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Structure of 1-Thia-*closo*-dodecaborane(11), 1-$SB_{11}H_{11}$, as Determined by Microwave Spectroscopy Complemented by Quantum Chemical Calculations

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The microwave spectrum of 1-thia-*closo*-dodecaborane(11), 1-$SB_{11}H_{11}$, has been investigated in the 23–62 GHz spectral region. The molecule is found to have C_{5v} symmetry. The spectra of several isotopomers have been assigned and a precise substitution structure of the non-hydrogen atoms has been determined. The structure is in quite good agreement with the one determined previously by electron diffraction. Density functional theory calculations at the B3LYP/cc-pVTZ level were found to predict a structure that is in good agreement with the substitution structure.

Introduction

Little is known about the structures of thiaboranes. The X-ray structure of the dimeric form of 1-thia-*closo*-decaborane(9), 2,2′-(1-SB_9H_8)$_2$, was determined in 1975 by Pretzer et al.[1] The substitution structure of the heavy-atom skeleton of 1-thia-*closo*-decaborane(9), 1-SB_9H_9, was determined very recently by microwave (MW) spectroscopy and found to be in good agreement with density theory calculations (B3LYP/cc-pVTZ level of theory).[2]

The title compound was studied by electron diffraction complemented by ab initio calculations 11 years ago.[3] C_{5v} symmetry was assumed in this work, and it was found that the molecule is distorted from a regular icosahedron mainly in a substantial expansion of the pentagonal belt adjacent to sulfur.

MW spectroscopy may in this case be used to determine an accurate substitution (r_s) structure of the non-hydrogen skeleton of gaseous 1-$SB_{11}H_{11}$ because the compound is sufficiently volatile, has a high dipole moment producing a sufficiently strong MW spectrum, and has no atoms close to a principal inertial axis (apart from S(1) and B(12) lying on the C_5 symmetry axis; see Figure 1). 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 and 4.2% ^{34}S). This is ideal because isotopomers in natural abundance can be used to determine the structure.

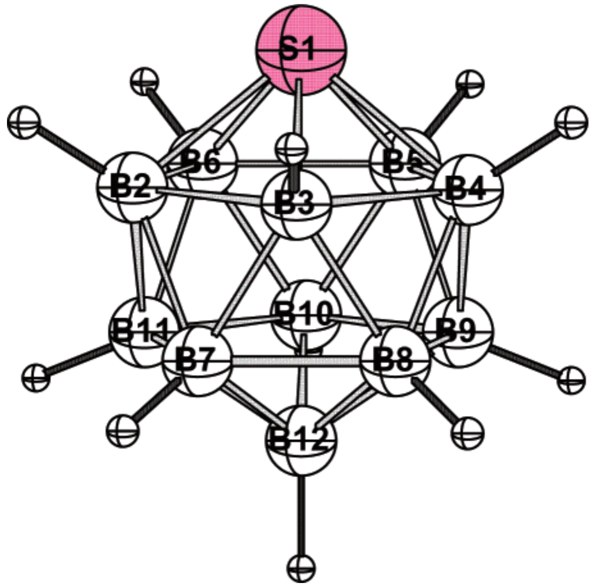

Figure 1. Structure of 1-$SB_{11}H_{11}$ with atom numbering.

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It was also found worthwhile to augment the MW study by quantum chemical calculations made at a much higher level of theory than previously reported.[3] Density functional theory calculations with large basis sets were successful in reproducing the structure of the related compound 1-SB_9H_9.[2] This quantum chemical procedure was therefore chosen in the present case as well.

Experimental Section

The sample of 1-thia-*closo*-dodecaborane(11) (purity >98% as assessed by TLC) was prepared following the literature.[4] The sublimation pressure of 1-$SB_{11}H_{11}$ is a few Pa at room temperature. This was sufficient to obtain the MW spectrum that was studied using the Oslo Stark spectrometer, which is described briefly in ref 5. A 3-m-long Stark cell made of brass was utilized. Radio frequency microwave double-resonance (RFMWDR) experiments were carried out as described in ref 6 using the equipment mentioned in ref 7. Measurements were made in the 23−62 GHz spectral 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.[8] The accuracy of the spectral measurements was better than ±0.10 MHz.

Results

Quantum Chemical Calculations. The quantum chemical calculations were made using the GAUSSIAN98 program package running on the HP superdome in Oslo.[9] Density functional theory calculations using Becke's three-parameter functional[10] and the correlation functional of Lee, Yang, and Parr,[11] which includes both local and nonlocal terms, were employed (B3LYP). Dunning's correlation consistent triple-ζ basis set with polarized valence electrons, cc-pVTZ,[12] was utilized. C_{5v} symmetry was confirmed by force field calculations.

The optimized structure found in these B3LYP/cc-pVTZ calculations is listed in the third column of Table 1. The second column of this table contains the electron diffraction r_g structure. The last column contains the substitution structure of 1-$SB_{11}H_{11}$, which was determined as described below.

Table 1. Structure[a] of 1-$SB_{11}H_{11}$ as Determined by Experiments and Theoretical Calculations

bonds	electron diffraction[b]	B3LYP/cc-pVTZ[c]	MW[c−e]
S(1)−B(2)	201.0(5)	202.0	201.3(2)
B(2)−B(3)	190.5(4)	189.0	188.9(1)
B(3)−B(7)	178.3(8)	175.6	174.8(2)
B(7)−B(8)	178.0(11)	178.8	179.7(1)
B(7)−B(12)	177.7(6)	178.0	179.1(3)

[a] Distances in pm. [b] r_g structure taken from ref 3. [c] This work. [d] Substitution (r_s) structure calculated from the entries in Table 4 assuming C_{5v} symmetry. [e] Uncertainties have been calculated according to ref 18; see text.

The dipole moment and a harmonic force field were also calculated (same level of theory). The dipole moment was predicted to be as large as 10.96×10^{-30} C m (3.29 D). The force field calculation predicts that 1-$SB_{11}H_{11}$ is remarkably rigid. The lowest vibrational frequency is, for example, calculated to be as high as 371 cm^{-1}. Further frequencies and intensities are given in Table 6S in the Supporting Information.

The Cartesian force field was transformed to an internal valence force field using the ASYM40 program[13,14] to calculate the harmonic (quartic) centrifugal distortion constants, whose values were found to be $D_J = 0.0285$, $D_{JK} = 0.00611$, and $D_K = 0.00292$ kHz, respectively.

Microwave Spectrum and Assignments. A MW spectrum of intermediate intensity characterized by complicated pile-ups of lines separated by roughly 2.6 GHz was observed in the first survey spectra. This behavior was expected for 1-$SB_{11}H_{11}$ because there are many possible distributions of the ^{11}B and ^{10}B isotopes in this compound that will result in independent spectra for the corresponding isotopomers. Moreover, the spectrum of each isotopomer is accompanied by weaker satellites belonging to vibrationally excited states.

The mixture of isotopomers consists of either symmetrical tops of C_{5v} symmetry or near-symmetrical tops. The $^{32}S^{11}B_{11}{}^{1}H_{11}$ species has the highest natural abundance factor of the isotopomers being 0.0847. This factor is 0.0207 for the $^{32}S^{11}B_{10}{}^{10}B^{1}H_{11}$ species. The natural abundance factor is considerably lower than these two values for species containing two or more ^{10}B atoms.

The spectrum of the symmetrical top $^{32}S^{11}B_{11}{}^{1}H_{11}$ should thus be about 4 times as strong as the similar symmetrical top isotopomer having a ^{10}B atom in position 12 (Figure 1). The spectra of the asymmetrical tops having one ^{10}B atom in either of the two belts should have a total intensity similar to that of $^{32}S^{11}B_{11}{}^{1}H_{11}$. Observations were subsequently found to be in agreement with these predictions.

The B3LYP rotational constant of $^{32}S^{11}B_{11}{}^{1}H_{11}$ (not given in Table 1) was 1281.3 MHz. This value was first used to predict the spectrum of this isotopomer. The strongest line in each of the pile-up regions was now immediately assigned as the $J + 1 \leftarrow J$ transition of the ground vibrational state of this species. Transitions with J-values between 9 and 24 were subsequently assigned.

The ^{11}B isotope has a spin of $^{3}/_{2}$ and will therefore have a quadrupole moment. However, none of the transitions of

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Table 2. Spectroscopic Constants[a] of Symmetrical Top Isotopomers of 1-$SB_{11}H_{11}$

isotopomer	$^{32}S^{11}B_{11}H_{11}$	$^{32}S^{11}B_{10}{}^{10}BH_{11}$[b]	$^{34}S^{11}B_{11}H_{11}$
B (MHz)	1279.6109(14)	1291.6512(19)	1261.7656(30)
D_J (kHz)	0.0287(17)	0.0188(23)	0.0295(33)
no. of trans. in fit	14	14	12
rms dev (MHz)	0.068	0.088	0.138

[a] Uncertainties represent one standard deviation. [b] ^{10}B in 12 position; see Figure 1.

$^{32}S^{11}B_{11}{}^{1}H_{11}$ were found to be resolvably split by quadrupole interaction presumably because the quadrupole coupling constants are quite small. This was also found to be the case for the other isotopomers studied here. The spectrum of $^{32}S^{11}B_{11}{}^{1}H_{11}$ is 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 the frequency of the transition, B is the rotational constant, and D_J is a centrifugal distortion constant.[15] The spectroscopic constants obtained this way are shown in Table 2. The experimental values of B and D_J are close to the B3LYP values (1281.3 MHz and 0.0285 kHz, respectively).

No resolved K-doublet splittings were observed, even for the $J = 24 \leftarrow 23$ transition. It was therefore not possible to determine the D_{JK} centrifugal distortion constant experimentally. This is in keeping with the comparatively small value for D_{JK} (0.0061 kHz) obtained from the B3LYP 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.

The shift in the B rotational constant of the theoretical structure caused by exchanging the ^{11}B isotope with the ^{10}B isotope at the 12 position (Figure 1) was used to predict the B rotational constant of the symmetrical top $^{32}S^{11}B_{10}{}^{10}B_1{}^{1}H_{11}$. This procedure made it possible to assign this species in a straightforward manner. Its spectrum is found in Table 2S in the Supporting Information. The corresponding spectroscopic constants are listed in Table 2. Assignment of the spectrum of the corresponding symmetrical top containing ^{34}S was made in an analogous manner. The spectrum is found in Table 3S. The spectroscopic constants are shown in Table 2.

The spectra of the two $^{32}S^{11}B_{10}{}^{10}B^{1}H_{11}$ isotopomers where the ^{10}B isotope is placed in either the 2 position or in the 7 position have to be assigned 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 structure. The fact that the distances from the symmetry axis to the B(2) and B(7) atoms are both quite large (Table 4) makes these ^{10}B isotopomers rather asymmetrical tops with the asymmetry parameter κ approximately equal to -0.92 in each case. This allows a rather accurate determination of the A rotational constants of these two species to be made (Table 3).

Table 3. Spectroscopic Constants[a] of $^{32}S^{11}B_{10}{}^{10}B\ H_{11}$ Asymmetrical Top Isotopomers

	position of ^{10}B[b]	
	2	7
A (MHz)	1503.84(21)	1503.16(25)
B (MHz)	1288.7777(21)	1290.4271(23)
C (MHz)	1280.2987(19)	1282.6264(24)
Δ_J (kHz)	0.0278(15)	0.0257(17)
Δ_{JK}[c] (kHz)	0.039(12)	0.037(16)
no. of trans. in fit	82	75
max value of J	24	24
rms (MHz)	0.107	0.105

[a] A reduction I^r representation.[16] Uncertainties represent one standard deviation. [b] Position of ^{10}B; see Figure 1. [c] Further quartic centrifugal distortion constants preset at zero.

Table 4. Kraitchman's Coordinates[a−c]

atom	Y (pm)	Z (pm)	atom	Y (pm)	Z (pm)
S(1)	0.0[d]	168.31(2)	B(2)	160.65(7)	47.06(23)
B(12)	0.0[d]	−191.64(6)	B(7)	152.87(7)	−98.26(11)

[a] The $^{32}S^{11}B_{11}H_{11}$ isotopomer is the parent species; see ref 17. [b] The Z-axis is the symmetry axis. The signs of the coordinates are arbitrary. [c] Uncertainties have been calculated as recommended by van Eijck.[18] [d] For symmetry reasons.

Only relatively 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[6] was employed to confirm the assignments made for these two species. The spectra are found in the Supporting Information, Tables 4S and 5S, respectively. The spectroscopic constants (A reduction I^r representation[16]) are listed in Table 3.

Structure Determination. The substitution coordinates of the heavy atoms were calculated using Kraitchman's equations[17] assuming C_{5v} symmetry. The $^{32}S^{11}B_{11}{}^{1}H_{11}$ isotopomer was used as the parent species. The rotational constants appearing in Tables 2 and 3 were employed to calculate the principal moments of inertia using 5053.7905 nm^2 u MHz as the conversion factor. The Kraitchman (substitution) coordinates that were calculated utilizing these moments of inertia are given in Table 4.

The uncertainties of the substitution coordinates reported in Table 4 have been calculated from the expression $\sigma(x) = K/|x|$. The K-values have been taken from van Eijck's compilation.[18]

The fact that the compound has C_{5v} symmetry implies that the Cartesian coordinates of the sulfur atom in position 1 and the three boron atoms in the 2, 7, and 12 positions are the only parameters needed to describe the full structure of the heavy-atom skeleton. The Cartesian coordinates in Table 4 can thus be used for this purpose. The substitution structure that is shown in Table 1 was calculated using the coordinates in Table 4. The uncertainties of the bond lengths were

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calculated from the van Eijck uncertainties[18] in Table 4 by the method of propagation of errors.

Discussion

The microwave spectrum confirms that the title compound has C_{5v} symmetry. The substitution structure of 1-$SB_{11}H_{11}$ (Table 1, fourth column) is not just precise, but it is also presumed to be close to the equilibrium structure because the molecule is remarkably rigid.

The B3LYP structure is close to the substitution structure as no theoretical distance deviates more than 1.1 pm from the r_s distance. A similar good agreement was found for the related compound 1-SB_9H_9.[2] It is concluded that B3LYP/cc-pVTZ calculations yield excellent predictions of the heavy-atom structures of these two compounds.

The electron diffraction r_g structure is in satisfactory agreement with the r_s structure with one exception, namely, the B(3)−B(7) bond length. The r_g value of this bond length is about 3.5 pm longer than the r_s value.

Several interesting structural features pointed out in the electron diffraction work[3] are confirmed here. It is, for example, noted that the axial position of the sulfur atom leads to a substantial expansion of the B_5 belt adjacent to sulfur, as the B(2)−B(3) bond length is 188.9(1) pm compared to 179.7(1) pm for the B(7)−B(8) bond length.

It has been pointed out[19] that the sulfur atom in this compound is positively charged relative to boron, although simple concepts such as electronegativity would have implied the opposite. A positively charged sulfur atom would drain electron density away from its surroundings. This draining should be most prominent for the boron atoms closest to the sulfur atom, resulting in a lengthening of the adjacent B(2)−B(3) bond as compared to the remote B(7)−B(8) bond length. The observed lengthening of 9.2 pm (from 188.9(1) to 179.7(1)) is consistent with this view. This view is supported by the present B3LYP calculations, which predict that the positive end of the dipole moment is directed toward sulfur.

Few S−B bond lengths of molecules in the gas phase have been reported. The S−B bond length (201.3(2) pm) of the title compound is considerably longer than the r_s value of 194.4(2) pm seen in 1-SB_9H_9, which has C_{4v} symmetry.[2] The S−B bond lengths of two linear transient molecules, ClBS and FBS, are known. This bond is as short as 160.6(1) pm (r_s) in ClBS[20] and 160.6(3) pm (r_s) in FBS.[21]

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Supporting Information Available: Tables 1S−5S contain the microwave spectra used to determine the spectroscopic constants shown in Tables 2 and 3. Table 6S contains the B3LYP normal vibrational frequencies and their predicted infrared intensities. This material is available free of charge via the Internet at http://pubs.acs.org.

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