# The Structure of 5-Phenyl-3-(5-phenyl-1,2-dithiol-3-ylidenmethyl)-1,2-dithiolium Iodide

ASBJØRN HORDVIK

Chemical Institute, University of Bergen, Bergen, Norway

The 5-phenyl-3-(5-phenyl-1,2-dithiol-3-ylidenemethyl)-1,2-dithiolium ion (I) contains two 5-phenyl substituted unsaturated five-membered cyclic disulphide rings connected in their 3-positions through a methine group. The structure is analogous to that of a mono-methine

(I)
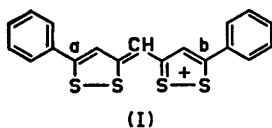
cyanine dye. In compounds of this type the methine hydrogen is known to be rather acid. The cation (II), for example, is stable in strong acid solution,[1] while in neutral solution the methine hydrogen ionizes completely, and the methine carbon valencies probably become linear.

(II)
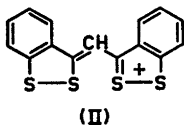
In the cation (I), the methine carbon should be mainly sp^2 hybridized, and the (a—b)-chain of sp^2-hybridized carbon atoms should be planar. Hence close contact between the two central sulphur atoms would be expected to occur. The structures of a series of compounds in which the sulphur atoms of an unsaturated five-membered cyclic disulphide participate in partial bonding with external atoms, have recently been investigated,[2,3] and it was hoped that a structure investigation of (I) might contribute to a better understanding of this partial bonding. Preliminary results of a complete structure determination of (I) is given here.

The iodide of (I) was prepared by Klingsberg,[4] who kindly provided a sample. It crystallized from methanol as purple

needles which by closer examination showed pronounced irregular growth. The crystals are monoclinic and probably belong to the space group $P2_1/c$. Due to the poor quality of the crystals, X-ray photographs has so far been taken around the needle axis only. The a axis, parallel the needle axis, is 5.25 Å, and the b and c spacings, without knowing which is which, are 17.43 Å (taken as b) and 23.26 Å (taken as d_{001}). Experimental error is estimated to be within 0.5 %. Four formula units in the unit cell and the density 1.645 g/cm³, found by flotation, yield a molecular weight of 527, which is 31 molecular weight units higher than corresponding to the formula $S_4C_{19}H_{13}I$. This seems to indicate one molecule of methanol (mol. wt. 32) of solvation.

The structure was solved by the heavy atom method. A Fourier map of the a-projection, based on phases calculated from the iodide position, showed well resolved peaks for the sulphur atoms. The carbon atoms were successively included in the structure factor calculations within four subsequent Fourier refinement cycles. Two electron density maxima which

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

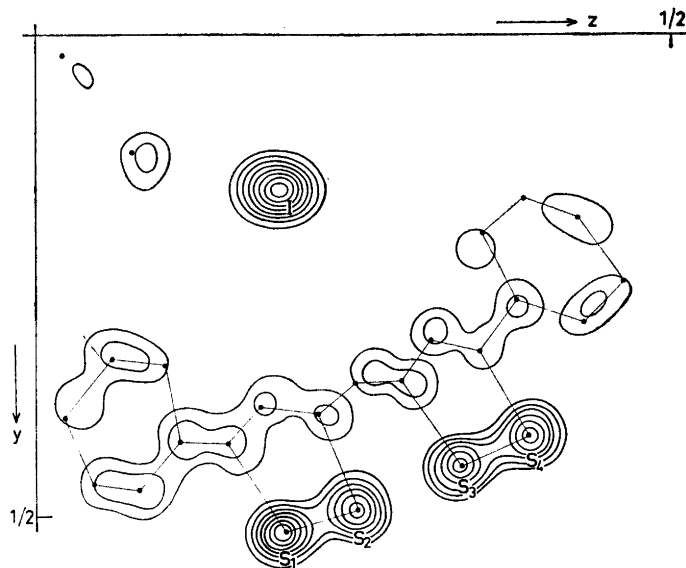|	y	z
I	0.1601	0.1886
S_1	0.5167	0.1952
S_2	0.4932	0.2520
S_3	0.4499	0.3342
S_4	0.4180	0.3869
C_1	0.475	0.081
C_2	0.468	0.045
C_3	0.400	0.022
C_4	0.338	0.594
C_5	0.343	0.102
C_6	0.424	0.113
C_7	0.425	0.145
C_8	0.388	0.176
C_9	0.395	0.222
C_{10}	0.364	0.248
C_{11}	0.361	0.287
C_{12}	0.318	0.309
C_{13}	0.331	0.348
C_{14}	0.275	0.377
C_{15}	0.207	0.351
C_{16}	0.171	0.384
C_{17}	0.192	0.426
C_{18}	0.256	0.462
C_{19}	0.300	0.431
C_{20}	0.121	0.076
C_{21}	0.520	0.478

Fig. 1. Electron density projection of 5-phenyl-3-(5-phenyl-1,2-dithiol-3-ylidenemethyl)-1,2-dithiolium iodide along the *a* axis. Plane group *pgg* and origin in center of symmetry. Contours at arbitrary but equal intervals. The atomic positions are those from the least squares refinement.

revealed themselves during this process, were interpreted as due to the "solvation atoms". These atoms were included in the structure factor calculation as carbon atoms. Least squares refinement was then applied, with anisotropic temperature factors for iodine and sulphur, and isotropic for carbon. After twelve 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 refinement are listed in Table 1. An electron density map of the *a*-projection is shown in Fig. 1.

Judging from Fig. 1, the two disulphide rings are coplanar, and the four sulphur atoms thus nearly colinear. The projected sulphur-sulphur distances are $S_1-S_2 = 1.38$ Å, $S_2-S_3 = 2.03$ Å, and $S_3-S_4 = 1.35$ Å. If one assumes the sulphur-sulphur bonds in the disulphide rings to be about 2.05 Å, this corresponds to a central S_2-S_3 distance of $3.00-3.10$ Å, which is considerably shorter than twice the van der Waals radius [5] of sulphur,

3.70 Å. There are thus obviously partial bonding between S_2 and S_3. The bonding may be both σ and π in character; an attempt is being made to calculate the bond orders by molecular orbital methods.

1. Schmidt, U. *Ann.* **635** (1960) 109.
2. Foss, O. and Tjomsland, O. *Acta Chem. Scand.* **12** (1958) 1799.
3. Work in press and to be published by A. Hordvik and coworkers (S. Joys, H. M. Kjøge, J. Sundsfjord and E. Sletten).
4. Klingsberg, E. *Private communication.*
5. Pauling, L. *The Nature of the Chemical Bond,* 3rd Ed., Cornell University Press, New York 1960.