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Molecular Structure of Gaseous Tris(methylthio)borane

R. JOHANSEN,[a] E. WISLØFF NILSSEN,[a] H. M. SEIP[a] and W. SIEBERT[b]

[a] *Department of Chemistry, University of Oslo, Oslo 3, Norway and* [b] *Institut für anorganische Chemie der Universität Würzburg, Würzburg, Germany*

Tris(methylthio)borane has been studied by gas electron diffraction. The molecular skeleton was found to be essentially planar with $r_a(B-S)=1.805(2)$ Å, $r_a(S-C)=1.825(3)$ Å, and $\angle BSC=104.5(3)°$. Mean amplitudes of vibration determined from the electron-diffraction data are in fairly good agreement with values computed from spectroscopic data.

The structure determination of tris(methylthio)borane, $B(SMe)_3$, *cf.* Fig. 1, by gas electron diffraction was carried out as a part of our studies of the nature of the $B-S$ bond, and in particular for comparison with the structure of methylthio-dimethylborane, Me_2BSMe, described in the previous paper.[1]

EXPERIMENTAL

The sample of $B(SMe)_3$ was synthesized by one of us (W.S.). The electron diffraction diagrams were recorded with the Balzer's Eldigraph KDG2 [2,3] in Oslo. The nozzle temperature was about 80°C. Four plates recorded with a nozzle-to-plate distance of 50 cm and wavelength 0.05847 Å and seven plates with a nozzle-to-plate distance of 25.0 cm (the vawelength was 0.05852 Å for five of these plates, 0.05828 Å for two of them) were used. The data were treated as described elsewhere.[4] The levelled intensity curves obtained from each plate were plotted and showed very satisfactory agreement. A composite intensity curve ranging from $s=2.25$ Å^{-1} to $s=29.0$ Å^{-1} was computed (see Fig. 2). The s intervals were 0.125 Å^{-1} for $s<10.0$ Å^{-1} and 0.25 Å for $s>10.0$ Å^{-1}.
The same scattering amplitudes were used as in the previous paper.[1]

STRUCTURE REFINEMENT

Most of the important interatomic distances may be estimated from the experimental radial distribution (RD) curve [4] shown in Fig. 1. The peaks near 1.81 Å and near 3.12 Å show that the BS_3 moiety is planar as expected and give reasonably accurate $B-S$ and $C-S$ bond lengths. The peak around 4.6 Å must correspond to distances of the type $S2\cdots C5$, and shows that the heavy atom skeleton must be nearly planar. The molecular parameters were refined by the least-squares method using a diagonal weight matrix. Very

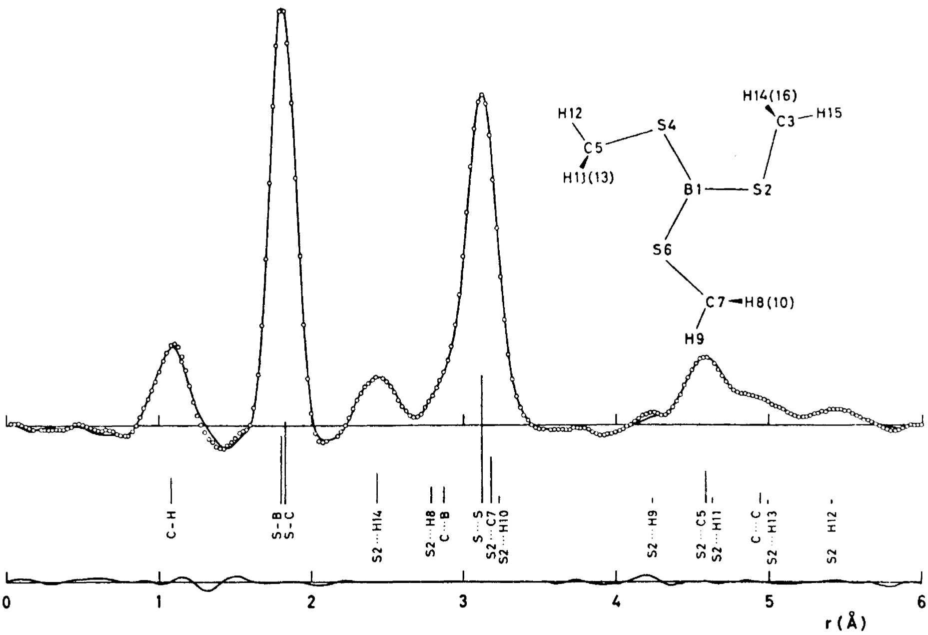

Fig. 1. Experimental (circles) and theoretical (full line) radial distribution functions for $B(SMe)_3$ calculated by Fourier transformation of the curves in Fig. 2 with an artificial damping constant [4] $k=0.002$ Å^2. The differences between experimental and theoretical values are also shown. The positions and the approximate areas of the peaks corresponding to the most important interatomic distances are indicated. The figure of the molecule corresponds to C_{3h} symmetry.

satisfactory agreement between experimental and theoretical curves was obtained for a model with C_3 symmetry. We assumed further that there was no tilt of the methyl groups. The Bastiansen-Morino shrinkage effect [5] was neg-

Table 1. Bond distances, angles, and mean amplitudes of vibration in tris(methylthio)borane. The standard deviations given in parentheses apply to the last decimal place. Mean amplitudes of vibration calculated from spectroscopic data are also given.

	r_a(Å)[8]	u(Å)	u_{calc}[b](Å)		angles (degrees)
$(C-H)_{av}$[a]	1.089 (4)	0.085 (5)	0.078	∠SCH	110.7 (6)
S−B[c]	1.805 (2)	0.050 } (3)	0.056	∠BSC	104.5 (3)
S−C[c]	1.825 (3)	0.047 }	0.054	ϕ (S4B1S2C3)	9.9 (30)
				ϕ (B1S2C3H15)	160.5 (40)

[a] An asymmetry constant, $\varkappa=0.000020$ Å,^{3} was assumed for the C−H bond distances; for all other distances $\varkappa=0$. [b] At 80°C. [c] If the shrinkage for the S···S distance is neglected, 1.804 Å and 1.826 Å are obtained for the S−B and S−C bond lengths.

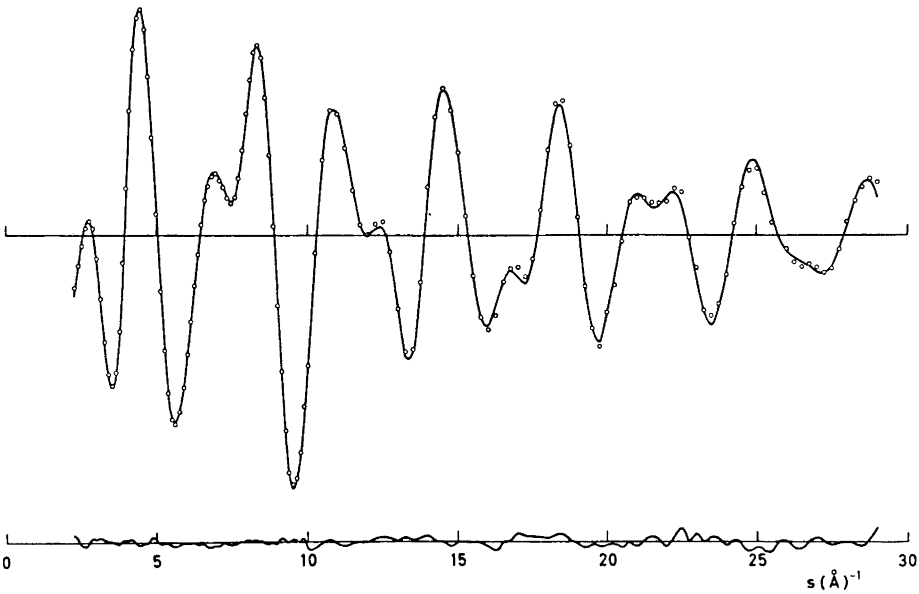

Fig. 2. Comparison of the experimental intensity values (circles) and the corresponding theoretical ones (full line) calculated with the parameters in Tables 1 and 2. The differences between experimental and theoretical values are also shown.

lected except for the S···S distance in some refinements where $\delta_a = 0.003$ Å was used. This value was calculated as described in the next section. Some assumptions about the mean amplitudes of vibration $(u)^5$ were also necessary (*cf.* the next section). The bond distances, the corresponding mean amplitudes of vibration, bond angles and torsional angles obtained are given in Table 1. The most important non-bonded distances with the corresponding u values are given in Table 2, and the atomic coordinates in Table 3.

Table 2. The most important non-bonded distances and mean amplitudes of vibration.

	r_a(Å)	u (Å)		u_{calc}(Å)
S···S	3.123[a]	0.074	(2)	0.075
S2···C5	4.585	0.096	(5)	0.095
S2···C7	3.184	0.146	(8)	0.145
C···B	2.870	0.065	(8)	0.096
C···C	4.944	0.160 [b]		0.147
S2···H14	2.433	0.114	(6)	0.107
S2···H8	2.793	0.280		0.28
S2···H9	4.250	0.190		0.16
S2···H10	3.232	0.280	} b	0.28
S2···H11	4.633	0.200		0.18
S2···H12	5.422	0.130		0.12
S2···H13	4.999	0.200		0.18

[a] A shrinkage of 0.003 Å is included. [b] The parameter was not refined.

Table 3. Atomic coordinates (Å) for $B(SMe)_3$.

	x	*y*	*z*
B1	0.0	0.0	0.0
S2	1.805	0.0	0.0
C3	2.262	1.740	0.304
S4	−0.903	1.563	0.0
C5	−2.638	1.089	0.304
S6	−0.903	−1.563	0.0
C7	0.376	−2.829	0.304
H8	1.088	−2.485	1.053
H9	−0.074	−3.754	0.662
H10	0.925	−3.050	−0.611
H11	−2.697	0.300	1.053
H12	−3.214	1.941	0.662
H13	−3.103	0.724	−0.611
H14	1.608	2.185	1.052
H15	3.288	1.812	0.662
H16	2.179	2.326	−0.611

VIBRATIONAL FREQUENCIES AND ROOT-MEAN-SQUARE AMPLITUDES OF VIBRATION

The IR and Raman spectra have been studied by Goubeau and Wittmeier [6] and by Vahrenkamp.[7] A calculation of the fundamental frequencies and root-mean-square amplitudes of vibration was carried out by the methods used for Me_2BSMe.[1] After some adjustments the force constants given in Table 4 were used. As in the case of Me_2BSMe, the torsional and out-of-plane force constants are very uncertain, giving considerable uncertainty in some of the mean ampli-

Table 4. Force constants used in the calculation of frequencies and mean amplitudes.

Stretching force constants (mdyn/Å)		Bending force constants (mdyn Å/rad²)		Repulsion force constants (mdyn/Å)	
B−S	2.50	SBS	0.9	S···H	0.54
S−C	1.80	BSC	0.9	H···H	0.20
C−H	4.35	SCH	0.35	C3···S4	0.007
		HCH	0.40		

Coupling constants (mdyn/Å)		Torsional force constants (mdyn Å/rad²)			Out-of-plane force constant (mdyn Å/rad²)		
BS/BS	0.40	SBSC	0.10	(two for each BS bond)	BS out of SBS plane:	0.07	(three contributions)
		BSCH	0.04	(three for each SC bond)			

Table 5. Observed [7] and calculated frequencies (in cm^{-1}) for $B(SCH_3)_3$ (C_{3h} symmetry).

		Symmetry	IR	Raman	Calculated
δ_s	(SBS_2)	E'		162	160
δ_s	(BSC)	A'		235	219
δ_{as}	(BSC)	E'	307	305	286
ν_s	(BS_3)	A'	410	430	429
γ	(BS_3)	A''	474	481	482
ν	(CS)	E', A'	709	705	710, 711
ν_{as}	(BS_3)	E'	905/930	906	915/945
ϱ	(CH_3)		990	984	977 – 991
δ_s	(CH_3)		1320	1317	1373
δ_{as}	(CH_3)		1430	1427	1406
ν_{as}	(CH_3)		2925	2925	2982
ν_{as}	(CH_3)		2995	2995	2965

tudes and in the correction terms necessary to obtain an r_α-structure.[8] In Table 5 the computed frequencies are compared to the experimental values using the assignment proposed by Vahrenkamp.[7] The agreement is fairly satisfactory, though improvement in the computed values for the methyl frequencies seems possible.

The computed root-mean-square amplitudes have been included in Tables 1 and 2. The agreement with the electron-diffraction results is acceptable for all parameters except perhaps for $u(C \cdots B)$.

By approximate methods Vahrenkamp [7] obtained 2.71 mdyn/Å and 2.57 mdyn/Å, respectively, for the B – S stretching force constants in $B(SMe)_3$ and Me_2BSH. He concluded that no π-bonding occurs between boron and sulphur. However, our calculations give a somewhat smaller value for $k(B-S)$ in $B(SMe)_3$ (2.50 mdyn/Å) compared to 2.85 mdyn/Å in Me_2BSMe.[1] Though both values depend to some extent on the values chosen for the other force constants, the results may perhaps be regarded as an indication of a slightly weaker B – S bond in $B(SMe)_3$ than in Me_2BSMe.

DISCUSSION

Tris(methylthio)borane is better suited for electron-diffraction studies than methylthio-dimethylborane. The quality of the observed data was also better, and the uncertainties in the main parameters in Tables 2 and 3 are smaller than in the corresponding parameters given in the previous paper.[1] The standard deviations have been corrected for the effect of correlation between the data.[9] and the uncertainty in the wavelength has been included.

The torsional angle ϕ (SBSC) of 9.9° cannot be regarded as significantly different from zero; oscillations about the B – S bonds may lead to an apparent angle of this size. To find if the equilibrium angle is zero, one might compute the r_α-structure, but as mentioned in the previous section most of the correction terms were considered to be too inaccurate.

The torsional angle about the S – C bonds (ϕ(B1S2C3H15) = 160.5°, *i.e.* about 20° from the staggered position) may possibly also be explained as a result of rather large oscillations. A model with ϕ(B1S2C3H15) negative was also tried. The angle refined to – 164°. The agreement was slightly poorer than for a positive torsional angle, and S2 ··· H10 became rather short (about 2.70 Å).

A comparison of the parameters in $B(SMe)_3$ and Me_2BSMe shows that the B – S bond is slightly longer in the former compound. The difference seems to be significant and is consistent with the difference in the force constants discussed in the previous section. It is tempting to ascribe these results to a lower π-bond order in the BS bonds in $B(SMe)_3$ than in Me_2BSMe_3. However, we have also found a bond length of 1.805 (4) Å in $Me_2BSSBMe_2$.[10] The B – S bond length in $B(SMe)_3$ is in good agreement with the average value of 1.807 Å obtained by Hess in $(HSBS)_3$.[11]

The C – S bond lengths in $B(SMe)_3$ and Me_2BSMe are equal as expected. The difference in the BSC angles may be real, but this angle is difficult to determine in Me_2BSMe.

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