

**4,6-DICARBA-8-THIA-*arachno*-NONABORANE(10) REVISITED.
THEORETICAL REFINEMENT OF ITS STRUCTURE**Drahomír HNYK^{a,*}, Matthias HOFMANN^{b1,+} and Paul von Ragué SCHLEYER^{b2,+}^a Institute of Inorganic Chemistry, Academy of Sciences of the Czech Republic,
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Dedicated to Professor Stanislav Heřmánek on the occasion of his 70th birthday.

The structure of the nine-vertex *arachno*-thiadicarbaborane $C_2SB_6H_{10}$ has been established employing the *ab initio*/IGLO/NMR method. Theoretical IGLO ^{11}B chemical shifts support C and S atom placements at the 4, 6 and 8 positions, respectively, and unambiguously rule out the 4,6,5- $C_2SB_6H_{10}$ structural alternative, suggested earlier on the basis of IR and Raman spectroscopy. Important structural features of the 4,6,8- $C_2SB_6H_{10}$ geometry include a small B(7)–S(8)–B(9) angle (MP2(fc)/6-31G*: 97.9°) and long S–B bonds (MP2(fc)/6-31G*: 1.905 and 1.924 Å) compared to B–B bonds spanning the 1.71–1.85 Å range.

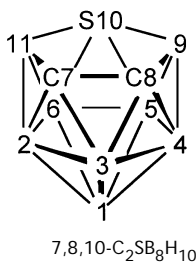
Key words: Boranes; Heteroboranes; Thiaboranes; *Ab initio* calculations; NMR spectroscopy; Structure elucidation.

The structural chemistry of polyhedral boranes has challenged chemists for many years. Lipscomb's pioneering contributions provided the basis for comprehending molecular structures of this class of compounds¹. X-Ray diffraction has played the dominant role in determining accurate molecular geometries; gas-phase electron diffraction as well as microwave spectroscopy also have been employed. The results were summarized in Beaudet's 1988 review². However, a subsequent examination using *ab initio* molecular orbital theory^{3,4} surprisingly revealed that many of the experimental structures were imperfect^{5,6}. Theoretical assessments of structures are based not

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only on computed geometries but also on IGLO (individual gauge for localized orbitals)⁷ chemical shift calculations. Since $\delta(^{11}\text{B})$ values are very sensitive to small geometric changes, the degree of agreement between calculated and experimental⁸ ^{11}B chemical shifts serves as a criterion of the accuracy of a particular geometry. Moreover, the combined *ab initio*/IGLO/NMR method^{6f} has the power to predict the correct boron cluster structure among various competing alternatives⁶. Although the calculations refer to isolated species, comparison with solution NMR data shows good agreement.

In contrast to the many recent applications of this structural tool to binary boron hydrides and carbaboranes^{5,6,9}, there are few such structural determinations of heterocarbaboranes. For example, only one thiacarbaborane, 7,8-dicarba-10-thia-*nido*-undecaborane(10), 7,8,10- $\text{C}_2\text{SB}_8\text{H}_{10}$ (Scheme 1) has been investigated in this fashion¹⁰. The *ab initio*/IGLO/NMR method was applied in conjunction with a gas-phase electron diffraction investigation as an additional refinement condition.

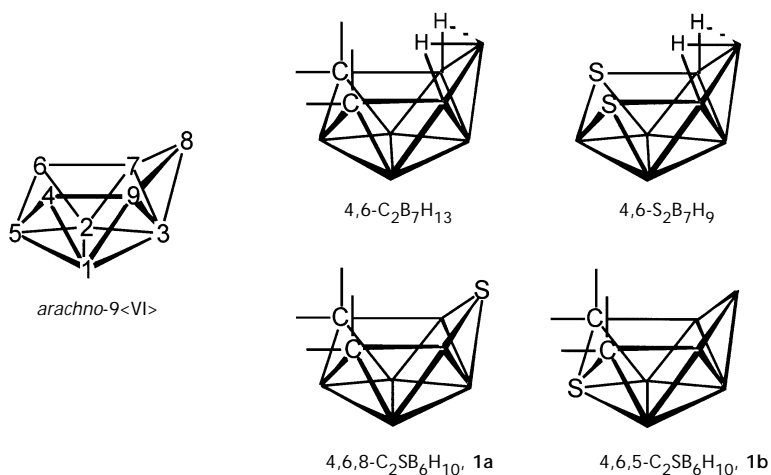


SCHEME 1

Baše *et al.*¹¹ reported the preparation of 4,6-dicarba-8-thia-*arachno*-nonaborane(10), 4,6,8- $\text{C}_2\text{SB}_6\text{H}_{10}$. The structure of the thiacarbaborane (derived from the hypothetical *arachno*- $[\text{B}_9\text{H}_9]$ ⁶⁻ in which the three $\{\text{BH}\}^{2-}$ vertices are formally replaced with the S and two $\{\text{CH}_2\}$ vertices) was proposed on the basis of experimental ^1H and ^{11}B NMR spectroscopy. Four ^{11}B NMR signals with relative intensities 1 : 2 : 2 : 1 indicated a symmetry plane bisecting the nonaborane skeleton in the 3,5,8 positions¹². This structure also agrees with empirical rules¹³ in accommodating sulfur at a low-coordinate site (Scheme 2, **1a**). However, the sulfur position has been debated: the alternative 4,6,5- $\text{C}_2\text{SB}_6\text{H}_{10}$ (**1b**) is suggested by IR and Raman evidence (*e.g.* a very strong Raman signal of 688 cm^{-1} attributable to symmetrical C-S-C valence vibration)¹¹. Since an X-ray diffraction study is lacking, we now report a theoretical assessment of *arachno*- $\text{C}_2\text{SB}_6\text{H}_{10}$ using the *ab initio*/IGLO/NMR method in order to establish the structure.

COMPUTATIONAL METHODS

Both geometrical alternatives **1a** and **1b** were fully optimized in C_s symmetry using standard *ab initio* methods³ beginning at the SCF level. Analytical frequency calculations with the 6-31G* basis set confirmed the structures to be energy minima on the $C_2SB_6H_{10}$ potential energy hypersurface (no imaginary frequencies). The final level of optimization employed second-order Møller-Pleset (MP2) perturbation theory in the frozen-core approximation denoted as MP2/6-31G*. These calculations were carried out with Gaussian94 (ref.¹⁴) on a Cray YMP-8 computer. Harmonic vibrational frequencies of **1a** were computed at the B3LYP/6-31G* density functional theory level¹⁵ using Gaussian98 (ref.¹⁶). This level was recommended¹⁷ on the basis of a study of 1 066 frequencies of 122 molecules comparing 19 different levels (including semi-empirical, *ab initio*, and DFT levels). A scaling factor of 0.9614 was determined for estimating fundamentals from B3LYP/6-31G* computed harmonic frequencies for comparison with experiment. Chemical shieldings were computed with the IGLO program⁶ using Huzinaga basis sets¹⁸: first the DZ basis set, *i.e.* (10s6p) contracted to [511111, 3111] for S, (7s3p) contracted to [4111, 21] for C, B and (3s) contracted to [21] for H, and second a larger basis set with polarization functions (II'), *i.e.* (11s7p2d) contracted to [5111111, 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. B_2H_6 served as the primary reference and the calculated δ values were converted to the



SCHEME 2

$\text{BF}_3\cdot\text{OEt}_2$ scale using the experimental value of $\delta(\text{BF}_3\cdot\text{OEt}_2) = 16.6$ ppm (ref.¹⁹). Some structural features are summarized in Table I and the IGLO results are presented in Table II.

RESULTS AND DISCUSSION

Since $\text{C}_2\text{SB}_6\text{H}_{10}$ has an *arachno* electron count, a nine-vertex cluster with an open IV-membered face (*arachno*-9<VI>, Scheme 2) can be expected¹³. The low coordination vertices 4, 6 and 8 should be the preferred sites for the one sulfur and the two carbon heteroatoms, consistent with the 4,6,8- $\text{C}_2\text{SB}_6\text{H}_{10}$ (**1a**) proposal based on NMR spectra¹². However, the 4,6,5-isomer (**1b**) also has been considered because the IR and Raman data seem to suggest a C–S–C arrangement¹¹.

The two geometries (**1a** and **1b**) optimized at MP2/6-31G* are depicted in Fig. 1 (the structural data only for **1a** are presented in Table I, which comes from the following).

Structure **1a** (Table I) involves an open hexagonal C(4)–B(5)–C(6)–B(7)–S(8)–B(9) face in a chair conformation, analogous both to 4,6- $\text{C}_2\text{B}_7\text{H}_{13}$, the first known *arachno* 9-vertex carbaborane²⁰ (with S in **1a** replaced by {BH})²⁻

TABLE I
Salient *ab initio* optimized internal coordinates for 4,6,8- $\text{C}_2\text{SB}_6\text{H}_{10}$

Model	Bond lengths (Å) and bond angles (°)					
	S(8)–B(3)	S(8)–B(7)	C(4)–B(1)	C(4)–B(5)	C(4)–B(9)	B(1)–B(2)
6-31G*	1.935	1.920	1.698	1.665	1.716	1.764
MP2/ 6-31G*	1.924	1.905	1.671	1.664	1.711	1.752
	B(1)–B(3)	B(1)–B(5)	B(1)–B(9)	B(3)–B(9)	B–H ^a	C–H ^a
6-31G*	1.797	1.800	1.747	1.875	1.181	1.076
MP2/ 6-31G*	1.777	1.777	1.737	1.852	1.188	1.087
	B(7)–S(8)–B(9)	C(4)–B(5)–C(6)	B(2)–B(1)–B(9)	B(1)–B(9)–S(8)	H–C–H	
6-31G*	98.0	110.4	109.0	111.3	111.0	
MP2/ 6-31G*	97.9	109.9	108.8	111.6	111.2	

^a Arithmetical mean value.

and two extra protons bridging B(8) with B(7) and B(9)), and to 4,6-S₂B₇H₉ (with S in **1a** replaced by {BH}²⁻ and the two {CH₂} replaced by two S, plus two extra bridge hydrogens between B(8) and B(7,9)) (ref.⁸). In contrast, optimization of a 4,6,5-C₂SB₆H₁₀ starting geometry converged to structure **1b** which did not retain the nine-vertex cluster. The **1b** geometry has an eight-membered open face (only B(1) does not participate in this octagonal belt) bearing a slight resemblance to the puckered structure of S₈ (ref.²¹). Energetically, **1a** is favored strongly over **1b** by 114.4 kcal/mol (MP2/6-31G* + 0.89 ZPE(HF/6-31G*)).

TABLE II
IGLO results for 4,6,8- (**1a**) and 4,6,5-C₂SB₆H₁₀ (**1b**) isomers

IGLO basis set/model employed	$\delta(^{11}\text{B})^a$, ppm				
	B(3)	B(7,9)	B(1,2)	B(5)	B(8)
4,6,8-C ₂ SB ₆ H ₁₀ (1a)					
DZ//6-31G*	-30.4	14.4	-15.1	10.4	-
DZ//MP2/6-31G*	-31.2	13.3	-16.6	8.8	-
II//MP2/6-31G*	-32.8	9.9	-15.4	7.8	-
Experimental ^b	-35.6 ^c	5.7 ^d	-21.7 ^c	7.6 ^c	-
4,6,5-C ₂ SB ₆ H ₁₀ (1b)					
DZ//MP2/6-31G*	-5.6	61.6	29.8	-	3.6

^a Relative to BF₃·OEt₂. ^b From ref.¹¹ (64.2 MHz, CDCl₃). ^c Intensity 1. ^d Intensity 2.

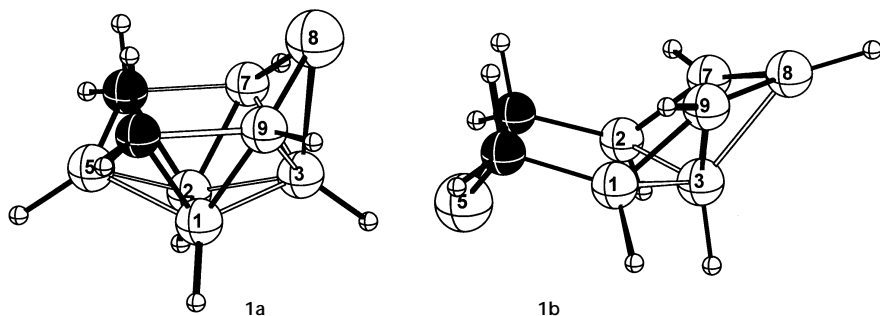


FIG. 1
4,6,8-C₂SB₆H₁₀ (**1a**) and 4,6,5-C₂SB₆H₁₀ (**1b**) geometries optimized at MP2(fc)/6-31G*

Further convincing support for structure **1a** comes from IGLO ^{11}B NMR chemical shift calculations. The correlation between theory and experiment is very good for structure **1a**, (Table II) considering the presence of the sulfur (a third-row element for which even the II' basis set may not be adequate) and the obviously lower quality experimental NMR data (at 64.2 MHz) recorded¹¹ in 1984. In contrast, computed chemical shifts for **1b** do not correlate with the experimental data at all (Table II). Hence, these calculations end the speculation about a 4,6,5- $\text{C}_2\text{SB}_6\text{H}_{10}$ structure and show that **1a** is the only cluster structure likely to be able to accommodate the three heteroatoms in *arachno*- $\text{C}_2\text{SB}_6\text{H}_{10}$. The boron-sulfur bonds in **1a** are longer than the boron-boron bonds and lead to a small B(6)-S(8)-B(7) angle (97.9° , see also Table I): comparable with a similar B(9)-S(10)-B(11) angle (MP2/6-31G*: 96.6) (ref.¹⁰) in 7,8,10- $\text{C}_2\text{SB}_8\text{H}_{10}$ (Scheme 1) relative to the 108° for a regular pentagon. The other angles involved in the B(1)-B(2)-B(7)-S(8)-B(9) pentagon are much closer to 108° . The S(8)-B(7) bond length (MP2/6-31G*: 1.905 \AA) is about the same as $r[\text{S}(10)\text{-B}(9)]$ (1.915 \AA) present in the C(7)-C(8)-B(11)-S(10)-B(9) pentagon of 7,8,10- $\text{C}_2\text{SB}_8\text{H}_{10}$ (Scheme 1, ref.¹⁰), shaped similarly to the B(1)-B(2)-B(7)-S(8)-B(9) ring of **1a**. Only a slight deviation from planarity of the B(1)-B(2)-B(7)-S(8)-B(9) ring in **1a** is apparent: S is 0.231 \AA out of the B(1)-B(2)-B(7)-B(9) plane, the B(1)-B(9)-B(7)-S(8) dihedral angle being 169.4° . For comparison, the C(7)-C(8)-B(11)-S(10)-B(9) pentagon in 7,8,10- $\text{C}_2\text{SB}_8\text{H}_{10}$ is nearly planar as well: S is out of the C(7)-B(8)-B(9)-B(11) plane by 0.078 \AA and the C(7)-B(9)-B(11)-S(10) dihedral angle is 176.5° (ref.¹⁰).

Speculations about a 4,5,6- $\text{C}_2\text{SB}_6\text{H}_{10}$ arrangement are based on a strong Raman band at 688 cm^{-1} attributable to a symmetrical C-S-C valence vibration. Applying the B3LYP/6-31G* density functional level, we compute a 4,6,8- $\text{C}_2\text{SB}_6\text{H}_{10}$ vibration at 696 cm^{-1} (which gives 669 cm^{-1} after scaling by 0.9614 (ref.¹⁷)) with a large Raman intensity ($21.1 \text{ A}^4/\text{amu}$) which may account for the observed band. Hence, the reported Raman band is not in contradiction with the 4,6,8- $\text{C}_2\text{SB}_6\text{H}_{10}$ structure. No further experimental/theoretical comparisons are possible because only one band at 688 cm^{-1} was reported¹¹. In summary, we presented convincing evidence that the 4,6,8- substitution pattern **1a** is correct for $\text{C}_2\text{SB}_6\text{H}_{10}$.

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