

## Molecular Structure of Gaseous Bis(dimethylboryl) Disulfane, $(\text{CH}_3)_2\text{BSSB}(\text{CH}_3)_2$

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Planar B–S arrangements have been found in a number of compounds by gas electron diffraction (ED).<sup>1–4</sup> The main reason is considerable  $\pi$ -bond character in the B–S bonds as shown by *ab initio* calculations on  $\text{H}_2\text{BSH}$ , which gave a barrier to internal rotation of nearly 20 kcal/mol.<sup>5</sup> The present study of  $(\text{CH}_3)_2\text{B}_2\text{S}_2$  was carried out for comparison with the BS compounds studied previously and to find the effect of delocalisation on the SS bond length and the torsional angle about this bond compared to other disulfides.

The compound was synthesised by one of us (W.S.),<sup>6</sup> and the electron-diffraction diagrams recorded with Balzers' eldigraph KD-G2 in Oslo.<sup>7,8</sup> The nozzle temperature was about 65°C. Three sets of plates were recorded: Set 1 (6 plates, electron wavelength 0.05849 Å, nozzle-to-plate distance 500 mm); Set 2 (4 plates, 0.05858 Å, 250 mm); and Set 3 (1 plate, 0.05839 Å, 250 mm). The plates in set 2 and set 3 were unfortunately too light to give quite satisfactory intensity data. The data were treated in the usual way.<sup>9</sup> A composite intensity curve was computed, and the  $s$ -range 1.75–26.0 Å used in the structure determination. The scattering amplitudes and modification function were the same as applied previously.<sup>3</sup>

Least-squares refinements of the structure were carried out assuming  $C_2$  symmetry. We assumed further the methyl groups to have a threefold symmetry axis coinciding with the B–C bond and planar arrangements about the boron atoms. In some calculation free rotation of the methyl groups was simulated and in other cases the torsional angles for the methyl groups were fixed. The results for the most important parameters were nearly the same in these refinements.

Mean amplitudes of vibration ( $u$ ) were computed as described by Stølevik *et al.*<sup>10</sup> The force constants assumed for the  $(\text{CH}_3)_2\text{BS}$ -moieties were essentially the same as used for  $(\text{CH}_3)_2\text{BSCH}_3$ .<sup>3</sup> The S–S stretching constant was taken from  $\text{H}_2\text{S}_2$ .<sup>11</sup> Various values were tried for the constant for torsion about the S–S bond. The best agreement between experimental and theoretical ED data was obtained for low torsional constants. The value used in the final calculations, 0.04 mdyne Å rad<sup>-2</sup>, is less than half of the constant found in  $\text{H}_2\text{S}_2$ .<sup>11</sup>

Table 1. Distances ( $r_a^{20}$ ), angles and mean amplitudes in  $(\text{CH}_3)_2\text{B}_2\text{S}_2$ . The standard deviations given in parentheses apply to the last digit given.

	$r$ (Å)	$u^{\text{ED}}$ (Å) <sup>a</sup>	$u^{\text{S}}$ (Å) <sup>b</sup>
S–B	1.805(5)	0.044(4)	0.055
S–S	2.078(4)	0.040(4)	0.051
C–B	1.573(5)	0.057(4)	0.058
C–H	1.090(5)	0.068(3)	0.078
C <sub>1</sub> ...S <sub>1</sub>	2.836(6)	0.083	0.080
C <sub>2</sub> ...S <sub>1</sub>	2.976(7)	0.083	0.076
C <sub>1</sub> ...S <sub>2</sub>	4.561(5)	0.095	0.098
C <sub>2</sub> ...S <sub>2</sub>	3.293(9)	0.17	0.17
B <sub>1</sub> ...S <sub>2</sub>	3.091(5)	0.10	0.10
C <sub>1</sub> ...C <sub>3</sub>	2.760(10)	0.076	0.082
C <sub>1</sub> ...B <sub>2</sub>	5.599(38)	0.24	0.23
C <sub>1</sub> ...C <sub>3</sub>	7.020(34)	0.24	0.23
C <sub>1</sub> ...C <sub>4</sub>	5.548(40)	0.41	0.39
C <sub>2</sub> ...B <sub>2</sub>	4.550(55)	0.39	0.38
C <sub>2</sub> ...C <sub>1</sub>	5.174(95)	0.54	0.53
B <sub>1</sub> ...B <sub>2</sub>	4.275(30)	0.25	0.24
Degrees			
$\angle \text{B}_1\text{S}_1\text{S}_2$	105.3(4)		
$\angle \text{S}_1\text{B}_1\text{C}_1$	114.0(6)		
$\angle \text{S}_1\text{B}_1\text{C}_2$	123.4(4)		
$\angle \text{BCH}$	109.8(6)		
$\phi(\text{BSSB})$	120(6)		
$\phi(\text{S}_2\text{S}_1\text{B}_1\text{C}_1)$	179(4)		

<sup>a</sup> Refined or assumed in the electron-diffraction investigation. <sup>b</sup> Calculated assuming a simple force field as described in the text. <sup>c</sup> The values were assumed equal.

The mean amplitudes for the bond distances were difficult to determine from the ED data because of the short  $s$ -range. The geometrical parameters obtained were nearly the same if these amplitudes were refined or kept at the values computed as described above. The results of the investigation given in Table 1 are averages of values obtained in several refinements. The standard deviations include the effect of correlation between the intensity data. Comparison of the experimental and theoretical radial distribution curves is shown in Fig. 1. The difference curve reflects the noise in the experimental data for  $s > 20 \text{ \AA}^{-1}$ .

As in related molecules the arrangements about the B–S bonds are planar in  $(\text{CH}_3)_2\text{B}_2\text{S}_2$ , indicating some  $\pi$ -bond character. The torsional angle about the S–S bond is about 120° (0° for the *syn* form). The standard deviation is quite large, but a planar *anti* form can be ruled out.

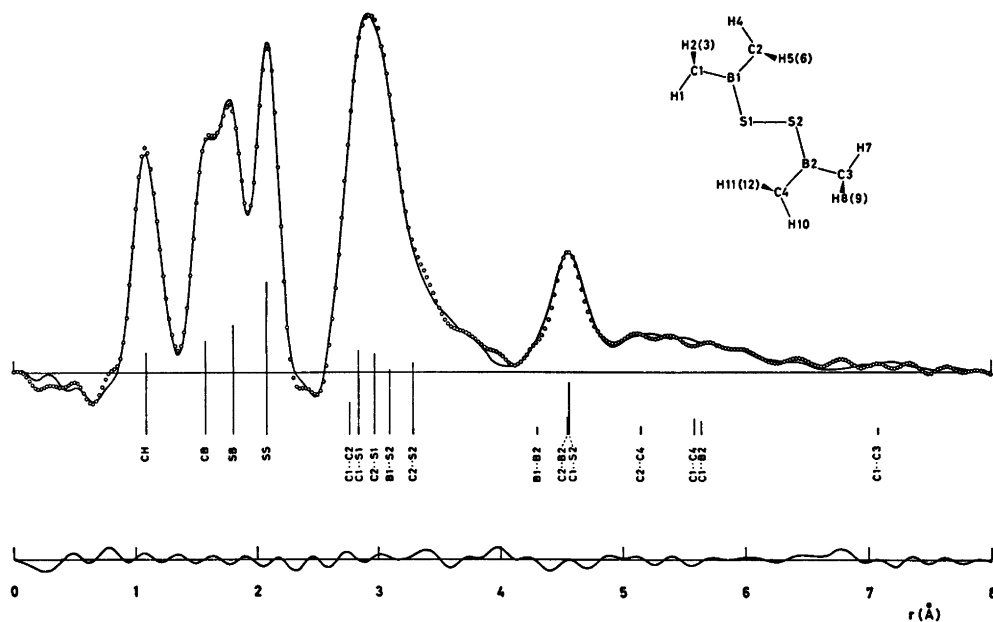
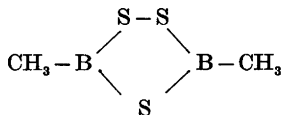


Fig. 1. Experimental (circles) and theoretical radial distribution functions for bis(dimethylboryl) disulfane (artificial damping constant  $k=0.003 \text{ \AA}^2$ ). The differences between experimental and theoretical values are also shown.

The bond distances are almost identical to those found in dimethyl-1,2,4-trithia-3,5-diborolane<sup>1</sup>

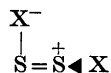


with a rather long S-S bond. In XSSX compounds this bond length varies considerably with the electronegativity of X. In  $\text{H}_2\text{S}_2$ ,  $(\text{CH}_3)_2\text{S}_2$ ,  $\text{Cl}_2\text{S}_2$ , and  $\text{F}_2\text{S}_2$  the S-S bond lengths are 2.05<sub>5</sub> Å,<sup>12</sup> 2.02<sub>2</sub> Å,<sup>13</sup> 1.93<sub>1</sub> Å,<sup>14</sup> and 1.88<sub>7</sub> Å,<sup>15</sup> respectively. The torsional angle is close to 90° in all these molecules.

No accurate experimental barriers have been reported for  $\text{H}_2\text{S}_2$ , though it seems clear that the *syn* and *anti* barriers are both fairly high;<sup>16</sup> a result also obtained by *ab initio* calculations. Veillard and Demuyne<sup>17</sup> obtained (in kcal/mol) 9.3 and 6.0 for the *syn* and *anti* barriers, respectively. Pappas<sup>18</sup> found 8.4 and 4.2 in  $\text{H}_2\text{S}_2$  and 16.0 and 9.2 in  $(\text{CH}_3)_2\text{S}_2$ . These results may be compared to preliminary values obtained by *ab initio* calculations on  $\text{H}_2\text{BSSBH}_2$ .<sup>19</sup> The equilibrium angle becomes about 102° and the barrier in the *anti* form is very low, about 0.7 kcal/mol. It should be noted that while this angle corresponds to the

minimum in the potential curve, a value averaged over the oscillations is obtained by electron diffraction.

The barriers in  $\text{X}_2\text{S}_2$  have been described to lone-pair-lone-pair repulsion in the planar forms and hyperconjugation of the type



in the orthogonal form.<sup>15,16</sup> The *ab initio* calculations seem to support this hypothesis to some extent.<sup>17,18</sup> The reduced barrier in the *anti* form of  $\text{H}_2\text{B}_2\text{S}_2$ , and probably also in  $(\text{CH}_3)_2\text{B}_2\text{S}_2$ , is most likely due to considerable delocalisation in the  $\pi$ -system. However, though the torsional angle becomes somewhat greater than 90°, the reduction is not large enough to give an equilibrium structure with planar skeleton. With considerable deviation from planarity the S-S bond length should depend largely on the electronegativity of the substituents; *i.e.* a bond length similar or slightly longer than found in  $\text{H}_2\text{S}_2$  is reasonable.

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