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$[C_2B_{10}]$–$[B_{12}]$ double cage boron compounds—a new approach to the synthesis of water-soluble boron-rich compounds for BNCT

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Dedicated to Professor M.F. Hawthorne on the occasion of his 75th birthday

Abstract

A new approach in the synthesis of water-soluble boron-rich compounds was proposed. The *closo*-dodecaborate cage is used as a hydrophilic substitutent providing for the water-solubility of the molecule whereas the carborane cage can be used for attachment to biomolecules using earlier developed methods. The double-cage molecules [*o*-, *m*-, and *p*-$CB_{10}H_{10}C(CH_2)_4OB_{12}H_{11}]^{2-}$ were prepared by the reaction of the tetramethylene oxonium derivative of the *closo*-dodecaborate anion, $[B_{12}H_{11}O(CH_2)_4]^-$, with the corresponding lithiated carboranes. The compounds obtained have doubled the boron contents and could serve for the synthesis of agents for boron neutron capture therapy (BNCT).

Keywords: Dodecahydro-*closo*-dodecaborate; *o*-Carborane; *m*-Carborane; *p*-Carborane; Boron neutron capture therapy

1. Introduction

The first icosahedral boron hydrides, dodecahydro-*closo*-dodecaborate anion $[B_{12}H_{12}]^{2-}$ and 1,2-, 1,7-, and 1,12-dicarba-*closo*-dodecaboranes $C_2B_{10}H_{12}$, have been known from the beginning of the 1960s [1,2]. However, up to now, the development of their chemistry, which has been connected mainly with boron neutron capture therapy (BNCT) [3,4], resembles two sprouts having the same root—they grow close together, their branches interlace here and there, but they look completely different, where one of them is grafted and rich in fruits and the other is wilding and practically fruitless. The first sprout is the carborane cage engrafted with organic chemistry through the two carbon atoms [5,6]. It should be noted, however, that not all fruits from the carborane tree are good for a BNCT compote. The inherent drawback of carboranes is their extreme lipophilicity, often rendering potentially bioactive structures, which contain them, water-insoluble. The exceptionally hydrophobic character and spherical geometry of carboranes may allow their use as a hydrophobic pharmacophore in biologically active molecules that can interact hydrophobically with the receptors [7]. However, one of the main requirements for BNCT agents is their water solubility. Previous methods of increasing the water solubility of carborane-containing molecules included the introduction of various hydrophilic substituents, such as a polyol cascade [8], polyamines [9], sugars [10], have been elaborated but in many cases these have failed to give good solutions to the problem. The salts of *closo*-dodecaborane anion and its derivatives, in contrast, have as high water solubility as the sodium salts of inorganic acids; however, in comparison with the carboranes there has been very little development. Several attempts have been made to develop the study of the $[B_{12}H_{12}]^{2-}$ chemistry further for the purposes of BNCT during recent years [11]; however, the problem still exists.

In this contribution, we propose to combine the advantages of these two boron cages in one molecule: the *closo*-dodecaborate cage serves as a hydrophilic

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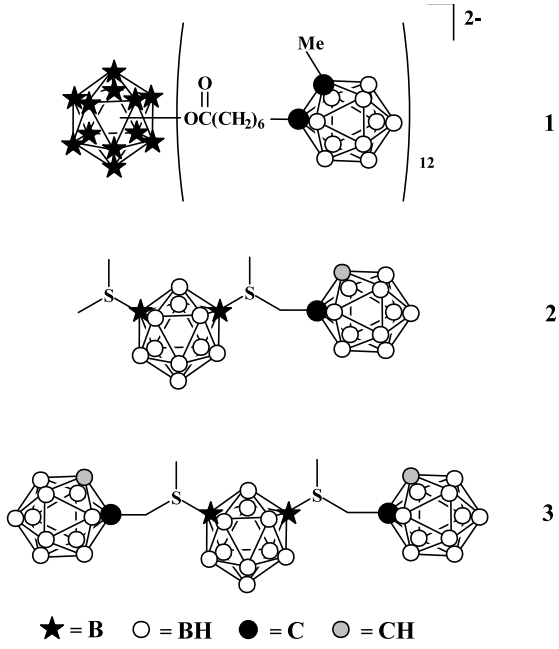
substitutent providing for the water solubility of the molecule and the carborane cage serves as the base for the attachment to biomolecules using the earlier developed methods. This also allows us to double the boron content of the biomolecule as compared to the single-cage approach. Moreover, by changing the type and the size of a spacer between these two boron cages, it is possible to control, to some extent, the hydrophilic–hydrophobic balance of the compounds. As the first step in the realization of this approach we have used the previously developed method of functionalization of the $[B_{12}H_{12}]^{2-}$ anion via its tetramethylene oxonium derivative [12].

2. Results and discussion

In spite of the 40-years of adjacent histories of carborane and *closo*-dodecaborate chemistry, no attempt to combine these boron clusters in one molecule was described until recently. The first system containing both the *closo*-dodecaborate and carborane cages was reported in 2001 by Hawthorne who prepared a dodeca(carboranyl)-substituted closomer $[B_{12}(\text{-}1\text{-}OCO(CH_2)_6\text{-}2\text{-}CH_3\text{-}1,2\text{-}C_2B_{10}H_{10})_{12}]^{2-}$ (**1**) (Scheme 1) by the reaction of dodecahydroxy dodecaborate $[B_{12}(OH)_{12}]^{2-}$ with the corresponding carborane-containing acid chloride [13]. Unfortunately, this compound is practically insoluble in water and has very limited resources for subsequent functionalization. More recently, in 2002, two more examples of systems containing both the *closo*-dodecaborate and carborane cages [1-(1,2-$C_2B_{10}H_{11}$-1-CH_2)(CH_3)S-7-$(CH_3)_2SB_{12}H_{10}$] (**2**) and



Scheme 1.

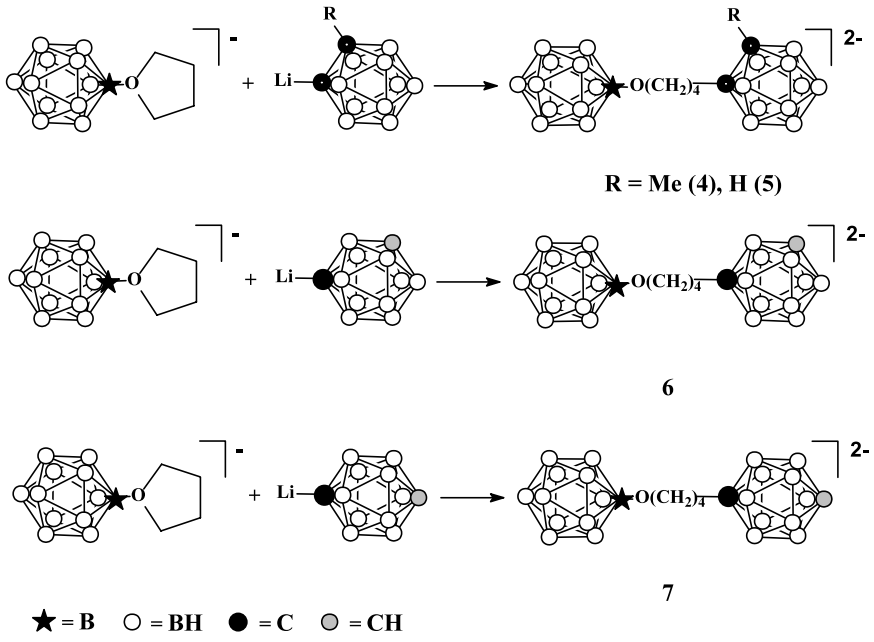
[1,7-{(1,2-$C_2B_{10}H_{11}$-1-CH_2)–$(CH_3)S\}_2B_{12}H_{10}$] (**3**) were reported [14]. These compounds have been accessible for subsequent functionalization CH carborane groups, but they are completely insoluble in water and their syntheses require multi-step procedures resulting in low yields of the goal compounds.

In this communication, we describe the synthesis of the $[C_2B_{10}]$–$[B_{12}]$ double cage compounds by the reaction of lithium derivatives of carboranes with tetramethylene oxonium derivative of the *closo*-dodecaborate anion, $[B_{12}H_{11}O(CH_2)_4]^-$. Recently, we have found that the attack of the tetramethylene oxonium derivative of the *closo*-dodecaborate anion, $[B_{12}H_{11}O(CH_2)_4]^-$, by nucleophilic reagents results in the ring opening reaction giving $[B_{12}H_{11}O(CH_2)_4Nu]^{2-}$ derivatives [12]. The same approach was used here to synthesize compounds containing the *closo*-dodecaborate and the carborane cages.

The addition of carboranes to electrophiles is one of the most important reactions in the synthesis of carborane-containing organic molecules. The C-metallated carboranes are widely utilized for the carbon–carbon bond formation [5]. Both ethylene oxide [15] and oxetane [16] cycles are known to react with the C-metallated carboranes giving primary alcohols via the ring opening reactions. We found here that lithium derivatives of carboranes are able to open the five-atom oxonium cycle in $[B_{12}H_{11}O(CH_2)_4]^-$ giving the corresponding $[C_2B_{10}]$–$(CH_2)_4O$–$[B_{12}]^{2-}$ derivatives.

Methyl-*o*-carborane was used as a model system to determine the possibility of the ring-opening reaction under steric hindrance conditions. The reaction of 1-lithio-2-methyl-*o*-carborane with $(Bu_4N)[B_{12}H_{11}O(CH_2)_4]$ in tetrahydrofuran was found to give, smoothly, the double-cage moiety $[B_{12}H_{11}O(CH_2)_4$-1,2-$CB_{10}H_{10}CMe]^{2-}$ (**4**) (Scheme 2) in a high yield. The *closo*-dodecaborate-*o*-carborane compound with a free *CH* group $[B_{12}H_{11}O(CH_2)_4$-1,2-$CB_{10}H_{10}CH]^{2-}$ (**5**) was prepared by the reaction of 1-lithio-*o*-carborane (prepared by treatment of *o*-carborane with one equivalent of *n*-butyllithium in 1,2-dimethoxyethane at 0 °C [17]) with $[B_{12}H_{11}O(CH_2)_4]^-$. The *closo*-dodecaborate-*m*- and -*p*-carboranes ($[B_{12}H_{11}O(CH_2)_4$-1,7-$CB_{10}H_{10}CH]^{2-}$ (**6**) and $[B_{12}H_{11}O(CH_2)_4$-1,12-$CB_{10}H_{10}CH]^{2-}$ (**7**)) were prepared by the reaction of 1-lithio-*m*- and -*p*-carboranes, respectively, with $[B_{12}H_{11}O(CH_2)_4]^-$ in tetrahydrofuran. A fourfold excess of the carborane was used to suppress the undesirable formation of the 1,7- and 1,12-dilithio derivatives. The unreacted carborane can be recycled easily during work-up of the reaction mixture.

The compounds prepared were isolated as tetra-*n*-butylammonium or cesium (in the case of *p*-carborane) salts. One equivalent of tetrabutylammonium bromide was added during the work-up to compensate for an increase of charge of the molecule from mono- to



Scheme 2.

dianionic one. In one of experiments with methyl-*o*-carborane without the addition of Bu_4NBr, the reaction products were isolated after the chromatography work-up as the lithium $Li_2[B_{12}H_{11}O(CH_2)_4$-1,2-$CB_{10}H_{10}CMe] \times nH_2O$ and tetrabutylammonium $(Bu_4N)_2[B_{12}H_{11}O(CH_2)_4$-1,2-$CB_{10}H_{10}CMe]$ salts. The tetrabutylammonium salt was converted to the corresponding sodium salt $Na_2[B_{12}H_{11}O(CH_2)_4$-1,2-$CB_{10}H_{10}CMe] \times nH_2O$ by passing a methanol solution through an ion-exchange column with Amberlite IR120(H^+) resin followed by neutralization of the acidic eluate with Na_2CO_3. The lithium and sodium salts were found to have good solubility in water (> 100 g l^{-1}) justifying, in a way, our approach to the synthesis of water-soluble carboranes.

The double-cage boron compounds described here can be attached to biomolecules via the free carborane carbon atom using earlier developed methods. The reverse approach that includes functionalization of the carborane cage at the first step and attachment of the *closo*-dodecaborate cage at the second step may serve as a reasonable alternative.

3. Experimental

Tetrabutylammonium tetramethyleneoxonium-undecahydro-*closo*-dodecaborate(1-), $(Bu_4N)[B_{12}H_{11}O(CH_2)_4]$, was prepared as described in the literature [12]. Both the THF and 1,2-dimethoxyethane were freshly distilled from sodium benzophenone ketyl immediately prior to use. The ^{1}H- and ^{13}C-NMR spectra were collected using a Varian Gemini 200 spectrometer and referenced to Me_4Si, whereas the ^{11}B-NMR spectra were collected using a Varian Unity 400 instrument with $BF_3 \cdot OEt_2$ as the external standard. IR spectra were obtained on a Perkin–Elmer 1760 FTIR spectrometer. Elemental analyses were performed in the Laboratory of Microanalysis of the Institute of Organoelement Compounds (Moscow).

3.1. Synthesis of $(Bu_4N)_2[B_{12}H_{11}O(CH_2)_4$-1,2-$CB_{10}H_{10}CMe]$ (4)

0.25 ml (0.6 mmol) 2.5 M solution of *n*-butyllithium in hexane was added at 0 °C to a solution of 94 mg (0.6 mmol) methyl-*o*-carborane in 50 ml THF and the solution was stirred at 0 °C for 1 h. 230 mg (0.5 mmol) $(Bu_4N)[B_{12}H_{11}O(CH_2)_4]$ was added and the reaction mixture was stirred at 0 °C for 1 h and at room temperature (r.t.) overnight. 0.5 ml 2 M HCl and 160 mg (0.5 mmol) Bu_4NBr were added to the solution obtained. The solvent was distilled off in vacuo and the crude product was purified by chromatography on silica column with CH_2Cl_2–MeOH 9:1 as the eluent to give 370 mg (89%) of off-white amorphous solid. ^{1}H-NMR ($CDCl_3$, ppm): 3.55 (2H, t, $-OCH_2CH_2CH_2CH_2-$), 3.22 (16H, m, Bu_4N^+), 2.25 (2H, t, $-OCH_2CH_2CH_2CH_2-$), 2.03 (3H, s, CH_3), 1.60 (16H, m, Bu_4N^+), 1.44 (20H, m, $-OCH_2CH_2CH_2CH_2- + Bu_4N^+$), 0.98 (24H, t, Bu_4N^+); ^{13}C-NMR (Me_2SO-d_6, ppm): 80.1, 76.1, 67.1, 57.5 (Bu_4N^+), 34.2, 30.7, 26.9, 23.1 (Bu_4N^+), 22.7, 19.2 (Bu_4N^+), 13.5 (Bu_4N^+); ^{11}B-NMR (Me_2SO-d_6, ppm): 6.7 (1B, s, B_{12}), −(4–11) (10B, m, C_2B_{10}), −16.5 (5B, d, B_{12}), −18.0 (5B, d, B_{12}), −22.7 (1B, d, B_{12}); IR ($CHCl_3$, cm^{-1}): 2580 (ν_{BH}-C_2B_{10}), 2477 (ν_{BH}-B_{12}). Anal. Calc.

for $C_{39}H_{104}B_{22}N_2O$: C, 54.78; H, 12.26; B, 27.81; N, 3.28. Found: C, 54.67; H, 12.29; B, 27.74; N, 3.35%.

3.2. Synthesis of $(Bu_4N)_2[B_{12}H_{11}O(CH_2)_4$-1,2-$CB_{10}H_{10}CH]$ (5)

0.37 ml (0.6 mmol) 1.6 M solution of *n*-butyllithium in hexane was added at 0 °C to solution of 85 mg (0.6 mmol) *o*-carborane in 50 ml 1,2-dimethoxyethane and the solution was stirred at 0 °C for 1 h. 230 mg (0.5 mmol) $(Bu_4N)[B_{12}H_{11}O(CH_2)_4]$ was added and the reaction mixture was stirred at 0 °C for 1 h and at r.t. overnight. 0.5 ml 2 M HCl and 160 mg (0.5 mmol) Bu_4NBr were added to the solution obtained. Solvent was distilled off in vacuo and the crude product was purified by column chromatography on silica with CH_2Cl_2–MeOH 9:1 as the eluent to give 360 mg (86%) of off-white solid. ^{1}H-NMR ($CDCl_3$, ppm): 3.95 (1H, s, CH_{carb}), 3.56 (2H, t, –OCH_2CH$_2$CH$_2$CH$_2$–), 3.25 (16H, m, Bu_4N^+), 2.31 (2H, t, –OCH$_2$CH$_2$CH$_2$CH_2–), 1.61 (16H, m, Bu_4N^+), 1.43 (20H, m, –OCH$_2$CH_2CH_2CH$_2$–+Bu_4N^+), 0.97 (24H, t, Bu_4N^+); ^{13}C-NMR ($CDCl_3$, ppm): 77.2, 67.9, 61.5, 58.8 (Bu_4N^+), 37.3, 30.5, 26.4, 24.0 (Bu_4N^+), 19.6 (Bu_4N^+), 13.7 (Bu_4N^+); ^{11}B-NMR ($CDCl_3$, ppm): 6.7 (1B, s, B_{12}), −2.8 (2B, d, C_2B_{10}), −9.6 (4B, d, C_2B_{10}), −11.2 (2B, d, C_2B_{10}), −13.6 (2B, d, C_2B_{10}), −16.4 (5B, d, B_{12}), −17.8 (5B, d, B_{12}), −22.7 (1B, d, B_{12}); IR ($CHCl_3$, cm^{-1}): 3040 (ν_{CH}-C_2B_{10}), 2575 (ν_{BH}-C_2B_{10}), 2475 (ν_{BH}-B_{12}). Anal. Calc. for $C_{38}H_{102}B_{22}N_2O$: C, 54.27; H, 12.22; B, 28.28; N, 3.33. Found: C, 54.13; H, 12.23; B, 28.30; N, 3.42%.

3.3. Synthesis of $(Bu_4N)_2[B_{12}H_{11}O(CH_2)_4$-1,7-$CB_{10}H_{10}CH]$ (6)

0.37 ml (0.6 mmol) 1.6 M solution of *n*-butyllithium in hexane was added at −78 °C to the solution of 360 mg (2.5 mmol) *m*-carborane in 50 ml THF and the solution was stirred for 2 h. The temperature was raised to −30 °C and 230 mg (0.5 mmol) $(Bu_4N)[B_{12}H_{11}O(CH_2)_4]$ was added. The reaction mixture was slowly warmed up to 10 °C overnight and then refluxed for 2 h. The reaction mixture was cooled to r.t. and 0.5 ml 2 M HCl and 160 mg (0.5 mmol) Bu_4NBr were added to the solution obtained. The solvent was distilled off in vacuo and the crude product was purified by column chromatography on silica with CH_2Cl_2–MeOH 6:1 as the eluent to give 300 mg (72%) of off-white solid. ^{1}H-NMR (MeOH-d_4, ppm): 3.49 (2H, t, –OCH_2CH$_2$CH$_2$CH$_2$–), 3.44 (1H, s, CH_{carb}), 3.26 (16H, m, Bu_4N^+), 1.98 (2H, m, –OCH$_2$CH$_2$CH$_2$CH_2–), 1.67 (16H, m, Bu_4N^+), 1.43 (20H, m, –OCH$_2$CH_2CH_2CH$_2$–+Bu_4N^+), 1.02 (24H, t, Bu_4N^+); ^{13}C-NMR (MeOH-d_4, ppm): 78.6, 69.6, 59.5 (Bu_4N^+), 56.7, 38.2, 32.0, 28.0, 24.9 (Bu_4N^+), 20.7 (Bu_4N^+), 14.1 (Bu_4N^+); ^{11}B-NMR (MeOH-d_4, ppm): 6.5 (1B, s, B_{12}), −4.2 (1B, d, C_2B_{10}), −11.0 (5B, d, C_2B_{10}), −13.6 (2B, d, C_2B_{10}), −15.2 (2B, d, C_2B_{10}), −16.4 (5B, d, B_{12}), −18.2 (5B, d, B_{12}), −23.0 (1B, d, B_{12}); IR ($CHCl_3$, cm^{-1}): 3033 (ν_{CH}-C_2B_{10}), 2598 (ν_{BH}-C_2B_{10}), 2482 (ν_{BH}-B_{12}). Anal. Calc. for $C_{38}H_{102}B_{22}N_2O$: C, 54.27; H, 12.22; B, 28.28; N, 3.33. Found: C, 54.19; H, 12.07; B, 28.23; N, 3.34%.

3.4. Synthesis of $Cs_2[B_{12}H_{11}O(CH_2)_4$-1,12-$CB_{10}H_{10}CH]$ (7)

The reaction was carried out as described above using 360 mg (2.5 mmol) *p*-carborane, 0.37 ml (0.6 mmol) 1.6 M solution of *n*-butyllithium in hexane, and 230 mg (0.5 mmol) $(Bu_4N)[B_{12}H_{11}O(CH_2)_4]$. The crude product after column chromatography (silica) was dissolved in 15 ml CH_3OH and treated with 300 mg (2.0 mmol) cesium fluoride in 10 ml CH_3OH. The precipitate formed was filtered, washed with CH_3OH and dried over P_2O_5 to give 230 mg (77%) of white solid. ^{1}H-NMR (Me_2SO-d_6, ppm): 3.62 (1H, s, CH_{carb}), 3.10 (2H, t, –OCH_2CH$_2$CH$_2$CH$_2$–), 1.57 (2H, t, –OCH$_2$CH$_2$CH$_2$CH_2–), 1.08 (4H, m, –OCH$_2$CH_2CH_2CH$_2$–); ^{13}C-NMR (Me_2SO-d_6, ppm): 85.0, 67.4, 58.8, 38.4, 31.1, 26.2; ^{11}B-NMR (Me_2SO-d_6, ppm): 6.3 (1B, s, B_{12}), −12.6 (5B, d, C_2B_{10}), −15.1 (5B, d, C_2B_{10}), −16.8 (5B, d, B_{12}), −18.2 (5B, d, B_{12}), −22.8 (1B, d, B_{12}); IR ($CHCl_3$, cm^{-1}): 3051 (ν_{CH}-C_2B_{10}), 2606 (ν_{BH}-C_2B_{10}), 2474 (ν_{BH}-B_{12}). Anal. Calc. for $C_6H_{30}B_{22}Cs_2$: C, 11.59; H, 4.86; B, 38.24. Found: C, 11.47; H, 4.88; B, 38.08%.

Acknowledgements

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