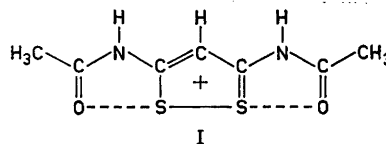


## The Structure of 3,5-Diacetamido-1,2-dithiolium Iodide

ASBJØRN HORDVIK and HANS M. KJØGE

Chemical Institute, University of Bergen,  
Bergen, Norway



Structure investigations, carried out on halogenides of positively charged unsaturated five-membered cyclic disulphides,<sup>1,2</sup> have shown that the sulphur atoms of the disulphide group are able to form partial covalent bonds with iodide and bromide ions. So far the strongest bond of this type has been found in a linear arrangement  $\text{S}-\text{S}\cdots\text{I}$  in 3-phenyl-1,2-dithiolium iodide.<sup>3</sup> The sulphur-iodide distance (3.37 Å) in this salt corresponds to a  $\sigma$ -bond order of 0.39 if one assumes a linear bond-order/bond-length relationship, but the bonding does not seem to have effected a lengthening of the sulphur-sulphur bond which is  $1.998 \text{ \AA} \pm 0.010 \text{ \AA}$ . In thio-thiophene<sup>3</sup> a linear trisulphur system  $\text{S}-\text{S}-\text{S}$  is present in which both sulphur-sulphur bond lengths are equal (2.36 Å). These bonds are longer than single bonds (2.08 Å), which shows that one of the sulphur-sulphur bonds is formed at the expense of the other. A nearly linear  $\text{S}-\text{S}\cdots\text{O}$  arrangement is present in 2,5-dimethyl-dithiofuroptene,<sup>4</sup> an isologue of thio-thiophene. The  $\sigma$ -bond order of the partial sulphur-oxygen bond (2.41 Å) in this compound is reported to be 0.55, and the bonding seems to have a significant although small effect on the sulphur-sulphur bond (2.12 Å) for which a  $\sigma$ -bond order of 0.95 is reported.

Structure investigations of unsaturated five-membered cyclic disulphides, in which both sulphur atoms form partial bonds with external atoms or ions in a linear arrangement  $\text{X}\cdots\text{S}-\text{S}\cdots\text{X}$ , may contribute to the understanding of the character of this kind of partial bonding. The degree to which the partial bonding affects the sulphur-sulphur bond may be more detectable when the bond is attacked from both sides. A structure investigation of the 3,5-diacetamido-1,2-dithiolium ion (I) is of interest in this respect.

Crystal data on 3,5-diacetamido-1,2-dithiolium iodide have been published elsewhere.<sup>5</sup> The salt crystallizes from water by slow evaporation as yellow needles. The crystals are monoclinic, with  $a = 24.68 \text{ \AA}$ ,  $b = 5.05 \text{ \AA}$ ,  $c = 21.41 \text{ \AA}$ , and  $\beta = 115.2^\circ$ . Experimental error is estimated to be within 0.5%. There are eight formula units per unit cell; density, calc. 1.89, found 1.89 g/cm<sup>3</sup>. The centrosymmetric space group  $C2/c$  has been found to be the correct one through Patterson and Fourier projections along the  $b$  axis. Preliminary results of a complete structure determination of 3,5-diacetamido-1,2-dithiolium iodide is given here.

The structure was solved by the "heavy atom method". A Fourier map of the  $b$ -projection, based on phases calculated from the iodide and sulphur positions, showed well resolved peaks for all the carbon, nitrogen and oxygen atoms. The projection was refined by least squares methods, using anisotropic temperature factors for iodide and sulphur, and isotropic for the light atoms. After ten refinement cycles  $R = \Sigma |F_o| - |F_c| / \Sigma |F_o|$  had reached 0.10 and did not improve. Coordinates corresponding to this stage of

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

	$x$	$z$
I	0.1473	0.1560
S <sub>1</sub>	0.2736	0.0692
S <sub>2</sub>	0.3587	0.1472
C <sub>1</sub>	0.248	0.107
C <sub>2</sub>	0.288	0.163
C <sub>3</sub>	0.343	0.192
C <sub>4</sub>	0.149	0.007
C <sub>5</sub>	0.082	-0.017
C <sub>6</sub>	0.448	0.270
C <sub>7</sub>	0.488	0.350
N <sub>1</sub>	0.192	0.071
N <sub>2</sub>	0.388	0.249
O <sub>1</sub>	0.166	-0.014
O <sub>2</sub>	0.454	0.245

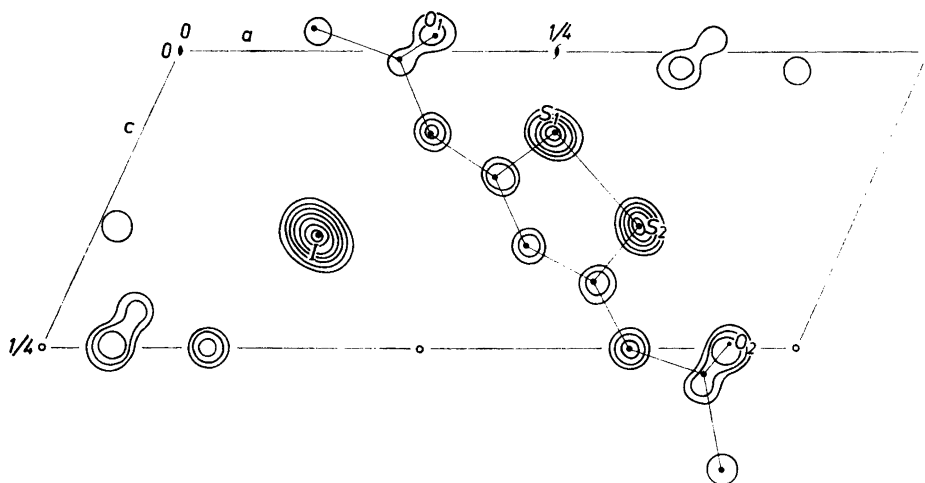


Fig. 1. Electron density projection of 3,5-diacetamido-1,2-dithiolium iodide along the  $b$  axis. Plane group  $p2$  and origin on twofold axis. Contours at arbitrary but equal intervals.

refinement are listed in Table 1. An electron density map of the  $b$ -projection is shown in Fig. 1.

The 3,5-diacetamido-1,2-dithiolium ion looks nearly planar according to Fig. 1, and the sulphur-sulphur bond seems to be approximately perpendicular to the  $b$  axis. There is obviously partial bonding between sulphur and oxygen, the projected sulphur-oxygen distances being 2.39 Å and 2.49 Å. The projection of the sulphur-sulphur bond length (2.055 Å), which according to the orientation of the ion should be very nearly the same as the bond length itself, is shorter than the sulphur-sulphur bond in 3,5-diamino-1,2-dithiolium iodide (2.08 Å).

In order to find out whether the sulphur-oxygen bonding in the 3,5-diacetamido-1,2-dithiolium ion has an effect on the sulphur-sulphur bond, it becomes important to obtain information which can lead to an estimate of the  $\pi$ -bond

order of the sulphur-sulphur bond in the ion. This implies accurate determinations of the sulphur-carbon and carbon-carbon bond lengths of the 1,2-dithiolium ring. Structure investigations will therefore also be carried out on 3,5-diacetamido-1,2-dithiolium bromide and chloride which both are isomorphous with the iodide.

1. Foss, O. and Tjomsland, O. *Acta Chem. Scand.* **12** (1958) 1799.
2. Work to be published by A. Hordvik and coworkers (H. Kjøge, S. Joys, J. Sundsfjord and E. Sletten).
3. Bezzi, S., Mammì, M. and Garbuglio, C. *Nature* **182** (1958) 247.
4. Mammì, M., Bardi, R., Traverso, G. and Bezzi, S. *Nature* **192** (1961) 1282.
5. Hordvik, A. *Acta Chem. Scand.* **17** (1963) 1809.

Received February 1, 1965.