

Synthesis and structure of halogen derivatives of 9-dimethylsulfonium-7,8-dicarba-*nido*-undecaborane [9-Me₂S-7,8-C₂B₉H₁₁]

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Abstract

Halogenation of 9-dimethylsulfonium-7,8-dicarba-*nido*-undecaborane [9-SMe₂-7,8-C₂B₉H₁₁] with *N*-chlorosuccinimide, bromine and iodine gave the expected corresponding halogen derivatives [9-SMe₂-11-X-7,8-C₂B₉H₁₀], where X = Cl (**1**), Br (**2**), I (**3**). In the bromination reaction, [9-SMe₂-6-Br-7,8-C₂B₉H₁₀] (**4**) was isolated as a minor product being the first example of substitution at a “lower” belt of the 7,8-dicarba-*nido*-undecaborate cage. The use of excess of bromine resulted in dibromo derivative [9-SMe₂-6,11-Br₂-7,8-C₂B₉H₉] (**5**). Structures of the compounds prepared were determined using ¹¹B–¹¹B COSY NMR spectroscopy (for all halogen derivatives) and single crystal X-ray diffraction (for compounds **2**, **3**, and **5**).

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1. Introduction

The dicarbollide anion [7,8-C₂B₉H₁₁]²⁻ has been extensively used as a ligand in organometallic chemistry for about 40 years because of their similarity with the formally isolobal cyclopentadienide anion [C₅H₅]⁻ (Cp). The capacity of the dicarbollide ligand to stabilize uncommon and high oxidation states of transition metals is well established [1,2]. Replacement of hydrogen atoms by other substituents is known to alter both the steric and electronic influences of the η⁵-cyclopentadienyl ring, resulting in differing reactivity and stability of the substituted cyclopentadienyl metal complexes [3]. The pentamethylcyclopenta-

dienide ligand [C₅Me₅]⁻ (Cp*) has a higher electron donating ability and a higher size than the parent cyclopentadienide. Similarly, substitution in the dicarbollide ligand will result in a change of the steric and electronic properties of the ligands. That is why there is a considerable interest in the chemical synthesis of substituted dicarbollide ligands and in the study how the electronic and steric properties of the ligands affect structure and properties of metal complexes on their base.

In contrast to the cyclopentadienide ligand, substituents in the pentagonal face of the dicarbollide ligand are not situated in the ligand plane, but directed out of the icosahedron center thus effectively reducing the cone angle of the ligand. On the other hand, it was shown that the reduction of the charge on the dicarbollide ligand by one unit through the incorporation of the charge-compensating

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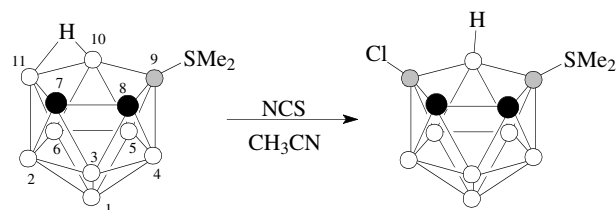
substituents ($-S^+R_2$, $-N^+R_3$) results in formation of neutral or cationic metallocarboranes with metals in accessible low oxidation states [4,5]. It is expected that combination of different types of substituents (including charge-compensating ones) in one dicarbollide moiety would give metallocarborane complexes having unusual structural characteristics and chemical properties.

There are two general approaches to synthesis of substituted metallocarboranes: (1) substitution in already available metallocarborane molecule and (2) the synthesis from substituted *nido*-carborane ligands and metal complexes [6]. Both these approaches can be used for synthesis of metallocarborane complexes having unusual structural characteristics and chemical properties. It was demonstrated recently that the reactions of neutral ferracarborane [4- Me_2S -3-Cp-3,1,2- $FeC_2B_9H_{10}$] with electrophilic reagents (bromine or mercury trifluoroacetate) result in substitution at the position 8 of the metallocarborane cage [7], which is equivalent to the position 10 in the “free” dicarbollide ligand. At the same time, halogenation of the parent 7,8-dicarba-*nido*-undecaborate is known to result in substitution at the position 9(11) [8–10] giving after deprotonation the corresponding dicarbollide ligands [10]. In order to prepare a series of neutral and cationic metallocarboranes based on isomeric heterosubstituted charge-compensated dicarbollide ligands we proposed to combine both abovementioned methodologies.

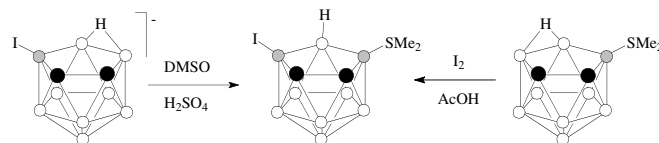
In this paper we report synthesis of the halogen-substituted charge-compensated 7,8-dicarba-*nido*-undecaboranes [9- Me_2S -11-X-7,8- $C_2B_9H_{10}$] (X = Cl, Br, I) by halogenation of the parent 9-dimethylsulfonio-7,8-dicarba-*nido*-undecaborane [9- Me_2S -7,8- $C_2B_9H_{11}$] for further use them as precursors to the corresponding monoanionic substituted dicarbollide ligands.

2. Results and discussion

Synthesis. The halogenation of the parent 7,8-dicarba-*nido*-undecaborate with elemental halogens [8,9] or *N*-halogensuccinimides [10] results in subsequent substitution at boron atoms in the positions 9 and 11 in the open pentagonal face of the ligand that are neighboring to the carbon atoms. An introduction of alkyl or aryl substituents at the carbon atoms of the carborane cage does not interfere with this pattern [11–14]. The halogenation of charge-compensated *nido*-carboranes is less studied [15], however the iodination of [9-Py-7,8- $C_2B_9H_{11}$] with elemental iodine has been reported recently to proceed at the position 11 giving [9-Py-11-I-7,8- $C_2B_9H_{10}$] [16]. Based on these data it could be expected that halogenation of [9- Me_2S -7,8- $C_2B_9H_{11}$] will proceed in the similar way. Indeed we found that its reaction with *N*-chlorosuccinimide in acetonitrile at room temperature produces [9- Me_2S -11-Cl-7,8- $C_2B_9H_{10}$] (1) isolated in 45% yield. The structure of the chloro derivative 1 was determined using ^{11}B - ^{11}B COSY NMR spectroscopy (see Fig. S1 in Supplementary material).



The reaction of [9- Me_2S -7,8- $C_2B_9H_{11}$] with elemental iodine requires stronger conditions than the iodination of the parent *nido*-carborane [8] and proceeds well only in boiling acetic acid giving [9- Me_2S -11-I-7,8- $C_2B_9H_{10}$] (3) as a single product isolated in 37% yield. No other products were found after refluxing of the reaction mixture over 4 days. The same compound was obtained in 78% yield coming from the opposite direction by the treatment of $(Me_4N)[9-I-7,8- $C_2B_9H_{11}$]$ in dimethylsulfoxide with concentrated sulfuric acid under conditions used for the introduction of the SMe_2 group into the parent *nido*-carborane [17]. The structure of the iodo derivative 3 was determined using methods ^{11}B - ^{11}B COSY NMR spectroscopy (Fig. S2) and single crystal X-ray diffraction (Fig. 1).



The reaction of [9- Me_2S -7,8- $C_2B_9H_{11}$] with equimolar amount of elemental bromine at ambient temperature in dichloromethane gave unexpectedly a mixture of two isomeric products. The major isomer is the expected [9- Me_2S -11-Br-7,8- $C_2B_9H_{10}$] (2), whereas the minor one

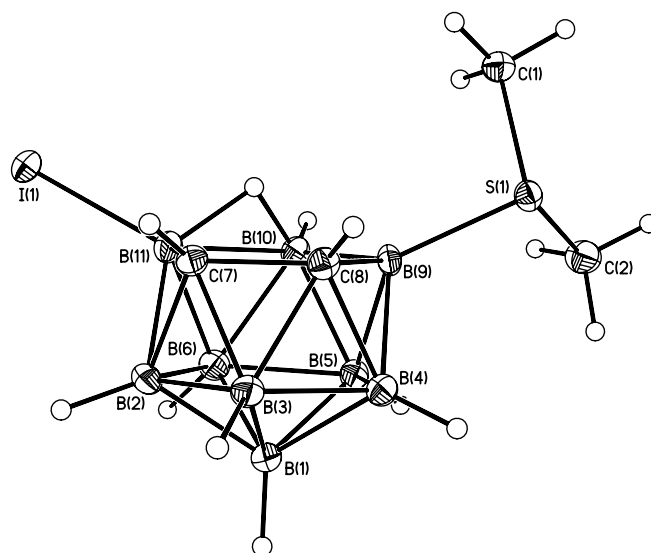


Fig. 1. Molecular structure of [9- Me_2S -11-I-7,8- $C_2B_9H_{10}$] (3).

was found to be a product of substitution at a “lower”¹ boron belt – [9-Me₂S-6-Br-7,8-C₂B₉H₁₀] (**4**). The structures of the bromo derivatives **2** and **4** were determined using the ¹¹B–¹¹B COSY NMR spectroscopy (Figs. S3 and 3, respectively) and the single crystal X-ray diffraction study of **2** was performed as well (Fig. 2).

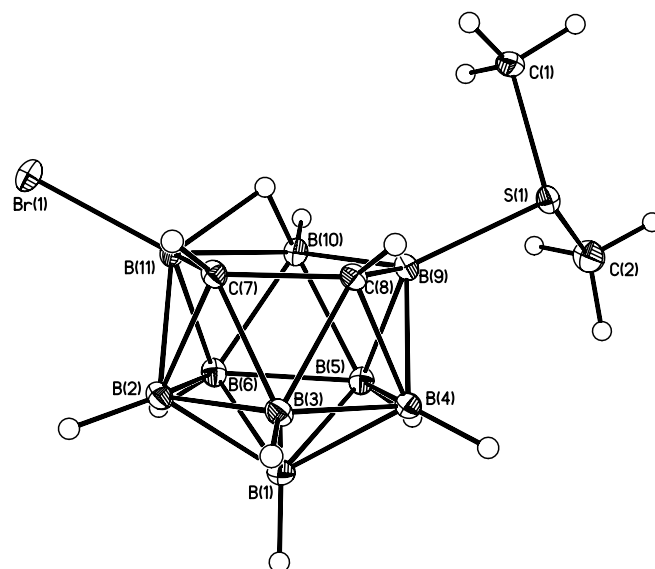
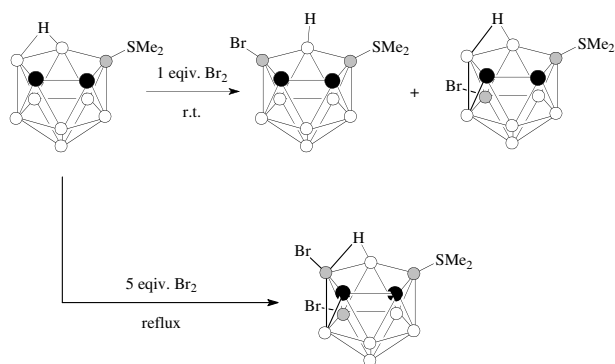


Fig. 2. Molecular structure of [9-Me₂S-11-Br-7,8-C₂B₉H₁₀] (**2**).

It is reasonable to suppose that the use of excess of bromine should result in the derivative containing bromine substituents both in the positions 6 and 11. Indeed, the reaction of [9-Me₂S-7,8-C₂B₉H₁₁] with the fivefold excess of bromine gives the corresponding dibromo derivative [9-Me₂S-6,11-Br₂-7,8-C₂B₉H₉] (**5**). The hydrogen atom at the position 5 was found to resist to substitution for bromine that can be explained by the deactivating effect of the SMe₂ group [18].

It should be noted that on our knowledge the bromination of [9-Me₂S-7,8-C₂B₉H₁₁] is the first documented example of an electrophilic substitution at the “lower” belt of the 7,8-dicarba-*nido*-undecaborate cage. The halogenation of the parent 7,8-dicarba-*nido*-undecaborate [8–10] and its C-substituted derivatives [11–14] was demonstrated to proceed only at the positions 9 and 11 of the open face (the “upper” belt) of the *nido*-carborane cage. The halogen derivatives contained halogen atoms at the positions 5, 6 [19], 2, 4 [20], and 3 [21] in the “lower” belt of the 7,8-dicarba-*nido*-undecaborate cage can be obtained by indirect methods. The bromination and iodination at the “lower” belt of [9-Py-7,8-C₂B₉H₁₁] was reported earlier by Volkov et al. [15], however, the proposed position of substitution was not supported by any reasonable arguments. Moreover, these results (at least in the iodination part) were disproved later by X-ray structure determination, which revealed the substitution at the position 11 of the “upper” belt [16].

The reason of the revealed “abnormality” in the halogenation of [9-Me₂S-7,8-C₂B₉H₁₁] is not very clear and probably connected with close values of atomic charges on the B(11) and B(6) atoms. It should be noted, however, that the formation of the 6,11-dibromo derivative correlates

well with the general order of reactivity of boron atoms towards electrophilic attack proposed on the base of selective proton–deuterium exchange in the [7,8-C₂B₉H₁₂][−] anion [22].

NMR spectra. The assignments of signals in the ¹¹B NMR spectra of the all compounds synthesized were carried out using the ¹¹B–¹¹B COSY NMR spectroscopy. The comparison of the ¹¹B NMR spectra of isomeric bromo derivatives **2** and **4** with the spectra of the parent [9-Me₂S-7,8-C₂B₉H₁₁] [23] (Fig. 5) revealed that the introduction of the bromo substituent at the position 6 (the “lower” belt) does not disturb significantly the spectrum pattern except the low-field shift of a signal corresponding to the substituted boron atom B(6) by 5.0 ppm. All other signals undergo high-field shifts by −(1.2–3.5) ppm. On the other hand, the introduction of the bromo substituent at the position 11 (the “upper” belt) produces drastic changes in the spectral pattern. Except the low-field shift of the signal corresponding to the substituted boron atom B(11) by 2.4 ppm, similar low-field shifts were found for the B(2) and B(4) atoms. At the same time, the signals corresponding to the B(5) and B(3) atoms displace to a high magnetic field by −8.3 ppm and −11.6 ppm, respectively, other signals undergo high-field shifts by −(0.8–3.5) ppm.

Similar spectral patterns were found for the chloro and iodo analogues **1** and **3**. Variation in chemical shifts of the corresponding boron atoms (except the signals of the substituted B(11) atoms) for compounds **1–3** does not exceed 2.0 ppm with the highest variation range for the B(3) atoms. It should be noted that the changes in the spectral pattern proceeding on substitution at the “upper” belt of the 7,8-dicarba-*nido*-undecaborate cage agree well with the general trends found in other substituted *nido*-carborane systems [24].

¹¹B NMR spectrum of the 6,11-dibromo derivative **5** resembles the spectra of **1–3**, except the signal of the B(6)

¹ Here and further, a “lower” belt is a pentagon including positions 2–6, while an “upper” belt is a pentagon including positions 7–11.

atom having chemical shift very close to one for the corresponding boron atom in the spectrum of the 6-bromo derivative **4**. It is not surprisingly taking to account much stronger disturbing effect of the halogen substituent located in the “upper” belt than in the “lower” one. The ^1H NMR spectra of all the compounds contain sets of signals corresponding methyl and CH_{carb} -groups as well as the broad signals of the bridge hydrogen atom BH^{10} in hydride range. It should be noted that the chemical shift of the last signal practically does not depend on halogen, whereas it is very sensitive to the position of substitution.

X-ray structure. Molecular crystal structures of compounds **2**, **3**, and **5** were determined by single crystal X-ray diffraction. All the three compounds were found to be isomorphous and their cell parameters (Table 1) are close. Some larger parameters of **5** could be explained by the presence of the second bulky halogen atom. General views of molecules **2**, **3**, and **5** are given in Figs. 1,2 and 4, respectively. The geometrical parameters of all the structures studied (Table 2) are close to one of the parent compounds – $[\text{9-Me}_2\text{S-7,8-C}_2\text{B}_9\text{H}_{11}]$ [25] and $[\text{9-I-7,8-C}_2\text{B}_9\text{H}_{11}]^-$ [8b]. One can notice that the introduction of a halogen to $[\text{9-Me}_2\text{S-7,8-C}_2\text{B}_9\text{H}_{11}]$ leads to noticeable changes in the carborane moiety. They are the most pronounced for the C–B bonds, which include the halogen-substituted boron atom (B(11) and B(6)) and also for C–B and C–C bonds. Although these bonds do not directly include substituted atoms they are very “sensitive” to the presence of electron-withdrawing substituents. The extent of alternation for the majority of bond lengths in the compounds studied does not exceed 0.03 Å. For example the $\text{C}_{\text{carb}}\text{--C}_{\text{carb}}$ bond elongates by 0.019, 0.016 and 0.012 Å for **2**, **3**, and **5**, respectively, in the comparison with $[\text{9-Me}_2\text{S-7,8-C}_2\text{B}_9\text{H}_{11}]$. The similar elongation of the $\text{C}_{\text{carb}}\text{--C}_{\text{carb}}$ bond (by 0.024 Å) was found to be produced

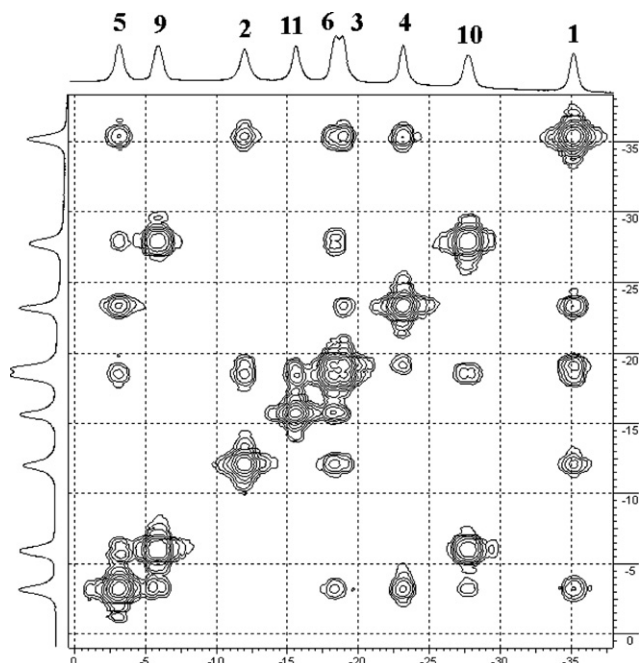


Fig. 3. $^{11}\text{B}\text{--}^{11}\text{B}$ NMR COSY spectrum of $[\text{9-Me}_2\text{S-6-Br-7,8-C}_2\text{B}_9\text{H}_{10}]$ (**4**).

by the introduction of the iodine substituent in the $[\text{9-Py-7,8-C}_2\text{B}_9\text{H}_{11}]$ molecule [16]. At the same time the $\text{C}_{\text{carb}}\text{--C}_{\text{carb}}$ bond lengths found in **2**, **3**, and **5** are very close to the one found in the crystal of $(\text{Me}_3\text{NH})[\text{nido-9,11-I}_2\text{-7,8-C}_2\text{B}_9\text{H}_{10}]$ (1.547(6) Å). The largest elongation was found for the C(8)–B(9) and B(2)–B(11) bonds (by 0.021 and 0.026 Å for **5** in the comparison with $[\text{9-Me}_2\text{S-7,8-C}_2\text{B}_9\text{H}_{11}]$). Unfortunately due to the fact that the variation of one bond in carborane cage alters automatically geometrical parameters of its nearest environment it is not always clear which bonds in particular initiate the changes.

Table 1

Crystal data and structure refinement for $[\text{9-Me}_2\text{S-11-Br-7,8-C}_2\text{B}_9\text{H}_{10}]$ (**2**), $[\text{9-Me}_2\text{S-11-I-7,8-C}_2\text{B}_9\text{H}_{10}]$ (**3**), and $[\text{9-Me}_2\text{S-6,11-Br}_2\text{-7,8-C}_2\text{B}_9\text{H}_9]$ (**5**)

Compound	2	3	5
Empiric formula	$\text{C}_4\text{H}_{16}\text{B}_9\text{BrS}$	$\text{C}_4\text{H}_{16}\text{B}_9\text{IS}$	$\text{C}_4\text{H}_{15}\text{B}_9\text{Br}_2\text{S}$
Formula weight	273.43	320.42	352.33
Color, habit	Colorless plate	Colorless plate	Colorless plate
Crystal size (mm)	$0.60 \times 0.45 \times 0.37$	$0.45 \times 0.40 \times 0.25$	$0.21 \times 0.15 \times 0.07$
Crystal system	Orthorhombic	Orthorhombic	Orthorhombic
Space group	<i>Pbca</i> (No. 61)	<i>Pbca</i> (No. 61)	<i>Pbca</i> (No. 61)
<i>a</i> (Å)	13.4963(13)	13.6579(16)	14.524(2)
<i>b</i> (Å)	11.0106(10)	11.2066(14)	11.1777(11)
<i>c</i> (Å)	16.7586(16)	16.926(2)	17.2573(18)
<i>V</i> (Å ³)	2490.4(4)	2590.7(5)	2801.7(6)
<i>Z</i>	8	8	8
D_{calc} (Mg m^{-3})	1.459	1.643	1.671
λ (Å)	0.71073	0.71073	0.71073
μ (mm^{-1})	34.20	25.87	58.95
θ Range (°)	2.43–28.00	2.64–26.00	2.36–28.00
Total number of reflections collected	26226	16555	13293
Number of independent reflections	2989	2474	3387
Number of reflections with $[I > 2\sigma(I)]$	2617	2237	2771
Number of parameters refined	136	136	145
Final $R_1(I > 2\sigma(I))$, wR_2	0.0231, 0.0589	0.0218, 0.0427	0.0222, 0.0457

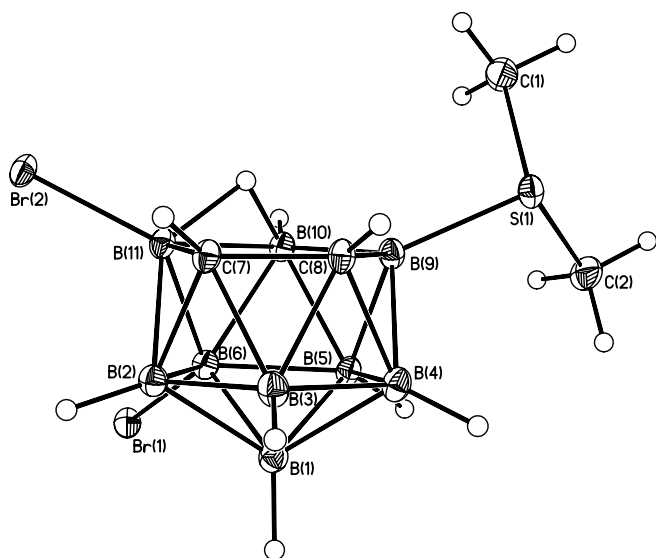


Fig. 4. Molecular structure of [9-Me₂S-6,11-Br₂-7,8-C₂B₉H₉] (**5**).

The B–I bond length in **3** is 2.197(3) Å, that is identical to a similar bond found in [9-Py-11-I-7,8-C₂B₉H₁₀] (2.197(3) Å) [16] and some shorter than in (Me₃NH)[nido-

Table 2
Selected bond distances (Å) for **2**, **3**, **5** and [9-Me₂S-7,8-C₂B₉H₁₁] (**D**) [25]

	2	3	5	D ^a
B(9)–S(1)	1.8763(18)	1.873(3)	1.883(3)	1.884(3)
B(11)–X(Br,I)	1.9855(17)	2.197(3)	1.978(3)	–
B(6)–X(Br)	–	–	1.971(2)	–
C(7)–C(8)	1.547(2)	1.544(3)	1.540(3)	1.528(4)
C(8)–B(9)	1.595(2)	1.595(3)	1.598(3)	1.577(4)
C(7)–B(11)	1.620(2)	1.620(3)	1.624(3)	1.618(5)
B(9)–B(10)	1.786(2)	1.785(4)	1.782(4)	1.774(4)
B(11)–B(10)	1.849(2)	1.848(4)	1.860(4)	1.847(5)
B(2)–C(7)	1.710(2)	1.700(3)	1.709(3)	1.685(5)
B(2)–B(11)	1.814(3)	1.808(4)	1.824(4)	1.798(5)
B(6)–B(11)	1.783(3)	1.778(4)	1.782(4)	1.776(5)

^a Average values for two independent molecules of **D**.

9-I-7,8-C₂B₉H₁₁] (2.309(9) Å) [8b]. The B–Br bond lengths in **2** (1.9855(17) Å) and **5** (1.978(3) and 1.971(2) Å) lie in the same range as the similar bonds in [1,7-(Me₂S)₂-9,10-Br₂B₁₂H₈] (1.966(11) and 1.982(10) Å) [18] and some shorter than those found in [3-Cp-4-Me₂S-7,8-Br₂-3,1,2-FeC₂B₉H₈] (1.992(3) and 1.998(3) Å) [7].

The crystal packing in compounds **2**, **3**, and **5** is defined mainly by the Van-der-Waals interactions, although one can notice the presence of C–H···X hydrogen bonds. For **2** and **3** they are similar and formed by the H(7) atom of the CH carborane group and the bromine (Br(1)) (**2**) or iodine (I(1)) (**3**) atoms (Fig. S5). The parameters of the hydrogen bond are: C(7)–H(7) 0.944, H(7)···Br(1A) 3.021, C(7)···Br(1A) 3.762(3) Å, angle C(7)–H(7)–Br(1A) 136° for **2** and C(7)–H(7) 0.869, H(7)···I(1A) 3.179, C(7)···I(1A) 3.865(2) Å, angle C(7)–H(7)–I(1A) 138° for **3**.

The intermolecular interaction network in structure of **5** differs from those found in **2** and **3**. Unlike to **2** and **3**, the bromine atom Br(2) bonded to B(11) does not form intermolecular interactions while the second bromine atom Br(1) is bonded to H(4) atom of the B–H group (distances: B(4A)–H(4A) 1.087, Br(1)···H(4A) 3.040, B(4A)···Br(1) 4.082(2) Å, angle B(4A)–H(4A)–Br(1) 161°) as well as to the *exo*-polyhedral hydrogen atom (distance H(10B)···Br(1) 2.877 Å) (see Fig. 6). At the first sight the formation of such intermolecular interactions seems unlikely as both interacting atoms have negative charges. However, recent investigations of crystal packages of carboranes have shown that similar B–H···H–B interactions do exist and contribute significantly to the overall lattice energy [26]. The similar type of intermolecular interaction was found recently in structure of [9-Py-11-I-7,8-C₂B₉H₁₀] [16]. So, the possibility of the formation of the B–H···Br hydrogen bonds in the case of **5** cannot be discarded especially taking into account their directionality.

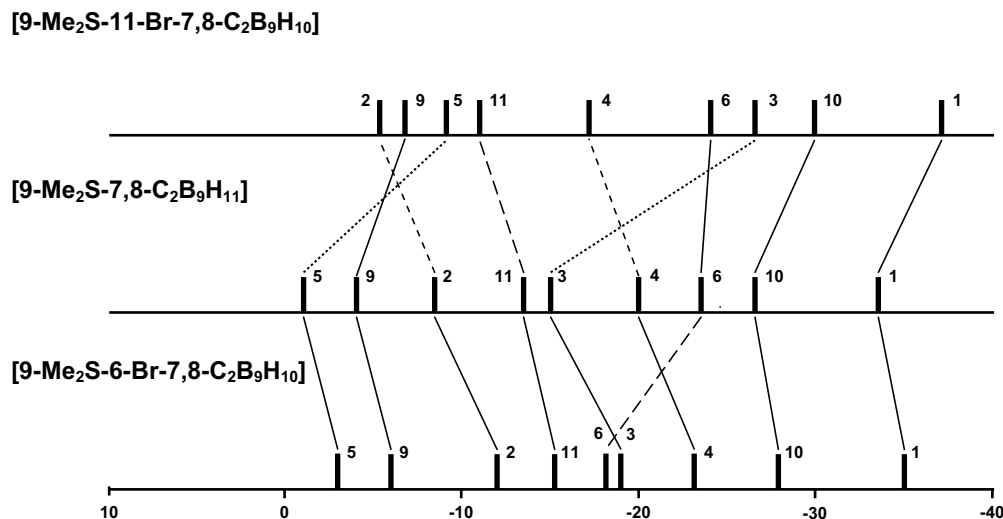


Fig. 5. Stick diagram of ¹¹B NMR chemical shifts for [9-Me₂S-7,8-C₂B₉H₁₁] [23], [9-Me₂S-11-Br-7,8-C₂B₉H₁₀] (**2**), and [9-Me₂S-6-Br-7,8-C₂B₉H₁₀] (**4**).

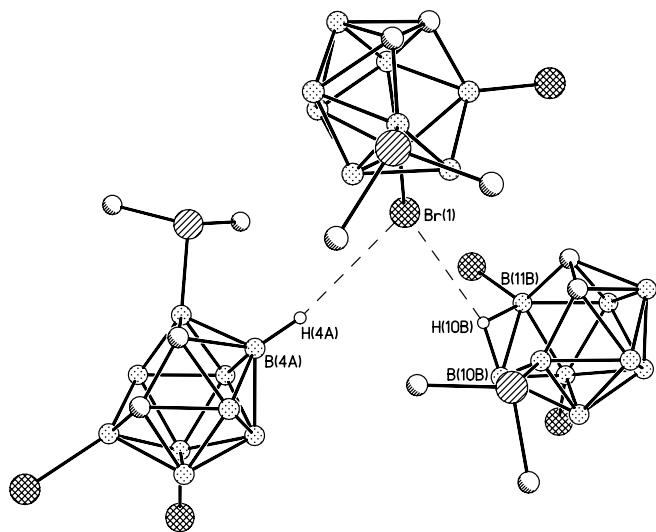


Fig. 6. Hydrogen bonding at the Br(1) bromine atom in the structure of [9-Me₂S-6,11-Br₂-7,8-C₂B₉H₁₁] (5).

3. Experimental

[9-SMe₂-7,8-C₂B₉H₁₁] [17] and (Et₄N)[9-I-7,8-C₂B₉H₁₁] [27] were prepared using the literature procedures. All other reagents were commercially available and used without further purification. ¹H and ¹¹B NMR spectra were collected using Bruker AM 360, Bruker Avance 400 and Bruker Avance 500 spectrometers. Elemental analyses were performed at Laboratory of Microanalysis of Institute of Organoelement Compounds (Moscow) and at Institute of Physical Organic Chemistry (Minsk).

3.1. Synthesis of [9-Me₂S-11-Cl-7,8-C₂B₉H₁₀] (1)

To the solution of 0.91 g (4.7 mmol) of [9-Me₂S-7,8-C₂B₉H₁₁] in 15 ml of acetonitrile 0.94 g (4.7 mmol) of *N*-chlorosuccinimide was added. The reaction mixture was stirred for 4 h and poured into cold water. The precipitate formed was filtered, dried and recrystallized from acetone–Et₂O mixture (1:1) giving 0.48 g (45%) of the product. M.p. 148–150 °C. ¹¹B NMR (acetone-*d*₆, ppm): −5.1 (1B, s, B(9)), −5.6 (1B, d, *J* = 146 Hz, B(2)), −10.4 (2B, d, *J* = 134 Hz, B(5, 11)), −17.4 (1B, d, *J* = 163 Hz, B(4)), −23.6 (1B, d, *J* = 153 Hz, B(6)), −26.3 (1B, d, *J* = 153 Hz, B(3)), −30.3 (1B, d, *J* = 146 Hz, B(10)), −36.3 (1B, d, *J* = 147 Hz, B(1)). ¹H NMR (acetone-*d*₆, ppm): 2.94 (3H, s, *Me*-S), 2.87 (1H, s, *CH*_{carb}), 2.77 (3H, s, *Me*-S), 2.48 (1H, s, *CH*_{carb}), −1.4 to −2.1 (1H, br. s, *BH*¹⁰). Anal. Calc. for C₄H₁₆B₉ClS: C, 20.98; H, 7.04; B, 42.49; Cl, 14.00; S, 15.48. Found: C, 20.94; H, 7.45; B, 42.64; Cl, 14.42; S, 15.09%.

3.2. Synthesis of [9-Me₂S-11-Br-7,8-C₂B₉H₁₀] (2) and [9-Me₂S-6-Br-7,8-C₂B₉H₁₀] (4)

Solution of 0.6 ml (11.5 mmol) of bromine in 2 ml of dichloromethane was added to solution of 1.96 g

(10.0 mmol) of [9-Me₂S-7,8-C₂B₉H₁₁] in 20 ml of dichloromethane at ambient temperature. The reaction mixture was stirred for 1 h and solvent was removed *in vacuo*. The residue was dissolved in 75 ml of dichloromethane, solution was dried over anhydrous K₂CO₃, and evaporated to dryness *in vacuo*. The isomers formed were separated by column chromatography on silica using the petroleum ether–dichloromethane mixture (1:1) as the eluent. The first fraction gave 1.67 g (61%) of isomer 2, and the second fraction gave 0.49 g (18%) of isomer 4.

2: M.p. 178 °C. ¹¹B NMR (CDCl₃, ppm): −5.7 (1B, d, *J* = 159 Hz, B(2)), −6.8 (1B, s, B(9)), −9.4 (1B, d, *J* = 167 Hz, B(5)), −11.1 (1B, s, B(11)), −17.6 (1B, d, *J* = 170 Hz, B(4)), −24.2 (1B, d, *J* = 149 Hz, B(6)), −26.8 (1B, d, *J* = 156 Hz, B(3)), −29.9 (1B, d, *J* = 138 Hz, B(10)), −36.2 (1B, d, *J* = 144 Hz, B(1)). ¹H NMR (CDCl₃, ppm): 2.80 (3H, s, *Me*-S), 2.61 (4H, s, *Me*-S+*CH*_{carb}), 2.53 (1H, s, *CH*_{carb}), −1.5 to −2.3 (1H, br. s, *BH*¹⁰). Anal. Calc. for C₄H₁₆B₉BrS: C, 17.57; H, 5.90; B, 35.58. Found: C, 17.54; H, 6.07; B, 35.50%.

4: M.p. 132 °C. ¹¹B NMR (acetone-*d*₆, ppm): −3.1 (1B, d, *J* = 142 Hz, B(5)), −5.9 (1B, s, B(9)), −11.9 (1B, d, *J* = 159 Hz, B(2)), −15.6 (1B, d, *J* = 143 Hz, B(11)), −18.4 (1B, s, B(6)), −18.8 (1B, d, *J* = 162 Hz, B(3)), −23.1 (1B, d, *J* = 119 Hz, B(4)), −27.7 (1B, d, *J* = 130 Hz, B(10)), −35.1 (1B, d, *J* = 146 Hz, B(1)). ¹H NMR (CDCl₃, ppm): 2.78 (3H, s, *Me*-S), 2.65 (3H, s, *Me*-S), 2.52 (1H, s, *CH*_{carb}), 2.35 (1H, s, *CH*_{carb}), −2.2 to −2.8 (1H, br. s, *BH*¹⁰).

3.3. Synthesis of [9-Me₂S-6,11-Br₂-7,8-C₂B₉H₉] (5)

Solution of 1.0 ml of bromine (20.0 mmol) in 20 ml of dichloromethane was added to solution of 0.98 g (5.0 mmol) of [9-Me₂S-7,8-C₂B₉H₁₁] in 25 ml of dichloromethane. The reaction mixture was stirred for 30 min at room temperature and heated under reflux for 1 h. Solvent removed *in vacuo*, 50 ml of ethanol was added, the mixture was poured in water and extracted with dichloromethane (3 × 50 ml), the organic phase was dried over anhydrous sodium sulfate, filtered and evaporated to dryness. The residue was recrystallized from CH₂Cl₂–hexane to give 1.55 g (88%) of the product. M.p. 152 °C. ¹¹B NMR (CDCl₃, ppm): −4.3 (1B, d, *J* = 149 Hz, B(2)), −6.9 (1B, s, B(9)), −8.8 (1B, d, *J* = 154 Hz, B(5)), −11.2 (1B, s, B(11)), −17.5 (1B, s, B(6)), −18.7 (1B, d, B(4)), −26.1 (1B, d, *J* = 162 Hz, B(3)), −27.6 (1B, d, *J* = 179 Hz, B(10)), −34.5 (1B, d, *J* = 148 Hz, B(1)). ¹H NMR (CDCl₃, ppm): 2.81 (3H, s, *Me*-S), 2.76 (1H, s, *CH*_{carb}), 2.66 (3H, s, *Me*-S), 2.59 (1H, s, *CH*_{carb}), −1.0 to −1.8 (1H, br. s, *BH*¹⁰). Anal. Calc. for C₄H₁₅B₉Br₂S: C, 13.64; H, 4.29; B, 27.61. Found: C, 13.60; H, 4.23; B, 27.53%.

3.4. Synthesis of [9-Me₂S-11-I-7,8-C₂B₉H₁₀] (3)

A. To solution of 1.96 g (10.0 mmol) of [9-Me₂S-7,8-C₂B₉H₁₁] in 50 ml of glacial acetic acid 3.92 g (15.4 mmol)

of iodine was added. The reaction mixture was heated at reflux for 4 days. The precipitate formed was filtered, washed by glacial acetic acid (2 × 15 ml) and hexane (2 × 40 ml) and recrystallized from dichloromethane–hexane to give 1.20 g (37%) of the product.

B. Twenty-five milliliters of concentrated sulfuric acid was added slowly at 30 ± 5 °C to the solution of 3.57 g (9.2 mmol) of (Et₄N)[9-I-7,8-C₂B₉H₁₁] in 35 ml of dimethylsulfoxide. The reaction mixture was stirred at room temperature overnight and diluted with water up to 250 ml. The precipitate obtained was filtered, washed with 3 × 20 ml of water, dissolved in 50 ml of acetone and precipitated with ether. The precipitate formed was filtered, recrystallized from acetone–Et₂O mixture (1:1) and dried *in vacuo* to give 2.29 g (78%) of the product. M.p. 187–189 °C. ¹¹B NMR (acetone-*d*₆, ppm): –5.0 (2B, d + s, B(2,9)), –10.2 (1B, d, *J* = 159 Hz, B(5)), –17.3 (1B, d, *J* = 163 Hz, B(4)), –23.5 (1B, d, *J* = 155 Hz B(6)), –24.8 (1B, d, *J* = 169 Hz, B(3)), –26.6 (1B, s, B(11)), –29.5 (1B, d, *J* = 143 Hz, B(10)), –36.0 (1B, d, *J* = 144 Hz, B(1)). ¹H NMR (acetone-*d*₆, ppm): 2.97 (4H, s, Me–S+CH_{carb}), 2.80 (3H, s, Me–S), 2.53 (1H, s, CH_{carb}), –1.4 to –2.3 (1H, br. s, BH¹⁰). Anal. Calc. for C₄H₁₆B₉IS: C, 14.99; H, 5.03; B, 30.36; I, 39.60; S, 10.01. Found: 15.25; H, 5.27; B, 30.42; I, 39.44; S, 10.35%.

3.5. X-ray diffraction study

Single crystals suitable for X-ray diffraction study were grown up by slow evaporation of solution in acetone for **3**, and by recrystallization from dichloromethane–heptane for **2** and **5**, respectively. X-ray data for compounds **2**, and **5** were recorded on a Bruker SMART APEX2 CCD area detector and **3** on Bruker SMART 1000 CCD area detector diffractometers, using Mo K α radiation (λ = 0.71073 Å) at 100(2) (for **2** and **5**) and 120(3) K (for **3**). The reflection intensities were integrated using SAINT software [28] and the absorption correction was applied semi-empirically using SADABS program [29]. The structure was solved by direct method and refined by the full-matrix least squares method against *F*² in anisotropic (for non-hydrogen atoms) and isotropic (for H atoms) approximation. All hydrogen atoms were located from the difference Fourier synthesis and refined in riding model. All calculations were performed using the SHELXTL software [30]. The data collection and refinement parameters are summarized in Table 1.

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Appendix A. Supplementary material

CCDC 642783, 642782 and 642784 contain the supplementary crystallographic data for **2**, **3** and **5**. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorgchem.2007.07.036.

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