$ Å, $b = 7.3377(3)$ Å, $c = 11.6245(4)$ Å, $V = 1099.39(7)$ Å$^3$, $Z = 4$, M = 302.02, $d_{\text{cryst}} = 1.825$ g cm$^{-3}$, $wR2 = 0.0622$ calculated on $I^2_{\text{ref}}$ for all 2784 independent
references with $2\theta < 58.0^\circ$, $(GOF = 1.026, R = 0.02976$ calculated on $F_{\text{obs}}$ for 2460 reflections with $I > 2\sigma(I)$).

**Supplementary Materials:** $^1$H, $^{11}$B, $^{13}$C NMR and MS spectra of 9,12-B$_2$ortho-C$_2$B$_{10}$H$_{10}$.

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