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A New Convenient Method for Preparing Tetrabutylammonium *closo*-Dodecaborate

Abstract

A new synthetic procedure for preparing tetrabutylammonium *closo*-dodecaborate $(Bu_4N)_2B_{12}H_{12}$ by the solvent-free pyrolysis of tetrabutylammonium tetrahydroborate Bu_4NBH_4 has been developed. The procedure also provides isolation of pure tetrabutylammonium octahydrotriborate $Bu_4NB_3H_8$ as a by-product. The main advantages of the route proposed are convenience and utilization of readily available starting materials. The compounds prepared have been characterized by NMR and IR spectroscopy. Based on the DFT calculations of normal modes of the $[B_3H_8]^-$ and $[B_{12}H_{12}]^{2-}$ anions, the assignment of the main absorption bands in the IR spectra of the compounds synthesized has been performed.

Keywords: *closo*-dodecaborate; octahydrotriborate; pyrolysis; DFT calculations

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Новий зручний спосіб отримання тетрабутиламоній *клозо*-додекаборату

Анотація

Розроблено нову синтетичну процедуру отримання тетрабутиламоній *клозо*-додекаборату $(Bu_4N)_2B_{12}H_{12}$ шляхом піролізу тетрабутиламоній тетрагідроборату Bu_4NBH_4 без розчинника. Процедура також передбачає виділення чистого тетрабутиламоній октагідротриборату $Bu_4NB_3H_8$ як побічного продукту. Основними перевагами запропонованого підходу є його зручність і використання легкодоступних вихідних матеріалів. Одержані сполуки схарактеризовано методами ЯМР- та ІЧ-спектроскопії. На основі DFT-розрахунків нормальних коливань аніонів $[B_3H_8]^-$ та $[B_{12}H_{12}]^{2-}$ визначено структурні фрагменти, яким відповідають основні смуги поглинання в ІЧ-спектрах синтезованих сполук.

Ключові слова: *клозо*-додекаборат; октагідротриборат; піроліз; DFT-розрахунки

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Introduction

Highly symmetric icosahedral *closo*-dodecaborate anion $[B_{12}H_{12}]^{2-}$ fills one of the central places among numerous boron hydrides [1–3]. Compounds based on the *closo*-dodecaborate core are not only of great theoretical interest, but are also promising for the use in medicine as therapeutic agents in cancer treatment by neutron-capturing therapy [4, 5]. An inestimable advantage of these compounds is their low toxicity, which is due to the high chemical stability of the icosahedral B_{12} cluster. The development of an inexpensive method for preparing *closo*-dodecaborate salts from commercially available reagents is an important task on the way to the introduction of such drugs into medical practice.

Synthetic routes to *closo*-dodecaborate salts can be classified roughly into 3 groups according to the starting materials, which could be either boron hydride B_xH_y, octahydrotriborate $[B_3H_8]^-$ or tetrahydroborate $[BH_4]^-$. In early works, triethylammonium *closo*-dodecaborate $(Et_3NH)_2B_{12}H_{12}$ was prepared by the interaction of triethylamine borane Et_3NBH_3 with boron hydrides, such as B_5H_9 [6] or $B_{10}H_{14}$ [7]. In a similar manner sodium salt $Na_2B_{12}H_{12}$ was synthesized by the treatment of $NaBH_4$ with $B_{10}H_{14}$ in boiling diglyme [1, 8]. Despite this route being featured with high yields, it requires working with hazardous, flammable, and commercially unavailable boron hydrides.

The second group of synthetic routes is based on the disproportionation of octahydrotriborate anion $[B_3H_8]^-$ into $[B_{12}H_{12}]^{2-}$ and $[BH_4]^-$ in boiling diglyme. In turn, octahydrotriborate is preliminarily synthesized in the same reactor by the oxidation of $NaBH_4$ with iodine [9] or hydrocarbon halides [10]. The yields of *closo*-dodecaborate are generally higher in the latter case: for example, a tetrabutylammonium salt $(Bu_4N)_2B_{12}H_{12}$ was prepared in the yield of 84, 82, 81, and 80% *via* application of $PhCH_2Cl$, Ph_3CCl, $C_{10}H_7CH_2Cl$ and *n*BuBr, respectively [10]. However, this process is moisture sensitive, and diglyme should be thoroughly dried beforehand, increasing the complexity and total cost of the process.

Synthetic procedures, which include the pyrolysis of tetrahydroborate salts form another group of routes for preparing *closo*-dodecaborates. The formation of a magnesium salt $MgB_{12}H_{12}$ was achieved by the pyrolysis of an equimolar mixture of $Mg(BH_4)_2$ and tetraglyme at 200 °C for 8 h although the yield was not very high [11]. The preparation of sodium and potassium *closo*-dodecaborates in up to the yield of 95% was reported by reactions of the corresponding tetrahydroborates with trialkylamine boranes in high-boiling alkanes (dodecane, hexadecane) at 200–250 °C [1]. The temperature of the process can be lowered by replacing the cation with tetraalkylammonium. For example, a tetraethylammonium salt $(Et_4N)_2B_{12}H_{12}$ can be prepared by heating the suspension of Et_4NBH_4 in triethylamine borane at 185 °C, and it plays a dual role of a reagent and a heat-transfer liquid medium [1]. The main drawback of the method mentioned is the low purity of the product, which is contaminated with other polyhedral boron hydrides ($B_9H_9^{2-}$, $B_{10}H_{10}^{2-}$, $B_{11}H_{14}^{-}$) [12], and thus requires additional chromatographic purification. The high cost of triethylamine borane as a solvent is an additional obstacle for a large-scale application of this synthetic procedure.

The composition of the solid residue after the pyrolysis of tetraalkylammonium tetrahydroborate is known to depend strongly on the nature of the cation [1, 13]. Our study has revealed that a tetrabutylammonium cation favored the formation of *closo*-dodecaborate. Based on these findings, a convenient synthetic procedure for preparing $(Bu_4N)_2B_{12}H_{12}$ by the solvent-free pyrolysis of Bu_4NBH_4 was elaborated. The products were identified by ^1H and ^{11}B NMR spectroscopy. In some cases, the formation of *closo*-decaborate $[B_{10}H_{10}]^{2-}$ was detected. This fact deserves more attention in future studies since this anion is a valuable starting compound for the synthesis of carboranes. It is worth noting that ^1H NMR spectra of all solid products obtained show solely 4 resonances of Bu_4N^+ cation at 0.93 (t, $J = 7.4$ Hz, 3H), 1.30 (sx, $J = 7.4$ Hz, 2H), 1.57 (m, 2H) and 3.17 (m, 2H) ppm, therefore, only ^{11}B NMR spectra are discussed herein.

Assignment of the vibrations in IR spectra of the boranes is also a non-trivial task. In this paper, we report the assignment of the main absorption bands in the IR spectra of $(Bu_4N)_2B_{12}H_{12}$ and $Bu_4NB_3H_8$ based on DFT calculations of normal modes of the corresponding hydroborate anion.

Materials and methods

Starting materials and solvents were obtained from commercial sources and used as received. Tetrabutylammonium tetrahydroborate Bu_4NBH_4 was prepared according to the literature procedure [14] and its purity was determined by the iodometric titration method [15].

Nuclear magnetic resonance (NMR) spectra were measured on a Varian Unity Plus 400 spectrometer. ^{1}H chemical shifts were referenced to tetramethylsilane, and ^{11}B chemical shifts were referenced to $BF_3 \cdot Et_2O$. Infrared (IR) spectra were recorded on an IR5 spectrometer (Edinburgh Instruments) within the range of 4000–600 cm^{-1}.

The synthesis of $(Bu_4N)_2B_{12}H_{12}$ and $Bu_4NB_3H_8$

A 250 mL pear-shaped flask was charged with 30.00 g of Bu_4NBH_4 and connected to a diaphragm pump through a condenser (a 250 mL round-bottom flask equipped with a receiver adapter). After the pump was turned on, the reaction mixture was heated to 170 °C and kept at this temperature for 6 h. The solid residue left after the pyrolysis was transferred to a 100 mL beaker and stirred with 50 mL of boiling ethanol. After cooling to room temperature, the precipitate was filtered off, washed with a small amount of ethanol, and dried in air to give 4.10 g of $(Bu_4N)_2B_{12}H_{12}$ as a white solid.

^{1}H NMR (DMSO-d_6, 400 MHz), δ, ppm: 0.93 (3H, t, J = 7.4 Hz), 1.30 (2H, sx, J = 7.4 Hz), 1.57 (2H, m), 3.17 (2H, m). ^{11}B NMR (DMSO-d_6, 192,4 MHz), δ, ppm: –15.56 (12B, d, J = 126.4 Hz). IR (KBr), ν_{max}, cm^{-1}: 2960, 2936, 2873, 2464, 1470, 1381, 1153, 1053, 882, 740, 710.

The filtrate was evaporated to dryness under reduced pressure, and the residue was stirred with 25 mL of boiling ethyl acetate. After cooling to room temperature, the suspension was filtered, and the filtrate was evaporated to dryness under reduced pressure to give 2.44 g of $Bu_4NB_3H_8$ as a white solid.

^{1}H NMR (DMSO-d_6, 400 MHz), δ, ppm: 0.93 (3H, t, J = 7.4 Hz), 1.31 (2H, sx, J = 7.4 Hz), 1.57 (2H, m), 3.16 (2H, m). ^{11}B NMR (DMSO-d_6, 192,4 MHz), δ, ppm: –29.40 (3B, nonet, J = 33.1 Hz). IR (KBr), ν_{max}, cm^{-1}: 2962, 2935, 2875, 2437, 2386, 2117, 2066, 1569, 1470, 1382, 1299, 1137, 1009, 882, 778, 737, 711, 681, 647.

Computation details

The geometry optimization and normal coordinate analysis in the harmonic approximation of $[B_3H_8]^-$ and $[B_{12}H_{12}]^{2-}$ anions were carried out in a GAMESS (US) program package [16] (version 2023 R1) with the ωB97X-D functional [17] and the Karlsruhe triple zeta basis with one polarization function (TZVP) [18]. No symmetry restrictions were applied.

■ Results and discussion

Within the project concerned with the development of a convenient route for multi-gram scale production of *closo*-dicarbadodecaboranes, we were studying the pyrolysis of tetraalkylammonium tetrahydroborates in order to find optimal conditions for the conversion of $[BH_4]^-$ into *closo*-decaborate $[B_{10}H_{10}]^{2-}$. Previously, it was argued that the presence of butyl groups in tetraalkylammonium cation promotes the formation of $[B_{10}H_{10}]^{2-}$ [13]. However, in our preliminary experiments on the autoclave pyrolysis of Bu_4NBH_4 (in a pure state, as well as in a mixture with toluene) *closo*-dodecaborate $(Bu_4N)_2B_{12}H_{12}$ was always found to be the main solid product. One possible reason was that the increased pressure in the autoclave could be responsible for these results. To check this supposition, experiments on the pyrolysis of Bu_4NBH_4 in the vacuum were carried out. Pyrolysis products were studied by ^{1}H and ^{11}B NMR spectroscopy.

Firstly, the pyrolysis was performed in the vacuum of a water jet pump. Bu_4NBH_4 melts at ~130 °C and, upon further heating, begins to decompose at ~160 °C liberating tributylamine. The latter could be collected in the trap. During the remaining time (12 h), the temperature was maintained at 180 °C. The weight loss upon the pyrolysis was about 85–87%; *i.e.*, typically, 0.45–0.55 g of a solid residue were obtained from 5.00 g of Bu_4NBH_4). After the pyrolysis, the solid residue contained $(Bu_4N)_2B_{12}H_{12}$ and $(Bu_4N)_2B_{10}H_{10}$, which were identified by ^{11}B NMR (*see* positions of signals and coupling constants in the Experimental Part). In addition, it was found that a significant quantity of the starting material was transformed into polyborate, presumably due to the hydrolysis caused by water vapor.

To reduce the possible effect of water vapors, the pyrolysis was performed under the same conditions, but for a shorter period of time (3 h) until the evolution of gas ceased, and the residue in the reaction flask solidified. By this means, 1.87 g of a solid residue were obtained from 10.40 g of Bu_4NBH_4 (the weight loss was 8.53 g, 82.0%). To separate borate impurities, the residue was intensively mixed with 25 mL of dichloromethane, the mixture was filtered, and the filtrate was evaporated to dryness under reduced pressure to give 1.27 g of a white powder. Its ^{11}B NMR spectrum exhibits only the resonances of $[B_{12}H_{12}]^{2-}$ (–15.6 ppm) and $[B_{10}H_{10}]^{2-}$ anions (–0.9 and –28.8 ppm). Based on the relative intensities of these signals, it can be concluded that pyrolysis product is comprised of about 85% $(Bu_4N)_2B_{12}H_{12}$ and 15% $(Bu_4N)_2B_{10}H_{10}$ (mass percentages).

In another experiment, the pyrolysis of Bu_4NBH_4 was carried out under conditions, which excluded the presence of water vapor (the vacuum of a continuously working diaphragm pump). The temperature was maintained at a level just above the beginning of decomposition (160–170 °C). In typical experiments, about 12 g of an off-white solid were obtained by heating 45.00 g of Bu_4NBH_4 at 170 °C for 6 h (the weight loss was 70–75%). This solid contained 60% $(Bu_4N)_2B_{12}H_{12}$ and 40% $Bu_4NB_3H_8$ (mass percentages), as evidenced by ^{11}B NMR. Taking into account that the pyrolysis product contains a minor quantity of impurities, the efficient procedure for isolation of the main component was elaborated. The separation is based on different solubility of tetrabutylammonium hydroborates in organic solvents: $(Bu_4N)_2B_{12}H_{12}$ was insoluble in ethanol, while $Bu_4NB_3H_8$ is soluble in ethanol and ethyl acetate (*see* the Experimental Part for a detailed description).

The main advantages of the procedure proposed for the synthesis of $(Bu_4N)_2B_{12}H_{12}$ include the pyrolysis without adding any high-boiling solvent and purification of the products by simple recrystallization. Another advantage offered by the procedure proposed is that not only *closo*-dodecaborate, but also the octahydrotriborate byproduct $Bu_4NB_3H_8$ can be isolated, which is a more convenient route for preparing octahydrotriborate compared to other known methods based on reactions of $NaBH_4$ with iodine [19] or CuCl [20] in diglyme, with $BH_3{\cdot}THF$ [21], alkali metals tetrahydroborates with $BH_3{\cdot}THF$ [22] or $BH_3{\cdot}DMS$ [23] and reduction of $BH_3{\cdot}THF$ by sodium dispersed on silica gel [24].

The identity of the $(Bu_4N)_2B_{12}H_{12}$ and $Bu_4NB_3H_8$ prepared was additionally confirmed by IR (**Figure 1**) spectroscopy. In order to perform an accurate assignment of IR absorption bands associated with vibrations of the hydroborate anions, the normal coordinate analysis of $[B_{12}H_{12}]^{2-}$ (**Table 1**) and $[B_3H_8]^-$ (**Table 2**) was performed at ωB97X-D/TZVP level of theory. The bands associated with vibrations of the Bu_4N^+ cation were assigned according to [25].

The *closo*-dodecaborate anion (**Figure 2**, *a*) possesses an icosahedral symmetry with calculated BB and BH bonds of 1.78 and 1.21 Å, respectively. It has 3 × 24 – 6 = 66 vibrational modes, but only 3 groups of them are IR active (**Table 1**). The most intense bands in the IR spectrum of $(Bu_4N)_2B_{12}H_{12}$ are due to antisymmetric BH stretching (2464 cm^{-1}) and the BBH bending (1053 cm^{-1}) vibrations. The medium-intensity band in the low-frequency region with a maximum at 710 cm^{-1} is assigned to skeletal vibrations of the B_{12} cluster. Other absorption bands are attributed to vibrations of the Bu_4N^+ cation.

Table 1. Experimental IR absorption bands of $(Bu_4N)_2B_{12}H_{12}$ and calculated normal modes (ν_i) of $[B_{12}H_{12}]^{2-}$ anion

Band (cm^{-1}), intensity[a]	Assignment[b]	ν_i	Calculated frequency (cm^{-1})	Calculated intensity (km mol^{-1})
2960, m 2936, m 2873, m	*ν*(C–H)	-	-	-
2464, s	*ν*(B–H)	ν_{65} ν_{64} ν_{63}	2532.9 2532.6 2532.1	1200 1200 1202
1470, s 1381, m	*δ*(CH)	-	-	-
1153, w	*ρ*(CH_3)	-	-	-
1053, s	*δ*(BH)	ν_{54} ν_{53} ν_{52}	1083.0 1081.3 1079.9	44.8 45.2 44.8
882, m	*ν*(C–N)	-	-	-
740, m	*ρ*(CH_2)	-	-	-
710, m	τ	ν_{17} ν_{16}	721.0 717.9	7.2 7.2

Notes: [a] s – strong, m – medium, w – weak; **[b]** ν – stretching, δ – scissoring, ρ – rocking, τ – skeletal

The octahydrotriborate anion (**Figure 2**, *b*) has a structure of isosceles BBB triangle with BH_2 moieties at vertices. The base of the triangle is a conventional covalent B–B bond, and vertices at the legs are linked by bridging hydrogens. Due to the formation of bent $B–H_b–B$ bonds, the legs are somewhat shorter (1.79 Å) than the base (1.83 Å). The calculated $H_2B–B(H)H_2$ stretching force constants (2.99 N cm^{-1}) are also larger than $H_2(H)B–B(H)H_2$ one (2.08 N cm^{-1}). The bent $B–H_b–B$ bond is asymmetric: the interatomic distances (stretching force constants) for constituent $B–H_b$

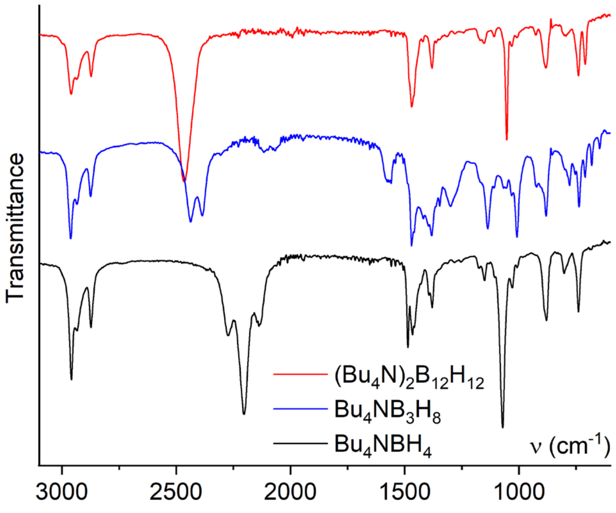

Figure 1. IR spectra of the tetrabutylammonium hydroborates prepared

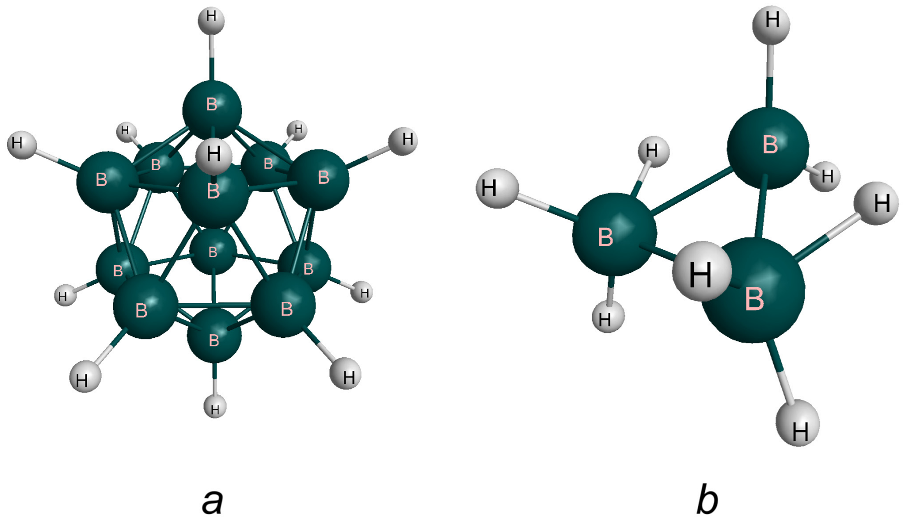

Figure 2. Optimized structures of $[B_{12}H_{12}]^{2-}$ (*a*) and $[B_3H_8]^-$ (*b*)

Table 2. Experimental IR absorption bands of $Bu_4NB_3H_8$ and calculated normal modes (ν_i) of $[B_3H_8]^-$ anion

Band (cm^{-1}), intensity[a]	Assignment[b]	ν_i	Calculated frequency (cm^{-1})	Calculated intensity (km mol^{-1})
2962, s 2935, m 2875, m	ν(C–H)	-	-	-
2437, s	$\nu_{as}(B{=}H_2)$	ν_{24}	2518.0	707
2386, s	$\nu_{as}(\{H\}B{=}H_2)$ $\nu_s(B{=}H_2)$	ν_{23} ν_{22}	2447.8 2445.1	175 409
2117, w	$\nu_s(B{-}H_b)$	ν_{21}	2248.6	153
2066, w	$\nu_{as}(B{-}H_b)$	ν_{20}	2204.2	42.3
1470, s 1382, s 1299, m	δ(CH)	-	-	-
1137, s	$\delta(BH_2)$	ν_{15}	1162.3	61.7
1009, s	$\omega(BH_2)$	ν_{12}	1042.5	85.8
882, s	ν(C–N)	-	-	-
778, m	ν(B–B)	ν_9 ν_8	823.8 812.8	8.0 11.0
737, s	$\rho(CH_2)$	-	-	-
711, m 681, m 647, w	τ	-	-	-

Notes: [a] s – strong, m – medium, w – weak; [b] *ν* – stretching, *δ* – scissoring, *ρ* – rocking, *ω* – wagging, *τ* – skeletal, *s* – symmetric, *as* – antisymmetric, *b* – bridging

parts are 1.26 Å (2.72 N cm^{-1}) and 1.48 Å (1.00 N cm^{-1}). For comparison, the length and force constant for the B–H bonds involving terminal hydrogen atoms are 1.21 Å and 3.36 N cm^{-1}, respectively. For the $[B_{12}H_{12}]^{2-}$ anion, the B–H force constant was calculated to be 3.46 N cm^{-1}. The computed values correspond to those previously reported in [26].

The IR spectrum of $Bu_4NB_3H_8$ is more complicated compared to $(Bu_4N)_2B_{12}H_{12}$ (**Figure 1**). The intense band in the 2330–2550 cm^{-1} range is split into 2 components. According to the calculations performed for $[B_3H_8]^-$, the higher frequency component (peaked at 2437 cm^{-1}) is attributed to the antisymmetric stretching of all three BH_2 moieties in the octahydrotriborate anion. The lower frequency component (peaked at 2386 cm^{-1}) is due to the symmetric counterpart of the previous vibration and antisymmetric BH_2 stretching in two BH_3 fragments. Two weak bands in the 2030–2150 cm^{-1} range are assigned to symmetric (higher frequency) and antisymmetric (lower frequency) B–H$_b$ stretching involving bridging hydrogens. Strong, sharp bands at 1137 and 1009 cm^{-1} are assigned to scissoring and wagging deformations of the BH_2 moieties, respectively. In the low-frequency region two intense bands at 882 and 737 cm^{-1} are due to vibrations of the Bu_4N^+ cation (as can be seen from **Figure 2**, these bands are common for all tetrabutylammonium compounds studied), while other less intense bands are associated with BB stretching (band at 778 cm^{-1}) or other skeletal vibrations of the octahydrotriborate anion (bands below 720 cm^{-1}).

■ Conclusions

Tetrabutylammonium *closo*-dodecaborate $(Bu_4N)_2B_{12}H_{12}$ can be conveniently prepared by the thermal decomposition of Bu_4NBH_4 in the vacuum of a diaphragm pump. When the process is carried out at temperatures not exceeding 175 °C, both the final $(Bu_4N)_2B_{12}H_{12}$ and the intermediate $Bu_4NB_3H_8$ products can be isolated from pyrolysis residue by simple recrystallization. The procedure proposed is easy to handle and does not require any sophisticated equipment.

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