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RESEARCH ARTICLE

Interaction of the anion $[2\text{-}B_{10}H_9O(CH_2)_4O]^-$ with secondary amines

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Abstract

Objectives. *One of the most promising methods of treating malignant tumors is ^{10}B-neutron capture therapy. While compounds based on cluster boron anions $[B_nH_n]^{2-}$ (n = 10, 12) are often used as boron-containing agents due to the very high specific concentration of boron atoms per particle, the use of such compounds is associated with the need to develop new methods for the functionalization of boron clusters associated with the production of boron-containing derivatives containing biologically active functional groups. One of the most convenient methods of modification of $[B_nH_n]^{2-}$ (n = 10, 12) anions is the interaction of their derivatives containing cyclic oxonium-type substituents with negatively charged or neutral nucleophilic reagents. The disclosure of substituents of this type leads to the formation of closo-borates with functional groups separated from the cluster by an alkoxyl spacer chain. The purpose of this study is to develop methods for the synthesis of derivatives of the closo-decaborate anion $[B_{10}H_{10}]^{2-}$ with pendant nitrogen-containing groups.*

Methods. *The general control of the reactions of the disclosure of cyclic substituents was carried out on the basis of ^{11}B nuclear magnetic resonance (NMR) spectroscopy data. The structure of the obtained derivatives, including the nature of the attached functional groups, was determined using ^{1}H, ^{13}C attached proton test (APT) NMR and infrared (IR) spectroscopy data. The molecular weight of the synthesized compounds was confirmed by electrospray ionization mass-spectrometry (ESI–MS).*

Results. *The interaction of the anion $[2\text{-}B_{10}H_9O(CH_2)_4O]^-$ with secondary amines (dimethylamine, dipropylamine, diallylamine, dibutylamine, diisobutylamine, morpholine, di-sec-butylamine) in an ethanol environment is investigated. As a result of the reactions, a cyclic substituent is shown to expand with the addition of a nucleophilic reagent. Seven new derivatives of the closo-decaborate anion with pendant nitrogen-containing groups have been synthesized.*

Conclusions. *A developed method for obtaining closo-decaborates with ammonium groups separated from the boron cluster by an alkoxyl spacer group is presented. It is shown that the use of amines of various structures does not fundamentally affect the course of the reactions, allowing the composition and structure of the target derivatives to be effectively regulated. The resulting compounds can be involved in further modification reactions due to a reactive pendant group, as well as being suitable for use as effective polydentate ligands. Closo-decaborates with pendant nitrogen-containing groups and their derivatives are of considerable interest in the synthesis of compounds for use in ^{10}B-neutron capture therapy of malignant tumors.*

Keywords: *cluster boron anions, closo-decaborate anion, oxonium derivatives of closo-decaborate anion, disclosure of cyclic substituent, secondary amines, ^{10}B-neutron capture therapy of malignant tumors*

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НАУЧНАЯ СТАТЬЯ

Взаимодействие аниона $[2\text{-}B_{10}H_9O(CH_2)_4O]^-$ с вторичными аминами

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Аннотация

Цели. *^{10}B-нейтронозахватная терапия является одним из наиболее перспективных методов лечения злокачественных опухолей. В качестве борсодержащих агентов нередко применяются соединения на основе кластерных анионов бора $[B_nH_n]^{2-}$ (n = 10, 12), как имеющие очень высокую удельную концентрацию атомов бора в расчете на одну частицу. Однако использование таких соединений связано с необходимостью разработки новых методов функционализации борных кластеров, связанных*

с получением борсодержащих производных с биологически активными функциональными группами. Одним из наиболее удобных методов модификации анионов $[B_nH_n]^{2-}$ (n = 10, 12) является взаимодействие их производных, содержащих циклические заместители оксониевого типа, с отрицательно заряженными или нейтральными нуклеофильными реагентами. Раскрытие заместителей данного типа приводит к образованию клозо-боратов с функциональными группами, отделенными от кластера алкоксильной спейсерной цепочкой. Целью настоящего исследования является разработка методов синтеза производных клозо-декаборатного аниона $[B_{10}H_{10}]^{2-}$ с пендантными азотсодержащими группами.

Методы. *Общий контроль протекания реакций раскрытия циклических заместителей осуществлялся на основании данных ^{11}B спектроскопии ядерного магнитного резонанса (ЯМР). Строение полученных производных, в том числе природу присоединенных функциональных групп определяли на основании данных ^{1}H, ^{13}C ЯМР с тестом на присоединенные протоны (АРТ) и инфракрасной спектроскопии (ИК). Молекулярную массу синтезированных соединений подтверждали методом масс-спектрометрии с ионизацией электрораспылением (ИЭР-МС).*

Результаты. *Исследовано взаимодействие аниона $[2\text{-}B_{10}H_9O(CH_2)_4O]^-$ с вторичными аминами (диметиламин, дипропиламин, диаллиламин, дибутиламин, диизобутиламин, морфолин, ди-втор-бутиламин) в среде этанола. Показано, что в результате реакций происходит раскрытие циклического заместителя с присоединением нуклеофильного реагента. Синтезированы семь новых производных клозо-декаборатного аниона с пендантными азотсодержащими группами.*

Выводы. *Разработан новый метод получения клозо-декаборатов с аммониевыми группами, отделенными от борного кластера алкоксильной спейсерной группой. Показано, что применение аминов различного строения принципиально не влияет на ход протекающих реакций и позволяет эффективно регулировать состав и строение целевых производных. Полученные соединения могут быть вовлечены в дальнейшие реакции модификации за счет реакционноспособной пендантной группы, а также могут быть использованы в роли эффективных полидентатных лигандов. Клозо-декабораты с пендантными азотсодержащими группами и их производные представляют значительный интерес в синтезе соединений, перспективных для применения в ^{10}B-нейтронозахватной терапии злокачественных опухолей.*

Ключевые слова: *кластерные анионы бора, клозо-декаборатный анион, оксониевые производные клозо-декаборатного аниона, раскрытие циклического заместителя, вторичные амины, ^{10}B-нейтронозахватная терапия злокачественных опухолей*

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INTRODUCTION

Cluster boron anions $[B_nH_n]^{2-}$ (n = 10, 12) are one of the unique examples of completely inorganic clusters that are highly resistant to oxidizing agents and tend to replace *exo*-polyhedral hydrogen atoms with various functional groups [1–3]. Derivatives based on boron polyhedra of this class are increasingly being used in science and technology, with the medical field, namely, ^{10}B neutron capture therapy of malignant tumors, remaining one of the most significant areas [4–14]. In this regard, it is very important to develop new methods for the synthesis of *closo*-borates containing biologically active groups that can also be modified.

As well as being associated directly with the boron cluster, the functionalization of boron

cluster anions can involve already introduced functional groups. One of the main methods for the direct functionalization of $[B_nH_n]^{2-}$ (n = 10, 12) anions is electrophilic-induced nucleophilic substitution (EINS) of *exo*-polyhedral hydrogen atoms for various functional groups [15–19]. While this method can be used to obtain a wide range of *closo*-borates, its disadvantages are associated with the possible interaction of nucleophilic reagents with Lewis acids used to initiate such processes. By modifying the already introduced *exo*-polyhedral groups, it becomes possible to significantly expand the range of obtained boron-containing compounds. For example, in recent years, the method of modifying thiol and nitrile derivatives of $[B_nH_n]^{2-}$ anions has gained popularity [20–23]. However, it is often necessary to obtain compounds containing so-called pendant functional groups separated by a relatively inert fragment from the boron cluster in order to avoid the influence of the latter. Therefore, one of the most convenient methods for the functionalization of boron clusters involves the substitution of *exo*-polyhedral hydrogen atoms for molecules of cyclic ethers, followed by the opening of the resulting oxonium-type cyclic substituents with the help of nucleophiles. As a result of such reactions, *closo*-borates are formed with pendant functional groups attached to the boron cluster through an alkoxy spacer chain. Derivatives of $[B_nH_n]^{2-}$ anions with a given structure can be obtained by using a wide range of nucleophilic reagents [24–30].

The purpose of this work is to reveal the conditions and features of the interaction of the 1,4-dioxane derivative of the *closo*-decaborate anion, $[2\text{-}B_{10}H_9O(CH_2)_4O]^-$, with secondary amines (dimethylamine, dipropylamine, diallylamine, dibutylamine, diisobutylamine, di-*sec*-butylamine, morpholine), during which *closo*-decaborates with pendant ammonium groups are formed.

EXPERIMENTAL SECTION

Physical and chemical analysis methods

The infrared (IR) spectra of the compounds were recorded on an Infralum FT-02 IR Fourier spectrometer (*Lumex*, Russia) in the range 400–4000 cm^{-1}. Samples were prepared in the form of tablets from a mixture of the test compound and KBr. ^1H, ^{11}B, ^{13}C nuclear magnetic resonance (NMR) spectra of test substance solutions in fully deuterated dimethyl sulfoxide (DMSO-d_6) with attached proton test (APT) were recorded on a DPX-300 NMR spectrometer (*Bruker*, Germany) at frequencies of 300.3, 96.32, and 75.49 MHz, respectively, with internal deuterium stabilization. Mass spectra were recorded using a TSQ Quantum Access MAX triple quadrupole mass spectrometer (*Thermo Fisher Scientific*, USA) equipped with an API source (HESI-II), an Agilent 1200 G1311A four-channel pump (*Agilent*, USA), and a 6-port injector with an external volume loop of 0.002 cm^3. Samples were introduced into the ion source by manual loop injection into the solvent stream. Acetonitrile (ACN) for the high-performance liquid chromatography (HPLC) and deionized water obtained on a Milli-Q unit (*Millipore*, USA) were used as solvents. The pump flow was set at 0.4 mL/min in ACN/H_2O isocratic mode (50:50). Electrospray ionization (ESI) was carried out in the negative ion detection mode under the following conditions: sputtering voltage –2.5 kV, ion transfer tube temperature 350 °C, evaporator temperature 300 °C, gas pressure (N_2) 35 a.u., auxiliary gas flow rate 10 a.u. Mass spectra (MS) in the full scan mode were recorded in the range m/z 100–600. Data collection and processing was carried out using Xcalibur software (version 2.0).

Elemental analysis of the sample was performed on an ELAN DRC-e inductively coupled plasma mass spectrometer (*PerkinElmer*, USA). The content of carbon, hydrogen, and nitrogen in the samples was determined on a EuroEA 3000 elemental CHNS analyzer (*Eurovector Instrument*, Italy).

Materials

Tetrabutylammonium [2-(1-(1,4-dioxanium))]-nonahydro-*closo*-decaborate, (n-Bu_4N)$[B_{10}H_9O(CH_2)_4O]$ was synthesized according to a previously developed procedure [31]. 1,4-dioxane was purified according to [32]. Dimethylamine (33% aqueous solution, *Sigma-Aldrich*, USA), dibutylamine (>99.5%, *Sigma-Aldrich*, USA), dipropylamine (99%, *Sigma-Aldrich*, USA), diallylamine (99%, *Sigma-Aldrich*, USA), di(*sec*-butyl)amine (99%, *Sigma-Aldrich*, USA), diisobutylamine (99%, *Sigma-Aldrich*, USA), morpholine (99%, *Sigma-Aldrich*, USA), ethanol (95%, *Sigma-Aldrich*, USA), 1-pentanol (99%, *Sigma-Aldrich*, USA), methanol (99.9%, *Merck*, Germany), cesium iodide (chemically pure, *Himmed*, Russia), tetraphenylphosphonium chloride (99.9%, *Sigma-Aldrich*, USA), dimethylformamide (99.8%, *Sigma-Aldrich*, USA).

Experiments

To a suspension of 45 mg (0.1 mmol) (Bu_4N)$[B_{10}H_9O(CH_2)_4O]$ in 10 mL of ethanol (95%)

was added 0.6 mmol of a secondary amine (40 μL of a 33% aqueous solution of dimethylamine or 85 μL of dipropylamine or 105 μL of dibutylamine or 105 μL of diisobutylamine or 52 μL of morpholine or 75 μL of diallylamine) and heated with stirring for 2 h at reflux temperature. 200 μL of a 2 *M* solution of cesium fluoride in methanol was then added the resulting colorless or light-yellow solution. The resultant white or light-yellow precipitate was filtered off, recrystallized from a mixture of water-methanol (1:1) and dried under high vacuum.

Cesium 2-[2-(2-dimethylammonioethoxy)ethoxy)]-nonahydro-*closo*-decaborate, $Cs[B_{10}H_9O(CH_2)_2O(CH_2)_2NH(CH_3)_2]$

Yield: 0.030 g (79%). ^{1}H NMR (DMSO-d_6, δ, ppm): 10.16 (s, 1H, NH), 3.65 (t, 2H, CH$_2$ (α)), 3.40 (t, 2H, CH$_2$ (γ)), 3.16 (m, 4H, CH$_2$ (β, δ)), 2.77 (s, 6H, CH$_3$ (ε)), from 1.00 to −0.50 (m, 9H, $B_{10}H_9$). ^{11}B {^{1}H} NMR (DMSO-d_6, δ, ppm): 0.8 (s, BO (2)), −0.3, −3.5 (both s, by 1B, BH (10, 1)), −21.5 (s, BH (3, 5, 6, 9)), −27.2 (s, 2B, BH (7, 8)), −31.5 (s, 1B, BH (4)). ^{13}C APT NMR, (DMSO-d_6, δ, ppm): 71.2 (CH$_2$ (β)), 70.1 (CH$_2$ (γ)), 63.2 (CH$_2$ (α)), 55.2 (CH$_2$ (δ)), 42.8 (CH$_3$ (ε)). IR (KBr, cm^{-1}): 3075, 2720 (ν(N$^+$–H)), 2467 (ν(B–H)), 1471 (δ(H–N$^+$–H)). Found (%): C, 18.59; H, 3.58; N, 3.61; B, 28.12; $C_6H_{24}B_{10}CsNO_2$. Calculated (%): C, 18.80; H, 3.61; N, 3.65; B, 28.20. ESI-MS. Found, *m*/*z*: 250.3 $[B_{10}H_9O(CH_2)_2O(CH_2)_2NH(CH_3)_2]^-$. ($C_6H_{24}B_{10}NO_2$). Calculated: *M* = 250.3.

Cesium 2-[2-(2-dipropylammonioethoxy)ethoxy)]-nonahydro-*closo*-decaborate, $Cs[B_{10}H_9O(CH_2)_2O(CH_2)_2NH(CH_2CH_2CH_3)_2]$

Yield: 0.036 g (81%). ^{1}H NMR (DMSO-d_6, δ, ppm): 9.81 (s, 1H, NH), 3.68 (t, 2H, CH$_2$ (α)), 3.38 (t, 2H, CH$_2$ (γ)), 3.20 (t, 2H, CH$_2$ (β)), 3.13 (t, 2H, CH$_2$ (δ)), 2.51 (t, 4H, CH$_2$ (ε)), 1.72 (m, 4H, CH$_2$ (ζ)), 0.93 (t, 6H, CH$_2$ (η)), from 1.00 to −0.50 (m, 9H, $B_{10}H_9$). ^{11}B {^{1}H} NMR (DMSO-d_6, δ, ppm): 1.4 (s, BO (2)), −0.1, −3.7 (both s, by 1B, BH (10, 1)), −21.3 (s, BH (3, 5, 6, 9)), −27.3 (s, 2B, BH (7,8)), −31.2 (s, 1B, BH (4)). ^{13}C APT NMR (DMSO-d_6, δ, ppm): 70.5 (CH$_2$ (β)), 70.1 (CH$_2$ (γ)), 54.9 (CH$_2$ (α)), 50.8 (CH$_2$ (δ)), 23.1 (CH$_3$ (ε)), 16.3 (CH$_3$ (ζ)), 10.9 (CH$_3$ (η)). IR (KBr, cm^{-1}): 3079, 2715 (ν(N$^+$–H)), 2449 (ν(B–H)), 1481 (δ(H–N$^+$–H)). Found (%): C, 27.14; H, 7.26; N, 3.15; B, 24.49; $C_{10}H_{32}B_{10}CsNO_2$. Calculated (%): C, 27.33; H, 7.34; N, 3.18; B, 24.60. ESI-MS. Found, *m*/*z*: 306.4 $[B_{10}H_9O(CH_2)_2O(CH_2)_2NH(C_3H_7)_2]^-$. ($C_{10}H_{32}B_{10}NO_2$). Calculated: *M* = 306.3.

Cesium 2-[2-(2-dibutylammonioethoxy)ethoxy)]-nonahydro-*closo*-decaborate, $Cs[B_{10}H_9O(CH_2)_2O(CH_2)_2NH(CH_2CH_2CH_2CH_3)_2]$

Yield: 0.38 g (82%). ^{1}H NMR (DMSO-d_6, δ, ppm): 9.80 (s, 1H, NH), 3.63 (t, 2H, CH$_2$ (α)), 3.35 (t, 2H, CH$_2$ (γ)), 3.17 (t, 2H, CH$_2$ (β)), 3.12 (t, 2H, CH$_2$ (δ)), 2.51 (t, 4H, CH$_2$ (ε)), 1.62 (m, 4H, CH$_2$ (ζ)), 1.33 (m, 4H, CH$_2$ (η)), 0.93 (t, 6H, CH$_3$ (θ)), from 1.00 to −0.50 (m, 9H, $B_{10}H_9$). ^{11}B {^{1}H} NMR (DMSO-d_6, δ, ppm): 1.9 (c, BO (2)), 0.1, −3.6 (both s, by 1B, BH (10, 1)), −21.4 (s, BH (3, 5, 6, 9)), −27.3 (s, 2B, BH (7,8)), −31.4 (s, 1B, BH (4)). ^{13}C APT NMR (DMSO-d_6, δ, ppm): 70.5 (CH$_2$ (β)), 57.6 (CH$_2$ (γ)), 53.2 (CH$_2$ (α)), 50.8 (CH$_2$ (δ)), 23.1 (CH$_2$ (ε)), 19.6 (CH$_2$ (ζ)), 19.2 (CH$_3$ (η)), 13.7 (CH$_3$ (θ)). IR (KBr, cm^{-1}): 3079, 2715 (ν(N$^+$–H)), 2449 (ν(B–H)), 1483 (δ(H–N$^+$–H)). Found (%): C, 30.65; H, 7.72; N, 2.93; B, 22.98; $C_{12}H_{36}B_{10}CsNO_2$. Calculated (%): C, 30.83; H, 7.76; N, 2.99; B, 23.12. ESI-MS. Found, *m*/*z*: 334.2 $[B_{10}H_9O(CH_2)_2O(CH_2)_2NH(CH_2CH_2CH_2CH_3)_2]^-$. ($C_{12}H_{36}B_{10}NO_2$). Calculated: *M* = 334.4.

Cesium 2-[2-(2-di(2-methylpropyl)ammonioethoxy)-ethoxy)]nonahydro-*closo*-decaborate, $Cs[B_{10}H_9O(CH_2)_2O(CH_2)_2NH(CH_2CH(CH_3)_2)_2]$

Yield: 0.36 g (77%). ^{1}H NMR (DMSO-d_6, δ, ppm): 9.82 (s, 1H, NH), 3.32 (t, 2H, CH$_2$ (α)), 3.17 (t, 2H, CH$_2$ (γ)), 3.07 (t, 2H, CH$_2$ (β)), 2.43 (t 2H, CH$_2$ (δ)), 2.08 (d, 4H, CH$_2$ (ε)), 1.61 (m, 2H, CH (ζ)), 0.82 (d, 6H, CH$_3$ (η)), from 1.00 to −0.50 (m, 9H, $B_{10}H_9$). ^{11}B {^{1}H} NMR (DMSO-d_6, δ, ppm): 0.6 (s, BO (2)), −0.4, −3.1 (both s, by 1B, BH (10, 1)), −21.3 (s, BH (3, 5, 6, 9)), −27.0 (s, 2B, BH (7, 8)), −31.6 (s, 1B, BH (4)). ^{13}C APT NMR (DMSO-d_6, δ, ppm): 72.2 (CH$_2$ (β)), 69.4 (CH$_2$ (γ)), 68.6 (CH$_2$ (α)), 64.0 (CH$_2$ (δ)), 54.0 (CH (ε)), 26.3 (CH$_3$ (ζ)), 20.7 (CH$_3$ (η)). IR (KBr, cm^{-1}): 3082, 2694 (ν(N$^+$–H)), 2448 (ν(B–H)), 1468 (δ(H–N$^+$–H)). Found (%): C, 30.62; H, 7.70; N, 2.94; B, 23.02; $C_{12}H_{36}B_{10}CsNO_2$. Calculated (%): C, 30.83; H, 7.76; N, 2.99; B, 23.12. ESI-MS. Found, *m*/*z*: 334.3 $[B_{10}H_9O(CH_2)_2O(CH_2)_2NH(CH_2CH(CH_3)_2)_2]^-$. ($C_{12}H_{36}B_{10}NO_2$). Calculated: *M* = 334.4.

Cesium 2-[2-(2-*N*-morpholylammonioethoxy)ethoxy)]-nonahydro-*closo*-decaborate, $Cs[B_{10}H_9O(CH_2)_2O(CH_2)_2NH(CH_2CH_2)_2O)]$

Yield: 0.36 g (85%). ^{1}H NMR (DMSO-d_6, δ, ppm): 4.55 (s, 1H, NH), 3.56 (t, 2H, CH$_2$ (ζ)), 3.35 (t, 2H, CH$_2$ (α)), 3.19 (t, 2H, CH$_2$ (γ)), 3.05 (t, 2H, CH$_2$ (β)), 2.36 (t, 2H, CH$_2$ (δ)), 2.32 (m, 2H, CH$_2$ (ε)), from 1.00 to −0.50 (m, 9H, $B_{10}H_9$). ^{11}B {^{1}H} NMR (DMSO-d_6, δ, ppm): 1.5 (s, BO (2)), −0.2, −3.2 (both s, by 1B, BH (10, 1)), −21.3 (s, BH (3, 5, 6, 9)), −27.0 (s, 2B, BH (7,8)), −31.4 (s, 1B, BH (4)). ^{13}C APT NMR

(DMSO-d_6, δ, ppm): 72.2 ($\underline{C}H_2$ (β)), 69.3 ($\underline{C}H_3$ (ζ)), 66.7 ($\underline{C}H_2$ (γ)), 65.9 ($\underline{C}H_2$ (α)), 58.0 ($\underline{C}H_2$ (δ)), 53.4 ($\underline{C}H_2$ (ε)). IR (KBr, cm^{-1}): 3071, 2726 (ν(N^+–H)), 2454 (ν(B–H)), 1456 (δ(H–N^+–H)). Found (%): C, 22.41; H, 6.10; N, 3.23; B, 25.24; $C_8H_{26}B_{10}CsNO_3$. Calculated (%): C, 22.59; H, 6.16; N, 3.29; B, 25.41. ESI-MS. Found, *m/z*: 292.2 $[B_{10}H_9O(CH_2)_2O(CH_2)_2NH(CH_2CH_2)_2O)]^-$. ($C_8H_{26}B_{10}NO_3$). Calculated: *M* = 292.3.

Cesium 2-[2-(2-diallylammonioethoxy)ethoxy)]-nonahydro-*closo*-decaborate, $Cs[B_{10}H_9O(CH_2)_2O(CH_2)_2NH(CH_2CH{=}CH_2)_2)]$

Yield: 0.34 g (79%). ^{1}H NMR (DMSO-d_6, δ, ppm): 9.85 (s, 1H, N$\underline{H}$), 5.83 (m, 2H, C$\underline{H}$ (ζ)), 5.12 (d, 4H, C$\underline{H}_2$ (η)), 3.38 (t, 2H, C$\underline{H}_2$ (α)), 3.20 (t, 2H, C$\underline{H}_2$ (γ)), 3.11 (t, 2H, C$\underline{H}_2$ (β)), 3.04 (d, 4H, C$\underline{H}_2$ (ε)), 2.52 (t, 2H, C$\underline{H}_2$ (δ)), from 1.00 to −0.50 (m, 9H, $B_{10}\underline{H}_9$). ^{11}B {^{1}H} NMR (DMSO-d_6, δ, ppm): 1.1 (s, $\underline{B}$O (2)), −0.3, −3.2 (both s, by 1B, $\underline{B}$H (10, 1)), −21.4 (s, $\underline{B}$H (3, 5, 6, 9)), −27.2 (s, 2B, BH (7, 8)), −31.7 (s, 1B, BH (4)). ^{13}C APT NMR (DMSO-d_6, δ, ppm): 135.7 ($\underline{C}$H (ζ)), 117.4 ($\underline{C}H_2$ (η)), 72.2 ($\underline{C}H_2$ (β)), 69.4 ($\underline{C}H_2$ (γ)), 67.9 ($\underline{C}H_2$ (α)), 56.4 ($\underline{C}H_2$ (δ)), 52.2 ($\underline{C}H_2$ (ε)). IR (KBr, cm^{-1}): 3079, 2716 (ν(N^+–H)), 3025 (ν(=C–H)), 2455 (ν(B–H)), 1446 (δ(H–N^+–H)). Found (%): C, 27.40; H, 6.42; N, 3.17; B, 24.68; $C_{10}H_{28}B_{10}CsNO_2$. Calculated (%): C, 27.58; H, 6.48; N, 3.21; B, 24.83. ESI-MS. Found, *m/z*: 302.4 $[B_{10}H_9O(CH_2)_2O(CH_2)_2NH(CH_2CH{=}CH_2)_2)]^-$. ($C_{10}H_{28}B_{10}NO_2$). Calculated: *M* = 302.3.

Cesium 2-[2-(2-di(2-butyl)ammonioethoxy)-ethoxy)]nonahydro-*closo*-decaborate, $Cs[B_{10}H_9O(CH_2)_2O(CH_2)_2NH(CH(CH_3)(CH_2CH_3))_2]$

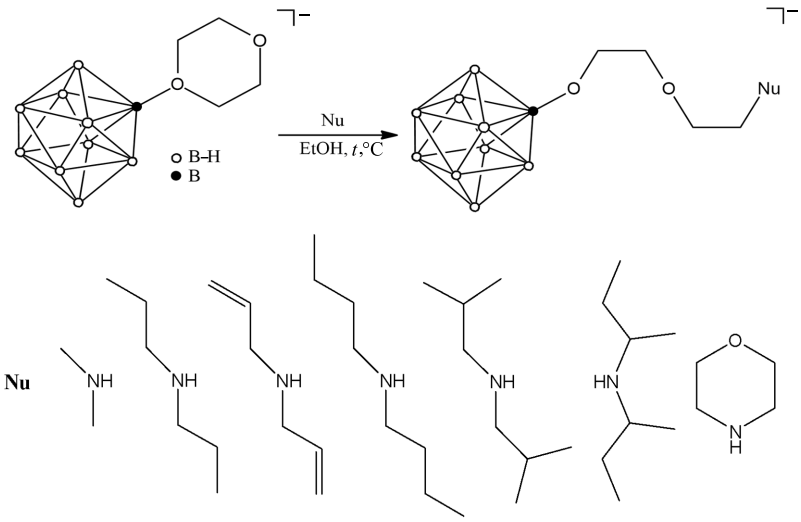
To a suspension of 45 mg (0.1 mmol) of (Bu_4N)[$B_{10}H_9O(CH_2)_4O$] in 10 mL of 1-pentanol (95%) was added 0.6 mmol (105 μL) of di-*sec*-butylamine and heated with stirring for 6 h at 110–120°C. To the resulting colorless solution was added 200 μL of a 2 *M* solution of cesium fluoride in methanol. The resulting white or light-yellow precipitate was filtered off, recrystallized from a mixture of water-methanol (1:1) and dried in a high vacuum.

Yield: 0.33 g (72%). ^{1}H NMR (DMSO-d_6, δ, ppm): 6.57 (s, 1H, N$\underline{H}$), 3.38 (t, 2H, C$\underline{H}_2$ (α)), 3.16 (t, 2H, C$\underline{H}_2$ (γ)), 3.06 (t, 2H, C$\underline{H}_2$ (β)), 2.55 (t, 2H, C$\underline{H}_2$ (δ)), 1.23 (t, 2H, C$\underline{H}$ (ε)), 1.09 (m, 4H, C$\underline{H}_2$ (ζ)), 0.89 (t, 6H, CHC$\underline{H}_3$ (η)), 0.80 (t, 6H, $CH_2C\underline{H}_3$ (θ)), from 1.00 to −0.50 (m, 9H, $B_{10}\underline{H}_9$). ^{11}B {^{1}H} NMR (DMSO-d_6, δ, ppm): 1.3 (s, $\underline{B}$O (2)), −0.4, −3.2 (both s, by 1B, $\underline{B}$H (10, 1)), −21.4 (s, $\underline{B}$H (3, 5, 6, 9)), −27.1 (s, 2B, $\underline{B}$H (7, 8)), −31.9 (s, 1B, $\underline{B}$H (4)). ^{13}C APT NMR (DMSO-d_6, δ, ppm): 72.2 ($\underline{C}H_2$ (β)), 69.4 ($\underline{C}H_2$ (γ)), 65.5 ($\underline{C}H_2$ (α)), 62.7 ($\underline{C}H_2$ (δ)), 28.6 ($\underline{C}$H (ε)), 18.1 ($\underline{C}H_2$ (ζ)), 17.3 (CH$\underline{C}H_3$ (η)), 11.7 ($CH_2\underline{C}H_3$ (θ)). IR (KBr, cm^{-1}): 3079, 2732 (ν(N^+–H)), 2456 (ν(B–H)), 1457 (δ(H–N^+–H)). Found (%): C, 30.63; H, 7.70; N, 2.91; B, 23.00; $C_{12}H_{36}B_{10}CsNO_2$. Calculated (%): C, 30.83; H, 7.76; N, 2.99; B, 23.12. ESI-MS. Found, *m/z*: 334.3 $[B_{10}H_9O(CH_2)_2O(CH_2)_2NH(CH(CH_3)(CH_2CH_3))_2]^-$. ($C_{12}H_{36}B_{10}NO_2$). Calculated: *M* = 334.4.

RESULTS AND DISCUSSION

We have studied the interaction of the 1,4-dioxane derivative of the *closo*-decaborate anion $[B_{10}H_9O(CH_2)_4O]^-$ with secondary amines in ethanol. In the course of research, it was shown that as a result of the reactions, the cyclic substituent of the oxonium type is opened, followed by the addition of pendant ammonium functional groups (see Scheme).

^{11}B {^{1}H} NMR spectroscopy is a very convenient method for the primary monitoring of 1,4-dioxane substituent opening reactions in the $[B_{10}H_9O(CH_2)_4O]^-$



Scheme. Interaction of the $[B_{10}H_9O(CH_2)_4O]^-$ anion with secondary amines.

anion. Here, it is important to note that, while the general form of the spectrum characteristic of monosubstituted *closo*-decaborates $[B_{10}H_9R]^{x-}$ (x = 1, 2) is preserved, a significant change in the chemical shifts of the signals is observed (Fig. 1).

Thus, the signals from apical boron atoms appear in the ^{11}B NMR spectrum of the starting compound $Bu_4N[B_{10}H_9O(CH_2)_4O]$ at 0.8 ppm and −6.4 ppm; and −3.1 ppm, respectively. The singlet from the ipso boron atom bonded to the oxygen atom is shifted from 7.9 ppm. up to 0.6 ppm. This is the only signal that does not split into a doublet in the absence of broadband suppression of the B–H spin-spin interaction. Signals from other equatorial atoms in a strong field are redistributed with respect to the spectrum of the initial $[B_{10}H_9O(CH_2)_4O]^-$ anion: three signals are observed in the spectrum of the reaction product at –21.3, –27.0, and –31.56 ppm., having a ratio of integral intensities of 4:2:1. Such changes in the spectral pattern can be explained by the redistribution of the electron density on boron atoms due to the change in the B–O bond type from oxonium to alkoxy.

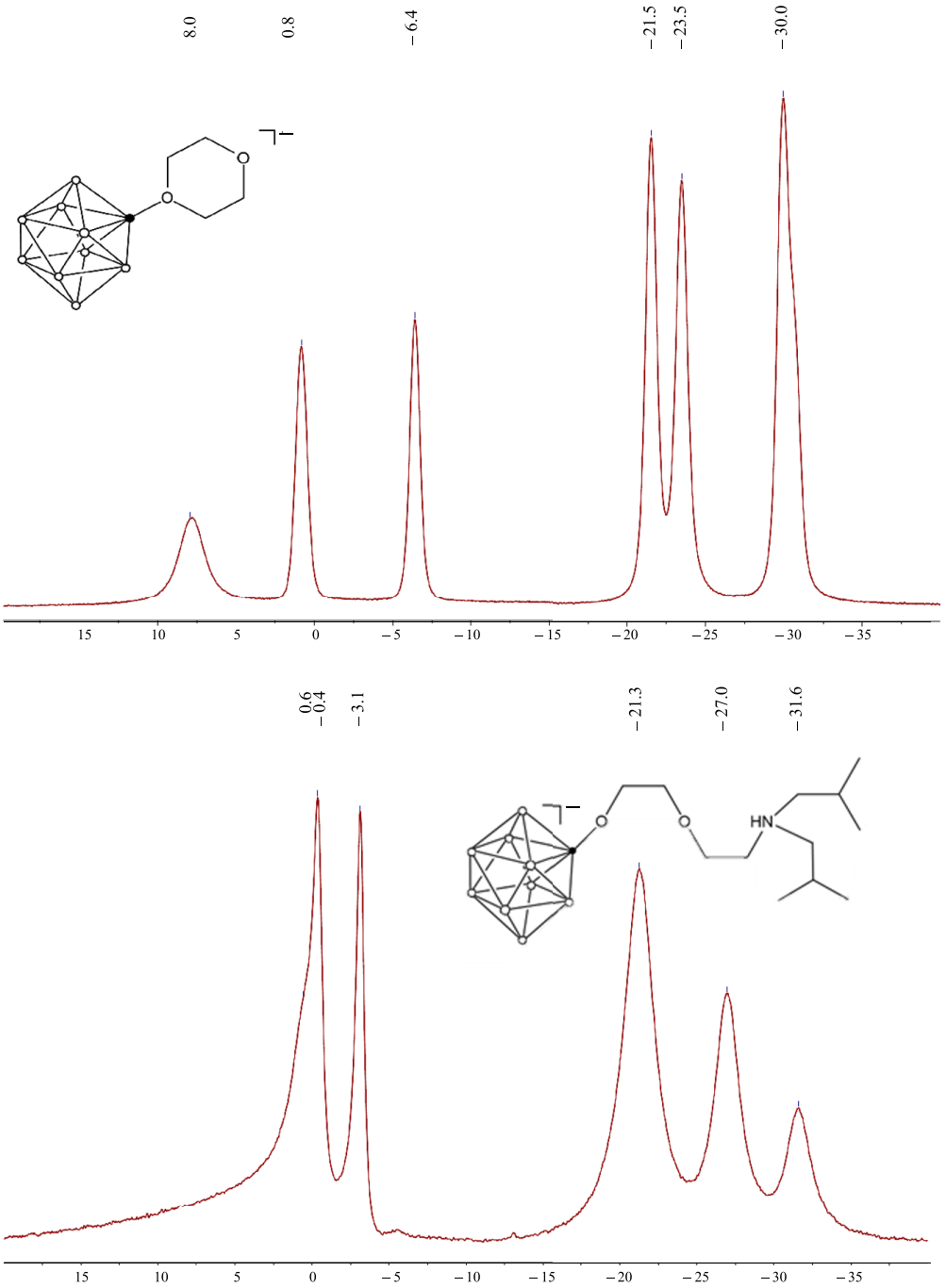


Fig. 1. ^{11}B {^1H} NMR spectra of $Bu_4N[B_{10}H_9O(CH_2)_4O]$ (top) and $Cs[B_{10}H_9O(CH_2)_2O(CH_2)_2NH(CH_2CH(CH_3)_2)_2]$ (bottom).

While the course of the opening of the cyclic substituent in the 1,4-dioxane derivative of the *closo*-decaborate anion can be unambiguously determined according to the described changes, practically no information about the structure of the alkoxy spacer and the introduced pendant group is provided, due to their similarity for all obtained connections. Accordingly, this data was obtained by analyzing the IR, ^{13}C APT and ^1H NMR spectra of the obtained derivatives.

Thus, the absorption bands in the regions of 2690–3100 cm^{-1} and 1440–1490 cm^{-1} in the IR spectra of the synthesized compounds with pendant ammonium groups can be related to stretching vibrations of the N^+–H bonds and bending vibrations of the H–N^+–H bonds, respectively. The boron cluster is represented in the IR spectra of the products by a high-intensity absorption band from B–H stretching vibrations in the range 2449–2467 cm^{-1}. This type of spectra indicates the opening of the cyclic substituent and the addition of pendant nitrogen-containing groups.

The ^1H NMR spectra of the obtained derivatives of the *closo*-decaborate anion undergo significant changes compared to the spectrum of the starting $[B_{10}H_9O(CH_2)_4O]^-$ anion. In particular, its ^1H NMR spectrum contains only two triplets at 3.85 ppm. and 4.31 ppm from nonequivalent methylene groups of the cyclic substituent, while in the spectrum of $Cs[B_{10}H_9O(CH_2)_2O(CH_2)_2NH(CH_2CH(CH_3)_2)_2]$ four triplets appear with equal integrated intensity from the protons of the alkoxy chain at 3.32 ppm (α), 3.17 ppm (γ), 3.07 ppm (β), and 2.43 ppm (δ), along with signals from the pendant group at 2.08 (d, CH_2 (ε)), 1.61 (m, 2H, CH (ζ)), and 0.82 (d, 6H, CH_3 (η)) ppm (Fig. 2). Similar changes are observed in the spectra of other obtained compounds. Since the signals from the hydrogen atoms of the boron cluster typically represent an extremely broad multiplet in the range from 1.00 to −0.50 ppm., they are not of significant interest.

The ^{13}C APT spectra of the synthesized compounds also depict interesting changes associated with the opening of the 1,4-dioxane substituent and the introduction of a terminal ammonium group. Thus, the spectrum of the cesium salt of the anion $[B_{10}H_9O(CH_2)_2O(CH_2)_2NH(CH_2CH(CH_3)_2)_2]^-$ contains four signals at 54.0, 26.3, and 20.7 ppm. from ε-, ζ-, and η-carbon atoms of the $–NH(CH_2CH(CH_3)_2)_2$ group. Signals from carbon atoms of the spacer chain are observed at 72.2 (β), 69.4 (γ), 68.6 (α), and 64.0 (δ) ppm (Fig. 3).

The composition of the synthesized derivatives of the *closo*-decaborate anion was confirmed using the ESI-MS method. For example, the mass spectrum of the compound $Cs[B_{10}H_9O(CH_2)_2O(CH_2)_2NH(CH_2CH_2CH_2CH_3)_2]$ in the negative ionization mode of ESI-MS shows an ion with a maximum intensity at *m*/*z* 334.22 from a singly charged anion of the composition $[B_{10}H_9O(CH_2)_2O(CH_2)_2NH(CH_2CH_2CH_2CH_3)_2]^-$ (Fig. 4).

It is interesting to note that the interaction of the anion $[B_{10}H_9O(CH_2)_4O]^-$ with di-*sec*-butylamine

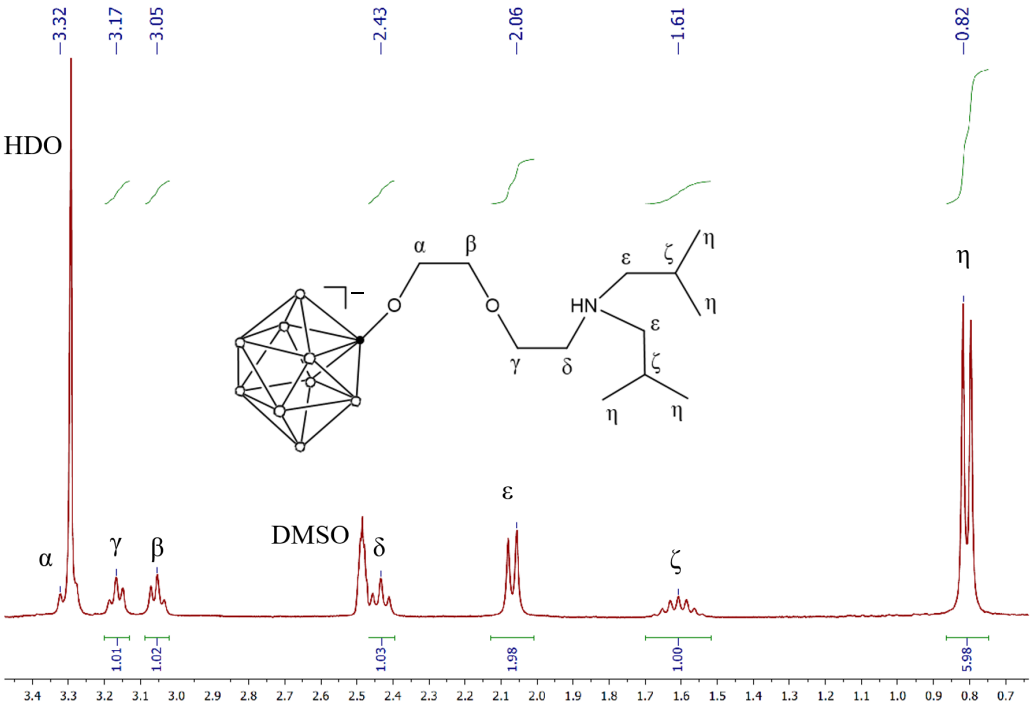


Fig. 2. ^1H NMR spectrum of $Cs[B_{10}H_9O(CH_2)_2O(CH_2)_2NH(CH_2CH(CH_3)_2)_2]$ in DMSO-d_6.

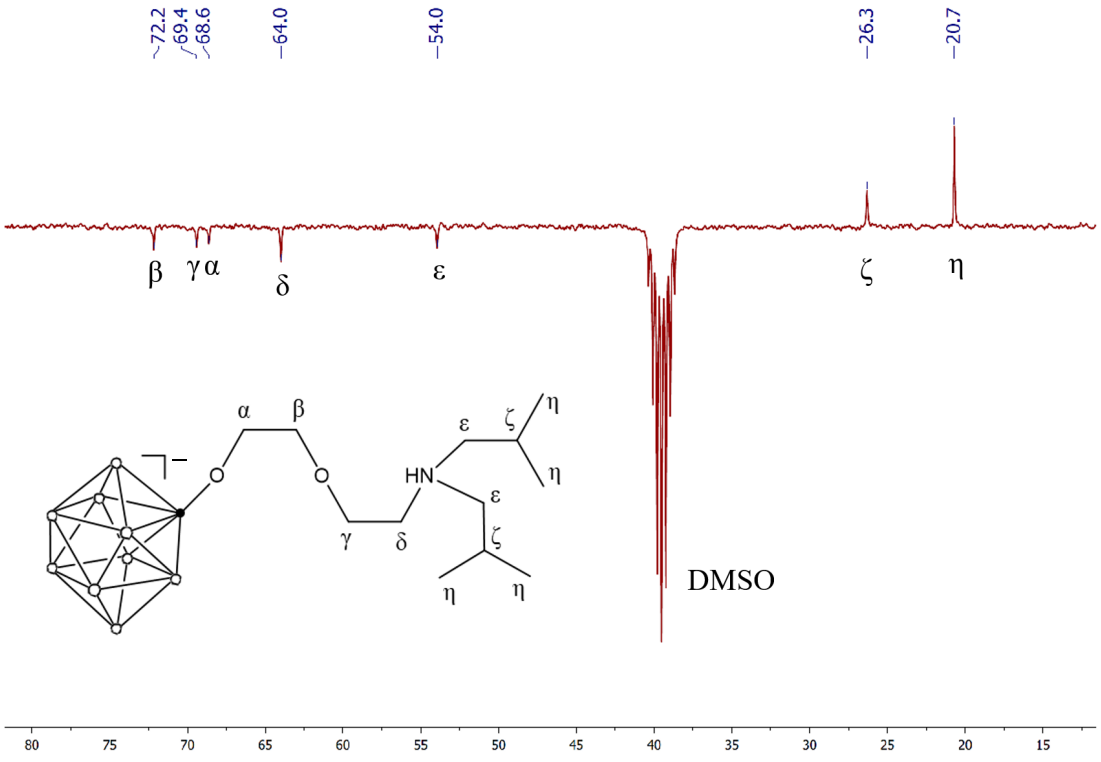


Fig. 3. ^{13}C ART NMR spectrum of $Cs[B_{10}H_9O(CH_2)_2O(CH_2)_2NH(CH_2CH(CH_3)_2)_2]$ in DMSO-d_6.

practically does not occur in ethanol at reflux for 8 h. For this reason, the corresponding reaction was carried out in a medium of a higher-boiling solvent (1-pentanol). This can be attributed to steric hindrance in the formation of the anion $[B_{10}H_9O(CH_2)_2O(CH_2)_2NH(CH(CH_3)(CH_2CH_3))_2]^-$.

CONCLUSIONS

Thus, in the present study, a method was developed for the synthesis of new derivatives of the *closo*-decaborate anion with secondary amine molecules (dimethylamine, dipropylamine, diallylamine,

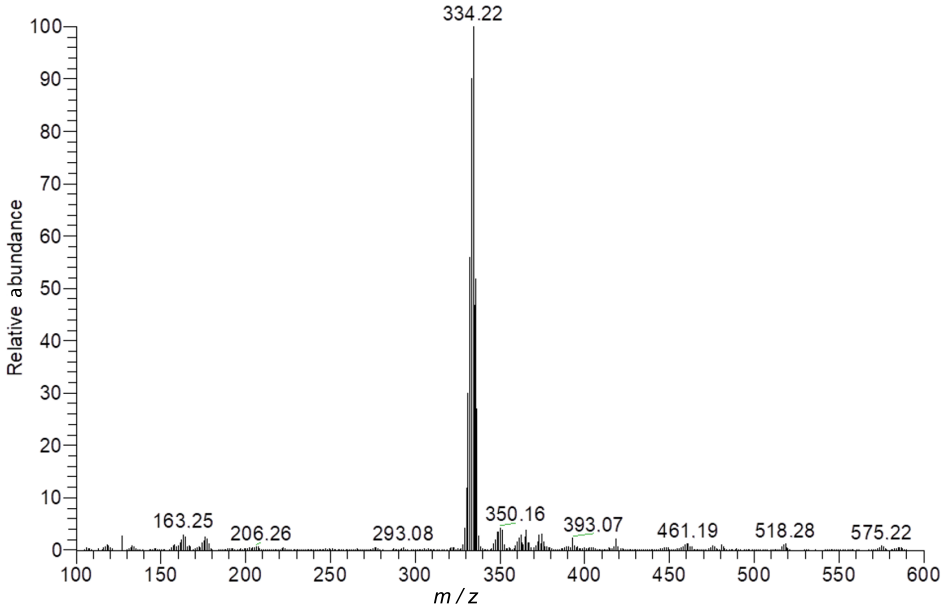


Fig. 4. ESI-MS spectrum of the $Cs[B_{10}H_9O(CH_2)_2O(CH_2)_2NH(CH_2CH_2CH_2CH_3)_2]$ in the negative ionization mode.

dibutylamine, diisobutylamine, morpholine, di-*sec*-butylamine) attached to the cluster anion as pendent groups.

The developed method is shown to achieve high yields of the target compounds (72–88%), simple execution, as well as allowing nitrogen-containing derivatives of the $[B_{10}H_{10}]^{2-}$ anion to be selectively obtained. Such compounds can be used as effective polydentate ligands, as well as being suitable for introduction into further modification reactions due to the attached pendant group.

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Authors' contributions

E.Yu. Matveev – formulation of the problem, development of the scientific concept, and writing the text of the article;

S.S. Novikov – performing experimental studies, collecting and analyzing the results;

V.Ya. Levitskaya – performing experimental studies, collecting and analyzing the results;

A.I. Nichugovskiy – obtaining and processing physicochemical characteristics of synthesized compounds;

I.E. Sokolov – obtaining and processing physicochemical characteristics of synthesized compounds;

K.Yu. Zhizhin – development of the scientific concept, consultation on research methodology;

N.T. Kuznetsov – development of the scientific concept, consultation on research methodology.

The authors declare no conflict of interest.

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