Synthesis and Characterization of *o*-Carboranylthioether Derivatives

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The reactions of the dithiolato-*o*-carborane salt $(Et_3NH)_2(S_2C_2B_{10}H_{10})$ (**2**) with alkyl halides $BrCH_2CH{=}CH_2$, $BrCH_2CH_2CH_2Cl$ and $C_6H_5CH_2Cl$, afford the *o*-carboranyl-bisthioether derivatives **3a** – **c**, which have been characterized by IR and NMR (^1H, ^{13}C, ^{11}B) spectroscopy, mass spectrometry, and single-crystal X-ray diffraction (**3c**). The photoluminescent properties of the known compound **3c** has been investigated. It exhibits a violet (chloroform solution) or blue (solid state) emission when excited with UV light.

Key words: *o*-Carborane, Thioether, Synthesis, Crystal Structure, Photoluminescence

Introduction

The chemistry of *closo*-carboranes $C_2B_{10}H_{12}$ (*ortho*-, *meta*-, and *para*-isomers) has been extensively studied due to the excellent thermal and chemical stability of the clusters and their potential applications especially in biomedical and materials science [1 – 4]. Among the many functionalized carborane compounds, the *C*-chalcogeno (S, Se, Te) derivatives of *ortho*-$C_2B_{10}H_{12}$ occupy a special position, and many related metal complexes have been reported [5 – 9]. The *ortho*-$C_2B_{10}H_{12}$ cluster is one of the few unique systems that allows a tuning of the carbon-carbon bond length [10]. It has been observed that the cage carbon-carbon bond lengths vary in a broad range with different substituents on the cage carbon atoms. The C_{cage}–C_{cage} distance in the parent *ortho*-$C_2B_{10}H_{12}$ has been determined to be 1.629(6)/1.630(6) Å [11], while with bulky ferrocenyl groups the corresponding distance is reported to be 2.156(4) Å [12]. In addition, it has been found that the electronic effect of the C-substituents plays a more important role in the lengthening of the C_{cage}–C_{cage} distance than the steric effect, although both effects are definitely involved [13 – 15]. For instance, when the C-substituent atom has electron lone pairs, as *e. g.* with sulfur and selenium atoms, the corresponding C_{cage}–C_{cage} distances are usually long (1.7 – 1.8 Å). We have recently reported the structure of the C-SePh-substituted *o*-carborane derivative 1,2-$(PhSe)_2C_2B_{10}H_{10}$ and found that the C_{cage}–C_{cage} bond length is 1.751(6) Å [16]. In order to further investigate the substituent effect on the corresponding C_{cage}–C_{cage} distance in the *o*-carboranylbisthioether derivatives, we have studied the reactions of the dithiolato-*o*-carborane salt $(Et_3NH)_2(S_2C_2B_{10}H_{10})$ (**2**) with several alkyl halides, and herein report on the details of the synthesis and on the characterization of the resulting *o*-carboranylthioethers.

Results and Discussion

*Synthesis and characterization of **3a** – **c***

In the literature there are generally four methods reported to prepare *o*-carboranylthioether derivatives: a) the reaction of carboranyllithium $Li_2C_2B_{10}H_{10}$ (or the monolithium analog) with organyldisulfides RSSR [5], b) the reaction of the dithiolatocarborane salt $Li_2S_2C_2B_{10}H_{10}$ or related ammonium salts with organyl halides RX to give the corresponding RS-substituted carboranes [5, 17] and c) the reaction of the *o*-carboranyldithiol $(HS)_2C_2B_{10}H_{10}$ with other reagents to produce the corresponding carboranylbisthioether products (for instance, the reaction with thiophosgene resulted in the formation of the cyclic product $(SC)S_2C_2B_{10}H_{10}$ [18]), and d) the reaction of transition metal complexes containing dichalcogenolato-*o*-carborane ligands (obtained from the reaction of $Li_2S_2C_2B_{10}H_{10}$ with organometallic species such as $CpCo(CO)I_2$) with alkynes to afford the corresponding *o*-carboranylbisalkenylthioether products [9]. In this paper we specifically used method b), namely, the reaction of an

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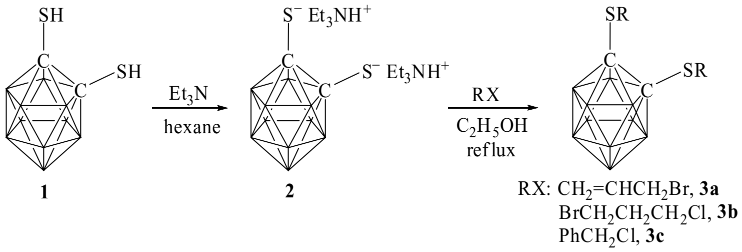

Scheme 1. Synthesis of *o*-carboranylbisthioethers **3**.

easily accessible ammonium dithiolatocarborane salt with alkyl halides (Scheme 1).

The carboranyldithiol **1** [5] was converted to the triethylammonium salt $(Et_3NH)_2(1,2\text{-}S_2\text{-}1,2\text{-}C_2B_{10}H_{10})$ (**2**) by treatment with 2 equiv. of triethylamine in hexane. Subsequently, the reactions of **2** with different alkyl halides in refluxing ethanol resulted in the expected *o*-carboranylthioethers (**3**) in moderate to good yields. The generated products **3** were characterized by IR and multinuclear (^1H, ^{13}C and ^{11}B) NMR spectroscopy, EI-MS, and X-ray structure analysis of **3c** (see below).

In the IR spectrum of compound **3a** (a yellow oil), the B–H stretching bands appear at 2597 cm^{-1}. The ^1H NMR spectrum exhibits signals for the allyl groups at 5.8–5.9 ppm as a multiplet, two doublets at 5.33 and 5.25 ppm, and a doublet at 3.54 ppm, and those for the B-bound protons at 1.66–2.92 ppm. The ^{11}B NMR spectrum of **3a** shows four signals at −3.46, −8.64, −9.91 and −11.02 ppm. The IR spectrum of compound **3b** (a yellow oil) presents the ν(B-H) absorption bands at 2600 cm^{-1}. In its ^1H NMR spectrum, the typical signals for the 3-chloropropyl groups and the B-bound protons are observed, and the ^{11}B NMR spectrum exhibits four broad signals at −3.30, −8.58, −9.76, and −11.34 ppm.

Compound **3c** (a colorless solid) is already known, but no spectroscopic data or structural details were reported [5]. In the IR spectrum of **3c** the ν(B-H) bands are observed at 2568 and 2613 cm^{-1}. The ^1H NMR spectrum shows the signals for the phenyl groups at 7.4–7.3 ppm, for the methylene moieties at 4.08 ppm and for the B-bound protons at 1.55–3.37 ppm. The ^{11}B NMR spectrum exhibits four signals at −3.33, −8.77, −9.84, and −11.00 ppm. The EI-MS spectra of **3a**–**c** all give the corresponding molecular ion peaks with correct isotopic patterns.

Crystal and molecular structure of **3c**

Single crystals of compound **3c** were grown by slow evaporation of a solution in hexane at r. t., and the solid-state structure has been established by an X-ray diffraction analysis (Fig. 1). Details of the crystal parameters, data collection and refinement are summarized in Table 1, and selected bond lengths and bond angles are given in Table 2.

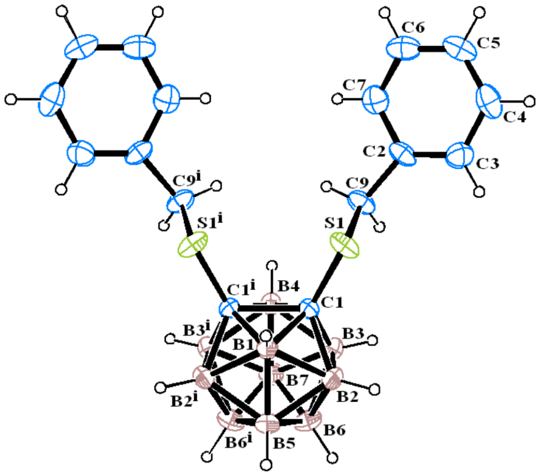

Fig. 1. The molecular structure of **3c**, with crystallographic atom labels and 30 % probability displacement ellipsoids.

As shown in Fig. 1, the structure has a crystallographic C_2 symmetry with the two-fold axis bisecting the C1–C1^i and B6–B6^i bonds. The cage C–C bond length (1.807(6) Å) is significantly longer than those found in the parent *o*-carborane (1.629(6)/1.630(6) Å) [11], similar to those in 1,2-$(PhS)_2$-*closo*-$C_2B_{10}H_{10}$ (1.799(3) Å) [14] and 1,2-$(CH_3S)_2$-*closo*-1,2-$C_2B_{10}H_{10}$ (1.8033(18) Å) [19], but slightly shorter than those in 1,2-μ-$SCH_2CH_2OCH_2CH_2S$-1,2-*closo*-$C_2B_{10}H_{10}$ (1.816(6) Å) [20] and 1,2-μ-$SCH_2(CH_2OCH_2)_2CH_2S$-1,2-*closo*-$C_2B_{10}H_{10}$ (1.826(5) and 1.858(5) Å) [21]. The data of some related examples are listed in Table 3. The comparison of the cage C–C bond lengths indicates that two thioether moieties usually have a more significant influence on the lengthening of the cage carbon-carbon bond than one of these units, and that *exo*-cyclic parts show longer C–C distances. It should also be noted, how-

Table 1. Crystal data and data collection and refinement details for **3c**.

Formula	$C_{16}H_{24}B_{10}S_2$
M_r	388.57
Crystal size, mm^3	$0.37 \times 0.35 \times 0.31$
Temperature, K	291(2)
Crystal system	monoclinic
Space group	$C2/m$
a, Å	16.0038(12)
b, Å	14.0964(12)
c, Å	10.6831(9)
β, deg	114.797(10)
V, Å^3	2187.9(3)
Z	4
D_{calcd}, g cm^{-3}	1.18
$\mu(\mathrm{Mo}K_\alpha)$, mm^{-1}	0.2
$F(000)$, e	808
hkl range	±19, ±17, ±13
θ range, deg	3.31 – 26.37
Reflections collected /unique / R_{int}	7064 / 2317 / 0.0286
Data / ref. parameters	2317 / 137
$R1$ / $wR2$ [$I \geq 2\sigma(I)$]^{a,b}	0.0742 / 0.2029
$R1$ / $wR2$ (all data)^{a,b}	0.0843 / 0.2120
Goodness-of-fit (GoF)^c on F^2	1.077
$\Delta\rho_{\mathrm{max/min}}$, e Å^{-3}	0.67 / −0.25

[a] $R1 = \Sigma\|F_o| - |F_c\|/\Sigma|F_o|$; [b] $wR2 = [\Sigma w(F_o{}^2 - F_c{}^2)^2/\Sigma w(F_o{}^2)^2]^{1/2}$, $w = [\sigma^2(F_o{}^2) + (0.1041P)^2 + 4.7792P]^{-1}$, where $P = (\mathrm{Max}(F_o{}^2,0) + 2F_c{}^2)/3$; [c] $\mathrm{GoF} = [\Sigma w(F_o{}^2 - F_c{}^2)^2/(n_{\mathrm{obs}} - n_{\mathrm{param}})]^{1/2}$.

ever, that in some bisthioether derivatives the cage C–C bond lengths are essentially unaffected when compared to those in the parent *o*-carborane [11].

Table 2. Selected bond lengths (Å) and angles (deg) for **3c** with estimated standard deviations in parentheses[a].

S1–C1	1.766(3)	C1–B4	1.723(5)
S1–C9	1.837(10)	C1–B1	1.725(5)
C1–B3	1.679(5)	C1–C1^i	1.807(6)
C1–B2	1.690(5)		
C1–S1–C9	103.6(3)	C2–C9–S1	104.7(6)
S1–C1–C1^i	116.7(1)		

[a] Symmetry code: ^{i} x, $-y$, z.

The S–C$_{\mathrm{cage}}$–C$_{\mathrm{cage}}$–S torsion angle in **3c** is found to be 0.0(3)°, indicating that the four atoms lie in one plane, but the two benzyl groups are pointing towards the same side of the carborane cluster, which is rare among the structurally characterized non-*exo*-cyclic carboranylbisthioethers (Table 3). As can be seen from Table 3, the only examples to have similar orientations are the MeS-substituted derivative and a few *exo*-cyclic compounds, whereas other dithioether structures exhibit S–C$_{\mathrm{cage}}$–C$_{\mathrm{cage}}$–S torsion angles of 10 – 17° and have the two sulfur-attached substituents pointing in the opposite direction with respect to the carborane cluster in order to minimize the steric repulsion of the sulfur electron lone pairs. There appears to be no apparent intermolecular interaction between the molecules of **3c** in the crystal. Although the intramolecular S···S distance in **3c** of 3.393(1) Å is somewhat shorter than most of the values in the related structures shown in Table 3, it is only slightly shorter

Table 3. Data of some structurally characterized *o*-carboranylthioethers[a].

Compound	Yield (%)	Synthetic method	Cage C–C distance (Å)	S–C–C–S Torsion angle (deg)	S···S Distance (Å)	Refs.
1,2-(MeS)$_2$-C$_2$B$_{10}$H$_{10}$	not given	a, b	1.8033(18)	1.07(13)	3.4359(6)	[5, 19]
1,2-(PhS)$_2$-C$_2$B$_{10}$H$_{10}$	76[b]	a, b	1.799(3)	10.6(2)	3.483(1)	[5, 14]
1-(C$_5$H$_4$NS)-C$_2$B$_{10}$H$_{11}$	35	a	1.643(3)	–	–	[22]
1,2-μ-SCH$_2$CH$_2$O-CH$_2$CH$_2$S-C$_2$B$_{10}$H$_{10}$	22	b	1.816(6)	0.3(5)	3.487(2)	[20]
1,2-μ-SCH$_2$(CH$_2$O-CH$_2$)$_2$CH$_2$S-C$_2$B$_{10}$H$_{10}$	–	b	1.826(5)	0.9(4)	3.434(5)	[21]
			1.858(5)	1.0(3)	3.435(3)	
1,2-(MeOOCHC=CHS)$_2$-C$_2$B$_{10}$H$_{10}$	27 – 34	d	1.790(4)	12.5(3)	3.420(2)	[9]
(three isomers)			1.793(3)	11.8(2)	3.368(1)	
			1.777(3)	12.9(2)	3.3979(9)	
1,2-μ-SHC=C(Fc)S-C$_2$B$_{10}$H$_{10}$[c]	70	d	1.683(4)	0.819(3)	3.250(1)	[9]
1,2-(FcC(=CH$_2$)S)$_2$-C$_2$B$_{10}$H$_{10}$[c]	10	d	1.820(6)	14.3(4)	3.460(2)	[9]
1,2-μ-SC(CH$_2$)FcS-C$_2$B$_{10}$H$_9$	40	d	1.637(9)	0.1(7)	2.881(2)	[23]
1,2-(FcCOHC=CHS)$_2$-C$_2$B$_{10}$H$_{10}$[c]	26	d	1.751(7)	13.1(5)	3.470(2)	[24]
1,2-μ-SHC=C-(COFc)S-C$_2$B$_{10}$H$_{10}$[c]	10	d	1.636(5)	1.8(5)	3.530(2)	[24]
1-(SHC=CHCOFc)-C$_2$B$_{10}$H$_{11}$[c]	28	d	1.661(3)	–	–	[24]
1,2-μ-S(COOMe)C=C(COOMe)-(COOMe)C=C(COOMe)S-C$_2$B$_{10}$H$_{10}$	30	d	1.717(3)	16.7(2)	3.571(2)	[24]
(S=C)S$_2$C$_2$B$_{10}$H$_{10}$	48	c	1.632(3)	–	–	[18]
1-Ph$_2$P-2-^{i}PrS-C$_2$B$_{10}$H$_{10}$	75	b	1.747(5)	–	–	[25]
1-PhS-2-Me-C$_2$B$_{10}$H$_{10}$	–	a	1.708(4)	–	–	[26]
1,2-[^{t}Bu$_2$(OH)C$_6$H$_2$-S]$_2$C$_2$B$_{10}$H$_{10}$	85	b	1.764(6)	−11.5(4)	3.437(3)	[27]

[a] See text for the synthetic methods a – d; [b] synthetic method a; [c] Fc: ferrocenyl group.

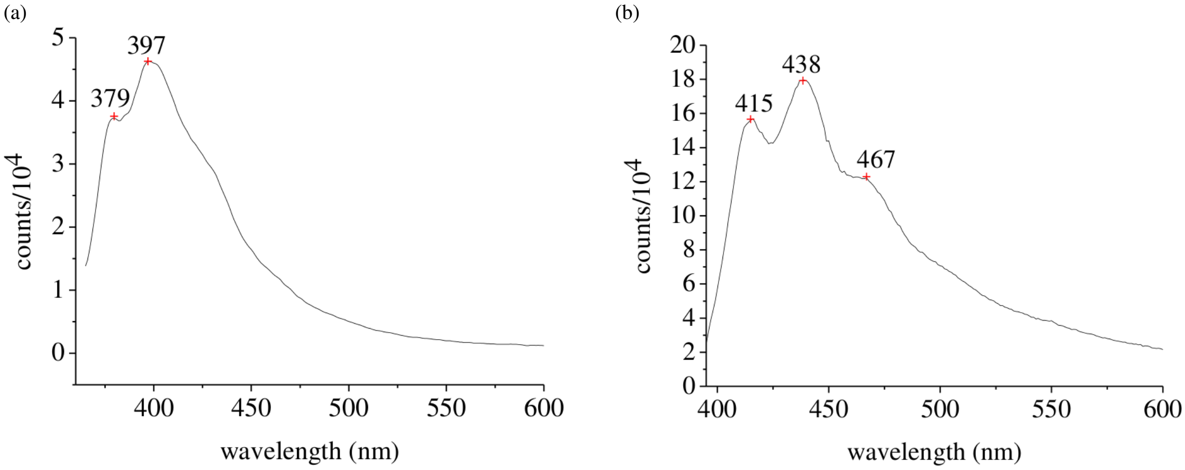

Fig. 2. The photoluminescence spectrum of **3c**. (a) The emission spectrum of **3c** in chloroform (λ_{ex} = 345 nm); (b) the solid-state emission spectrum of **3c** (λ_{ex} = 379 nm).

than the sum of the van der Waals radii of two sulfur atoms (3.6 Å) and considerably longer than the sum of covalent radii of two S atoms (2.04 Å), indicating that there is essentially no bonding interaction between the S atoms.

Photophysical properties of ***3c***

The photophysical properties of **3c** were investigated at r. t. The UV/Vis spectrum of **3c** in chloroform solution shows an absorption band with the maximum at 242 nm. The photoluminescence spectrum of **3c** (Fig. 2a) in chloroform solution exhibits a broad emission band with the highest peak around 397 nm on excitation with UV light (λ_{ex} = 345 nm), which is similar to that reported for 1,2-$(PhS)_2$-*closo*-$C_2B_{10}H_{10}$ [16]. The corresponding spectrum of a solid sample displays a blue emission with vibrational structures (Fig. 2b).

The synthesis and characterization of the *o*-carboranylthioether derivatives **3a – c** will allow further reactivity studies including their ligand properties. A comparison of the structural data of some related carboranylbisthioethers has shown that the cage carbon-carbon bond length is also influenced by the formation of *exo*-polyhedral cycles as well as by the size and nature of the cycles.

Experimental Section

The solvent diethyl ether was dried over sodium/benzophenone and distilled under nitrogen prior to use. Other analytically pure reagents were commercially available. IR spectra were recorded in the range 400 – 4000 cm^{-1} on a Perkin Elmer Spectrum RX I spectrometer using KBr pellets. NMR analyses were performed on a Bruker Avance 400 MHz spectrometer with tetramethylsilane (TMS) as internal standard (^{1}H) and $BF_3 \cdot OEt_2$ as external standard (^{11}B). Chemical shifts are given in ppm. UV/Vis spectra were recorded on a TU-1900 spectrometer. Fluorescence was determined on an Edinburgh FLS920 spectrometer. Melting points were measured with an SGW X-4 apparatus and are not corrected. The mass spectra were recorded on Agilent 5973N MSD (low resolution) and Waters Micromass GCT Premier (high resolution) instruments. The starting material **1** was prepared according to the literature method [5].

Synthesis of ***2***

To solution of **1** (629 mg, 3.02 mmol) in hexane (20 mL) at r. t., Et_3N (638 mg, 6.3 mmol) was added dropwise and the mixture stirred for 30 min and filtered. The colorless precipitate **2** was washed with hexane and dried (954 mg, 76.9 % yield). – IR (KBr): ν = 3436, 2981, 2582, 2470, 1632, 1446, 1382, 1159, 1019, 875, 725 cm^{-1}. – $^{11}B\{^1H\}$ NMR (128.4 MHz, acetone, 293.8 K): δ = −1.48, −8.54, −10.94.

Synthesis of ***3a***

To a solution of **2** (204 mg, 0.5 mmol) in ethanol (30 mL), $BrCH_2CH{=}CH_2$ (130 mg, 1.1 mmol) was added, and the resulting solution was stirred at reflux for 46 h. The reaction mixture was cooled to r. t. and evaporated to dryness *in vacuo*. The residue was treated with CH_2Cl_2 (30 mL) and water (30 mL). The organic layer was separated and the water phase extracted with CH_2Cl_2 (3 × 20 mL), dried over anhydrous Na_2SO_4 and evaporated *in vacuo*. The crude product was purified using preparative TLC on silica gel with CH_2Cl_2/petroleum ether (60 – 90 °C) (1 : 4, $V : V$) as eluent. A colorless band (R_f = 0.77) was separated and washed with CH_2Cl_2. The solvent was evaporated *in vacuo* and **3a** was obtained as a yellow oil (111 mg, 77 % yield). – IR (KBr): ν = 3087, 2597, 1637, 1409, 1232, 985, 929, 724 cm^{-1}. – ^{1}H NMR (400.1 MHz, $CDCl_3$, 293.3 K): δ = 5.78 – 5.89 (m, 2H, C-CH=C), 5.33 (d, J = 16.8 Hz, 2H, C-C=CH), 5.25 (d, J = 10.0 Hz, 2H, C=CH), 3.54 (d, J= 7.2 Hz, 4H, CH_2S), 1.6 – 2.9 (br, 10H, BH). – $^{11}B\{^1H\}$ NMR (128.4 MHz, CH_2Cl_2, 293.5 K): δ = −3.46, −8.64, −9.91, −11.02. – ^{13}C NMR (100.6 MHz, $CDCl_3$, 294.0 K): δ = 130.66, 120.71, 92.18, 40.22. – EI-MS (70 eV): m/z (%) = 288 (8) $[M]^+$, 246 (100) $[M–CH_2=CH-CH_2–H]^+$. – HRMS ((+)-EI): m/z = 290.1935 (calcd. 290.1937 for $C_8H_{20}S_2^{11}B_{10}$, $[M]^+$).

Synthesis of ***3b***

The procedure was analogous to that described for the synthesis of **3a** using **2** (204 mg, 0.5 mmol) and $BrCH_2CH_2CH_2Cl$ (166 mg, 1.05 mmol). The crude product was purified using preparative TLC on silica gel with CH_2Cl_2/petroleum ether (60 – 90 °C) (1 : 6, $V : V$) as eluent. A yellow band (R_f = 0.46) was separated and washed with CH_2Cl_2. The solvent was evaporated *in vacuo*, and **3b** was obtained as a yellow oil (96 mg, 53 % yield). – IR (KBr): ν = 2960, 2600, 1434, 1270, 1079, 889, 725 cm^{-1}. – ^{1}H NMR (400.1 MHz, $CDCl_3$, 293.2 K): δ = 3.64 (t, J= 6.2 Hz, 4H, CH_2Cl), 3.04 (t, J= 7.0 Hz, 4H, CH_2S), 2.07 – 2.21 (m, 4H, CH_2), 1.71 – 2.84 (br, 10H, BH). – $^{11}B\{^1H\}$ NMR (128.4 MHz, $CDCl_3$, 293.2 K): δ = −3.30, −8.58, −9.76, −11.34. – ^{13}C NMR (100.6 MHz, $CDCl_3$, 295.3 K): δ = 92.11, 42.82, 34.23, 30.99. – EI-MS (70 eV): m/z(%) = 361 (19) $[M]^+$, 285 (65) $[M–C_3H_6Cl+2H]^+$. – HRMS ((+)-EI): m/z = 362.1474 (calcd. 362.1471 for $C_8H_{22}S_2Cl_2^{11}B_{10}$, $[M]^+$).

Synthesis of ***3c***

The procedure was analogous to that described for the synthesis of **3a** using **2** (208 mg, 0.51 mmol) and $C_6H_5CH_2Cl$ (165 mg, 1.30 mmol). The crude product was purified using preparative TLC on silica gel with CH_2Cl_2/petroleum ether (60 – 90 °C) (1 : 6, $V : V$) as eluent. A colorless band (R_f = 0.52) was separated and washed with CH_2Cl_2. The solvent was evaporated *in vacuo*, and **3c** was obtained as a colorless solid (157 mg, 79 % yield). M. p. 94 – 103 °C (lit.: 102 – 104 °C [5]). – UV/Vis ($CHCl_3$): λ_{max} (ε_{max}) = 242 nm (5823 L · mol^{-1} · cm^{-1}). – IR (KBr): ν = 3436, 2936, 2613, 2568, 2366, 1632, 1456, 1068, 888, 702 cm^{-1}. – ^{1}H NMR (400.1 MHz, $CDCl_3$, 294.9 K): δ = 7.31 – 7.38 (m, 10H, Ph), 4.08 (s, 4H, CH_2), 1.55 – 3.37 (br, 10H, BH). – $^{11}B\{^1H\}$ NMR (128.4 MHz, $CDCl_3$, 294.9 K): δ = −3.33, −8.77, −9.84, −11.00. – ^{13}C NMR (100.6 MHz, $CDCl_3$, 295.8 K): δ = 133.18, 129.45, 128.92, 128.30, 91.76, 41.79. – EI-MS (70 eV): m/z (%) = 389 (2) $[M]^+$, 297 (11) $[M–C_6H_5CH_2–H]^+$. – HRMS ((+)-EI): m/z = 390.2254 (calcd. 390.2250 for $C_{16}H_{24}S_2^{11}B_{10}$, $[M]^+$).

Crystal structure determination of ***3c***

A suitable single crystal of **3c** was selected and mounted on an Oxford Gemini E diffractometer for data collection (graphite-monochromatized MoK_α radiation, λ = 0.71073 Å, ω scan mode). The structure was solved by Direct Methods and expanded using Fourier difference techniques with the SHELXTL-97 program package [28]. The non-hydrogen atoms were refined anisotropically by full-matrix least-squares calculations on F^2. The hydrogen atoms on the benzyl rings were placed in geometric positions, the B-bound hydrogen atoms were located in difference Fourier maps, and all were refined isotropically. A disorder of three carbon atoms of the phenyl ring was found, but alternative refinement models gave no significant improvement. As a result of this disorder there seems to be an apparent void of *ca.* 57 Å^3 in the crystal structure in the vicinity of the disordered atoms.

CCDC 823091 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

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