

## The Sulphur-Sulphur Bond in 3,5-Diamino-1,2-dithiolium Iodide

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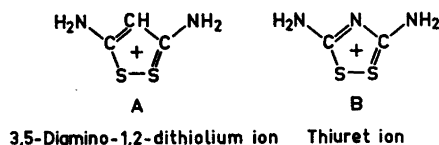
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An X-ray crystallographic investigation of the unsaturated five-membered cyclic disulphide, 3,5-diamino-1,2-dithiolium iodide, has been undertaken. The crystals are orthorhombic, space group  $Pnma$  with four formula units in the unit cell, and  $a = 5.46 \text{ \AA}$ ,  $b = 9.23 \text{ \AA}$ ,  $c = 14.17 \text{ \AA}$ .

The disulphide group lies across the crystallographic mirror plane, and the length of the sulphur-sulphur bond has been found through least squares refinement of the  $0kl$  data.

The derived sulphur-sulphur bond length,  $2.08 \pm 0.02 \text{ \AA}$ , shows that the presence of amino groups in 3- and 5-positions reduces the  $\pi$ -bond character of the sulphur-sulphur bond relatively to the equivalent bond in the unsubstituted 1,2-dithiolium ion.

It has been found, in the course of X-ray crystallographic studies of some dithiolium salts,<sup>1</sup> that crystals of 3,5-diamino-1,2-dithiolium iodide are isomorphous with those of thiuret hydroiodide.<sup>2</sup> The analogous five-membered rings of A and B both possess a sextet of  $\pi$ -electrons and the rings are pseudo-aromatic. According to molecular orbital calculations carried out on the



unsubstituted 1,2-dithiolium ion by Bergson,<sup>3</sup> one should expect the sulphur-sulphur bond to be shortened through  $\pi$ -bonding. However, the sulphur-sulphur bond length of  $2.088 \pm 0.012 \text{ \AA}$  found in thiuret hydroiodide,<sup>2</sup> indicates that the sulphur-sulphur bond is a pure single bond. It might be of interest to obtain additional experimental evidence for the length of this bond. The present X-ray crystallographic investigation of 3,5-diamino-1,2-dithiolium iodide, was undertaken with this view.

## EXPERIMENTAL

Crystal data on 3,5-diamino-1,2-dithiolium iodide have been published earlier.<sup>1</sup> The crystals are orthorhombic, space group *Pnma*, and the unit cell dimensions are  $a = 5.46 \text{ \AA}$ ,  $b = 9.23 \text{ \AA}$ , and  $c = 14.17 \text{ \AA}$ . Experimental error is estimated to be within 0.5%. There are four formula units per unit cell; density, calc. 2.33, found 2.20–2.30 g/cm<sup>3</sup>. The crystals were rather unstable and became opaque and gave powder pattern after a few hours. It was therefore rather difficult to obtain X-ray photographs good enough for intensity measurements. The intensities of the  $0kl$  reflections were estimated visually from a single Weissenberg photograph, taken with unfiltered copper radiation ( $\mu = 438 \text{ cm}^{-1}$ ) of a crystal with cross-section  $0.08 \times 0.05 \text{ mm}$ . Both  $\alpha$  and  $\beta$  reflections were measured, and the average value of the ratios between  $\alpha$  and  $\beta$  intensities for equivalent reflections was used to put the intensities on a relative scale. 69 of the 90  $0kl$  reflections obtainable with  $\text{CuK}\alpha$  radiation were observed and measured. The intensities were corrected for Lorentz and polarization factors, but not for absorption.

## STRUCTURE REFINEMENT

The sulphur-sulphur bond in 3,5-diamino-1,2-dithiolium iodide lies, as in thiuret hydroiodide, across the mirror plane *m* which passes through the crystal normal to the *b* axis, and the length of this bond can be determined

Table 1. Atomic coordinates in fractions of corresponding cell edges, and temperature factors.

| Atom           | <i>y</i> | <i>z</i> | Temperature factor                        |
|----------------|----------|----------|---|
| I              | 0.2500   | -0.1050  | $\exp-(0.0035k^2 + 0.0028l^2)$            |
| S              | 0.1373   | 0.0790   | $\exp-(0.0018k^2 + 0.0036l^2 - 0.0013kl)$ |
| N              | -0.011   | 0.159    | $\exp-2(\sin^2\theta/\lambda^2)$          |
| C <sub>1</sub> | 0.250    | 0.154    | $\exp-2(\sin^2\theta/\lambda^2)$          |
| C <sub>2</sub> | 0.094    | 0.144    | $\exp-5(\sin^2\theta/\lambda^2)$          |

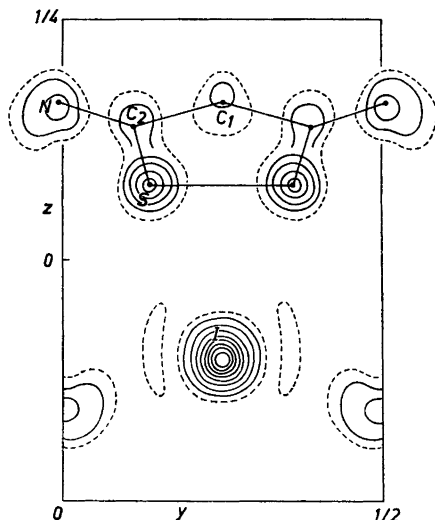


Fig. 1. Electron density projection of 3,5-diamino-1,2-dithiolium iodide along the *a* axis. Contours at arbitrary but equal intervals.

Table 2. Observed and calculated structure factors for 3,5-diamino-1,2-dithiolium iodide. The values are based on four asymmetric units.

| $k$ | $F_o$  | $0k0$ | $F_c$   | $l$ | $F_o$  | $05l$    | $F_c$  |
|-----|--------|-------|---------|-----|--------|----------|--------|
| 2   | 61.4   |       | - 85.1  | 1   | 62.2   |          | 57.9   |
| 4   | 47.0   |       | 53.7    | 3   | 90.4   |          | 9.22   |
| 6   | 44.4   |       | - 49.0  | 5   | < 14.9 |          | 9.4    |
| 8   | 81.1   |       | 79.3    | 7   | 61.1   |          | - 61.1 |
| 10  | 51.3   |       | - 51.3  | 9   | 35.2   |          | - 36.8 |
|     |        |       |         | 11  | 20.1   |          | 19.7   |
|     |        |       |         | 13  | 19.3   |          | 26.0   |
|     |        |       |         | 15  | < 12.8 |          | - 3.0  |
| $l$ |        | $00l$ |         | $l$ |        | $06l$    |        |
| 2   | 42.5   |       | 38.4    | 2   | < 15.3 |          | - 8.4  |
| 4   | 145.8  |       | - 133.3 | 4   | 48.6   |          | 47.7   |
| 6   | 78.2   |       | - 62.2  | 6   | 30.0   |          | 26.1   |
| 8   | 23.8   |       | 17.4    | 8   | 36.7   |          | - 34.9 |
| 10  | 42.0   |       | 40.6    | 10  | 32.8   |          | - 36.2 |
| 12  | 27.2   |       | 21.1    | 12  | < 16.4 |          | 10.3   |
| 14  | < 17.7 |       | - 17.5  | 14  | 27.5   |          | 29.1   |
| 16  | < 14.8 |       | - 17.6  |     |        |          |        |
| $l$ |        | $01l$ |         | $l$ |        | $07l$    |        |
| 1   | 20.3   |       | - 44.1  | 1   | 18.7   |          | - 22.5 |
| 3   | 51.1   |       | 40.5    | 3   | 48.3   |          | - 40.0 |
| 5   | 27.2   |       | - 19.9  | 5   | < 17.5 |          | 2.4    |
| 7   | 78.9   |       | - 63.3  | 7   | 47.5   |          | 44.0   |
| 9   | < 14.9 |       | - 5.8   | 9   | < 17.6 |          | 12.2   |
| 11  | 55.7   |       | 53.3    | 11  | 30.4   |          | - 32.9 |
| 13  | 27.0   |       | 27.3    | 13  | 16.8   |          | - 18.1 |
| 15  | 21.9   |       | - 23.9  |     |        |          |        |
| 17  | 22.1   |       | - 27.1  |     |        |          |        |
| $l$ |        | $02l$ |         | $l$ |        | $08l$    |        |
| 2   | 32.7   |       | - 35.3  | 2   | 20.0   |          | 20.7   |
| 4   | 65.8   |       | 65.0    | 4   | 59.0   |          | - 54.0 |
| 6   | 73.7   |       | 66.4    | 6   | 37.9   |          | - 41.2 |
| 8   | 36.2   |       | - 30.0  | 8   | < 17.1 |          | 9.5    |
| 10  | 53.5   |       | - 53.4  | 10  | 26.3   |          | 30.4   |
| 12  | < 17.9 |       | 3.5     | 12  | 11.1   |          | 12.2   |
| 14  | 24.6   |       | 30.0    |     |        |          |        |
| 16  | < 14.1 |       | 8.4     |     |        |          |        |
| $l$ |        | $03l$ |         | $l$ |        | $09l$    |        |
| 1   | 59.4   |       | - 67.0  | 1   | 15.4   |          | 16.9   |
| 3   | 83.4   |       | - 101.1 | 3   | 15.2   |          | 15.5   |
| 5   | < 12.1 |       | 0.7     | 5   | 14.8   |          | - 21.6 |
| 7   | 75.0   |       | 72.1    | 7   | 27.2   |          | - 28.2 |
| 9   | 27.2   |       | 29.5    | 9   | < 13.7 |          | 6.4    |
| 11  | 29.3   |       | - 31.1  | 11  | 30.7   |          | 31.3   |
| 13  | 24.4   |       | - 26.5  |     |        |          |        |
| 15  | < 15.4 |       | 7.6     |     |        |          |        |
| 17  | < 10.3 |       | 15.5    |     |        |          |        |
| $l$ |        | $04l$ |         | $l$ |        | $0,10,l$ |        |
| 2   | 13.0   |       | - 7.8   | 2   | 23.0   |          | - 19.1 |
| 4   | 49.9   |       | - 55.8  | 4   | 38.0   |          | 34.7   |
| 6   | < 14.1 |       | - 4.2   | 6   | 42.5   |          | 37.4   |
| 8   | 39.9   |       | 43.0    | 8   | < 11.3 |          | - 6.9  |
| 10  | 34.4   |       | 32.2    | 10  | 17.6   |          | - 26.7 |
| 12  | < 17.9 |       | - 12.0  |     |        |          |        |
| 14  | 37.0   |       | - 38.2  |     |        |          |        |
| 16  | < 11.8 |       | - 13.1  |     |        |          |        |
|     |        |       |         | $l$ |        | $0,11,l$ |        |
|     |        |       |         | 1   | 21.2   |          | - 16.9 |
|     |        |       |         | 3   | 37.1   |          | - 27.6 |
|     |        |       |         | 5   | < 9.3  |          | 3.1    |
|     |        |       |         | 7   | 35.5   |          | 30.3   |

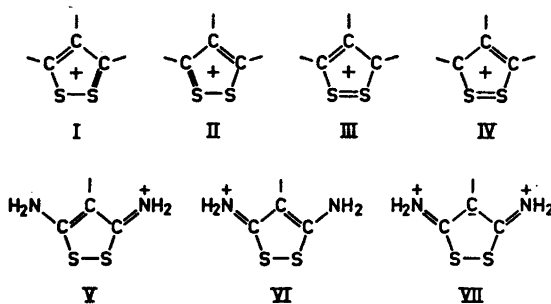
through a refinement of the  $a$ -axis projection. As a first approximation the coordinates of the isomorphous thiuret hydroiodide<sup>2</sup> were used with an overall isotropic temperature factor  $\exp[-3(\sin^2\theta/\lambda^2)]$ . The parameters were refined by least squares methods on an IBM 1620<sup>11</sup> computer, using a program designed by Mair.<sup>4</sup> Weighting scheme No. 3, recommended by Mair, was used with  $a = 128$  and  $b = 80$ . Three refinement cycles with isotropic temperature factors were carried out first. After four subsequent cycles with anisotropic temperature factors for iodine and sulphur, the agreement factor  $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$  had reached 0.11 and did not improve. There were, however, at this point, still small shifts in the sulphur coordinates, although smaller than the corresponding standard deviations. In order to secure that the remaining shifts did not accumulate in a specific direction, five additional refinement cycles were carried out. During this process all coordinate shifts became negligible, and no accumulating tendency was noticed. The final atomic coordinates and temperature parameters are listed in Table 1. A Fourier map of the  $a$  axis projection, corresponding to the last stage of refinement is shown in Fig. 1. The observed and calculated structure factors in Table 2 are based on the scattering curves for sulphur, nitrogen and carbon given in *International Tables*,<sup>5</sup> the first set of the listed scattering factors for carbon being used. For the iodide ion, a curve was constructed from Thomas-Fermi values for xenon at small scattering angles and electroneutral iodine at intermediate and large angles.

The structure of thiuret hydroiodide was refined by two-dimensional difference methods.<sup>2</sup> It was therefore of interest for the purpose of the present study to refine the structure of thiuret hydroiodide by the same procedure as employed for 3,5-diamino-1,2-dithiolium iodide. Professor Foss kindly provided unpublished  $h0l$  data for thiuret hydroiodide, and three-dimensional least squares refinement could thus be carried out on data for the three principal zones. This refinement gave a value of  $2.083 \pm 0.015$  Å for the sulphur-sulphur bond in thiuret hydroiodide, in agreement with the value  $2.088 \pm 0.012$  Å reported by Foss and Tjomsland.<sup>2</sup> The length of the sulphur-sulphur bond in 3,5-diamino-1,2-dithiolium iodide is, according to the coordinates in Table 1,  $2.08 \pm 0.02$  Å.

#### DISCUSSION

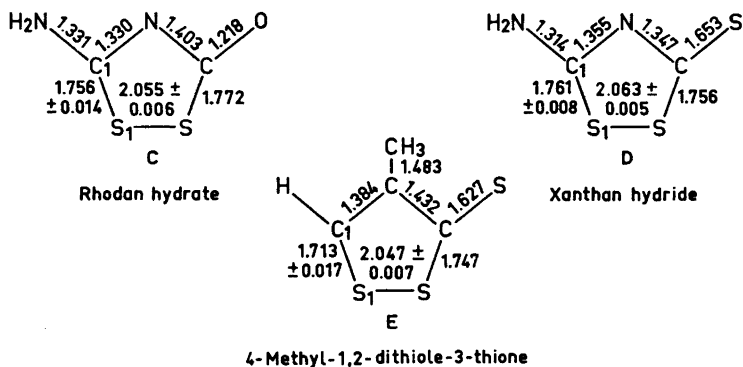
The  $\pi$ -bond order of the sulphur-sulphur bond in the 1,2-dithiolium ion is calculated to be 0.35–0.42 by molecular orbital methods,<sup>3</sup> corresponding to a bond length of 2.01–2.00 Å if one assumes a linear bond-length/bond-order relationship. The sulphur-sulphur bond is thus significantly longer in the 3,5-diamino-1,2-dithiolium ion, where it is found to be  $2.08 \pm 0.02$  Å, than in the unsubstituted 1,2-dithiolium ion. A look at the resonance forms of the ions may explain this difference in bond length.

The structure of the 1,2-dithiolium ion may according to the calculated  $\pi$ -bond orders for its different bonds,<sup>3</sup> be regarded as mainly based on the resonance forms I, II, III, and IV. The introduction of amino substituents in 3- and 5-positions leads to the additional resonance forms V, VI, and VII, which all contain a sulphur-sulphur single bond. The relative weight of resonance forms containing sulphur-sulphur double bonds should thus be smaller



in the 3,5-diamino-1,2-dithiolium ion than in the unsubstituted 1,2-dithiolium ion, and the sulphur-sulphur bond longer.

This line of argument derives support from the results of crystal structure analyses of 3-phenyl-1,2-dithiolium iodide,<sup>6</sup> 4-phenyl-1,2-dithiolium iodide,<sup>7</sup> and 4-phenyl-1,2-dithiolium bromide,<sup>7</sup> which show that the bond lengths in the dithiolium ring of these compounds are in agreement with the calculated  $\pi$ -bond orders for the corresponding bonds in the 1,2-dithiolium ion. Experimental evidence for the contribution of the resonance forms V, VI, and VII to the structure of the 3,5-diamino-1,2-dithiolium ion arises from structure investigations of thiuret hydro-iodide,<sup>2</sup> -bromide,<sup>7</sup> and -chloride.<sup>7</sup> It may be concluded that the conjugation in the 3,5-diamino-1,2-dithiolium ion is most pronounced in the nitrogen-carbon part of the ion, due to the presence of the amino groups.



Further support for the reduction of the  $\pi$ -bond order of the sulphur-sulphur bond, and probably also of the sulphur-carbon bond, in the 3,5-diamino-1,2-dithiolium ion relative to the unsubstituted 1,2-dithiolium ion, derives from structure investigations of rhodan hydrate (C),<sup>8</sup> xanthan hydride (D)<sup>9</sup> and 4-methyl-1,2-dithiole-3-thione (E).<sup>10</sup> The sulphur-sulphur bond in E, which contains no amino group, is shorter than in C and D which both contain one amino group. The difference is small, but in the direction indicated on the basis of

the above picture. The  $S_1-C_1$  bonds in C and D are both more than three times the respective standard deviations longer than the equivalent bond in E; this indicates that  $\pi$ -bonding between  $C_1$  and the amino nitrogen is formed partly at the expense of the  $C_1-S_1$   $\pi$ -bonding.

The sulphur-sulphur bond lengths,  $2.08 \pm 0.02$  Å in 3,5-diamino-1,2-dithiolium iodide and  $2.083 \pm 0.015$  Å in thiuret hydroiodide indicate that the conjugation in these compounds does not extend over the sulphur-sulphur bond. Before this can be more safely concluded, however, it becomes necessary to find out to which degree the sulphur-iodide close contacts which occur in thiuret hydroiodide<sup>2</sup> and probably also in the isomorphous 3,5-diamino-1,2-dithiolium iodide, affect the lengths of the sulphur-sulphur bond. Structure investigations of thiuret hydrobromide and hydrochloride<sup>7</sup> are almost completed, and may give further information on this point.

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