

phosphate before precipitation of the alkylated DNA did not influence the rate constant determined, and since, further, the rate constants for EMS and MMS were confirmed by an independent method (determination of alkylguanines formed in hydrolysis). In a preliminary investigation the rate constants were determined by separation of alkylated DNA from low-molecular labelled compounds by means of Sephadex G-25. This technique gave higher values, which in the case of iPMS were reduced to about the present values by addition of cold  $i\text{PrOPO}_3^{2-}$  before separation.

The preliminary higher values obtained were used for a calculation of degrees of alkylation in a previous communication.<sup>4</sup> More correct degrees of alkylation used in that case should therefore be: Me-DNA 0.2–1.4; Et-DNA 0.4–2.9; and iPr-DNA 0.9–3.7 alkyls per 100 DNA phosphates.

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## The Crystal and Molecular Structure of 4-Phenyl-1,2-dithiolium Bromide

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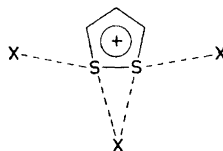
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In crystals of 4-phenyl-1,2-dithiolium iodide<sup>1</sup> there are sulphur-iodine close contacts similar to those present in crystals of thiuret hydrohalides.<sup>2–4</sup> They occur in roughly linear halogen-sulphur-sulphur-halogen arrangements and triangular sulphur-halogen-sulphur arrangements, cf. Scheme 1.



Scheme 1. Arrangements of halide ions (X) relative to disulphide group.

The  $X \cdots S$  distances in the linear arrangements in thiuret hydroiodide<sup>2</sup> and hydrobromide<sup>3</sup> are 0.4 Å shorter than the corresponding van der Waals distances. In thiuret hydrochloride hemihydrate<sup>4</sup> there is a close contact, 0.1 Å shorter than the van der Waals distance, on one side of the disulphide group only. The fact that the sulphur-sulphur bonds in the hydroiodide,  $S-S=2.088 \pm 0.012$  Å, and in the hydrobromide,  $S-S=2.081 \pm 0.008$  Å, are found to be longer than that in the hydrochloride hemihydrate,  $S-S=2.063 \pm 0.004$  Å, indicates that the halogen-sulphur close contacts have caused a small lengthening of the sulphur-sulphur bonds. Such a lengthening might be anticipated if charge is partially transferred from the halide ions into the antibonding sulphur-sulphur  $\sigma$ -orbital.

Crystals of 4-phenyl-1,2-dithiolium bromide,<sup>5</sup> chloride monohydrate,<sup>6</sup> and

thiocyanate<sup>8</sup> are isomorphous with those of 4-phenyl-1,2-dithiolium iodide.<sup>1</sup> The environment of the disulphide group in these compounds should therefore be similar to that in the iodide. Structure determinations of 4-phenyl-1,2-dithiolium bromide, chloride monohydrate,<sup>7</sup> and thiocyanate<sup>8</sup> have been carried out in order to find to which degree the sulphur-sulphur bonds are subject to interaction with external atoms, and the results from the study of 4-phenyl-1,2-dithiolium bromide are given here.

The arrangement of 4-phenyl-1,2-dithiolium bromide units in the unit cell, viewed along *c*, is shown in Fig. 1. Inter- and

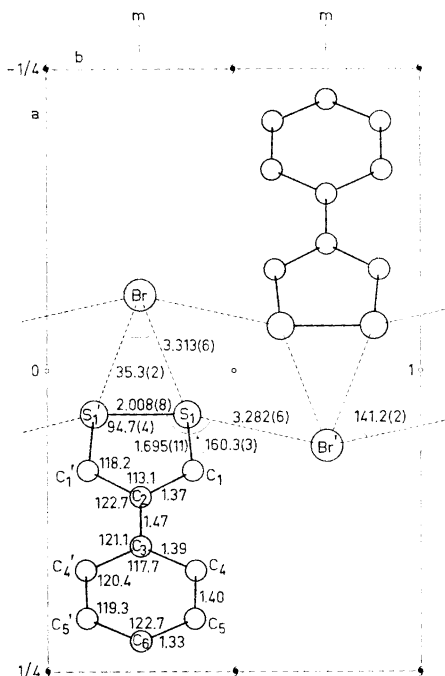


Fig. 1. The arrangement of 4-phenyl-1,2-dithiolium bromide units viewed along *c*, with atomic distances (Å) and angles (°). Standard deviations referring to last digits, are given in parentheses. The standard deviation in C—C bond lengths is  $\pm 0.02$  Å and in C—C—C angles  $\pm 1.2^\circ$ .

intramolecular atomic distances and angles are given in the figure. The 4-phenyl-1,2-dithiolium ion lies across the mirror plane *m* which passes through the central carbon

atoms and the midpoint of the sulphur-sulphur bond. The equation for the least squares plane of the ion with double weight on sulphur and hydrogens neglected is

$$-0.65921 X + 0.75196 Z = -1.40416$$

with *X* and *Z* in Å units. The deviations (Å) from the plane for S (−0.008), C<sub>1</sub> (0.006), C<sub>2</sub> (0.007), C<sub>3</sub> (0.012), C<sub>4</sub> (0.015), C<sub>5</sub> (0.001) and C<sub>6</sub> (−0.036) are not significant, and one may conclude that the ion is planar.

Br...S =  $3.282 \pm 0.006$  Å in the Br...S—S...Br arrangements is 0.52 Å shorter than the corresponding van der Waals distance. A shortening of 0.50 Å was found for the equivalent iodine-sulphur contacts in 4-phenyl-1,2-dithiolium iodide.<sup>1</sup>

S—S =  $2.008 \pm 0.008$  Å in the present structure is somewhat shorter than the S—S bond,  $2.028 \pm 0.010$  Å, in the iodide.<sup>1</sup> It is, however, slightly longer than the S—S

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

Atom	<i>x</i>	<i>y</i>	<i>z</i>
Br	−0.06278	0.25000	−0.59951
S	0.03609	0.37244	−0.22254
C(1)	0.08362	0.38928	0.01853
C(2)	0.10472	0.25000	0.12413
C(3)	0.14601	0.25000	0.33177
C(4)	0.16625	0.39467	0.43369
C(5)	0.20619	0.39244	0.62917
C(6)	0.22518	0.25000	0.71312
H(1)	0.0924	0.4793	0.0383
H(2)	0.1517	0.4894	0.3640
H(3)	0.2186	0.5084	0.6794
H(4)	0.2500	0.2500	0.8500

bond,  $2.004 \pm 0.005$  Å, in the thiocyanate,<sup>8</sup> which is not subject to interaction with external atoms. Thus a small, although hardly significant lengthening of the S—S bond in 4-phenyl-1,2-dithiolium bromide is indicated.

The bromine-sulphur distances of  $3.313 \pm 0.006$  Å in the triangular arrangements, with the bromide ion 0.40 Å above the plane of the 4-phenyl-1,2-dithiolium ion, indicate weak three-center two-electron bonds between the bromide ion and the sulphur atoms of the disulphide group. They may be established through partial transfer of charge from the bromide

Table 2. Temperature parameters  $\beta_{ij}$ . The expression used is

$$\exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + hk\beta_{12} + kl\beta_{23} + hl\beta_{13})].$$

	$\beta_{11}$	$\beta_{22}$	$\beta_{33}$	$\beta_{12}$	$\beta_{23}$	$\beta_{13}$
Br	0.0024	0.0179	0.0692	0.0000	0.0000	-0.0067
S	0.0016	0.0170	0.0491	0.0007	-0.0030	-0.0019
C(1)	0.0017	0.0198	0.0543	-0.0005	-0.0127	-0.0014
C(2)	0.0014	0.0201	0.0351	0.0000	0.0000	-0.0028
C(3)	0.0016	0.0250	0.0208	0.0000	0.0000	0.0034
C(4)	0.0022	0.0270	0.0471	-0.0041	0.0154	-0.0032
C(5)	0.0020	0.0359	0.0709	-0.0062	0.0256	-0.0078
C(6)	0.0013	0.0513	0.0578	0.0000	0.0000	-0.0066

For the hydrogen atoms, temperature factors  $\exp[-B(\sin^2\theta/\lambda^2)]$  were used with  $B$  equal to 1.6, 7.3, 5.0, and 7.0 Å<sup>2</sup> for H(1), H(2), H(3), and H(4), respectively.

ion into the  $p$ -orbitals on the sulphur atoms already engaged in the sulphur-carbon  $\sigma$ -bond.

Crystals of 4-phenyl-1,2-dithiolium bromide belong to the orthorhombic space group  $Pnma$ .<sup>5</sup> The unit cell dimensions (redetermined) are,  $a = 26.54$  Å,  $b = 8.20$  Å, and  $c = 4.66$  Å to within 0.2%. There are four formula units per unit cell; density, calc. 1.70, found 1.70 g/cm<sup>3</sup>.

The intensities of the  $hk0$ - $hk2$  and  $h0l$  reflections were estimated visually from Weissenberg photographs taken with  $\text{CuK}\alpha$  radiation ( $\mu = 92.7$  cm<sup>-1</sup>). Small crystals of cross-section  $0.05 \times 0.10$  mm were used in order to minimize absorption effects, and no absorption correction was applied. The intensities were corrected in the usual way to give sets of relative structure factors. Common reflections were used to put the reflections on the same scale. The data comprise 680 observed  $hk0$ - $hk2$  and  $h0l$  reflections.

The structure was solved by Patterson syntheses in the  $c$ - and  $b$ -projections, and the atomic parameters were refined by least squares methods using Mair's program.<sup>9</sup> Weighting scheme No. 3, recommended by Mair, was used throughout the entire least squares process. Final atomic coordinates and temperature parameters are given in Tables 1 and 2, respectively. The atomic

distances and angles in Fig. 1 correspond to the coordinates in Table 1.

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