

TWO FORGOTTEN TEN-VERTEX *arachno* TRIHETEROBORANES: *arachno*-5,6,9-C₂SB₇H₁₁ AND *arachno*-5,6,9-C₃B₇H₁₃, THEIR MOLECULAR STRUCTURE DETERMINATION BY *ab initio*/NMR APPROACH AND SYNTHESIS OF THE THIACARBABORANEDrahomír HNYK^{1,*} and Josef HOLUB²*Institute of Inorganic Chemistry, Academy of Sciences of the Czech Republic, 250 68 Řež, Czech Republic; e-mail: ¹ hnyk@iic.cas.cz, ² holub@iic.cas.cz*

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This piece of work is dedicated to Jaromír Plešek on the occasion of his 75th birthday in recognition of his outstanding achievements in the area of cluster-boron chemistry and his "life-dimension".

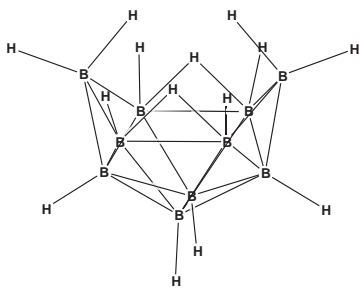
A solution of *nido*-5,6-C₂B₈H₁₂ reacted in the presence of Et₃N with sulfur to yield the first mixed triheteroborane based on the [*arachno*-B₁₀H₁₄]²⁻ framework (C_{2v} symmetry), *i.e.* *arachno*-5,6,9-C₂SB₇H₁₁. This compound is isoelectrolobal with known *arachno*-5,6,9-C₃B₇H₁₃. The structures of these two ten-vertex *arachno* triheteroboranes have been established by the *ab initio*/IGLO (and GIAO-SCF)/NMR method. The presence of three heteroatoms and the absence of the hydrogen atom bridging the 5 and 10 atoms are responsible for a symmetry reduction from C_{2v} to C₁ in both compounds. The carbon atoms are compressed toward the center and the sulfur atom is pushed away from the center of the respective cluster relative to the positions they would have in [*arachno*-B₁₀H₁₄]²⁻. These distortions from the parent compound are well described by the MP2/6-31* geometrical parameters. A good fit between the computed and measured ¹¹B chemical shifts revealed that the MP2/6-31G* internal coordinates are good representations of the molecular geometries of these two ten-vertex *arachno* heteroboranes.

Keywords: Boranes; Carboranes; Thiaboranes; Thiacarboranes; Heteroboranes; *Ab initio* calculations; NMR spectroscopy; Structure elucidation.

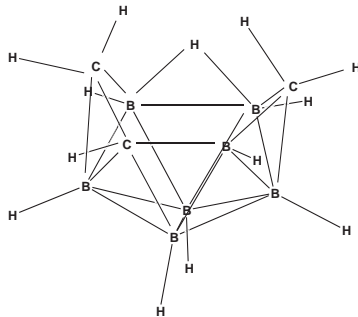
The *arachno*-ten-vertex series of boranes and heteroboranes represents an important class of materials in the chemistry of boron clusters due to their decisive roles in systematic building and degradation procedures leading to clusters of larger or smaller dimensions¹. This family of compounds is based on the parent [*arachno*-B₁₀H₁₄]²⁻ (1), from which the family members can be formally derived by replacing the {BH₂}⁻ cluster vertices by such units that are isoelectrolobal³ with {BH₂}⁻, *e.g.* by {CH₂}, {NH}, {S}, *etc.*⁴ According to Gimarc's topological rule⁵, elements more electronegative than boron (C,

N, S) prefer cluster sites of the highest electronegativity. As revealed by the natural population analysis (NPA) carried out for **1**⁶, a ten-vertex *arachno* heteroborane of an [*arachno*-B₁₀H₁₄]²⁻-type deltahedral shape will prefer its heteroatoms to reside in positions 6 and 9. Indeed, various synthetic routes lead both to anionic monoheteroatom species such as [6-CB₉H₁₄]⁻⁷, [6-NB₉H₁₃]⁻⁸, and [6-SB₉H₁₂]^{-8a,9} and neutral species represented by diheteroatom compounds 6,9-C₂B₈H₁₄¹⁰, 6,9-N₂B₈H₁₂¹¹, and similar mixed diheteroboranes 6,9-CNB₈H₁₃ and 6,9-CSB₈H₁₂¹². Additionally, Štíbr *et al.* reported the synthesis of the first example of the triheteroatom compound based on **1**, *i.e.* *arachno*-5,6,9-C₃B₇H₁₃ (**2**)¹³. This compound is isoelectrolobal with *arachno*-5,6,9-C₂SB₇H₁₁ (**3**), the latter being mentioned for the first time at the IMEBORON VIII meeting¹⁴ but the synthetic procedure has not been published yet.

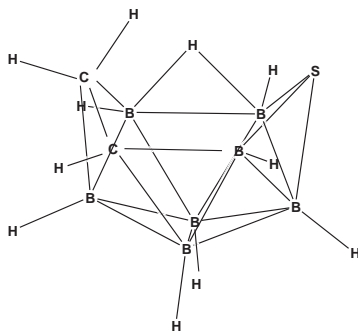
Very little is known about the structures of the compounds notionally derived from **1**. This is also true for **2** and **3**: the corresponding structural data are lacking. On one hand, single crystals of these two compounds are very difficult to grow, which precludes their molecular structure determination in the solid state. On the other hand, structural assignments based on the *ab initio*/IGLO^{15,16} (or GIAO¹⁷)/NMR method “quickly approach a confi-



1



2



3

dence level that rivals that of modern X-ray analysis"¹⁸. Theoretical assessments of structures are based not only on computed geometries but also on chemical shift calculations (IGLO or GIAO) since $\delta(^{11}\text{B})$ values are very sensitive to small geometric changes. The degree of agreement between calculated and experimental¹⁹ ^{11}B chemical shifts serves as a criterion of the accuracy of a particular geometry. These facts provide a good ground for undertaking a structural study of **2** and **3** using the *ab initio*/IGLO (and GIAO)/NMR method for derivation of the internal coordinates of these two unique triheteroboranes.

EXPERIMENTAL

Synthesis of *arachno*-5,6,9- $\text{C}_2\text{SB}_7\text{H}_{11}$ (**3**)

A solution of *nido*-5,6- $\text{C}_2\text{B}_8\text{H}_{12}$ (5.0 g, 40.3 mmol) in CHCl_3 (50 ml) was treated with elemental sulfur (2.0 g, 62.5 mmol) and Et_3N (6.0 ml, 42.5 mmol) and the mixture was stirred at ambient temperature for 24 h. The mixture was then decomposed carefully with dilute HCl (40 ml, 1 : 3) under cooling to 0 °C. The organic layer was separated, rotaevaporated, and the residual solid was separated by column (2.5 × 30 cm) chromatography on silica gel. Elution with hexane resulted in the separation of main fraction of R_f 0.35 (hexane) which was evaporated to dryness and identified by ^{11}B NMR spectroscopy as *arachno*-5,6,9- $\text{C}_2\text{SB}_7\text{H}_{11}$ (1.2 g, 20.7%). Melting point 199 °C.

Physical Measurements

^1H and ^{11}B NMR spectroscopies were employed and were performed at ca 11.75 T on a Varian XL-500 instrument. The procedure for $^1\text{H}\{-^{11}\text{B}(\text{selective})\}^{20}$ NMR experiment was essentially as described in other recent papers from our laboratories²¹. Chemical shifts (in CDCl_3) are given in ppm, relative to $\text{BF}_3\cdot\text{OEt}_2$ (± 0.05 ppm) and SiMe_4 (± 0.05 ppm) for ^{11}B and ^1H , respectively. $^1\text{H}\{-^{11}\text{B}(\text{selective})\}$ NMR (assignment): δ +3.20 (H2), +2.85 (H8), +2.48 (H4), +2.43 (H10), +2.36 (H7), +2.17 (H1), +0.38 (H3), +1.72 (CH5), +1.50 (*exo*-CH6), +1.17 (*endo*-CH6), -0.45 (μH (7,8)). $\delta(^{11}\text{B})$ values are given in Table II. High- and low-resolution mass spectra were obtained on a JEOL HP-5985 instrument (70 eV, EI). Exact mass: calculated for $^{12}\text{C}_2\text{}^{32}\text{S}^{11}\text{B}_7\text{}^1\text{H}_{11}$ 144.1232, found 144.1233.

Computational Details

Both the molecules were fully optimized in C_1 symmetry using standard *ab initio* methods²² beginning at the SCF level with the 3-21G and 6-31G* basis sets. Analytical frequency calculations with the 6-31G* basis set confirmed the structures to be energy minima on the respective potential energy hypersurfaces (no imaginary frequencies). The final level of optimization employed the second-order Møller-Pleset (MP2) perturbation theory in the frozen-core approximation denoted as MP2/6-31G*. These calculations were carried out with Gaussian94 suite of programs²³ on the Power ChallengeXL computer of the Supercomputing Centre of the Charles University in Prague (Czech Republic). The chemical shieldings were computed both with the IGLO (individual gauge for localized orbitals) program²⁴ and with

the GIAO (gauge-invariant atomic orbitals) method incorporated in the Gaussian94 package. The IGLO method employed a II' Huzinaga basis set²⁵ - (11s7p2d) contracted to [51111111, 211111, 11] for S (d exponents 0.4, 1.6), (9s5p1d) contracted to [51111, 2111, 1] for C, B (d exponents 1.0, 0.5, respectively) and (3s) contracted to [21] for H. The GIAO method used a II Huzinaga basis set - the same as II' but for H 5s is contracted to [311]. B₂H₆ served as the primary reference and the calculated δ values were converted to the BF₃·OEt₂ scale using the experimental value of B₂H₆ = 16.6 ppm²⁶. Some structural features are summarized in Table I and the IGLO and GIAO results are presented in Table II. The natural population analysis (NPA)²⁷ performed for **1** at the MP2/6-31G* level is discussed.

TABLE I

Salient MP2/6-31G*-optimized internal coordinates for *arachno*-5,6,9-C₃B₇H₁₃ (**2**) and *arachno*-5,6,9-C₂SB₇H₁₁ (**3**)

Atoms	<i>arachno</i> -5,6,9-C ₃ B ₇ H ₁₃	<i>arachno</i> -5,6,9-C ₂ SB ₇ H ₁₁
	Bond lengths, Å ^a	
5-6	1.569	1.569
6-7	1.780	1.781
5-1	1.721	1.723
5-10	1.607	1.598
8-9	1.712	1.925
9-10	1.702	1.918
7-8	1.852	1.826
4-9	1.671	1.935
4-10	1.760	1.861
B-H ^b	1.189	1.189
B7-H _b	1.300	1.281
B8-H _b	1.323	1.356
C-H ^b	1.089	1.090
	Bond angles, °	
5-6-7	107.9	108.7
8-9-10	111.4	97.8
H-C-H	109.3 ^b	111.1

^a The remaining nearest-neighbor separations (B-B) are smaller than 1.800 Å. ^b Arithmetical mean value.

RESULTS AND DISCUSSION

As far as we know, **2** and **3** are the only known representatives of the parent ten-vertex *arachno* triheteroboranes. The *arachno* count is reflected in the molecular shapes: **2** and **3** possess open six-membered faces in boat conformations, which is in accord with the qualitative connectivity considerations of Williams²⁸. Low-coordination vertices are preferred sites for the three heteroatoms, as partly confirmed by Gimarc's rule of topological charge stabilization (see above). Further convincing support for structures **2** and **3** comes from IGLO and GIAO-SCF ¹¹B chemical shifts calculations. The correlation between theory and experiment is satisfactory even for **3** (see Table II), the maximum deviation amounting to only *ca* 5 ppm, considering the presence of sulfur (a third-row element for which both the basis sets and mainly the level of theory for chemical shift computations (SCF) may not be adequate). GIAO-SCF gives results that are comparable to IGLO (an SCF method) for both the molecules. It has been demonstrated quite recently that the GIAO-MP2/II calculations (*i.e.* electron correlated chemical shifts) for compounds containing a third-row element improve agreement with experimental data considerably²⁹.

TABLE II
IGLO and GIAO-SCF results for *arachno*-5,6,9-C₃B₇H₁₃ (**2**) and *arachno*-5,6,9-C₂SB₇H₁₁ (**3**)

Level of theory/ basis set employed	$\delta(^{11}\text{B})^a$, ppm						
	B1	B2	B3	B4	B7	B8	B10
<i>arachno</i> -5,6,9-C ₃ B ₇ H ₁₃							
IGLO/II ^b	-28.2	6.2	-49.9	0.0	-16.4	-11.8	-11.0
GIAO-SCF/II ^b	-25.9	7.5	-47.6	1.3	-14.9	-10.5	-10.0
Experimental ^c	-29.4	1.0	-49.1	-5.3	-17.6	-14.1	-12.4
<i>arachno</i> -5,6,9-C ₂ SB ₇ H ₁₁							
IGLO/II ^b	-23.0	7.2	-51.1	-9.1	-20.7	-6.9	-11.6
GIAO-SCF/II ^b	-20.8	8.6	-48.9	-6.8	-19.0	-5.3	-9.9
Experimental ^d	-24.8	3.7	-49.5	-11.9	-22.2	-10.0	-13.4

^a Relative to BF₃·OEt₂ (see text). ^b MP2/6-31G* geometry employed. ^c Ref.¹³. ^d This work.

The geometries of **2** and **3** optimized at the MP2/6-31G* level are depicted in Figs 1 and 2, respectively. Vertex substitution and absence of the hydrogen atom bridging the linkage between atoms 5 and 10 in the parent $[\text{B}_{10}\text{H}_{14}]^{2-}$ skeleton lowered the C_{2v} symmetry, adopted by **1**, to C_1 . Whereas the presence of sulfur in **3** has not changed much the geometry of the 8–9–10 triangle with respect to **1**³⁰, the carbon atoms both in **2** and **3** produced substantial deviations of the 5–6–7 and 8–9–10 triangles in **2** and the

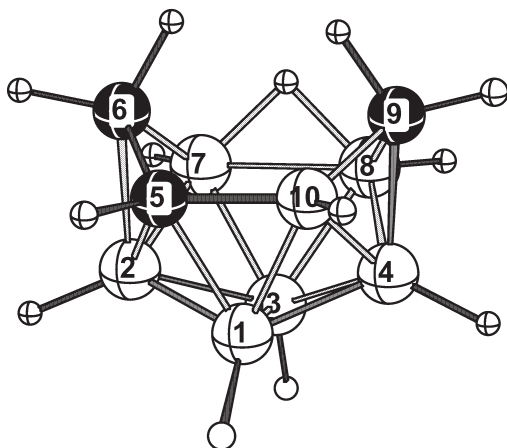


FIG. 1
arachno-5,6,9-C₃B₇H₁₃ (**2**) optimized at MP2/6-31G*

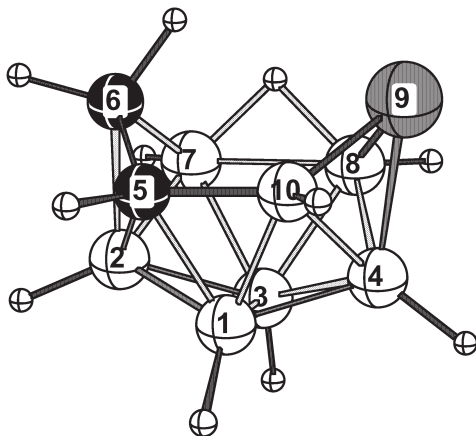


FIG. 2
arachno-5,6,9-C₂SB₇H₁₃ (**3**) optimized at MP2/6-31G*

8–9–10 triangle in **3** from that in **1**. Thus, the longer S(9)–B(8) and S(9)–B(10) bond lengths in **3** (1.925 and 1.918 Å, respectively at MP2/6-31G*) than $r[\text{B}(5)\text{--B}(6)]$ in **1** lead to a smaller B(8)–S(9)–B(10) angle (97.8°) than the analogous angle in **1** (see ref.³⁰). This angle is almost identical with the B(6)–S(8)–B(7) angle in *arachno*-4,6,8-C₂SB₆H₈ computed at the same level (97.6°)³¹. In effect, the sulfur atom in **3** is pushed away from the center of the cluster relative to the position it would have in **1**. The longest separation in **3** ($r[\text{S}(9)\text{--B}(4)] = 1.935 \text{ \AA}$) also reflects this feature (see ref.³⁰ for comparison). On the other hand, carbon atoms both in **2** and **3** are compressed toward the center of the cluster. This is accompanied by shorter C–B bond lengths and greater C–C–B and B–C–B angles than the corresponding parameters in **1** (see Table I). Summarizing, all these deformations occurring within **2** and **3** with respect to **1** are well described by the MP2/6-31G* parameters that may be deemed good representations of molecular geometries of **2** and **3**, as revealed by good fits between the computed and experimental ¹¹B chemical shifts. Further research aimed at the preparation of other heteroboranes of this class of compounds with diverse combinations of electron-rich main group elements as well as at cluster degradations, metal insertions, and exopolyhedral substitutions is in progress.

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- negatively charged and the topological charge stabilization rule of Gimarc cannot be unambiguously applied to the preferences of further vertex substitution. However, on the basis of chemical experience (e.g. position of the hydrogen bridge), symmetry considerations (e.g. the third heteroatom cannot occupy the positions 1 and 3 in **2** and with respect to the correlation between the corresponding ^{11}B NMR spectra also in **3**), and connectivity rules according to ref.²⁸, the position 5 remains as the only alternative for accommodating the third heteroatom.
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