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Methods of Creating *closo*-Decaborate Anion Derivatives with Bridging and Terminal Exopolyhedral Cyclic Substituents of Sulfonium Type

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Abstract—New methods of creation of cyclic bridging and terminal exopolyhedral sulfur-containing substituents in the *closo*-decaborate anion have been suggested. It has been shown that the reaction of $[\text{B}_{10}\text{H}_9\text{SH}]^{2-}$ with 1,2-dibromoethane leads to crosslinking of two cluster anions to give the $[\text{B}_{10}\text{H}_9\text{S}(\text{CH}_2)_2\text{SB}_{10}\text{H}_9]^{2-}$ dimer. An analogous reaction with 1,4-dibromobutane yields a derivative with the cyclic tetrahydrothiophene substituent $[\text{B}_{10}\text{H}_9\text{S}(\text{CH}_2)_4]^-$. Its interaction with tetrahydrothiophene in the presence of a small excess of trifluoroacetic acid leads to the formation of the neutral disubstituted derivative $[\text{B}_{10}\text{H}_8(\text{S}(\text{CH}_2)_4)_2]$.

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Previously [1–3], we have shown that the interaction of the $[\text{B}_{10}\text{H}_9\text{SH}]^{2-}$ anion with monohaloalkanes $\text{Hal}-\text{R}$ ($\text{Hal} = \text{Cl}, \text{Br}$, $\text{R} = n\text{-C}_4\text{H}_9$, $n\text{-C}_8\text{H}_{17}$, $n\text{-C}_{12}\text{H}_{25}$, $n\text{-C}_{18}\text{H}_{37}$, $-\text{CH}_2\text{CHCH}_2$, $-\text{CH}_2\text{CCH}$, $-\text{CH}_2\text{Ph}$, $-\text{CH}_2(4\text{-PhNO}_2)$, $-\text{CH}_2\text{CH}_2\text{OH}$, $-\text{CH}_2\text{CN}$, $-\text{CH}_2\text{CH}_2\text{CN}$, $-\text{CH}_2\text{COOEt}$) gives sulfonium di-S,S-substituted derivatives $[\text{B}_{10}\text{H}_9\text{SR}_2]^-$.

In the present study, we found that the reaction of the sulfonyl-*closo*-decaborate anion with 1,2-dibromoethane leads to crosslinking of two cluster anions to form a dithioxanium derivative (Fig. 1).

The ^{11}B NMR spectrum of the $[\text{B}_{10}\text{H}_9\text{S}(\text{CH}_2\text{CH}_2)_2\text{SB}_{10}\text{H}_9]^{2-}$ anion shows five signals with integrated intensity ratio 1 : 1 : 1 : 4 : 3: two signals of apical boron atoms at 4.6 and -2.8 ppm, the signal of the ipso-boron atom at -15.2 ppm, and two signals

of the unsubstituted boron atoms in the equatorial belt -24.8 and -28.4 ppm.

The ^1H NMR spectrum of $(n\text{-Bu}_4\text{N})_2[\text{B}_{10}\text{H}_9\text{S}(\text{CH}_2\text{CH}_2)_2\text{SB}_{10}\text{H}_9]$ shows two types of signals of the anionic part: two doublets at 3.53 and 2.91 ppm ($J = 12.15$ Hz) corresponding to two chemically nonequivalent apical and equatorial hydrogen atoms of the chair conformation of the cyclic substituent and a multiplet at 3.26 ppm corresponding to analogous signals of the boat conformation (Fig. 2). The ^{13}C NMR spectrum shows two closely spaced signals (34.2 and 34.1 ppm), which presumably reflects the presence of different conformers in solution (Fig. 2).

The reaction of the $[\text{B}_{10}\text{H}_9\text{SH}]^{2-}$ anion with 1,4-dibromobutane leads to the formation of a cyclic tetrahydrothiophene derivative (Fig. 3), which can also be obtained by the reaction of the $[\text{B}_{10}\text{H}_{11}]^-$ or $[\text{B}_{10}\text{H}_{10}]^{2-}$ anion with tetrahydrothiophene in the presence of a Lewis acid [4, 5].

The ^{11}B NMR spectrum of the $[\text{B}_{10}\text{H}_9\text{S}(\text{CH}_2)_4]^-$ anion is similar to the spectrum of the $[\text{B}_{10}\text{H}_9\text{S}(\text{CH}_2\text{CH}_2)_2\text{SB}_{10}\text{H}_9]^{2-}$ anion since a sulfonium substituent is formed in both cases. There is only a slight difference in chemical shifts between analogous signals.

Like in the case of synthesis of disubstituted oxonium derivatives [5], the tetrahydrothiophene deriva-

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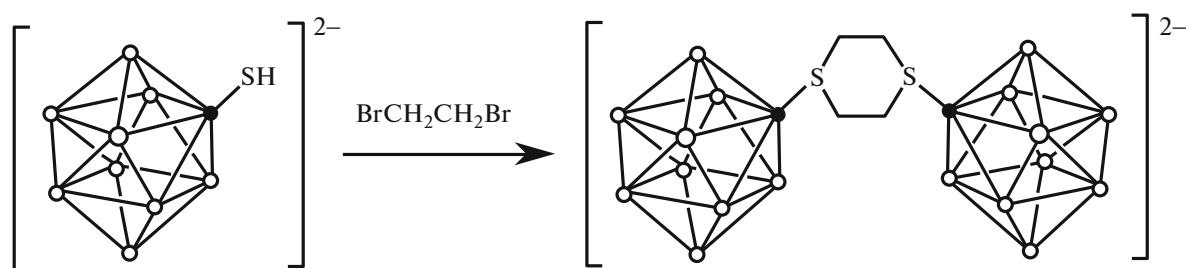


Fig. 1. Scheme of interaction of the $[\text{B}_{10}\text{H}_9\text{SH}]^{2-}$ anion with 1,2-dibromoethane.

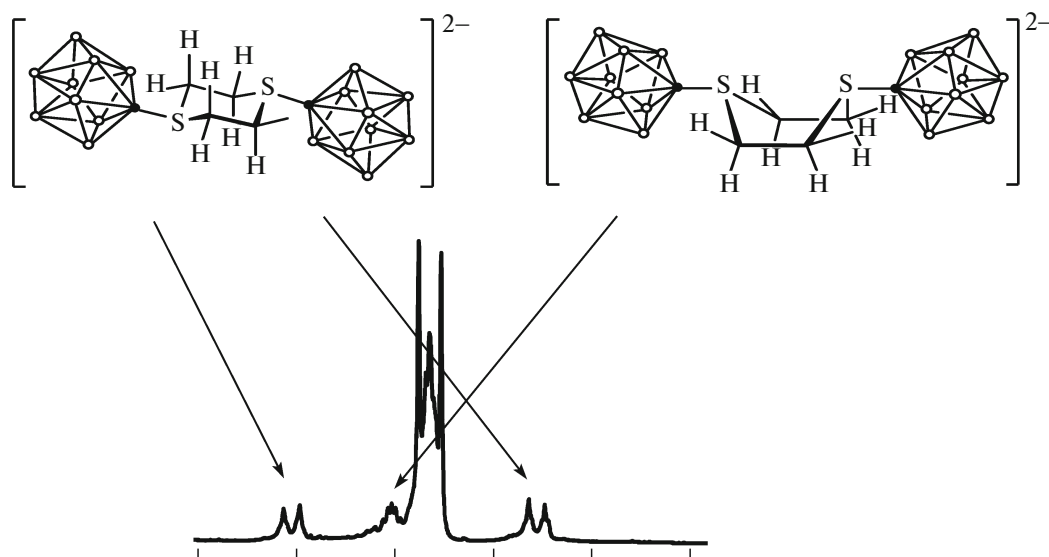


Fig. 2. Fragment of the ^1H NMR spectrum of $(n\text{-Bu}_4\text{N})_2[\text{B}_{10}\text{H}_9\text{S}(\text{CH}_2\text{CH}_2)_2\text{SB}_{10}\text{H}_9]$.

tive $[\text{B}_{10}\text{H}_9\text{S}(\text{CH}_2)_4]^-$ can further react with tetrahydrothiophene in the presence of trifluoroacetic acid or dry hydrogen chloride on heating (Fig. 3).

The ^{11}B NMR spectrum of this derivative shows four signals with the integrated intensity ratio 2 : 2 : 2 : 4: the signal of equivalent apical vertices (B1, B10) at 0.2 ppm, the signal at -12.9 ppm due to the ipso-boron atoms (B2, B7), the signal at -22.2 ppm of the B4 and B9 atoms, and the signal at -26.5 ppm arising from the other four atoms.

The structure of the $(n\text{-Bu}_4\text{N})_2[\text{B}_{10}\text{H}_9\text{S}(\text{CH}_2\text{CH}_2)_2\text{SB}_{10}\text{H}_9]$ compound was determined by single crystal X-ray diffraction (Fig. 4).¹

The monoclinic unit cell of $(n\text{-Bu}_4\text{N})_2[\text{B}_{10}\text{H}_9\text{S}(\text{CH}_2\text{CH}_2)_2\text{SB}_{10}\text{H}_9]$ contains two anions and four cations. The asymmetric unit comprises one half of the $[\text{B}_{10}\text{H}_9\text{S}(\text{CH}_2\text{CH}_2)_2\text{SB}_{10}\text{H}_9]^{2-}$ anion and one $n\text{-Bu}_4\text{N}$ cation. The cyclic dithionium substituent has a chair conformation with the equato-

rial arrangement of the $[\text{B}_{10}\text{H}_9]$ substituents. The B–S bond lengths are $1.896(2)$ Å, which corresponds to the bond lengths in other derivatives of the *closo*-decaborate anion with *exo*-polyhedral substituents containing a boron–sulfur bond. The sulfur atoms are located at the vertices of trigonal pyramid at a distance of 0.805 Å from the base plane, which is evidence that the positive charge is localized on sulfur atoms.

¹ Sets of reflection intensities for crystal I were collected on an automated Bruker APEX2 CCD diffractometer ($\lambda\text{MoK}\alpha$, ω -scan) [6] of the Shared Facility Center, Institute of General and Inorganic Chemistry, RAS. Reflection arrays were processed with the SAINT software [6]. Absorption corrections were applied with the SADABS program [6]. The structure was solved by direct methods using the SHELXS program package [7]. Non-hydrogen atoms were refined by least-squares calculations in the anisotropic approximation; the H atoms were refined as riding on their bonded atoms, $U_{\text{iso}}(\text{H})$ being 1.2 or 1.5 (CH_3 groups) times as large as U_{eq} of the corresponding non-hydrogen atom. One of the terminal methyl groups of the cation is disordered over two positions with equal site occupancy factors [8].

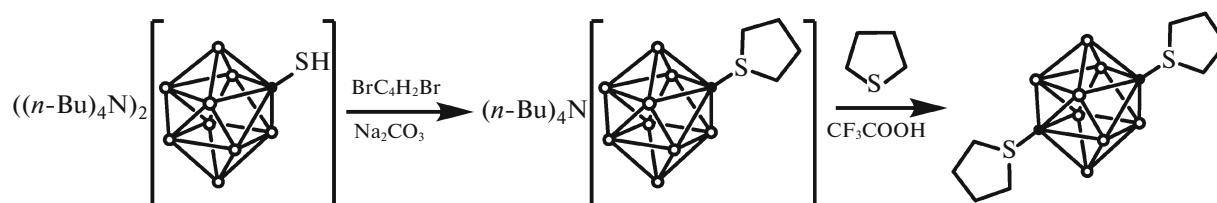


Fig. 3. Scheme of synthesis of mono- and disubstituted tetrahydrothiophene derivative.

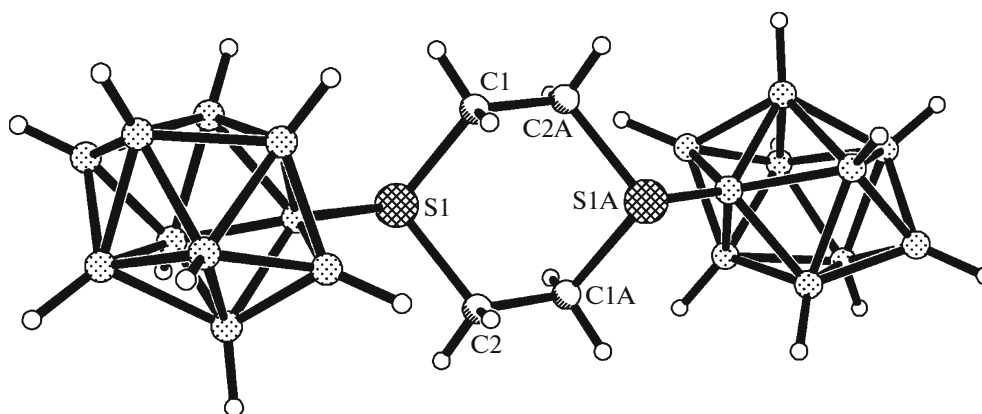


Fig. 4. Structure of the $[B_{10}H_9S(CH_2CH_2)_2SB_{10}H_9]^{2-}$ anion according to single crystal X-ray diffraction data.

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