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Synthesis and derivatization of the 2-amino-*closo*-decaborate anion $[2\text{-}B_{10}H_9NH_3]^-$

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Dedicated to the memory of Professor Leonid I. Zakharkin in recognition of his significant contribution to boron chemistry

Abstract

A novel high-yield method of synthesis of the $[2\text{-}B_{10}H_9NH_3]^-$ anion was elaborated. The method proposed includes reaction of the *closo*-decaborate anion with acetonitrile in the presence of acid, followed by hydrolysis of the formed nitrilium derivative $[2\text{-}B_{10}H_9NCMe]^-$ first to the acetamide derivative $[2\text{-}B_{10}H_9NH_2COMe]^-$ and then to the amine. The crystal molecular structure of $(Bu_4N)[2\text{-}B_{10}H_9NH{=}C(OH)Me]$ was determined by single crystal X-ray diffraction method. In the solid state, the acetamide derivative exists in the *O*-protonated tautomeric form and has a *Z*-configuration where the NH proton and the OH group are *trans* around the C=N bond. The reaction of the $[2\text{-}B_{10}H_9NH_3]^-$ anion with aromatic aldehydes in methanol in the presence of catalytic amounts of alkali gives *N*-protonated Schiff bases $[2\text{-}B_{10}H_9NH{=}CHR]^-$ (R = C_6H_5, C_6H_4-2-OMe, C_6H_4-4-NHCOMe). Reduction of the Schiff bases with $NaBH_4$ in aqueous methanol gives the corresponding monoalkylamino derivatives $[2\text{-}B_{10}H_9NH_2CH_2R]^-$ (R = C_6H_5, C_6H_4-2-OMe, C_6H_4-4-NHCOMe). The approach developed can be used in the synthesis of functional derivatives of the *closo*-decaborate anion for applications in nuclear medicine.

Keywords: *Closo*-decaborate; Derivatization; Amine; Acetamide; Schiff bases

1. Introduction

The decahydro-*closo*-decaborate anion $[B_{10}H_{10}]^{2-}$ has for a long time been considered as potential boron moiety for boron neutron capture therapy, a binary system for the treatment of cancer based upon the interaction of two relatively harmless species: a ^{10}B nucleus and a thermal neutron resulting in highly energetic ^4He and ^7Li products, which destroy the malignant cells [1,2]. Another important potentiality is connected with the possibility of applying this boron cluster as radiohalogen label carrier in the diagnosis and treatment of cancer [3]. However, after the explosive development of the *closo*-decaborate chemistry in the 1960s, the decahydro-*closo*-decaborate anion is at present in the shadow of its 'older brother', the dodecahydro-*closo*-dodecaborate anion $[B_{12}H_{12}]^{2-}$.

Recently, we developed an effective method for synthesis of various functional derivatives of the *closo*-dodecaborate anion based on its amino derivative $[B_{12}H_{11}NH_3]^-$ [4]. Planning to use this approach for synthesis of functional derivatives of the *closo*-decaborate anion we found in the literature that only one of the two isomeric amino derivatives, namely $[1\text{-}B_{10}H_9NH_3]^-$, can be prepared in high yield [5,6], whereas the second isomer, $[2\text{-}B_{10}H_9NH_3]^-$, was produced only in 38% yield by direct amination of the parent *closo*-decaborate with hydroxylamine-*O*-sulfonic acid [7]. It is known from the literature that the chemistry of the $[2\text{-}B_{10}H_9NH_3]^-$ anion is poorly studied: only alkylation [7–9] and acylation [8] reactions, as well as a reaction with ethylene oxide resulting in

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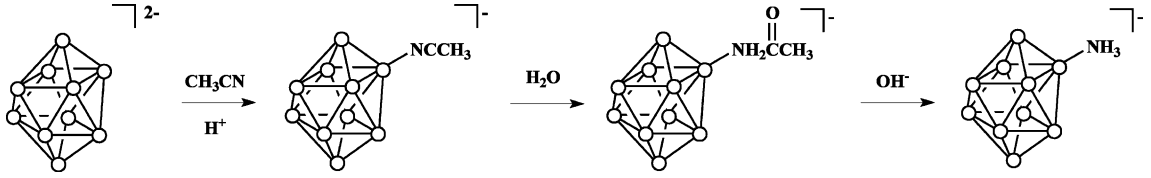
substitution at boron atoms [8], have been reported. In this paper, we discuss a new preparative method of synthesis of the $[2\text{-}B_{10}H_9NH_3]^-$ anion as well as some chemical properties of this anion.

2. Results and discussion

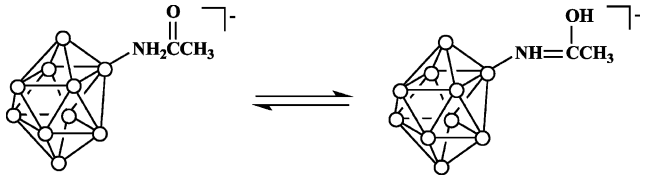
One of the possible methods of synthesis of $[2\text{-}B_{10}H_9NH_3]^-$ consists in the hydrolysis of the equatorially substituted nitrilium derivative of the *closo*-decaborate anion.



The synthesis of the stable nitrilium derivative $[2\text{-}B_{10}H_9N{\equiv}CCH_3]^-$ in high yield (93% as the triethylammonium salt) under an acid-catalyzed reaction of the parent *closo*-dodecaborate anion and acetonitrile was reported recently [10]. We used this reaction as the first step of the amino derivative synthesis and determined some spectral characteristics of the nitrilium derivative that had not been reported. The ^{1}H-NMR spectrum of $(Et_3NH)[2\text{-}B_{10}H_9N{\equiv}CCH_3]$ contains the methyl singlet at 2.68 ppm, and the ^{13}C-NMR spectrum contains signals of the methyl group at 3.2 ppm and the nitrilium carbon at 115.4 ppm, which is in good agreement with known spectral data on known nitrilium hexachloroantimonates [11] and triflates [12]. We also re-examined the IR spectrum of $(Et_3NH)[2\text{-}B_{10}H_9N{\equiv}CCH_3]$ and assigned the absorptions at 2537, 2505, and 2471 cm^{-1} to the BH stretching vibrations and the absorption at 2348 cm^{-1} to the nitrilium C≡N stretching vibration (2330–2400 cm^{-1} in $[R{-}C{\equiv}N^+{-}R']X^-$ [11,12]).

The nitrilium derivative was found to hydrolyze smoothly to the corresponding amide. The hydrolysis of the nitrilium derivative to the acetamide derivative was described as early as the 1960s by Miller et al. [13]; however, at that time, both compounds were assigned wrongly as the 1-isomers due to poor availability of NMR data.

According to the ^{1}H and ^{11}B-NMR data (DMSO-d_6), an equilibrium between the *N*-protonated $[2\text{-}B_{10}H_9NH_2COCH_3]^-$ (^{1}H-NMR (ppm): 8.82 (2H, s, $-NH_2COCH_3$) and 2.06 (3H, s, $-NH_2COCH_3$); ^{11}B-NMR (ppm): 1.85 (1B, d, $J = 148$ Hz), −6.33 (1B, d, $J = 140$ Hz), −17.42 (1B, s), −25.55, and −28.88) and the *O*-protonated $[2\text{-}B_{10}H_9NH{=}C(OH)CH_3]^-$ (^{1}H-NMR (ppm): 9.62 (1H, s, $-NH{=}C(OH)CH_3$), 7.98 (1H, s, $-NH{=}C(OH)CH_3$), and 2.15 (3H, s, $-NH_2COCH_3$); ^{11}B-NMR (ppm): −0.51 (1B, d, $J =$ 147 Hz), −3.53 (1B, d, $J = 140$ Hz), −14.83 (1B, s), −25.55, and −28.88) tautomeric forms exist in the solution. The ^{1}H-NMR assignment for the *O*-protonated form was performed on the basis of the literature data on protonated amide tetrafluoroborates [14]. The ratio of the *N*- and *O*-protonated forms at room temperature was estimated to be ca. 1.3:1 based on the ^{1}H-NMR spectrum.



It is known that the 2-acrylamide derivative of the *closo*-decaborate anion in the solid state exists as the *O*-protonated form $[2\text{-}B_{10}H_9NH{=}C(OH)CH{=}CH_2]^-$ [15]. It should be noted that the recently reported 1-acetamide derivative $[1\text{-}B_{10}H_9NH_2COCH_3]^-$ [16], according to the NMR data, exists in acetonitrile solution as

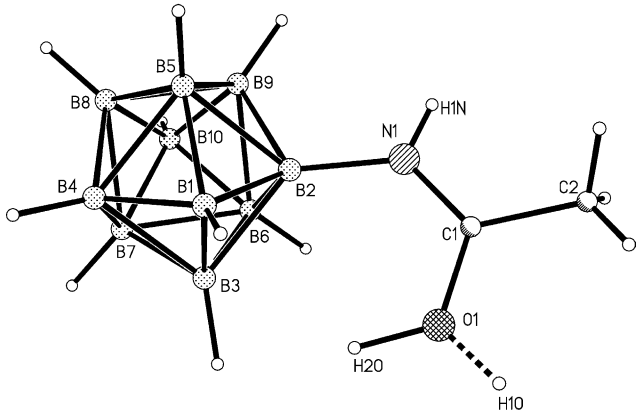


Fig. 1. Molecular structure of the $[2\text{-}B_{10}H_9NH{=}C(OH)Me]^-$.

single, presumably the *N*-protonated form. Probably, the protonation site in solution depends on the solvent as well as the electronic effect of the boron substituent, which is different for the 1- and 2-decaboranyl groups.

The crystal molecular structure of $(Bu_4N)[2\text{-}B_{10}H_9NH_2COCH_3]$ was determined by single crystal X-ray diffraction method (Fig. 1). In the solid state, the acetamide derivative was found to exist as the *O*-protonated form. The *exo*-polyhedral B–N distance of 1.520 Å is comparable with the B–N distances in known derivatives of the *closo*-decaborate anion (1.523 Å in $(Et_4N)[2\text{-}B_{10}H_9NH{=}C(OH)CH{=}CH_2]$ [15], 1.515 Å in $(Et_3NH)[2\text{-}B_{10}H_9NCCH_3]$ [10], 1.541 and 1.505 Å in $(Ph_4P)[2,9\text{-}\{N,N'\text{-}(2\text{-}NH{-}(C_5H_4N))\}B_{10}H_8]$ [17], and 1.498 Å in $(Et_3NH)_2[2\text{-}B_{10}H_9NCO]$ [18]). The nitrogen–carbon bond in $[2\text{-}B_{10}H_9NHC(OH)CH_3]^-$ is 1.303 Å, which is typical for the C=N double bonds [19] and is close to the C=N bond in $(Et_4N)[2\text{-}B_{10}H_9NH{=}C(OH)CH{=}CH_2]$ (1.288 Å) [15]. The B–N(H)=C(OH)–Me fragment in the $[2\text{-}B_{10}H_9NHC(OH)CH_3]^-$ anion is ca. planar and, as in the case of $[2\text{-}B_{10}H_9NH{=}C(OH)CH{=}CH_2]^-$ [15], $[Me_3NBH_2C(OH){=}NHEt]Cl$ [20], and known organic structures containing similar double protonated amide moiety [21–23], has a *Z*-configuration where the NH proton and the OH group are *trans* about the C=N bond. The C–O distance is 1.343 Å. The OH hydrogen atom is disordered between two equivalent positions (Table 1).

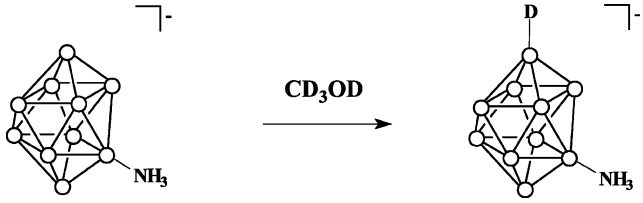
The alkaline hydrolysis of the amido derivative was found to give a mixture of the corresponding amine $[2\text{-}B_{10}H_9NH_2]^{2-}$ ($\delta_{B(2)}$ −14.99 ppm) and its protonated form $[2\text{-}B_{10}H_9NH_3]^-$ ($\delta_{B(2)}$ −16.97 ppm), which can be easily converted into $[2\text{-}B_{10}H_9NH_3]^-$ by addition of a small amount of acid. The method developed allows one to prepare the $[2\text{-}B_{10}H_9NH_3]^-$ anion in 85% yield.

Table 1
Bond lengths (Å) and selected angles (°) for the $[2\text{-}B_{10}H_9NH{=}C(OH)CH_3]^-$ anion

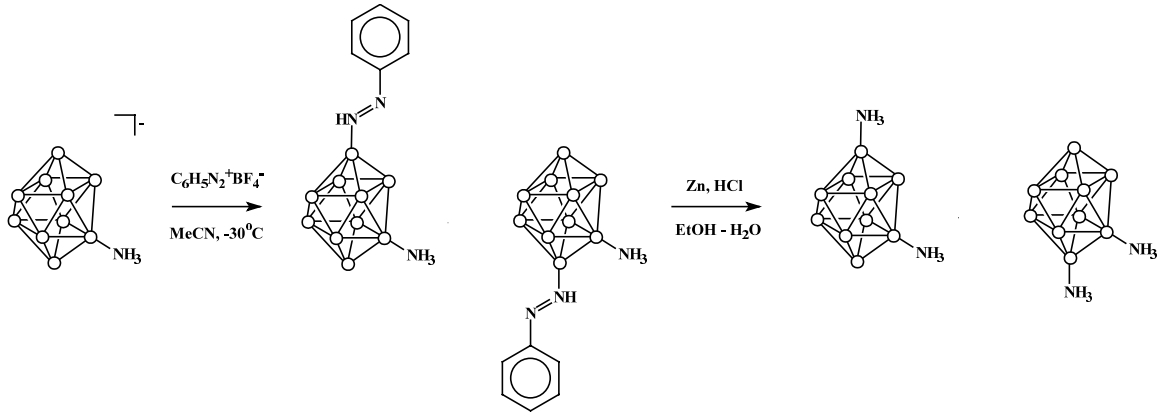
Bond lengths			
B(2)–N(1)	1.520(2)	B(3)–B(6)	1.819(3)
N(1)–C(1)	1.303(2)	B(5)–B(9)	1.817(3)
C(1)–O(1)	1.343(2)	B(3)–B(7)	1.815(3)
C(1)–C(2)	1.493(3)	B(5)–B(8)	1.818(3)
B(1)–B(2)	1.695(3)	B(4)–B(7)	1.822(3)
B(1)–B(3)	1.706(3)	B(4)–B(8)	1.824(3)
B(1)–B(5)	1.699(3)	B(6)–B(9)	1.831(3)
B(1)–B(4)	1.689(3)	B(6)–B(7)	1.826(3)
B(2)–B(3)	1.828(3)	B(8)–B(9)	1.826(3)
B(2)–B(5)	1.821(3)	B(7)–B(8)	1.842(3)
B(3)–B(4)	1.833(3)	B(6)–B(10)	1.699(3)
B(4)–B(5)	1.842(3)	B(9)–B(10)	1.705(3)
B(2)–B(6)	1.820(3)	B(7)–B(10)	1.698(3)
B(2)–B(9)	1.804(3)	B(8)–B(10)	1.697(3)
Bond angles			
B(2)–N(1)–C(1)	128.38(16)	N(1)–C(1)–C(2)	121.23(18)
N(1)–C(1)–O(1)	120.68(17)	O(1)–C(1)–C(2)	118.09(17)

As it was mentioned previously, the chemistry of the $[2\text{-}B_{10}H_9NH_3]^-$ anion is poorly studied [7–9]. The potential application of the $[2\text{-}B_{10}H_9NH_3]^-$ anion for synthesis of medicinal preparations requires more detailed study of its chemistry. In this connection, two aspects are important: (1) the possibility of selective substitution at the other boron atoms, and (2) transformation of the amino substituent into other functionalities, such as Schiff bases, and alkylamines.

Recently, we found that the $[B_{10}H_{10}]^{2-}$ anion in methanol-d_4 undergoes a regiospecific proton-deuterium exchange at the apical vertices giving $[1,10\text{-}B_{10}H_8D_2]^{2-}$ [24]. Under the same conditions, the proton-deuterium exchange in $[2\text{-}B_{10}H_9NH_3]^-$ proceeds selectively at one of the apical vertices. The deuteration position determined using ^{11}B–^{11}B TOCSY NMR spectroscopy was found to be the apical boron atom, which is the most distant from the substituted one and the deuteration product is $[1\text{-}D\text{-}6\text{-}ND_3\text{-}B_{10}H_8]^-$. This result is in good agreement with the strong deactivating effect of the NH_3^+ group.

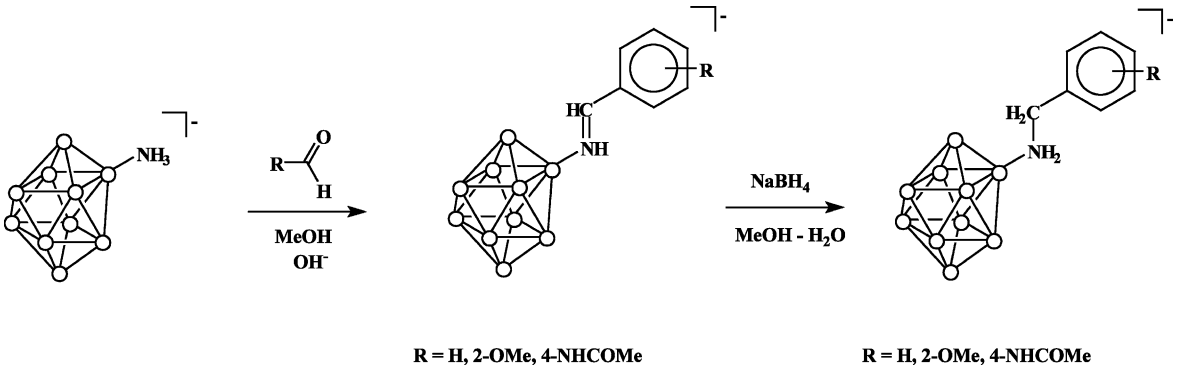


The reaction of $[B_{10}H_{10}]^{2-}$ with aryldiazonium tetrafluoroborate, giving $[1\text{-}B_{10}H_9NHNAr]^-$ in close to quantitative yield, is known to be the best way to introduce selectively substituents at the apical boron of the *closo*-decaborate anion [5]. The arylazo group can be easily converted into diazonium [25], amino [5], alkylamino [16], and mercapto [26] groups. It was shown previously that the $[2\text{-}B_{10}H_9NMe_3]^-$ anion can be substituted selectively at one of the apical boron vertices giving $[1,6\text{-}N_2B_{10}H_8NMe_3]$ [25]. This prompted us to study the possibility of regioselective synthesis of bifunctional derivatives on the base of the $[2\text{-}B_{10}H_9NH_3]^-$ anion using phenyldiazonium tetrafluoroborate. However, the reaction with phenyldiazonium tetrafluoroborate was found to be not regiospecific and the product isolated after reduction of the phenylazo derivative formed with tin in hydrochloric acid solution consisted of a mixture of 1,6- and 1,2-$[B_{10}H_8(NH_3)_2]$ at a ratio of ca. 4:1. The lack of regioselectivity can be explained by a weaker electron-withdrawing effect of the NH_3^+ group in comparison with the NMe_3^+ group. However, it leaves us to hope that there is a possibility of selective substitution in the $[2\text{-}B_{10}H_9NMe_2R]^-$ derivatives, where R is containing functional group substituent.



It was shown previously [7–9] that alkylation of the amino group in the $[2\text{-}B_{10}H_9NH_3]^-$ anion as a rule results in the formation of mixtures of mono-, di-, and trialkylamino derivatives $[2\text{-}B_{10}H_9NH_{3-n}R_n]^-$ ($n = 1-3$). Recently, we described the synthesis of monoalkylamino derivatives of the *closo*-dodecaborate anion via the Schiff bases [4].

In this work, we used a similar approach to produce the Schiff bases and monoalkylamino derivatives of the *closo*-decaborate anion and found that the reaction of $(Bu_4N)[2\text{-}B_{10}H_9NH_3]$ with aromatic aldehydes Ar-C(O)H (Ar=C_6H_5, C_6H_4-2-OMe, C_6H_4-4-NHCOMe) in methanol in the presence of catalytic amounts of sodium hydroxide indeed gave the corresponding Schiff bases $(Bu_4N)[2\text{-}B_{10}H_9NH{=}CHAr]$. These bases can be reduced to the corresponding benzylamine derivatives $(Bu_4N)[2\text{-}B_{10}H_9NH_2CH_2Ar]$ with sodium tetrahydroborate in aqueous methanol.



R = H, 2-OMe, 4-NHCOMe

R = H, 2-OMe, 4-NHCOMe

At present, we are using this approach to synthesize functional derivatives of the *closo*-decaborate anion for nuclear medicine. The results of this study will be published elsewhere.

3. Experimental

The NMR spectra were recorded on a Varian Gemini 200, Varian Unity 400, and Bruker AMX 400 spectrometers. The chemical shifts were referenced to $SiMe_4 = 0.00$ ppm for ^1H and ^{13}C and to $BF_3 \cdot Et_2O = 0.0$ ppm for ^{11}B. The infrared spectra of samples were recorded using a Perkin–Elmer 1760 and Specord IR75 FTIR spectrometers as suspensions in Nujol or films in CH_2Cl_2.

3.1. $[Et_3NH][2\text{-}B_{10}H_9NCCH_3]$

$[Et_3NH][2\text{-}B_{10}H_9NCCH_3]$ was prepared as described in the literature [10]. ^{1}H-NMR (DMSO-d_6, ppm): 3.09 (6H, m, N–CH_2–CH_3), 2.68 (3H, s, –N≡C–CH_3), 1.16 (9H, t, N–CH_2–CH_3). ^{13}C-NMR (DMSO-d_6, ppm): 115.4 (–N≡C–CH_3), 45.7 (N–CH_2–CH_3), 8.6 (N–CH_2–CH_3), 3.2 (–N≡C–CH_3). IR (CH_2Cl_2, cm^{-1}): 3081 (s, ν_{NH}, Et_3NH^+), 3019 (m), 2976 (m), 2907 (m), 2859 (w), 2790 (w), 2721 (w), 2663 (w), 2537 (m, ν_{BH}), 2505 (s, ν_{BH}), 2471 (s, ν_{BH}), 2348 (m, $\nu_{C\equiv N}$), 1672 (w),

1474 (m), 1463 (m), 1452 (m), 1435 (w), 1405 (m), 1396 (m), 1380 (w), 1364 (m), 1298 (w), 1216 (s), 1173 (m), 1157 (m), 1087 (w), 1073 (m), 1059 (w), 1032 (m), 1001 (m), 930 (w), 893 (w), 879 (w), 836 (m), 809 (w), 757 (s), 668 (m).

3.2. Synthesis of [Et_3NH][2-$B_{10}H_9NH_2COCH_3$]

[Et_3NH][2-$B_{10}H_9NCCH_3$] (0.40 g, 1.5 mmol) was dissolved in 40 ml of water and the solution was stirred at room temperature (r.t.) for 6 h. The solvent evaporated in vacuo to dryness and the residue was dried over P_2O_5 giving 0.41 g (96% yield) of the product. IR (Nujol, cm^{-1}): 3569 (w), 3332 (s, ν_{NH}, $-NH_2COMe$), 3093 (s, ν_{NH}, Et_3NH^+), 2955 (s), 2923 (s), 2854 (s), 2727 (w), 2679 (w), 2472 (s, ν_{BH}), 1652 (s), 1513 (m), 1461 (s), 1431 (m), 1402 (m), 1375 (s), 1309 (w), 1291 (w), 1238(s), 1203 (m), 1182 (m), 1172 (m), 1153 (m), 1119 (m), 1084 (w), 1053 (m), 1031 (m), 1002 (m), 994 (m), 936 (w), 896 (w), 838 (m), 791 (m), 724 (m), 706 (w), 674 (m), 666 (m).

3.3. Synthesis of [Bu_4N][2-$B_{10}H_9NH_2COCH_3$]

[Et_3NH][2-$B_{10}H_9NCCH_3$] (0.26 g, 1.0 mmol) was dissolved in 20 ml of water and the solution was stirred at r.t. for 6 h. 0.32 g (1.0 mmol) of Bu_4NBr in 10 ml of water was added. The precipitate formed was filtered off and dried in vacuo over P_2O_5. Yellow single crystals suitable for X-ray diffraction analysis were obtained by recrystallization from methanol.

3.4. Synthesis of [Bu_4N][2-$B_{10}H_9NH_3$]

a) [Et_3NH][2-$B_{10}H_9NH_2COCH_3$] (0.28 g, 1.0 mmol) was heated overnight in 70 ml of the refluxing 2 M ethanolic sodium hydroxide. To this solution 0.48 g (1.5 mmol) of Bu_4NBr in 10 ml of water was added. The reaction mixture was adjusted to pH 6 by addition of 1 M hydrochloric acid and extracted twice with 100 ml of dichloromethane. The organic phase was dried over Na_2SO_4, filtered, and evaporated to dryness under reduced pressure. The residue was recrystalized from ethanol and dried over P_2O_5 giving 0.33 g (88%) of the product. ^{11}B-NMR (CD_3OD, ppm): −2.07 (1B, B(10), d, $J = 141$ Hz), −3.80 (1B, B(1), d, $J = 146$ Hz), −15.49 (1B, B(2), s), −25.27 (2B, B(7,8), d, $J = 145$ Hz), −26.77 (2B, B(3,5), d, $J = 180$ Hz), −30.08 (2B, B(6,9), d, $J = 129$ Hz), −31.60 (1B, B(4), d, $J = 170$ Hz).

b) To 5.33 g (16.5 mmol) $(Et_3NH)_2[B_{10}H_{10}]$ in 50 ml of acetonitrile 20 ml of trifluoroacetic acid was added and the solution was heated at 60 °C for 4 h. Solution was cooled to −30 °C and evaporated to dryness under reduced pressure. The residue was dissolved in 100 ml of 2 M ethanolic sodium hydroxide and the solution was heated under reflux overnight. To this solution 6.5 g (19.8 mmol) of Bu_4NBr in 50 ml of water was added. The reaction mixture was adjusted to pH 6 by addition of 1 M hydrochloric acid and extracted twice with 100 ml of dichloromethane. The organic phase was dried over Na_2SO_4, filtered, and evaporated to dryness under reduced pressure. The residue was recrystalized from ethanol and dried over P_2O_5 giving 5.38 g (85%) of the product.

3.5. Synthesis of [Bu_4N][1-D-6-D_3N-$B_{10}H_9$]

(Bu_4N)[2-$B_{10}H_9NH_3$] (37 mg, 0.1 mmol) was dissolved in 2 ml methanol-d_4 and solution was allowed to stand at r.t. for 1 week. Solvent was evaporated to dryness at r.t. under N_2 stream giving 37 mg (quantitative yield) of the product. ^{11}B-NMR (CD_3OD, ppm): −2.07 (1B, s), −3.80 (1B, d), −15.49 (1B, s), −25.27 (2B, d), −26.77 (2B, d), −30.08 (2B, d), −31.60 (1B, d).

3.6. Secondary amination of [2-$B_{10}H_9NH_3$]$^-$

To the solution 0.74 g (2.0 mmol) (Bu_4N)[2-$B_{10}H_9NH_3$] in 150 ml of acetonitrile at 0 °C was added solution 0.40 g (2.1 mmol) phenyldiazonium tetrafluoroborate in 50 ml of acetonitrile and formed deep violet solution was stirred at r.t. overnight. The acetonitrile was removed in vacuo, residue was taken up in 70 ml of methanol, to this solution were added 2.36 g (20 mmol) tin and 30 ml of concentrated hydrochloric acid and stirred for 3 h. The reaction mixture was filtered and the solvent was removed in vacuo, the residue was recrystallized from aqueous ethanol and dried in vacuo over P_2O_5 giving 70 mg (23%) of white solid consisting of mixture of 1,2- and 1,6-[$B_{10}H_8(NH_3)_2$]. ^{11}B-NMR (D_2O, ppm): 6.2 (s, minor isomer), 2.0 (s, major isomer), −6.6 (d, major isomer), −9.3 (d, minor isomer), −18.8 (s), −26.7 to −32.7 (m).

3.7. Synthesis of [Bu_4N][2-$B_{10}H_9NH{=}CHC_6H_4$-2-OCH_3]

To the stirred solution of 0.37 g (1.0 mmol) (Bu_4N)[2-$B_{10}H_9NH_3$] and 0.15 g (1.1 mmol) of 2-methoxy benzaldehyde in 4 ml methanol three drops of 5% aqueous solution of sodium hydroxide was added. The solution became orange and the reacton mixture was stirred for 1 h. The yellow precipitate formed was filtered, washed with diethyl ether and dried in air, giving 0.29 g (59%) of the product. ^{1}H-NMR (DMSO-d_6, ppm): 11.54 (1H, d, $J = 19.2$ Hz), 8.40 (1H, d, $J = 19.2$ Hz), 7.99 (1H, d, $J = 8.0$ Hz), 7.62 (1H, t, $J = 8.0$ Hz), 7.19 (1H, d, $J = 8.8$ Hz), 7.05 (1H, t, $J = 8.8$ Hz), 3.90 (3H, s), 3.15 (8H, m) (Bu_4N^+), 1.55 (8H, m) (Bu_4N^+), 1.30 (8H, m) (Bu_4N^+), 0.92 (12H, t) (Bu_4N^+). ^{13}C-NMR (DMSO-d_6, ppm): 163.1, 159.6,

136.5, 130.2, 121.0, 117.5, 112.5, 57.5 (Bu_4N^+), 56.3, 23.1 (Bu_4N^+), 19.2 (Bu_4N^+), 13.5 (Bu_4N^+). ^{11}B-NMR (DMSO-d_6, ppm): 1.8 (1B, d, $J = 145$ Hz), −1.1 (1B, d, $J = 145$ Hz), −10.8 (1B, s), −23.0 (4B, m), −27.0 (3B, m). ^{11}B-NMR (CD_3OD, ppm): 2.1 (1B, d, $J = 143$ Hz), −1.3 (1B, d, $J = 145$ Hz), −11.4 (1B, s), −23.1 (2B, d, $J = 135$ Hz), −24.8 (2B, d, $J = 140$ Hz), −27.3 (3B, d, $J = 127$ Hz). IR (CH_2Cl_2, cm^{-1}): 3608 (m), 3305 (m), 3052 (m), 2962 (s), 2875 (s), 2472 (vs), 1636 (s), 1601 (s), 1576 (s), 1494 (s), 1483 (s), 1462 (s), 1416 (w), 1381 (m), 1341 (m), 1311 (m), 1267 (s), 1248 (s), 1218 (m), 1166 (m), 1128 (m), 1105 (w), 1047 (s), 1015 (s), 977 (m), 887 (m), 773 (m), 736 (s), 701 (m).

3.8. Synthesis of [Bu_4N][2-$B_{10}H_9NH$=CHC_6H_4-4-$NHCOCH_3$]

To the stirred solution of 0.37 g (1.0 mmol) (Bu_4N)[2-$B_{10}H_9NH_3$] and 0.18 g (1.1 mmol) of 4-acetamidobenzaldehyde in 4 ml methanol three drops of 5% aqueous solution of sodium hydroxide was added. The solution became orange and the reacton mixture was stirred overnight. The yellow precipitate formed was filtered, washed with diethyl ether and dried in air, giving 0.38 g (73%) of the product. ^{1}H-NMR (DMSO-d_6, ppm): 11.67 (1H, d), 10.38 (1H, s), 7.99 (3H, m), 7.68 (2H, d), 3.15 (8H, m) (Bu_4N^+), 2.07 (3H, s), 1.55 (8H, m) (Bu_4N^+), 1.29 (8H, m) (Bu_4N^+), 0.92 (12H, t) (Bu_4N^+). ^{13}C-NMR (DMSO-d_6, ppm): 169.2, 166.1, 144.5, 131.6, 124.2, 118.5, 57.6 (Bu_4N^+), 24.2, 23.1 (Bu_4N^+), 19.2 (Bu_4N^+), 13.5 (Bu_4N^+). ^{11}B-NMR (CD_3OD, ppm): −0.6 (1B, d), −2.1 (1B, d), −12.1 (1B, s), −24.8 (2B, d), −26.2 (2B, d), −28.9 (3B, d). IR (CH_2Cl_2, cm^{-1}): 3314 (m), 3290 (m), 3241 (m), 3219 (w), 3188 (w), 3101 (w), 3054(m), 2959 (m), 2977 (m), 2837 (m), 2464 (vs), 1694 (s), 1639 (s), 1600 (m), 1590 (s), 1531 (m), 1514 (m), 1481 (s), 1420 (s), 1377 (m), 1347 (m), 1323 (s), 1308 (s), 1266 (s), 1236 (m), 1225 (m), 1187 (s), 1151 (w), 1033 (m), 1006 (m), 981 (m), 890 (m), 880 (m), 855 (w), 831 (m), 739 (s), 704 (s).

3.9. Synthesis of [Bu_4N][2-$B_{10}H_9NH$=CHC_6H_5]

To the stirred solution of 0.18 g (0.5 mmol) (Bu_4N)[2-$B_{10}H_9NH_3$] and 0.06 g (0.55 mmol) of benzaldehyde in 4 ml methanol three drops of 5% aqueous solution of sodium hydroxide was added. The solution became orange and the reacton mixture was stirred for 4 h. The reaction mixture was poured into 20 ml of ether. The yellow precipitate formed was filtered, washed with diethyl ether and dried in air, giving 0.15 g (65%) of the product. ^{1}H-NMR (DMSO-d_6, ppm): 12.10 (1H, br s), 8.14 (1H, br s), 8.00 (2H, d), 7.63 (1H, t), 7.51 (2H, t), 3.14 (8H, m), 1.54 (8H, m), 1.29 (8H, m), 0.91 (12H, t). ^{13}C-NMR (DMSO-d_6, ppm): 167.0, 134.4, 130.3, 129.7, 129.4, 57.6 (Bu_4N^+), 23.2 (Bu_4N^+), 19.3 (Bu_4N^+), 13.6 (Bu_4N^+). ^{11}B-NMR (CD_3OD, ppm): −0.3 (1B, d), −1.8 (1B, d), −12.1 (1B, s), −24.8 (2B, d), −26.3 (2B, d), −28.8 (3B, d). IR (CH_2Cl_2, cm^{-1}): 3230 (m), 3203 (m), 3053 (m), 2965 (s), 2877 (s), 2504 (s), 2471 (vs), 1638 (s), 1600 (m), 1478 (s), 1452 (m), 1416 (m), 1382 (m), 1345 (m), 1266 (s), 1218(m), 1151 (w), 1105 (w), 1034 (m), 1003 (m), 977 (m), 895 (m), 737 (s), 703 (s).

3.10. Synthesis of [Bu_4N][2-$B_{10}H_9NH_2CH_2C_6H_4$-2-OCH_3]

To 0.20 g (0.4 mmol) [Bu_4N][2-$B_{10}H_9NH$=CHC_6H_4-2-OCH_3] in 5 ml of the mixture methanol-water (4:1) 0.05 g (1.2 mmol) $NaBH_4$ was added and stirred for 30 min until the solution became colourless. The solution was adjusted to pH 5 with diluted hydrochloric acid and stirred for 30 min. Methanol was removed under reduced pressure, the precipitate formed was filtered off, dried in air, and extracted twice with 5 ml dichloromethane. The extract was evaporated to dryness giving 0.17 g (85%) of white product. ^{1}H-NMR (DMSO-d_6, ppm): 7.24 (1H, d, $J = 7.6$ Hz), 7.22 (1 H, t, $J = 8.0$ Hz), 6.91 (1H, d, $J = 8.0$ Hz), 6.83 (1H, t, $J = 7.6$ Hz), 5.90 (2H, m), 3.75 (3H, s), 3.64 (2H, m), 3.15 (8H, m) (Bu_4N^+), 1.55 (8H, m) (Bu_4N^+), 1.30 (8H, m) (Bu_4N^+), 0.92 (12H, t) (Bu_4N^+). ^{13}C-NMR (DMSO-d_6, ppm): 156.8, 129.8, 129.0, 123.8, 119.9, 110.3, 57.5 (Bu_4N^+), 55.3, 46.6, 23.1 (Bu_4N^+), 19.2 (Bu_4N^+), 13.5 (Bu_4N^+). ^{11}B-NMR (CD_3OD, ppm): −1.6 (1B, d, $J = 140$ Hz), −4.7 (1B, d, $J = 144$ Hz), −12.4 (1B, s), −25.4 (2B, d), −26.8 (2B, d), −30.4 (2B, d), −31.5 (1B, d). IR (CH_2Cl_2, cm^{-1}): 3265 (s), 3177 (s), 3052 (m), 2963 (s), 2875 (s), 2463 (vs), 1605 (m), 1585 (w), 1495 (s), 1467 (s), 1372 (m), 1314 (w), 1294 (m), 1269 (s), 1248 (s), 1197 (w), 1179 (m), 1161 (w), 1117 (m), 1100 (w), 1043 (w), 1021 (s), 992 (m), 978 (m), 973 (w), 885 (m), 757(s), 736 (s), 701 (m).

3.11. Synthesis of [Bu_4N][2-$B_{10}H_9NH_2CH_2C_6H_4$-4-$NHCOCH_3$]

To 0.26 g (0.5 mmol) [Bu_4N][2-$B_{10}H_9NH$=CHC_6H_4-4-$NHCOCH_3$] in 5 ml of the mixture methanol-water (4:1) 0.06 g (1.5 mmol) $NaBH_4$ was added and stirred for 30 min until the solution became colourless. The solution was adjusted to pH 5 with diluted hydrochloric acid and stirred for 30 min. Methanol was removed under reduced pressure, the precipitate formed was filtered off, dried in air, and extracted twice with 5 ml dichloromethane. The extract was evaporated to dryness giving 0.21 g (81%) of white product. ^{1}H-NMR (DMSO-d_6, ppm): 9.87 (1H, s), 7.42 (2H, d, $J = 8.4$ Hz), 7.19 (2H, d, $J = 8.4$ Hz), 6.17 (2H, m), 3.54 (2H, m), 3.15 (8H, m) (Bu_4N^+), 2.00 (3H, s), 1.55 (8H, m) (Bu_4N^+), 1.29 (8H, m) (Bu_4N^+), 0.92 (12H, t) (Bu_4N^+). ^{13}C-NMR (DMSO-d_6): 168.2, 138.5, 130.5,

129.3, 118.4, 57.5 (Bu_4N^+), 50.9, 24.0, 23.1 (Bu_4N^+), 19.2 (Bu_4N^+), 13.5 (Bu_4N^+). ^{11}B-NMR (CD_3OD, ppm): −1.8 (1B, d, $J = 144$ Hz), −4.6 (1B, d, $J = 144$ Hz), −12.2 (1B, s), −25.4 (2B, d), −26.6 (2B, d), −30.4 (3B, d). IR (CH_2Cl_2, cm^{-1}): 3513 (w), 3338 (m), 3278 (m), 3189 (m), 3106 (m), 3053 (s), 2965 (s), 2877 (s), 2472 (vs), 1674 (s), 1600 (s), 1521 (s), 1480 (s), 1414 (s), 1380 (s), 1318 (s), 1267 (s), 1181 (w), 1152 (w), 1106 (w), 1019 (m), 980 (s), 882 (m), 838 (w), 501 (s), 734 (s).

3.12. Synthesis of $[Bu_4N][2\text{-}B_{10}H_9NH_2CH_2C_6H_5]$

To 115 mg (0.25 mmol) $[Bu_4N][2\text{-}B_{10}H_9NH{=}CHC_6H_5]$ in 5 ml of the mixture methanol-water (4:1) 40 mg (1.0 mmol) $NaBH_4$ was added and stirred for 30 min until the solution became colourless. The solution was adjusted to pH 5 with diluted hydrochloric acid and stirred for 30 min. The solution was evaporated to dryness, the residue was treated with 15 ml of water and 15 ml of dichloromethane, the aqueus phase was extracted with 20 ml of dichloromethane, the organic layer was dried over $MgSO_4$, filtered, and evaporated to dryness giving 100 mg (86%) of white solid. ^{1}H-NMR (DMSO-d_6, ppm): 7.26 (5H, m), 6.26 (2H, m), 3.61 (2H, m), 3.15 (8H, m) (Bu_4N^+), 1.56 (8H, m) (Bu_4N^+), 1.30 (8H, m) (Bu_4N^+), 0.92 (12H, t) (Bu_4N^+). ^{13}C-NMR (DMSO-d_6, ppm): 136.0, 128.7, 127.9, 127.3, 57.5 (Bu_4N^+), 51.2, 23.1 (Bu_4N^+), 19.2 (Bu_4N^+), 13.5 (Bu_4N^+). ^{11}B-NMR (DMSO-d_6, ppm): −0.2 (1B, d, $J = 144$ Hz), −4.9 (1B, d, $J = 143$ Hz), −11.9 (1B, d), −24.9 (4B, m), −29.6 (3B, m). IR (CH_2Cl_2, cm^{-1}): 3265 (m), 3176 (m), 3050 (w), 2962 (s), 2933 (s), 2875 (s), 2509 (s), 2466 (vs), 1605 (m), 1585 (m), 1495(s), 1466 (s), 1372 (m), 1289 (m), 1268 (s), 1247 (s), 1202 (w), 1179 (m), 1161 (m), 1117 (m), 1047 (w), 1022 (m), 977 (m), 884 (m), 752 (s), 734 (s), 696 (m).

3.13. Crystal structure determination of $(Bu_4N)[2\text{-}B_{10}H_9NHC(OH)CH_3]$

Crystal data: $(Bu_4N)[2\text{-}B_{10}H_9NHC(OH)CH_3]$, $C_{18}H_{50}B_{10}N_2O$ ($M = 418.70$), monoclinic, $P2_1/c$ (No. 14), $a = 13.106(3)$, $b = 11.474(3)$, $c = 18.185(4)$ Å, $\beta = 99.421(6)^\circ$, $V = 2697.9(11)$ Å^3, $Z = 4$, $d_{calc} = 1.031$ g cm^{-3}, $\mu = 0.056$ mm^{-1}, $F(000) = 920$, crystal size $0.25 \times 0.35 \times 0.50$ mm.

Single-crystal X-ray diffraction experiments were carried out with a SMART 1000 CCD area detector, using graphite monochromated Mo–K_α radiation ($\lambda = 0.71073$ Å, ω-scans with a 0.3° step in ω and 10 s per frame exposure, $2\theta < 60^\circ$) at 110 K. Low temperature of the crystals was maintained with a Cryostream (Oxford Cryosystems) open-flow N_2 gas cryostat. Reflection intensities were integrated using SAINT software [27] and semi-empirical method SADABS [28]. A total of 20 564 reflections were measured, 7206 ($R_{int} = 0.0511$) independent reflections were used in further calculations and refinement. The structures were solved by direct method and refined by the full-matrix least-squares method against F^2 in anisotropic (for nohydrogen atoms) and isotropic (for H atoms) approximation. All the hydrogen atoms were located from the difference Fourier syntheses. The final refinements were converged to $R_1 = 0.0684$ (from 3719 unique reflections with $I > 2\sigma(I)$) and $wR_2 = 0.1538$ (from all 7206 unique reflections). All the calculations were performed on an IBM PC/AT using the SHELXTL software [29].

4. Supplementary material

Crystallographic data for $(Bu_4N)[2\text{-}B_{10}H_9NHC(OH)CH_3]$ have been deposited with the Cambridge Crystallographic Data Centre, CCDC-169348. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www:http://www.ccdc.cam.ac.uk).

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