

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

A. ALMENNINGEN, H. M. SEIP, and P. VASSBOTN

Department of Chemistry, University of Oslo, Oslo 3, Norway

An electron diffraction investigation of dichloro-1,2,4-trithia-3,5-diborolane showed that the molecule is at least approximately planar. The B-S bond distances must be nearly equal; the average was found to be 1.794(0.005) Å. The other bond distances and angles are: $r_a(\text{S}-\text{S}) = 2.069(0.003)$ Å, $r_a(\text{B}-\text{Cl}) = 1.756(0.009)$ Å, $\angle \text{BSB} = 96.9(0.6)^\circ$, $\angle \text{SBS} = 121.7(0.5)^\circ$, $\angle \text{BSS} = 99.9(0.3)^\circ$, and $\angle \text{S}_4\text{BCl} = 120.8(0.5)^\circ$.

The investigation of dimethyl-1,2,4-trithia-3,5-diborolane ($\text{Me}_2\text{B}_2\text{S}_3$) discussed in the previous paper,¹ showed that the B-S bond lengths are nearly equal and the five-membered ring is at least approximately planar. It seemed worthwhile to study another compound with the same ring, and we chose dichloro-1,2,4-trithia-3,5-diborolane. Though it was realized that it would not be possible to determine the B-S and B-Cl bond lengths very accurately, small deviations from planarity might be easier to determine in this compound than in the methyl derivative. Possible differences in the ring structures in the two compounds would also be of interest.

EXPERIMENTAL

The sample of dichloro-1,2,4-trithia-3,5-diborolane was kindly synthesized by W. Siebert.² The diffraction data were recorded with the Oslo apparatus,³ the nozzle temperature being about 80°C and the electron wave length 0.06462 Å. Four and five plates were used for the long (48.06 cm) and short (23.05 cm) nozzle-to-plate distances, respectively. The data were treated in the usual way,⁴ and the modified molecular intensity were calculated using the modification function⁴

$$s/|f_s'|^2$$

The agreement between the obtained intensity curves was satisfactory, and most of the calculations were carried out on a composite intensity curve ranging from $s = 1.5$ Å⁻¹ to 38.0 Å⁻¹. The s intervals were 0.125 Å⁻¹ for $s < 10.0$ Å⁻¹ and 0.25 Å⁻¹ for larger s values.

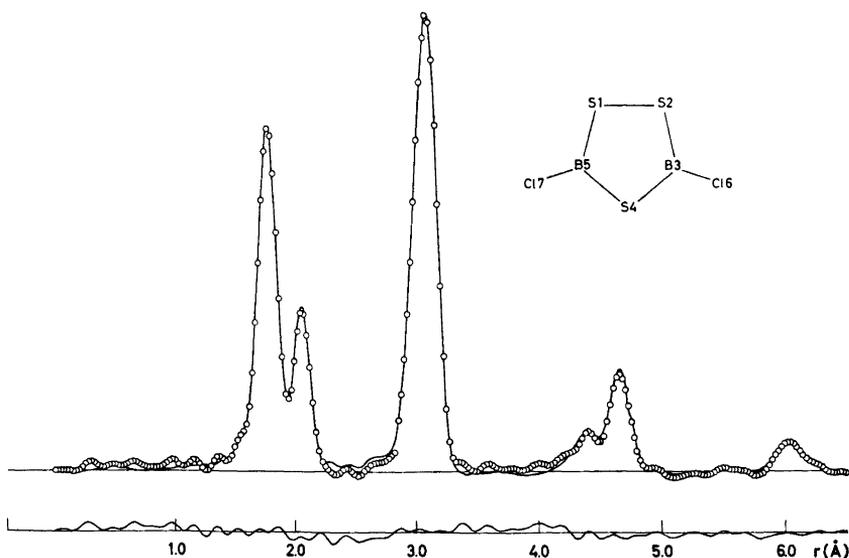


Fig 1. Experimental (circles) and theoretical radial distribution curves (artificial damping $k=0.001 \text{ \AA}^2$). The differences between experimental and theoretical curves are also shown.

STRUCTURE REFINEMENT

The experimental radial distribution (RD) curve (Fig. 1) calculated by Fourier inversion of the observed intensities (Fig. 2), showed that no appreciable deviations from planarity occur in this molecule. Very satisfactory agreement was obtained by least-squares refinement on the intensity data assuming a planar model (C_{2v} symmetry).

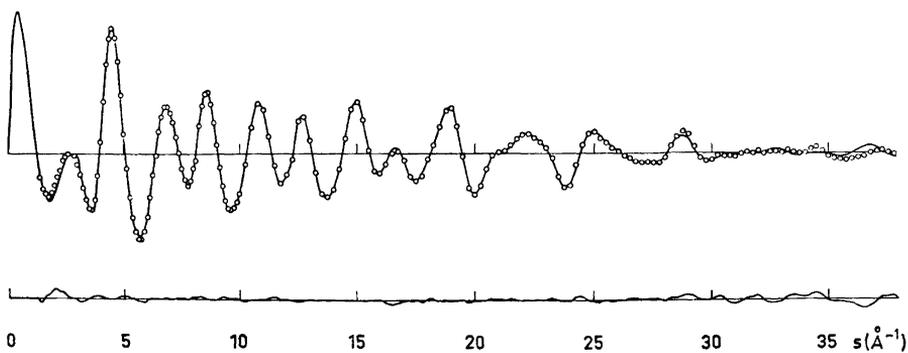


Fig. 2. Experimental (circles) and theoretical intensity curves. The difference curve is also given.

Table 1. Interatomic distances (r_a^s), mean amplitudes of vibration (u^{obs}), and bond angles with estimated standard deviations. Mean amplitudes calculated from spectroscopic data are given as u^{calc} .

	r_a (Å)	u^{obs} (Å)	u^{calc} (Å)
$S_4 - B_3$	1.794(0.005) ^a	0.042(0.005) ^a	0.051
$S_2 - B_3$			0.051
S-S	2.069(0.003)	0.041(0.004)	0.055
B-Cl	1.756(0.009)	0.047(0.007)	0.054
S...S	3.133(0.007)	0.051(0.003)	0.061
B...S	2.962(0.009)	0.057(0.012)	0.074
B...B	2.685(0.017)	0.051 ^b	0.077
$S_4 \cdots Cl$	3.087(0.007)	0.067(0.006) ^a	0.081
$S_2 \cdots Cl_6$			0.083
B...Cl	4.390(0.009)	0.071(0.008)	0.081
$S_1 \cdots Cl_6$	4.658(0.006)	0.070(0.003)	0.079
Cl...Cl	6.032(0.010)	0.104(0.007)	0.092
Angles (degrees)			
$\angle BSB$	96.9(0.6)		
$\angle SBS$	121.7(0.5)		
$\angle BSS$	99.9(0.3)		
$\angle S_4BCl$	120.8(0.5)		

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

The main difficulty in the structure determination lies in the similarity of 3 of the 4 bond distances; only the S-S bond being uniquely identifiable in the RD curve. There is also considerable overlap between the non-bonded distances (see Table 1 and Fig. 1). As in $Me_2B_2S_3$ ¹ the B-S bond lengths must be nearly equal, but the possibility of a difference of 0.02-0.03 Å cannot be excluded. The results in Table 1 were obtained assuming equal B-S bond lengths, and neglecting the shrinkage effect⁵ as for $Me_2B_2S_3$. The standard deviations in Table 1 are based partly on the formula^{6,7} used for $Me_2B_2S_3$ ¹ and partly on least-squares refinements with a weight matrix of the type discussed in Ref. 6.

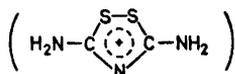
Further calculations were carried out for non-planar models (C_2 symmetry) with fixed values for the torsional angle (ϕ) about the $S_4 - B$ bond. The plot of the relative R factor is given in Fig. 3 of the previous paper.¹ The minimum in R corresponds to $\phi = 0$, but R increases very slowly for $\phi < 4^\circ$ also for this molecule. For $\phi = 8^\circ$ the relative R value is somewhat smaller for $Cl_2B_2S_3$ than for $Me_2B_2S_3$. However, some of the refined parameters corresponding to this ϕ value were rather unreasonable for the former molecule.

DISCUSSION

The results in Table 1 may be compared to the structure given for $Me_2B_2S_3$ in the previous paper.¹ The B_2S_3 ring is at least nearly planar in both compounds. The bond lengths in the rings are nearly equal, though the average

B-S distance may be slightly shorter in the Cl-compound. The SBS bond angles are somewhat increased and both the BSB and the SSB angles correspondingly decreased in $\text{Cl}_2\text{B}_2\text{S}_3$ compared to $\text{Me}_2\text{B}_2\text{S}_3$, possibly because of the difference in electronegativity between Cl and Me. Theoretical calculations by the CNDO/2 method gave a difference in the charges on Cl and on Me of about 0.14 electrons.⁹ A somewhat similar opening of a bond angle is found in fluorobenzene compared to benzene; the CCC angle at fluorine is found to be 123.4° .¹⁰

The S-S bond distances are in both compounds slightly longer than in H_2S_2 where 2.055 Å has been reported,¹¹ and approximately the same as found in the somewhat similar ring in the 3,5-diamino-1,2,4-dithiazolium cation (DADT^+):



This ring is planar in $\text{DADT}^+\text{Cl}^- \cdot \frac{1}{2}\text{H}_2\text{O}$,¹² DADT^+Br^- ,¹³ and DADT^+I^- .^{14,15} The S-S bond lengths (uncorrected for thermal motion) are 2.063(4) Å, 2.081(8) Å, and 2.083(3) Å, resp. In some other related planar rings the S-S bond may have more π -character as for example in 4-phenyl-1,2-dithiolium chloride, where the S-S bond is 2.021(4) Å.¹⁶

The B-Cl distance in $\text{Cl}_2\text{B}_2\text{S}_3$ is nearly the same as found in B_2Cl_4 (1.750 (0.005) Å¹⁷) and slightly longer than in BCl_3 (1.742 (0.004) Å¹⁸), but the difference is less than two times the standard deviation.

The obtained mean amplitudes (u) are smaller than expected for most distances both in $\text{Cl}_2\text{B}_2\text{S}_3$ and $\text{Me}_2\text{B}_2\text{S}_3$. Using the tentative assignment given by Sacher *et al.*^{19,20} and the calculation method described by Stølevik *et al.*²¹ the values denoted by u^{calc} in Table 1 were computed. These values are not very accurate, but at least for the bond distances the calculated mean amplitudes seem more reasonable than those obtained by electron diffraction. Likely sources of errors in the mean amplitudes are the "blackness correction"⁴ and the applied scattering amplitudes. In the investigations of $\text{Me}_2\text{B}_2\text{S}_3$ and $\text{Cl}_2\text{B}_2\text{S}_3$ plates of rather low density were used, and the blackness correction is therefore small. The scattering amplitudes were calculated in the usual way⁴ with Hartree-Fock atomic potentials;²² a method which usually gives fairly reliable results except perhaps for atoms considerably heavier than chlorine. We have thus at present no explanation for the unusual mean amplitudes. Possible errors in these values should not affect the geometrical parameters in $\text{Me}_2\text{B}_2\text{S}_3$ very much, but may be more serious in $\text{Cl}_2\text{B}_2\text{S}_3$ because of the large number of overlapping distances in the latter compound.

Acknowledgements. The authors are grateful to Dr. W. Siebert for supplying the sample of $\text{Cl}_2\text{B}_2\text{S}_3$ and to Dr. R. E. Sacher for sending his preliminary assignment for the fundamental vibrations of $\text{Cl}_2\text{B}_2\text{S}_3$.

REFERENCES

1. Seip, H. M., Seip, R. and Siebert, W. *Acta Chem. Scand.* **27** (1973) 15.
2. Schmidt, M. and Siebert, W. *Chem. Ber.* **102** (1969) 2752.
3. Bastiansen, O., Hassel, O. and Risberg, E. *Acta Chem. Scand.* **9** (1955) 232.

4. Andersen, B., Seip, H. M., Strand, T. G. and Stølevik, R. *Acta Chem. Scand.* **23** (1969) 3224.
5. Cyvin, S. J. *Molecular Vibrations and Mean Square Amplitudes*, Universitetsforlaget, Oslo 1968.
6. Seip, H. M., Strand, T. G., and Stølevik, R. *Chem. Phys. Lett.* **3** (1969) 617.
7. Seip, H. M. and Stølevik, R. In Cyvin, S. J., Ed., *Molecular Structures and Vibrations*, Elsevier, Amsterdam 1972, Chapter 11.
8. Kuchitsu, K. and Cyvin, S. J. In Cyvin, S. J., Ed., *Molecular Structures and Vibrations*, Elsevier, Amsterdam 1972, Chapter 12.
9. Gropen, O. and Vassbotn, P. *To be published*.
10. Nygaard, L., Bojesen, I., Pedersen, T. and Rastrup-Andersen, J. *J. Mol. Struct.* **2** (1968) 209.
11. Haase, W. *Z. Naturforsch.* **23a** (1968) 56.
12. Hordvik, A. and Sletten, J. *Acta Chem. Scand.* **20** (1966) 1907.
13. Hordvik, A. and Joys, S. *Acta Chem. Scand.* **19** (1965) 1539.
14. Foss, O. and Tjomsland, O. *Acta Chem. Scand.* **12** (1958) 1799.
15. Rodesiler, P. F. and Amma, E. L. *Acta Cryst.* **B 27** (1971) 1687.
16. Grundtvig, F. and Hordvik, A. *Acta Chem. Scand.* **25** (1971) 1567.
17. Ryan, R. R. and Hedberg, K. *J. Chem. Phys.* **50** (1969) 4986.
18. Konaka, S., Murata, Y., Kuchitsu, K. and Morino, Y. *Bull. Chem. Soc. Japan* **39** (1966) 1134.
19. Miller, F. A., Sacher, R. E. and Siebert, W. *Unpublished results*.
20. Sacher, R. E. *Private communication*.
21. Stølevik, R., Seip, H. M. and Cyvin, S. J. *Chem. Phys. Lett.* **15** (1962) 263.
22. Strand, T. G. and Bonham, R. A. *J. Chem. Phys.* **40** (1964) 1686.

Received June 8, 1972.