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Molecular Structure of Gaseous Methylthio-dimethylborane

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Methylthio-dimethylborane has been studied by gas electron diffraction. The skeleton is probably planar, though values for the torsional angle about the B–S bond up to about 25° cannot be ruled out. The results obtained for the most important parameters are (standard deviations in parentheses):
r_a(B–S) = 1.779(5) Å, r_a(C–S) = 1.825(4) Å, r_a(C–B) = 1.570(4) Å, ∠BSC = 107.2(10)°, ∠SBC4 = 124.0(8)°, ∠SBC5 = 115.3(6)°.
Mean amplitudes of vibration computed from spectroscopic data are also given.

Two compounds with B_2S_3 rings (dimethyl-1,2,4-trithia-3,5-diborolane [1] and dichloro-1,2,4-trithia-3,5-diborolane [2]) have recently been studied by electron diffraction in Oslo. Apart from methyl hydrogens, both molecules were found to be essentially planar. Considering the potential to internal rotation about S–S bonds,* one should expect a puckered B_2S_3 ring if the barrier to rotation about the B–S bonds is zero. Theoretical calculations using the CNDO/2 method indicated considerable π bond orders in the B–S bonds in the trithiadiborolane ring.[4] We have now studied this problem further by electron-diffraction investigations of methylthio-dimethylborane (Me_2BSMe), tris(methylthio)borane ($B(SMe)_3$),[5] and bis(dimethylboryl)-disulphane (Me_2BSSMe_2).[6]

EXPERIMENTAL

The sample of Me_2BSMe was kindly supplied by W. Siebert, University of Würzburg. The electron diagrams were recorded with the Balzer's Eldigraph KDG2 [7,8] in Oslo. The nozzle-temperature was about 20°C. Two sets of plates were used recorded with nozzle-to-plate distances of 50.0 cm and 25.0 cm and wavelengths of 0.05846 Å and 0.05833 Å (accelerating potential about 42kV) respectively. The data were treated in the usual way.[9] The levelled intensity curves obtained from each plate were plotted. We were not quite content with the quality of the data, but four curves from each set were considered fairly satisfactory, and composite intensity curves ranging from $s = 2.25$ Å^{-1} to $s = 29.0$ Å^{-1} were computed from these data. The s intervals were 0.125 Å^{-1} for $s < 7.25$ Å^{-1} and 0.25 Å^{-1} for $s < 7.25$ Å^{-1}.

* *ab initio* calulactions on H_2S_2 give a barrier of about 9.3 kcal/mol corresponding to the *syn* form.[3]

The elastic scattering amplitudes were calculated for an accelerating potential of 42 kV by the partial wave method.[9,10] The atomic potentials were taken from Ref. 11 except for hydrogen where the values in Ref. 12 were used. The modified molecular intensities were calculated using the modification function [9] $s/(|f'_B||f'_S|)$.

STRUCTURE REFINEMENT

The experimental radial distribution (RD) curve [9] in Fig. 1, obtained by Fourier transformation of the experimental intensity curve in Fig. 2, gives a rough idea of the main structural parameters. The structure was refined by

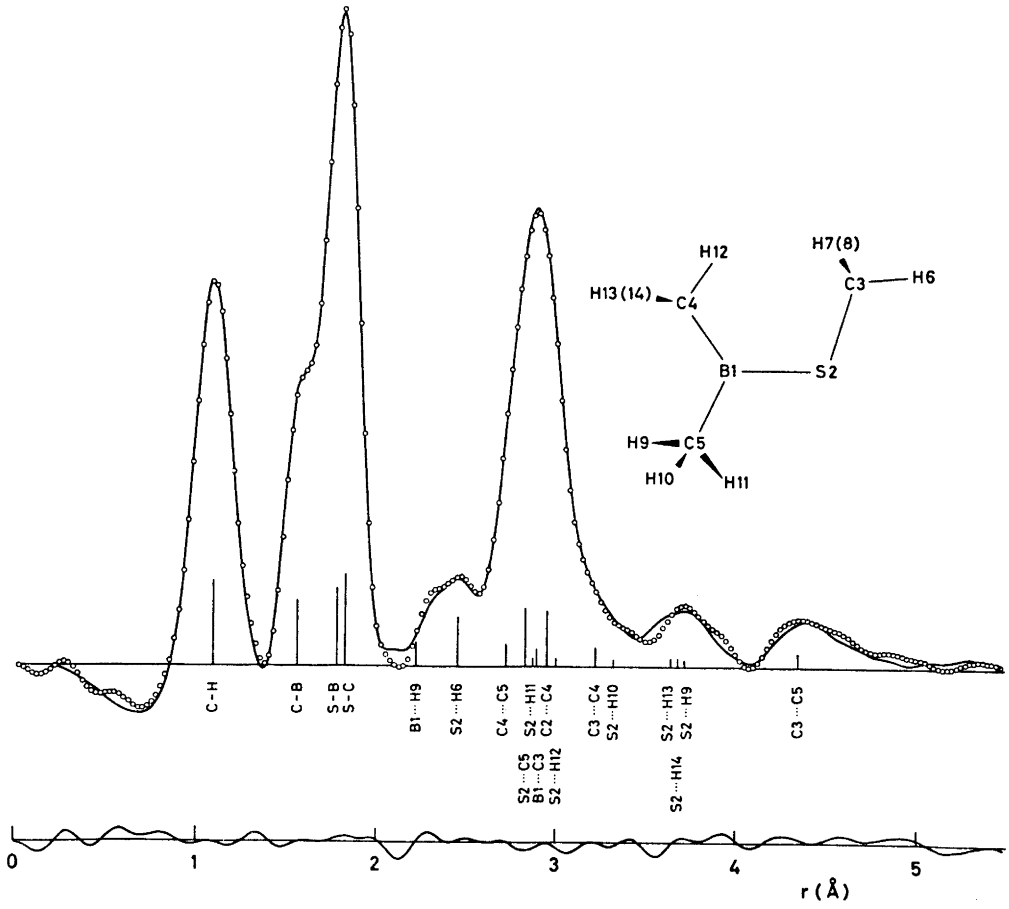

Fig. 1. Experimental (circles) and theoretical (full line) radial distribution functions for Me_2BSMe calculated by Fourier transformation of the curves in Fig. 2 with an artificial damping constant [9] $k = 0.002$ Å^2. The differences between experimental and theoretical values are also shown. The positions and approximate areas of the peaks corresponding to the most important distances are indicated.

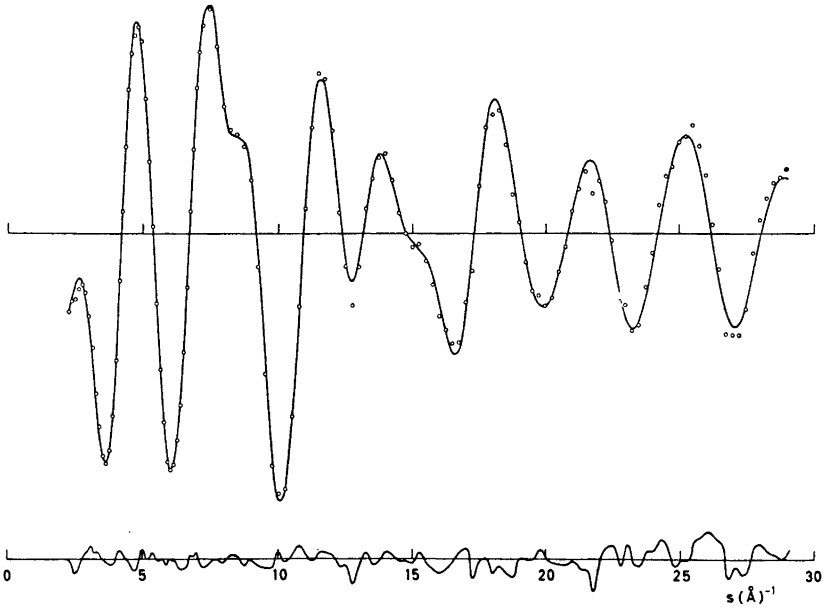

Fig. 2. Comparison of the experimental intensity values (circles) and the corresponding theoretical ones (full line) calculated with the parameters in Tables 1 and 2. The differences between experimental and theoretical values are also shown.

the least-squares method using a diagonal weight matrix. The molecule has little symmetry, at most a symmetry plane, and the number of parameters necessary to describe the geometry is large for a molecule of this size. Some assumptions were therefore necessary (*cf.* Tables 1 and 2). Thus the following parameters were assumed equal:

(1) B1 – C4 and B1 – C5
(2) All C – H bonds
(3) All BCH angles
(4) All SCH angles

The Bastiansen-Morino shrinkage effect [13–15] was neglected; this approximation is discussed in more detail later. Some assumptions about the mean amplitudes of vibration were also necessary (*cf.* the next section).

The possibility of tilt of the methyl groups was considered. However, this led to too many parameters, and it was necessary to assume threefold symmetry in the methyl groups with the axis coinciding with the B – C or S – C bonds. The thiomethyl group was assumed to be staggered with respect to the B – S bond. Free rotation was tried for the two other methyl groups, but with this assumption, we were unable to obtain satisfactory agreement in the outer part of the RD curve (Fig. 1). The experimental curve has a peak near 3.70 Å. To reproduce this peak theoretically several S···H distances must contribute in this region. If the torsional angle about B1 – C4 is such that one of the

hydrogens in this methyl group (say H12) lies *syn* to the sulphur atom (see Fig. 1), the distances S···H13 and S···H14 give contributions around 3.70 Å. The other methyl group is probably oscillating with a very large amplitude, avoiding positions where the torsional angle ϕ(SBC5H) for one of the hydrogens is close to zero. The distances given in Table 2 correspond to ϕ(SBC5H11) = $-30°$; S2···H9 is then about 3.75 Å. The agreement, as well as the other molecular parameters, was virtually independent of this angle within the interval $-20°$ to $-100°$.

VIBRATIONAL FREQUENCIES AND ROOT-MEAN-SQUARE AMPLITUDES OF VIBRATION

The IR and Raman spectra of Me_2BSMe have been given by Vahrenkamp.[16] A calculation of the fundamental frequencies was carried out using a computer program developed by Gwinn.[17] After some adjustments the force constants given in Table 4 were used. The force constants for torsional and out-of-plane motion, especially perhaps the force constant for methyl torsion about B–C bonds, are very uncertain. In Table 5 the computed frequencies are compared to the experimental values.

The value of the B–S stretching force constant is of some interest in the discussion of the π-bond order of the B–S bond. Unfortunately, values deviating considerably from 2.85 mdyn/Å may give reasonable fit for the frequencies if the B–C stretching constant and the BS/BC coupling constant are properly adjusted (*cf.* the discussion of the force field in $B(SMe)_3$ [5]).

The root-mean-square amplitudes of vibration were computed as described by Stølevik *et al.*[18] The results have been included in Tables 1 and 2. The u values which depend critically on one or more of the most uncertain

Table 1. Bond distances, angles, and mean amplitudes of vibration in methylthiodimethylborane. 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)[19]	u (Å)	u_{calc} (Å)[b]		Angles (degrees)
$(C-H)_{av}$[a]	1.092(4)	0.074(3)	0.078	∠BSC	107.2(10)
C–B	1.570(4)	0.051	0.058	∠SBC4	124.0(8)
S–B	1.779(5)	0.047 (3)[b]	0.054	∠SBC5	115.3(6)
S–C	1.825(4)	0.047	0.053	∠BCH, ∠SCH	111.7[c]
				ϕ(C4BSC)	0[c]
				ϕ(SBC4H12)	−5[c]
				ϕ(SBC5H11)	−30[c]
				ϕ(BSC3H6)	180[c]

[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 20°C. [c] The parameter was not refined at the same time as the other parameters. [d] The differences between the u-values were assumed.

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

	r_a (Å)	u (Å)	u_{calc} (Å)[a]
B1···C3	2.901(18)	0.095[b]	0.095
S2···C4	2.959(8)	0.059 (10)[c]	0.073
S2···C5	2.831(6)	0.062	0.076
C3···C4	3.227(20)	0.125(19)	0.151
C3···C5	4.352(14)	0.120(20)	0.093
C4···C5	2.729(11)	0.077[b]	0.080
B1···H9	2.219(5)	0.150[b]	0.109
S2···H6	2.449(5)	0.098(9)	0.106
S2···H9	3.731	0.13[b]	0.12
S2···H10	3.330	0.20[b]	0.18
S2···H11	2.875	0.18[b]	0.17
S2···H12	3.006	0.16[b]	0.15
S2···H13	3.644	0.205 (60)[c]	0.16
S2···H14	3.706	0.205	0.14

[a] At 20°C. [b] The parameter was not refined at the same time as the other parameters. [c] The difference between the u values was assumed.

force constants (say u(S2···H10)) must be regarded as rough estimates only. The computer program gives also the terms necessary to obtain an r_α-structure,[19] and thus avoid the shrinkage problem. However, the mentioned uncertainties in some of the force constants lead to very unrealiable correction terms.

DISCUSSION

Our final results for the structure parameters are given in Tables 1 and 2. The standard deviations have been corrected for the effect of correlation between the intensity data,[20] and the uncertainty in the wavelength has been included. The atomic coordinates for the final model are given in Table 3.

Table 3. Atomic coordinates (Å) for Me_2BSMe.

	x	y	z
B1	0.0	0.0	0.0
S2	1.779	0.0	0.0
C3	2.319	1.743	0.0
C4	−0.878	1.302	0.0
C5	−0.671	−1.419	0.0
H6	3.407	1.829	0.0
H7	1.953	2.279	0.879
H8	1.953	2.279	−0.879
H9	−1.638	−1.409	−0.507
H10	−0.844	−1.784	1.015
H11	−0.049	−2.160	−0.507
H12	−0.266	2.202	−0.088
H13	−1.459	1.397	0.920
H14	−1.586	1.311	−0.831

Table 4. Force constants used in the calculation of frequencies and root-mean-square amplitudes of vibration.

Stretching force constants (mdyn/Å)			Bending force constants (mdyn Å/rad²)		Repulsion force constants (mdyn/Å)	
B–S	2.85		BSC	0.90	S···H	0.54
S–C	1.80		CBC	0.80	B···H	0.46
B–C	1.85		CBS	0.80	H···H	0.20
C–H	4.20	(B–CH_3 groups)	SCH, BCH	0.35		
C–H	4.30	(S–CH_3 group)	HCH	0.40		

Coupling constant (mdyn/Å)		Torsional force constants (mdyn Å/rad²)			Out-of-plane force constant (mdyn Å/rad²)
BS/BC	0.55	CBSC	0.10	(two contributions)	CB out of CBS plane: 0.18 (two contributions)
		BSCH	0.04	(three contributions)	BS out of CCB plane: 0.18
		SBCH	0.01	(three for each	
		CBCH	0.01	BC bond)	

Table 5. Observed [16] and calculated frequencies (cm^{-1}) for $(CH_3)_2BSCH_3$.

	IR	Raman	Calculated
τ(BS)			124
$\delta_s(BC_2)$		210	181
$\delta_{as}(BC_2)$		298	306
δ(BSC)		352	353
$\gamma(C_2BS)$	455	452	466
ν(BS)	575	574	573
ν(SC)	712	716	714
$\varrho(CH_3)$	824–961	825–964	769–1008
$\nu_s(BC_2)$[a]	1089/1119	1087	1097/1123
$\nu_{as}(BC_2)$[a]	1129/1161	1122	1121/1157
$\delta_s(CH_3)$	1301	1297	1364, 1367, 1389
$\delta_{as}(CH_3)$	1375, 1436	1432	1382–1402
ν(CH)	2890–3000	2890–2996	2911–2970

[a] Frequencies corresponding to ^{11}B and ^{10}B are given.

The agreement between experimental and theoretical intensity and RD curves is not entirely satisfactory (*cf.* Figs. 1 and 2). The discrepancies may be due to noise in the observed data or to unsatisfactory assumptions about the structure. By refining a very limited number of parameters simultaneously, it is possible to refine more parameters than are indicated in Tables 1 and 2, and thus obtain slightly better agreement. However, it is not obvious which new parameters to include, and we preferred to use u values in reasonable agreement with the computed ones, and the seemingly reasonable assumptions listed previously.

The value used for u(B···H) is somewhat larger than that calculated from spectroscopic data. If the latter value is used, the disagreement around 2.2 Å is more evident. The large u value may perhaps be regarded as an indication of tilt of these methyl groups.

The peak around 3.70 Å contains mainly S···H contributions. The peak was, as mentioned, rather difficult to reproduce theoretically. The peak seems to exclude free rotation about the B – C bonds though the actual equilibrium positions and the amplitudes of the oscillations of those methyl groups remain rather uncertain.

The C3···C5 distance gives the main contribution to the outer peak around 4.35 Å. The position of the peak shows that the heavy atom skeleton is essentially planar. However, the agreement is not much changed if ϕ(C4BSC3) is varied in the range 0 – 25°. An angle of 30° may be rejected a level well below 0.5 % according to Hamilton's R-factor test.[21] An equilibrium form with a planar skeleton is in agreement with theoretical calculations. A barrier to rotation about the B – S bond in H_2BSH of about 20 kcal/mol has been found both by *ab initio* and CNDO/2 calculations while the CNDO/2 method gives a slightly lower barrier in Me_2BSMe.[22]

The B – S bond seems to be slightly shorter than found in the trithiadiborolane system,[1,2] while the B – C bond is about twice the standard deviation smaller than found in $B(CH_3)_3$ (1.578(1) Å).[23] The C – S bond length and the bond angle BSC differ somewhat from the corresponding values in methyl vinyl sulphide (1.806(6) Å and 104.5(7)°),[24] but the standard deviations are rather large. The two CBS angles differ significantly, presumably for steric reasons.

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