# Molecular Structure of Gaseous Bis(methylthio)methylborane

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Bis(methylthio)methylborane has been studied by gas electron diffraction. The molecular skeleton was found to be at least nearly planar, and only a *syn-anti* form was observed. The average $B-S$ and $C-S$ bond distances are 1.796(7) and 1.818(6) Å, respectively.

A series of compounds with BS bonds, *i.e.* $(CH_3)_2B_2S_3$,[1] $Cl_2B_2S_3$,[2] $(CH_3)_2BSCH_3$,[3] $B(SCH_3)_3$,[4] and $(CH_3)_2BSSB(CH_3)_2$,[5] has been investigated by gas electron diffraction at this institute. As a natural extension of these investigations we have now studied bis(methylthio)methylborane. From the previous investigations of boron-sulfur compounds both conformers I and II seem possible, and we were particularly interested in determining which is the more stable one.

I   II
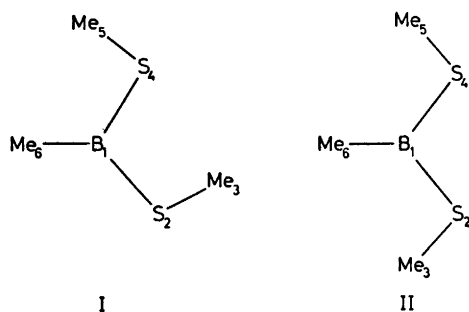
EXPERIMENTAL AND STRUCTURE ANALYSIS

Two sets of photographic plates were recorded with Balzers' eldigraph KD-G2.[6,7] Set 1 consisted of 5 plates, made at an electron wavelength of 0.05847 Å, and a nozzle-to-plate distance of 579.69 mm; set 2 of 4 plates, wavelength 0.05853 Å, and distance 189.78 mm. The nozzle temperature was about 50 °C. The data

were treated in the usual way using the modification function $s/(|f_C'||f_B'|)$.[8] The scattering amplitudes were those used previously.[3] Two average intensity curves were computed, one from each set of plates. The curves covered the s intervals $1.0-13.75$ Å^{-1} and $3.25-40$ Å^{-1}, respectively. Finally a composite intensity curve was computed (see Fig. 1). The data for $s > 35$ Å^{-1} were discarded in the refinements because of noise.

The experimental radial distribution (RD) function[8] calculated by Fourier inversion of the composite intensity curve given in Fig. 1, is shown in Fig. 2. The outer part of the curve is particularly interesting since it shows that form I must be the dominant one: In conformer II the distances S2...C5 and S4...C3 would be equal and cause a larger peak near 4.5 Å than found in the experimental curve.

To carry out least-squares refinements some assumptions about the geometry were necessary. Convenient and plausible ones, shown by the RD curve to be essentially correct, were:

(1) planar arrangement of C6B1S4S2,
(2) the $S-B$ distances are equal,
(3) the $S-C$ distances are equal,
(4) all $C-H$ distances are equal,
(5) local C_{3v} symmetry for the SCH$_3$ groups and for the BCH$_3$ group
(6) equal SCH angles.

The fifteen parameters given in Table 1 are then necessary to describe the molecular geometry.

The results of least-squares refinement with a diagonal weight matrix are given in Tables 1 and 2. Only a few of the mean amplitudes (u) could be refined simultaneously with the geometrical parameters. The other u values were either kept at values close to those calculated from spectroscopic data (see the next section) or adjusted somewhat in separate calculations.

The perpendicular amplitude correction coefficients calculated as described in the next section, were used to find the r_α structure[9] which is geometrically consistent. The shrinkage effect is therefore included in the calculation of the results given in the Tables 1 and 2.
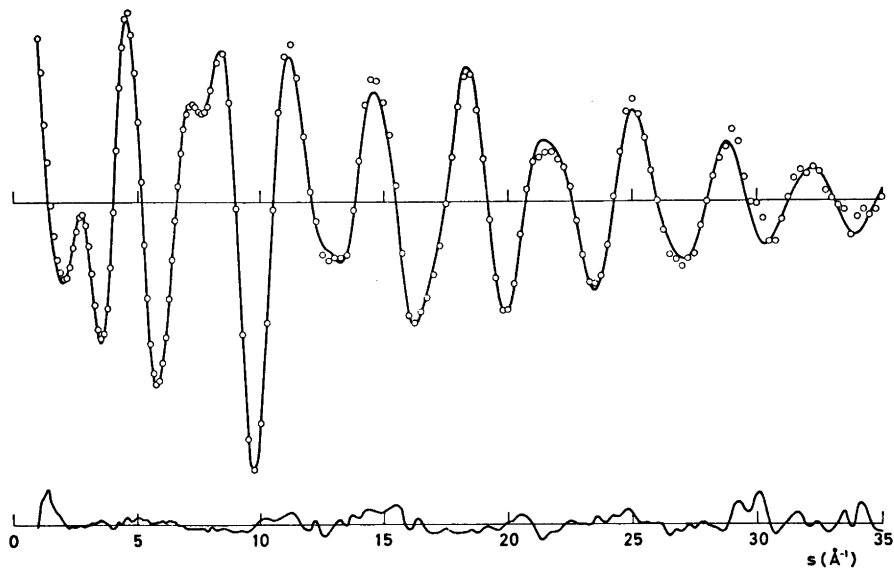
Fig. 1. Comparison of the experimental intensity values (circles) and the corresponding theoretical ones (full line) calculated with the parameters in Tables 1 and 2. The differences between experimental and theoretical values are also shown.
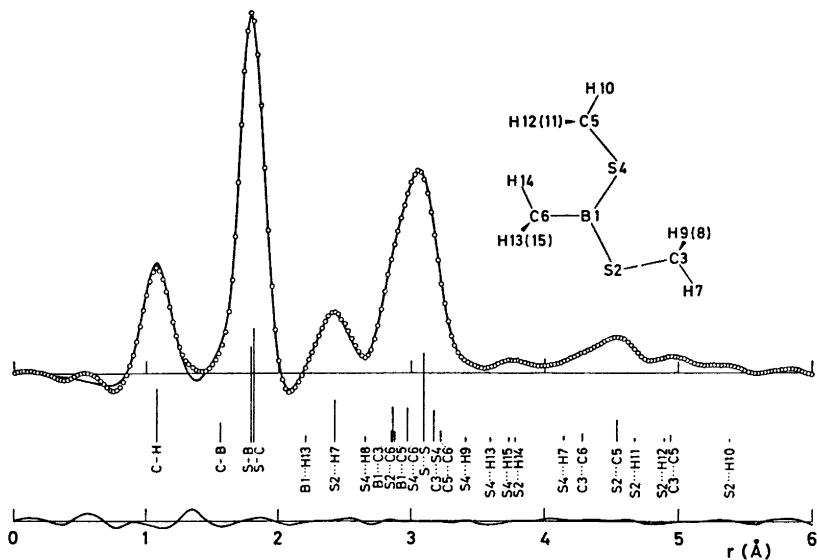

Fig. 2. Experimental (circles) and theoretical (full line) radial distribution functions calculated with an artificial damping constant [8] $k = 0.003$ Å². The differences between experimental and theoretical values are also shown. The positions and approximate areas of the peaks corresponding to the most important interatomic distances are indicated.

Table 1. Bond distances, the corresponding mean amplitudes of vibration and angle parameters in bis-(methylthio)methylborane.[a]

| | Distances and amplitudes | | |
	r_a (Å) [a]	u^{ED} (Å)[b]	u^S (Å)[c]
C−H	1.086(5)	0.074(5)	0.079
C−B	1.567(10)	0.053(10)	0.056
S−B	1.796(7)	0.052 }(2)[d]	0.055
S−C	1.818(6)	0.050 }	0.053
	Angles (degrees)		(degrees)
∠S2BC	116.4(4)	ϕ(CBS2C)	196.7(55)
∠S4BC	124.4(4)	ϕ(CBS4C)	−17.3(66)
∠BS2C	104.5(10)	ϕ(BS2CH7)	200.0[e]
∠BS4C	106.2(14)	ϕ(BS4CH10)	190.0[e]
∠SCH	112.0(5)	ϕ(S2BCH13)	75.0[e]
∠BCH	112.5[e]		

[a] The standard deviations given in parentheses correspond to the last digit given. The values were corrected for the correlation between the intensity data as described in Ref. 10. For C−H an asymmetry constant $\varkappa = 0.00002$ Å³ was applied, in all other cases $\varkappa = 0$. [b] Mean amplitudes from the electron-diffraction investigation. [c] Mean amplitudes calculated from spectroscopic data as described in the text for model I with planar skeleton. [d] The difference between the u values was assumed. [e] The value was not refined simultaneously with the other parameters.

Table 2. Non-bonded distances and the corresponding mean amplitudes of vibration.[a]

	r_a (Å)	u^{ED} (Å)	u^S (Å)
S···S	3.096	0.073(3)	0.072
S2···C5	4.550	0.099(10)	0.089
S2···C6	2.858	0.073	0.079
S4···C3	3.163	0.126	0.136
S4···C6	2.974	0.070	0.075
B···C3	2.849	0.099	0.090
B···C5	2.882	0.100	0.091
C3···C5	4.938	0.099(27)	0.139
C3···C6	4.284	0.100(25)	0.092
C5···C6	3.242	0.147	0.139
S2···H7	2.431	0.090(8)	0.106
S2···H10	5.381	0.082	0.117
S2···H11	4.648	0.147	0.175
S2···H12	4.942	0.138	0.175
S2···H13	3.222	0.218	0.194
S2···H14	3.779	0.137	0.112
S2···H15	2.999	0.208	0.184
S4···H7	4.134	0.145	0.156
S4···H8	2.629	0.236	0.266
S4···H9	3.423	0.249	0.266
S4···H13	3.579	0.193	0.167
S4···H14	3.051	0.183	0.157
S4···H15	3.757	0.162	0.138
B···H13	2.216	0.106	0.108

[a] The u values with standard deviations given in parentheses have been refined with the geometrical parameters; cf. Table 1.

However, since the torsional frequencies are not known, some of the correction terms are rather uncertain.

MEAN AMPLITUDES OF VIBRATION AND PERPENDICULAR AMPLITUDE CORRECTION COEFFICIENTS

The IR and Raman spectra of $CH_3B(SCH_3)_2$ have been studied by Vahrenkamp.[11] We computed the fundamental frequencies (see Table 3) by the program written by Gwinn,[12] and the mean amplitudes and correction coefficients as described by Stølevik et al.,[13] starting with force constants obtained for $(CH_3)_2BSCH_3$ [3] and $B(SCH_3)_3$.[4] Table 4 gives the values used in the final calculations. Vahrenkamp assigned the frequencies near 280 cm⁻¹ and 295 cm⁻¹ to torsions about the BS bonds. Using the force constants given in Table 4, these frequencies became 103 and 129 cm⁻¹, respectively, which seems more reasonable. We believe δ_{as} (CBS₂) and δ_{as} (BSC) to be about 295 and 332 cm⁻¹, respectively. The weak band near 383 cm⁻¹ is then unexplained. The value seems too high to correspond to methyl torsion which is more likely to be about 250 cm⁻¹, and may possibly be a combination band.

Table 3. Vibration spectrum (frequencies in cm^{-1}) of bis(methylthio)methylborane.[a]

Tentative assignment		IR	Raman	Calculated
τ(BS)				103
τ(BS)				129
δ_s(CBS$_2$)			165 s	167
δ_s(BSC)			235 s	223
τ(SCH$_3$)?	[τ(BS)]		280 w	248, 267
δ_{as}(CBS$_2$)	[τ(BS)]	295 vw	292 s	293
δ_{as}(BSC)	[δ_{as}(CBS$_2$)]	332 w	331 s	330
combination?	[δ_{as}(BSC)]	384 w	382 w	
γ(CBS$_2$)			431 vw	423
ν_s(BS$_2$)		519 m	517 vs	504
ν(CS)		708 m	713 vs	709, 718
ν_{as}(BS$_2$)		1026/1052 vs	1029 vw	1057/1082
ν(BC)		1073/1105 s	1074 w	1078/1116

[a] Most of the frequencies corresponding to hydrogen vibrations have not been included here. The observed values are taken from Vahrenkamp's work.[11] In some cases our proposed assignment differs from that of Vahrenkamp (given in square brackets).

Table 4. Force constants used in the calculations of frequencies, mean amplitudes of vibration and correction coefficients.[a]

Stretching (mdyn/Å)		Bending (mdyn Å/rad^2)		Repulsion (mdyn/Å)	
B−S	2.50(2)	BSC	1.05(2)	S···H	0.54(6)
C−S	1.80(2)	SBS	0.95(1)	B···H	0.46(3)
B−C	2.20(1)	SBC	0.80(2)	H···H	0.20(9)
C−H[b]	4.20(3)	SCH	0.35(6)	C3···S4	0.07(1)[d]
C−H[c]	4.30(6)	BCH	0.35(3)	C5···C6	0.04(1)
		HCH	0.35(9)		

Coupling (mdyn/Å)		Torsional (mdyn Å/rad^2)		Out-of-plane (mdyn Å/rad^2)	
BC/BS	0.25(2)	CBSC	0.10(2)	BS/CBS[e]	0.06(2)
BS/BS	0.40(1)	SBSC	0.10(2)	BC/SBS	0.05(1)
		BSCH	0.04(6)		
		SBCH	0.01(6)		

[a] The number of contributions is given in parentheses. [b] B−CH$_3$ group. [c] S−CH$_3$ group. [d] This value was also applied for B(SCH$_3$)$_3$. The value given in Table 4 of Ref. 4 is a misprint. [e] BS bond out of the CBS plane.

Table 5. Comparison of BS and CS bond lengths.

	(CH$_3$)$_2$BSCH$_3$	CH$_3$B(SCH$_3$)$_2$	B(SCH$_3$)$_3$
B−S	1.779(5)	1.796(7)	1.805(2)
C−S	1.825(4)	1.818(6)	1.825(3)
Average	1.802	1.807	1.815

DISCUSSION

The investigation shows conformer I to be the dominant one. Radial distribution curves calculated for mixtures of I and II showed that the amount of conformer II must certainly be less than 20 %. Preliminary results obtained by electron diffraction for $N_3B(OCH_3)_2$[14] and by *ab initio* calculations for $HB(OH)_2$[15] show that these molecules also prefer form I; in the latter case the energy difference is about 2 kcal/mol.

The skeleton of bis(methylthio)methylborane is certainly nearly planar. Table 1 shows that when the torsional angles about the BS bonds are refined, deviations of about 17° from planarity are obtained. A least-squares refinement was also carried out with these torsional angles fixed at 180° and 0°, respectively. The ratio between the R factors was 1.021. According to Hamilton's test[16] the model with a planar skeleton can therefore not be rejected at the 5 % significance level. When in addition the assumptions made about the structure and the rather large uncertainties in the perpendicular amplitude correction coefficients are considered, we conclude that an essentially planar skeleton is consistent with the experimental data.

The bond lengths in $(CH_3)B(SCH_3)_2$ are similar to the values found in $(CH_3)_2BSCH_3$ and $B(SCH_3)_3$ (Table 5). The slight tendency for an increase in the BS bond lengths with increasing number of SCH_3 groups is in agreement with the results of Kroner *et al.*[17] obtained by photoelectron spectroscopy and semi-empirical MO calculations. It should be noted, however, that the very similar lengths of the BS and CS bonds makes it difficult to determine the individual values with high accuracy, except in $B(SCH_3)_3$ where the BS distance follows from the value found for the $S\cdots S$ distance. The uncertainties in the BS stretching force constants in the three compounds are too large to justify a discussion of the variation.

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