Molecular Structure of Gaseous Dimethyl-1,2,4-trithia-3,5-diborolane

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Dimethyl-1,2,4-trithia-3,5-diborolane has been shown by electron diffraction to have an at least approximately planar skeleton. The $B-S$ bond distances are nearly equal; the average was found to be 1.803(0.003) Å. Some other important parameters are: $r_a(S-S) = 2.076(0.003)$ Å, $r_a(B-C) = 1.569(0.005)$ Å, $\angle BSB = 101.6(0.4)°$, $\angle SBS = 117.7(0.2)°$, $\angle BSS = 101.5(0.4)°$, and $\angle S_4BC = 122.8(1.6)°$.

Though considerable π-bond order has been established for $B-N$,[1] $B-O$,[2-4] $B-F$[5] bonds, and probably also for $B-Cl$ bonds,[6,7] there is still doubt about the magnitude of a similar effect in $B-S$ bonds. Siebert *et al.*[8] have proposed that the double bond character of the $B-S$ bonds is of importance for the structure and reactivity of thioboranes, while Vahrenkamp finds that the NMR [9] and vibrational spectra [10] indicate negligible π-bond order. As a contribution to the clarification of this problem we are studying boron-sulphur compounds, and report here our results for two 1,2,4-trithia-3,5-diborolane derivatives,[11] *i.e.* $Me_2B_2S_3$ and $Cl_2B_2S_3$,[12] by electron diffraction.

EXPERIMENTAL

The sample of dimethyl-1,2,4-trithia-3,5-diborolane was synthesized by one of us (W.S.), and the electron-diffraction diagrams were recorded with the Oslo apparatus.[13] The nozzle temperature was about 75°C and the electron wave length 0.06458 Å. Four and five plates were used for the long (48.05 cm) and short (25.06 cm) nozzle-to-plate distance, respectively. The data were treated in the usual way,[14] and the modified molecular intensities were calculated using the modification function [14] $s/(|f_{B}'||f_{S}'|)$. The agreement between the observed intensity curves was satisfactory, and most of the calculations were carried out on a composite intensity curve ranging from $s = 2.50$ Å^{-1} to $s = 35.0$ Å^{-1}. The s intervals were 0.125 Å^{-1} for $s < 7.50$ Å^{-1} and 0.250 Å^{-1} for s above this value.

STRUCTURE REFINEMENT

The molecule was assumed to have at least a twofold axis of symmetry, *i.e.* either C_2 or C_{2v} symmetry when the H atoms are not taken into consideration. A C_s model was not considered, since the potential function for rotation
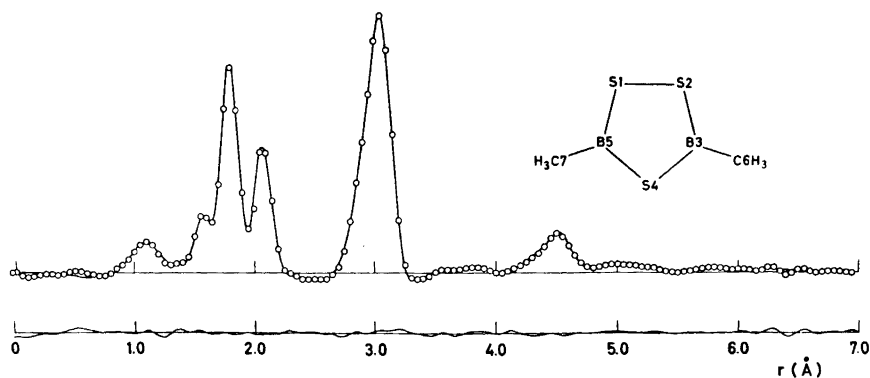
Fig. 1. Experimental (circles) and theoretical radial distribution curves (artificial damping $k = 0.0015$ Å²). The difference curve is also given.

about the $S-S$ bond has a considerable barrier corresponding to the *syn* form in most molecules (about 9 kcal/mol in H_2S_2 [15]). Models with the methyl groups in fixed positions as well as models with freely rotating groups were tried. It was assumed to be no tilt of these groups. The shrinkage effect [16] was neglected. This approximation seemed justified according to calculations (mainly for the corresponding chloro-compound [12]) by the method described by Stølevik *et al.*[17] using frequencies obtained by Sacher *et al.*[18],[19]

The experimental radial distribution (RD) curve (see Fig. 1) calculated by Fourier inversion of the observed intensities (Fig. 2), showed that the $B-S$ bond distances must be nearly equal. Least-squares refinements carried out for various values of the difference, showed that the difference must be less than 0.03 Å. Satisfactory agreement between theoretical and observed intensity and RD curves was obtained assuming a planar ring. The fit was very nearly the same for a model with the methyl groups in fixed positions
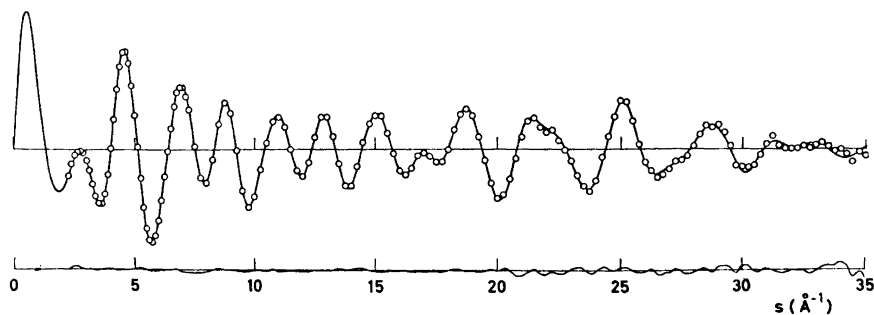

Fig. 2. Experimental (circles) and theoretical intensity curves. The differences between experimental and theoretical curves are also shown.
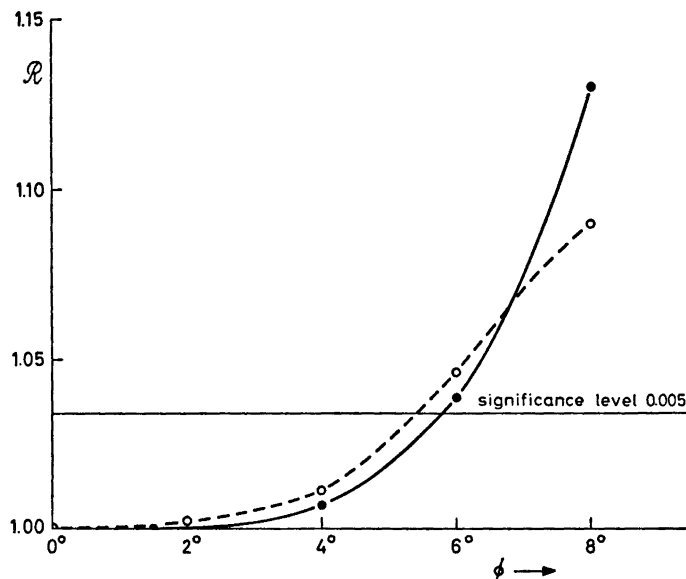
Fig. 3. The relative R factor [20] for various values of the torsional angle $\phi(S_4-B)$ for $Me_2B_2S_3$ (dots) and for $Cl_2B_2S_3$ (open circles). The R values corresponding to $\phi=0$ are put equal to 1 for both compounds.

and a model with freely rotating methyl groups.* However, it seems reasonable to assume that the barrier is low, and most of the subsequent calculations were carried out assuming free rotation.

The torsional angle about S_4-B (ϕ) was then refined as an additional parameter. The result was $\phi=1.4°$ with a standard deviation of $3.7°$. Refinements were then carried out for various fixed values of ϕ; the planar arrangement about the boron atoms was kept. Fig. 3 shows a plot of the relative R factor [20] against ϕ for a model with freely rotating methyl groups. The variation in R is very small up to $\phi=4°$. However, a torsional angle of $6°$ may be rejected at the 0.5 % level. Though one should not take this number too seriously, since the basic assumptions for the test are not fulfilled, the plot shows that the ring must be nearly planar.

The final electron diffraction results are given in Table 1, and the corresponding theoretical RD and intensity curves are compared to the observed values in Figs. 1 and 2. Since the least-squares refinements were carried out using a diagonal weight matrix, the standard deviations were multiplied by [22],[23]

$$F = \left(\frac{2a}{\Delta s}\right)^{\frac{1}{2}} \exp\left(-\frac{a^2}{2\pi}R^2\right)$$

with $a=0.5$ Å^{-1}. The uncertainty in the electron wave-length is also included.

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* The free rotation was simulated by having each methyl group in 6 different rotational positions.

Table 1. Interatomic distances ($r_a{}^{21}$), mean amplitudes of vibration (u), and bond angles with estimated standard deviations.

	r_a (Å)	u (Å)
$S_4 - B_3$ $S_2 - B_3$	1.803(0.003)[a]	0.040(0.003)[a]
S – S	2.076(0.003)	0.047(0.003)
B – C	1.569(0.005)	0.045[b]
C – H	1.104(0.012)	0.120(0.012)
S···S	3.086(0.004)	0.054(0.003)
B···S	3.008(0.007)	0.065[b]
B···B	2.795(0.007)	0.065[b]
S_4···C S_2···C_6	2.963(0.022) 2.916(0.024)	0.083(0.010)[a]
B···C	4.314(0.012)	0.068[b]
S_1···C_6	4.526(0.008)	0.075[b]
C···C	5.779(0.022)	0.100[b]
	Angles (degrees)	
∠BSB	101.6(0.4)	
∠SBS	117.7(0.2)	
∠BSS	101.5(0.4)	
∠S_4BC	122.8(1.6)	
$\phi(S_4 - B)$	1.4(3.7)	
∠HCH	108.0[b]	

[a] The parameters were assumed equal. [b] The parameter was not refined simultaneously with the other parameters.

DISCUSSION

The investigation shows that the five-membered ring in dimethyl-1,2,4-trithia-3,5-diborolane is at least nearly planar. The same result is obtained for $Cl_2B_2S_3$.[12] (See Fig. 3.) 1,2,4-Trioxa-3,5-diborolane ($B_2O_3H_2$) is also planar, as has been shown by spectroscopic methods.[24,25] The planarity of this compound in contrast to the puckered 1,2,4-trioxacyclopentane,[26] has been explained by partial π-bond character in the B – O bonds.[3] This is in agreement with the appreciable barriers to rotation about B – O bonds.[4]

It seems difficult to explain the planarity of the B_2S_3 ring without proposing some degree of π-character in the ring bonds. This is in agreement with theoretical calculations by the CNDO/2 method which gives a planar equilibrium conformation of the B_2S_3 ring and a considerable π-bond order for the B – S bonds.[27]

The ring puckering to be expected if the barrier to rotation about the B – S bonds is zero, was estimated using the Westheimer-Hendrickson approach.[28,29] Only torsional and bending contributions to the potential energy were included. The results obtained for three sets of constants are given in Table 2. The potential for rotation about the S – S bond was in the two first calculations taken from the *ab initio* results for the potential in H_2S_2.[15] This ex-

Table 2. Calculated bond angles and torsional angles in the B_2S_3 ring assuming zero barrier about the $B-S$ bonds. "Natural" angles were $\theta°_{SBS} = 120°$ and $\theta°_{SSB} = \theta°_{BSB} = 100°$ in all the calculations.

	I	II	III
$k_{BSB} = k_{SSB}{}^a$	0.035	0.50	0.050
$k_{SBS}{}^a$	0.035	0.055	0.050
$V°(SS)^b$	9.3^c	9.3^c	5.0^d
$\angle BSB$	97.4	97.5	98.0
$\angle SSB$	115.6	116.7	98.0
$\angle SBS$	95.1	96.2	118.0
$\phi(S_4-B)$	17.3	15.6	12.2
$\phi(S_2-B)$	-38.5	-34.6	-26.9
$\phi(S-S)$	41.3	36.9	28.6

[a] In kcal mol^{-1} degree^{-2}. [b] In kcal mol^{-1}. [c] The potential given in Ref. 15 was used.
[d] A potential of the form $V(\phi) = \frac{1}{2}V°(1-\cos(2\phi))$ was used.

pression for the potential includes terms up to $\cos(4\phi)$, and gives a barrier of about 9.3 kcal/mol corresponding to the *syn* form. The results in column III were obtained with a simple twofold potential. The bending force constants were similar to those used for tetrahydrothiophene [30] in the first calculation; in the other calculations larger values were used to avoid overestimating the puckering corresponding to a given rotational potential.

The torsional angles in the columns I and II are much too large to be consistent with the electron-diffraction data. Even in column III, corresponding to a considerably reduced barrier about the $S-S$ bond, the puckering is unacceptably large. With the same constants as used in this calculation, but introducing a twofold potential about the $B-S$ bonds, we found that the ring becomes planar when the barrier to rotation about $B-S$ is approximately 2.5 kcal/mol.

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