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Article

The Structure of 1-Thia-*closo*-decaborane(9), 1-SB_9H_9, as Determined by Microwave Spectroscopy and Quantum Chemical Calculations

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The microwave spectrum of 1-thia-*closo*-decaborane(9), 1-SB_9H_9, has been investigated in the 12–61 GHz spectral region. The molecule has C_{4v} symmetry. The spectra of five isotopomers have been assigned, and a precise substitution structure of the non-hydrogen atoms has been determined. It was found that the axial sulfur atom causes a substantial expansion of the B_4 belt adjacent to sulfur and hence leads to a significant distortion from a regular bicapped square antiprismatic structure. The experimental work has been supplemented by high-level ab initio (MP2/6–311G**) and density functional theory calculations (B3LYP/6–311G** and B3LYP/cc-pVTZ). The agreement between the substitution structure and the two DFT calculations is very good in each case. The agreement is considerably poorer for the MP2/6–311G** calculations, particularly for the sulfur–boron bond length.

Introduction

The existence of 1-thia-*closo*-decaborane(9), 1-SB_9H_9,was predicted in 1971.[1] The compound was assumed to have a bicapped Archimedian antiprismatic structure[1] of C_{4v} symmetry (Figure 1). Already two years later 1-SB_9H_9 was synthesized.[2] The predicted structure was confirmed by elemental analysis, mass spectrometry, IR and ^{11}B NMR spectroscopy.[2] 1-SB_9H_9 was found to be a white, volatile solid, stable in air, dissolving in a variety of organic solvents but lacking solubility in water.

The physical properties of the title compound have been the object of several studies: Its ultraviolet photoelectron spectrum[3] was assigned using MNDO calculations.[4] Hartree–Fock calculations of geometries and ^{11}B NMR chemical shifts have been made.[5] The bicapped Archimedian antiprismatic structure was again found to be preferred in these theoretical studies. The calculations also indicated that the title compound has a rather large dipole moment (approximately 11 × 10^{-30} C m; note units) and is quite rigid, since the lowest calculated vibrational frequencies are higher than 300 cm^{-1}.

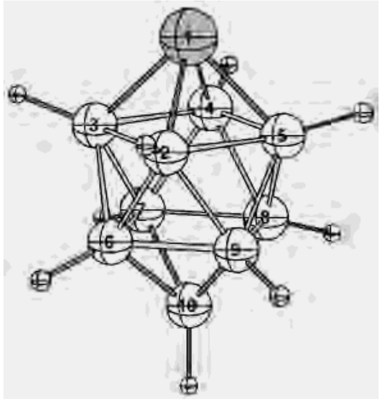

Figure 1. The structure of 1-SB_9H_9 with atom numbering.

An accurate experimental geometry of this compound has not been determined previously. However, the solid-state X-ray structure of the dimeric form of 1-SB_9H_9, 2,2′-(1-$SB_9H_8)_2$, is available.[6] A short B−B bond link between the two bicapped square antiprismatic frameworks of the SB_9H_8 moieties exists in this dimer.[6]

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Microwave (MW) spectroscopy may in this case be used to determine an accurate substitution[7] (r_s) structure of the non-hydrogen skeleton of gaseous 1-SB_9H_9, because the compound is volatile, has a high dipole moment producing a strong MW spectrum, and has no atoms close to a principal inertial axis (apart from B(10) and S(1) lying on the C_4 symmetry axis). Moreover, naturally occurring isotopes are fairly abundant for boron (80.4% ^{11}B and 19.6% ^{10}B) as well as for sulfur (95.0% ^{32}S, 4.2% ^{34}S, and 0.8% for ^{33}S). This is ideal, because isotopomers are used to determine the substitution structure.[7]

It was also found worthwhile to augment the MW study by quantum chemical calculations done at a much higher level of theory than previously reported.[4,5] Both density functional theory and ab initio calculations where carried out in order to compare the two different methods of calculations with the accurate structure that is possible to determine for the heavy-atom skeleton in this case.

Experimental Section

The sample of 1-thia-*closo*-decaborane(9) was prepared following the literature.[8] It was found to have a purity >98% as assessed by TLC and the $^1H\{^{11}B(\text{selective})\}$, ^{11}B, and two-dimensional [$^{11}B-^{11}B$] COSY NMR experiments.

The sublimation pressure of 1-SB_9H_9 is roughly 50 Pa at room temperature. This is a relatively high pressure for a compound with a melting point of 217 °C.[2,9]

The MW spectrum was studied using the Oslo Stark spectrometer which is described briefly in ref 10. A 3 m Stark cell made of brass was utilized. Radio frequency microwave double resonance (RFMWDR) experiments were carried out as described in ref 11 using the equipment mentioned in ref 12. Measurements were made in the 12−61 GHz region. The spectra were recorded at room temperature at a pressure of about 2−4 Pa and stored electronically using the program written by Waal.[13] The accuracy of the spectral measurements was better than ± 0.10 MHz.

Results

Quantum Chemical Calculations. The quantum chemical calculations were made using the GAUSSIAN94 program package.[14] Several calculations at different levels of theory were performed in order to compare the results with the accurate substitution structure. The theoretical structures were fully optimized in each case. The results of the three most advanced calculations are given in Table 1.

Hartree−Fock calculations followed by Møller−Plesset correlation energy corrections[15] where all electrons are included, and truncated at second order, are reported in the second column of this table. A triple-ζ wave function with polarization, (6−311G**), was used in these MP2 calculations.

In the second approach, density functional theory calculations using Becke's three-parameter functional[16] and the correlation functional of Lee, Yang, and Parr, which includes both local and nonlocal terms,[17] were employed (B3LYP). The results using the 6−311G** wave function in this approach are given in the third column of Table 1. Finally, Dunning's correlation consistent triple-ζ basis set with polarized valence electrons,[18] cc-pVTZ, was utilized. The results of the advanced B3LYP/cc-pVTZ calculations are found in the fourth column of the said table.

The next column contains the substitution structure of 1-SB_9H_9, which was determined as described below. This structure has been calculated from the Cartesian coordinates shown in Table 5.

In the last column the "average" X-ray structure of the 2,2′-(1-SB_9H_8)$_2$ dimer is shown. This compound has C_i symmetry. The bond distances and angles reported in Table 1 are average values of similar distances and angles determined in the original X-ray work of this dimer.[6]

A harmonic force field was also calculated at the B3LYP/cc-pVTZ level of theory. The calculated frequencies are given in Table 2 without any scaling. Our tentative assignment of the reported IR spectrum[2] obtained using a KBr disk is included in this table.

The Cartesian force field was transformed to an internal valence force field using the ASYM40[19,20] program in order to calculate the harmonic (quartic) centrifugal distortion constants. The results of these calculations are also included in Table 1 together with the rotational constants as well as dipole moments calculated at the three different levels of theory.

Microwave Spectrum and Assignments. A fairly strong MW spectrum characterized by very complicated pile-ups of lines separated by roughly 3.05 GHz was observed in the first survey spectra. This behavior was expected for 1-SB_9H_9, because there are many possible distributions of the ^{11}B and ^{10}B isotopes in this compound that will result in independent

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[8] In accordance with the C_{4v} symmetry, the ^{11}B NMR spectrum of 1-SB_9H_9 consists of 1:4:4 patterns of doublets (assignment, J(Hz)): $\delta = +71.8$ (B(10), J_{BH} 171), −7.6 (B(2,3,4,5), J_{BH} 177), −20.9 (B(6,7,8,9), J_{BH} 159). Application of the two-dimensional ^{11}B NMR COSY spectroscopy together with $^1H\{^{11}B\text{-selective decoupled}\}$ spectroscopy assigned all resonances to individual BH vertexes. [^{11}B-^{11}B] COSY cross peaks: B(10)−B(6,7,8,9), B(6,7,8,9)−B(2,3,4,5). $^1H\{^{11}B(\text{selective})\}$ NMR (multiplicity, intensity, assignment): $\delta = +7.99$ (s, 1H, H(10)), +2.50 (s, 4H, H(2,3,4,5)), +1.41 (s, 4H, H(6,7,8,9)). Proton and boron NMR spectroscopy was performed at 11.75 T on a Varian XL-500 instrument. Chemical shifts (in $CDCl_3$) are given in parts per million, with respect to $BF_3\cdot OEt_2$ (quoted ±0.05 ppm) and $SiMe_4$ (quoted ±0.05 ppm) for ^{11}B and ^1H, respectively. Coupling constants J_{BH} are taken from resolution-enhanced ^{11}B spectra with digital resolution ±8 Hz and are given in hertz. See also ref 9.

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Table 1. Structure,[a] Rotational Constants, Centrifugal Distortion Constants, and Dipole Moment of 1-SB_9H_9 as Determined by Experiment and Theoretical Calculations

	MP2(full)/ 6−311G**	B3LYP/ 6−311G**	B3LYP/ cc-pVTZ	MW[b]	X-ray of 2,2′-(1-$SB_9H_8)_2$[c]
S(1)−B(2)	199.4	195.2	194.2	194.4(2)	192
B(2)−B(3)	192.1	194.4	193.7	193.7(1)	193
B(2)−B(6)	178.0	177.7	177.5	176.5(3)	178
B(6)−B(7)	185.1	185.6	185.0	185.0(2)	184
B(6)−B(10)	171.8	171.2	170.7	170.7(1)	169
B-plane[d]	145.8	144.9	144.8	143.5(3)	
B(2)−S(1)−B(3)	59.6	59.7	59.8	59.66(5)	60
B(2)−S(1)−B(4)	89.2	89.5	89.7	89.41(5)	90
B(2)−B(6)−B(3)	65.3	66.3	66.1	66.44(5)	65
B(6)−B(2)−B(9)	62.7	62.9	62.8	63.58(7)	62
B(6)−B(10)−B(7)	65.2	65.7	65.6	65.46(10)	66
B(6)−B(10)−B(8)	99.2	100.1	100.0	99.76(2)	
S(1)−B(2)−H(2)	110.6	110.7	110.8		112
B(10)−B(6)−H(6)	120.3	119.7	119.7		122
B(6)−B(10)−H(10)	130.3	123.0	123.0		130
Rotational Constants of the $^{32}S^{11}B_9H_9$ Isotopomer					
A/MHz	2472.1	2443.6	2458.0		
$B = C$/MHz	1512.0	1510.9	1519.3	1513.7310(18)	
Centrifugal Distortion Constants[e]					
D_J/kHz				0.046	
D_{JK}/kHz				0.043	
D_K/kHz				0.044	
Dipole Moment[f]					
$\mu/10^{-30}$ C m	11.9	10.9	11.1		

[a] Distances in picometers and angles in degrees. [b] Calculated from the entries in Table 5 assuming C_{4v} symmetry. Uncertainties have been calculated according to ref 24; see text. [c] Average values of bond distances and angles in 2,2′-(1-$SB_9H_8)_2$ taken from ref 6; see text. [d] Distance between the two B-planes. [e] From B3LYP/cc-pVTZ force field using the ASYM40 program.[19,20] [f] 1 D = 3.33564 × 10^{-30} C m.

spectra. Moreover, each isotopomer spectrum is accompanied by weaker satellites belonging to vibrationally excited states.

The resulting mixture of isotopomers consists of either symmetrical tops of C_{4v} symmetry or near-symmetrical tops. Calculations showed that the isotopomer containing exclusively ^{11}B isotopes has the highest concentration (about 14% of the total of the ^{32}S species), followed by the species containing one ^{10}B and three ^{11}B atoms in either of the two belts (8%). All other species have lower concentrations.

The theoretical rotational constants shown in Table 1 were first used to predict the spectrum of the $^{32}S^{11}B_9H_9$ isotopomer. The strongest line in each of the pile-ups was then readily assigned as the ground vibrational $J + 1 \leftarrow J$ transition of this species. Transitions with J values between 3 and 20 were identified. The ^{11}B isotope has a spin of $^3/_2$ and will therefore have a quadrupole moment. However, none of the transitions was found to be split by quadrupole interaction. This was also found to be the case for the other isotopomers. The spectral data for the $^{32}S^{11}B_9H_9$ isotopomer are given in Table 1S in the Supporting Information.

The observed transitions were fitted by the method of least squares to the simple expression

$$\nu = 2B(J + 1) - 4D_J(J + 1)^3 \tag{1}$$

where ν is frequency of the transition, B is the rotational constant, and D_J is a centrifugal distortion constant.[21] The spectroscopic constants obtained this way are shown in Table 3. The experimental values of B and D_J are close to the theoretical values shown in Table 1.

No resolved K-doublet splittings were observed even for the $J = 20 \leftarrow 19$ transition. It was therefore not possible to determine the D_{JK} centrifugal distortion constant[21] experimentally. This is in keeping with the comparatively small value for D_{JK} (0.043 kHz; Table 1) obtained from the B3LYP/cc-pVTZ force field. Such a small constant would produce insufficient resolution of the K-doublet splittings in agreement with the observations. The small values of D_J and D_{JK} are caused by the rigidity of the compound, as remarked above.

The shift in the B rotational constant of the theoretical structure caused by changing the ^{11}B isotope with the ^{10}B isotope at the 10-position (Figure 1) was used to predict the B rotational constant of the symmetrical top $^{32}S^{10}B^{11}B_8H_9$ isotopomer. This procedure made it possible to assign this species in a straightforward manner. Its spectral data are found in Table 2S in the Supporting Information. The corresponding spectroscopic constants are listed in Table 3. Assignments of the spectra of the symmetrical tops $^{33}S^{11}B_9H_9$ and $^{34}S^{11}B_9H_9$ were made in an analogous manner. The spectral data are found in Tables 3S and 4S, respectively. Their spectroscopic constants are listed in Table 3.

The spectra of the two $^{32}S^{10}B^{11}B_8H_9$ isotopomers where the ^{10}B isotope is placed in either the 2- or the 6-position has to be assigned in order to determine a full structure for the heavy-atom skeleton. These species were assigned next. They are asymmetrical tops whose rotational constants were initially predicted from the theoretical structures. Only the

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Table 2. Fundamental Frequencies and Infrared Intensities from B3LYP/cc-pVTZ Calculations for 1-$\mathrm{SB_9H_9}$

no.	sym	calcd freq/cm^{-1}	int/km mol^{-1}	obsd freq[a]/cm^{-1}
1	a_1	2728.0	4.84	
2	a_1	2720.5	4.77	
3	e	2716.5	86.91	2600 (vs)
4	b_2	2712.9	0.00	
5	a_1	2676.6	27.25	
6	e	2672.2	89.24	2560 (vs)
7	b_1	2667.8	0.00	
8	a_1	1034.1	7.29	1011 (w)
9	e	984.2	4.40	972 (m, sh)
10	a_1	979.5	33.17	958 (s)
11	b_2	935.0	0.00	
12	e	930.9	2.61	902 (m)
13	a_2	915.9	0.00	
14	b_1	903.4	0.00	
15	e	898.9	0.86	873 (vw)
16	e	878.9	0.01	
17	b_2	878.5	0.00	
18	e	857.6	0.00	
19	a_2	851.7	0.00	
20	b_1	836.5	0.00	
21	a_1	822.7	14.18	810 (s)
22	e	763.1	0.78	750 (w,sh)
23	a_1	747.4	1.67	738 (m)
24	b_2	733.3	0.00	
25	e	695.8	6.71	685 (s)
26	b_1	692.3	0.00	
27	a_1	687.0	0.15	660 (w)
28	b_1	679.5	0.00	
29	a_1	661.2	7.79	610 (s)
30	e	618.3	6.09	603 (s)
31	b_2	606.5	0.00	
32	e	558.2	0.10	
33	e	548.2	3.53	532 (m)
34	b_2	527.3	0.00	
35	a_2	488.2	0.00	
36	b_1	483.1	0.00	
37	a_1	466.1	0.23	
38	e	330.4	0.12	

[a] Tentative assignments of the IR frequencies (KBr disk) listed in ref 2. Intensities given in ref 2 as s = strong, m = medium, w = weak; v = very, sh = shoulder.

Table 3. Spectroscopic Constants[a] of Symmetrical Top Isotopomers of 1-$\mathrm{SB_9H_9}$

isotopomer	$^{32}\mathrm{S}^{11}\mathrm{B_9H_9}$	$^{33}\mathrm{S}^{11}\mathrm{B_9H_9}$	$^{34}\mathrm{S}^{11}\mathrm{B_9H_9}$	$^{32}\mathrm{S}^{10}\mathrm{B}^{11}\mathrm{B_8H_9}$[b]
B/MHz	1513.7310(18)	1499.6119(46)	1485.9995(22)	1534.9792(19)
D_J/kHz	0.0526(33)	0.0386(73)	0.0509(38)	0.0503(33)
no. of trans in fit	15	6	11	13
rms dev/MHz	0.072	0.100	0.082	0.072

[a] Uncertainties represent 1 standard deviation. [b] ^{10}B in 10-position; see text.

low-K_{-1} transitions were well resolved from the high-K_{-1} pile-ups in these cases and, hence, used to determine the spectroscopic constants. The MWRFDR technique[11] was employed to confirm the assignments made for these two isotopomers. The spectra are found in the Supporting Information, Tables 5S and 6S, respectively. The spectroscopic constants (*A* reduction I^r representation[22]) are listed in Table 4. It is noted that it was not possible to obtain an accurate value for the Δ_{JK} centrifugal distortion constants in these cases, presumably because it is so small. Only its magnitude can be determined, as seen in this table. This is in accord with the force field calculations alluded to above.

Table 4. Spectroscopic Constants[a] of $^{32}\mathrm{S}^{10}\mathrm{B}^{11}\mathrm{B_8H_9}$ Isotopomers

position of ^{10}B:[b]	2	6
A/MHz	2477.8(13)	2478.6(21)
B/MHz	1523.0185(21)	1526.6092(28)
C/MHz	1514.4394(21)	1518.5811(28)
Δ_J/kHz	0.0460(26)	0.0419(36)
Δ_{JK}[c]/kHz	−0.09(12)	0.17(25)
no. of trans in fit	43	37
max value of *J*	19	19
rms/MHz	0.088	0.110

[a] *A* reduction I^r representation.[22] Uncertainties represent 1 standard deviation. [b] Position of ^{10}B; see text. [c] Further quartic centrifugal distortion constants preset at zero.

Table 5. Kraitchman's Coordinates[23,a,b,c]

isotopomer	*y*/pm	*z*/pm
$^{33}\mathrm{S}^{11}\mathrm{B_9H_9}$	0.0[g]	177.98(2)[h]
$^{34}\mathrm{S}^{11}\mathrm{B_9H_9}$	0.0[g]	177.94(2)
$^{32}\mathrm{S}^{10}\mathrm{B}^{11}\mathrm{B_8H_9}$[d]	0.0[g]	−214.60(5)
$^{32}\mathrm{S}^{10}\mathrm{B}^{11}\mathrm{B_8H_9}$[e]	136.78(8)	39.73(28)
$^{32}\mathrm{S}^{10}\mathrm{B}^{11}\mathrm{B_8H_9}$[f]	131.51(8)	−103.78(11)

[a] The $^{32}\mathrm{S}^{11}\mathrm{B_9H_9}$ isotopomer is the parent species. [b] The signs of the coordinates are arbitrary. [c] Uncertainties have been calculated as recommended by van Eijck.[24] [d] ^{10}B in 10-position; see text. [e] ^{10}B in 2-position. [f] ^{10}B in 6-position. [g] For symmetry reasons. [h] Uncertainty assumed to be the same as for the $^{32}\mathrm{S}-^{34}\mathrm{S}$ substitution pair; see ref 24.

No attempts were made to assign species containing two ^{10}B atoms. Sometimes such doubly substituted species produce independent information that is useful in the structure determination procedure, especially when atoms have small Cartesian principal-axis coordinates. This is not the case here since the smallest coordinate is about 40 pm (Table 5), and this was the reason why no attempts were made to assign these very weak asymmetrical top isotopomers.

Structure Determination. The changes of the rotational constants upon isotope substitution are relatively small in this case owing to the relatively large molecular weight of the compound. The substitution coordinates were calculated using Kraitchman's equations assuming C_{4v} symmetry.[23] The 1-$^{32}\mathrm{S}^{11}\mathrm{B_9H_9}$ isotopomer was used as the parent molecule. The coordinates are given in Table 5.

The *z*-coordinates (Table 5) of the sulfur atom obtained from either the $^{32}\mathrm{S}-^{34}\mathrm{S}$ or the $^{32}\mathrm{S}-^{33}\mathrm{S}$ pairs are practically identical as expected. Moreover, it is easy to decide whether the ^{10}B isotope of the two 1-$^{32}\mathrm{S}^{10}\mathrm{B}^{11}\mathrm{B_8H_9}$ isotopomers is located in position 2 or in position 6, because the *z*-coordinates are quite different (39.73(28) versus 103.78(11) pm; Table 5).

The uncertainties of the coordinates reported in Table 5 have been calculated from the expression $\sigma(x) = K/|x|$. The *K* values have been taken from van Eijck's compilation.[24]

The assumption that the compound has C_{4v} symmetry implies that the Cartesian coordinates of the sulfur atom and

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the boron atoms in the 2-, 6-, and 10-positions are needed to describe the full structure of the heavy-atom skeleton. The substitution structure that is shown in Table 1 was calculated using the coordinates in Table 5. The uncertainties of the bond lengths and angles were calculated from the van Eijck uncertainties in Table 5 by the method of propagation of errors.

Discussion

The substitution structure of 1-SB_9H_9 (Table 1) not only is precise but also is presumed to be close to the equilibrium structure because the molecule is quite rigid with its lowest normal mode predicted to be about 330 cm^{-1} (Table 2).

Several interesting structural features are found in this compound. It is, e.g., noted that the axial position of the sulfur atom leads to a substantial expansion of the B_4 belt adjacent to sulfur, as the B(2)−B(3) bond length is 193.7(1) pm compared to 185.0(2) pm for the B(6)−B(7) bond length. This rather large bond length difference is nearly 9 pm. An even larger expansion of about 12.5 pm of the B_5 belt adjacent to the sulfur atom was observed in the electron-diffraction geometry of 1-$SB_{11}H_{11}$,[25] where the sulfur atom leads to a considerable distortion from a regular icosahedron, just as in the present case.

Few S−B bond lengths of molecules in the gas phase have been reported. The S−B bond length (194.4(2) pm) of the title compound is considerably shorter than 201.0(5) pm (r_g value) seen in 1-$SB_{11}H_{11}$,[25] but much longer than 160.6(1) pm (r_s value) found for ClBS[26] and 160.6(3)pm (r_s value) determined for FBS,[27] respectively.

The advanced B3LYP/cc-pVTZ structure (Table 1) is in remarkably good agreement with the substitution structure. The same is true for the B3LYP/6−311G** structure. Although the MP2/6−311G** structure is capable of reproducing most of the structural parameters satisfactorily, the S(1)−B(2) bond length exhibits the largest discrepancy with respect to the experimental value among these three theoretical structures: This bond is calculated to be as much as 5 pm longer than the substitution value. The sulfur atom is obviously problematic at this level of ab initio calculations, whereas the B3LYP calculations are much more successful in reproducing the experimental data.

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Supporting Information Available: Tables 1S−6S containing the microwave spectral data used to determine the spectroscopic constants shown in Tables 3 and 4. This material is available free of charge via the Internet at http://pubs.acs.org.

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