

The Crystal and Molecular Structure of 3-Phenyl-1,2-dithiolium Iodide

ASBJØRN HORDVIK and HANS M. KJØGE

Chemical Institute, University of Bergen, Bergen, Norway

The crystal and molecular structure of 3-phenyl-1,2-dithiolium iodide has been solved by Patterson projections along the *b* and *a* axes and refined by least squares methods using anisotropic temperature parameters. The refinement comprises the *h0l*, *h1l*, *h2l*, and *0kl* reflections.

The C—C bonds in the 1,2-dithiolium ring are 1.39 ± 0.04 Å, the C—S bonds are 1.67 Å and 1.71 ± 0.03 Å and the S—S bond is 1.998 ± 0.010 Å. The 1,2-dithiolium ring is planar within the experimental error, and the bond lengths show that the ring is stabilized through π -orbital delocalization.

Average length of the C—C bonds in the benzene ring is 1.40 Å, and the angle between the plane of the benzene ring and that of the 1,2-dithiolium ring is 27°. The C—C bond connecting the two rings is 1.40 ± 0.04 Å, and is coplanar with the two rings within the limits of error.

Two 3-phenyl-1,2-dithiolium ions and two iodide ions are in the crystal arranged across a centre of symmetry through weak covalent bonding between iodine and sulphur. The length of the three iodine-sulphur distances which indicate bonding are 3.37 Å, 3.49 Å, and 3.62 Å. The shortest iodine sulphur distance occurs in an approximately linear I...S—S arrangement, and this bonding between iodine and sulphur seems to be analogous to the bonding in a linear trihalide ion. The other two short iodine-sulphur distances involve the same iodide ion and both sulphur atoms of the other, symmetry-related cation, and the indicated bonding may be explained in terms of three-center two electron bonds.

The bonding between sulphur and iodine in the crystal does not seem to have caused a lengthening of the sulphur-sulphur bond in the dithiolium ring.

So far no X-ray crystallographic structure investigation of a 1,2-dithiolium salt has been reported. A least squares refinement of the *a*-projection of 3,5-diamino-1,2-dithiolium iodide has been undertaken by one of the authors,¹ and for this compound as well as for thiuret hydroiodide,² which is analogous to and isomorphous with 3,5-diamino-1,2-dithiolium iodide, the sulphur-sulphur bond is found to be 2.08 Å and is thus apparently a pure single bond. Molecular orbital calculations, carried out for the unsubstituted 1,2-dithiolium ion by Bergson,³ show that one should expect the sulphur-sulphur bond to

be shortened by π -bonding and that a probable bond length would be about 2.00 Å. The deviation from this value may, with respect to 3,5-diamino-1,2-dithiolium iodide, be explained by the presence of additional resonance forms involving the amino groups. This would cause the π -bonding to be more pronounced in the nitrogen-carbon part of the ion, and the sulphur-sulphur π -bonding to be reduced relatively to the equivalent bonding in the unsubstituted ion. Support for this idea derives from the structure investigations of xanthane hydride⁴ and rhodan hydrate.⁵

In order to secure experimental evidence for the dimensions of the 1,2-dithiolium ring, attention has been paid to some monophenyl-substituted salts of which Dr. Klingsberg⁶ most generously offered us samples. It was also thought that the investigation of 3-phenyl-1,2-dithiolium iodide might reveal close contacts between divalent sulphur and iodide ions. Such close contacts are present in 3,5-diamino-1,2-dithiolium iodide and thiuret hydroiodide, and seem to indicate weak covalent bonding between iodine and sulphur.

EXPERIMENTAL

Crystal data on 3-phenyl-1,2-dithiolium iodide have been reported elsewhere.⁷ The salt crystallizes from ethanol as needles and flakes elongated along b and with (001) predominant. The crystals are monoclinic, with the unit cell dimensions (redetermined): $a = 8.28$ Å, $b = 5.51$ Å, $c = 22.52$ Å, $\beta = 98.4^\circ$. The experimental error is estimated to be within 0.5%. There are four formula units per unit cell; density, calc. 2.00, found 1.99 g/cm³. The space group, from systematic absences, is $P2_1/c$.

The intensities of the $h0l$, $h1l$, $h2l$, and $0kl$ reflections were estimated visually from Weissenberg photographs taken with $\text{CuK}\alpha$ radiation ($\mu = 299$ cm⁻¹). Small crystals of cross-section 0.07×0.03 mm were used in order to minimize absorption effects, and no absorption correction was applied. 913 of the 1.221 reflections obtainable with $\text{CuK}\alpha$ radiation were estimated, with a range of intensities of 10 000 to 3. The intensities were corrected in the usual way to give sets of relative structure factors. Common reflections in $h0l$, $h1l$, $h2l$, and $0kl$ were used to put all the reflections on the same scale.

The calculated structure factors in Table 6 are based on the atomic scattering curves for sulphur, carbon and hydrogen which are given in the *International Tables*,⁸ the first set of the listed scattering factors for carbon being used. For iodide ion a curve was constructed from the Thomas-Fermi values for xenon at small scattering angles and electroneutral iodine at intermediate and large angles.

DETERMINATION OF THE STRUCTURE

Coordinates for the iodide ion and the sulphur atoms were found from Patterson maps, and the positions of the carbon atoms revealed themselves during subsequent Fourier refinements of the a and b -axis projections. The structure was thereafter refined by least squares methods on an IBM 1620¹¹ computer, using a program designed by Mair.⁹ Weighting scheme No. 3, recommended by Mair, was used with $a = 36$ and $b = 22.5$. The refinement comprised the $h0l$, $h1l$, $h2l$, and $0kl$ reflections, and was carried out with isotropic temperature factors for five cycles before the iodide ion and the sulphur atoms were given anisotropic temperature parameters. After ten cycles all together, the agreement factor $R = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|$ had reached 0.11.

Hydrogen atoms are usually neglected in structure investigations of compounds which contain an atom as heavy as iodine, but since there are seven

hydrogen atoms in the present structure they might have some significance for low order reflections. The hydrogen positions were accordingly calculated, taking $C-H = 1.1 \text{ \AA}$, and their scattering contribution were included in the structure factor calculation, but the hydrogen parameters were not refined. Another reason to include the hydrogen contribution was that we thought it worth while to try to apply anisotropic temperature factors to the carbon atoms, in which case it might be an advantage that the hydrogen atoms had been accounted for. The agreement factor improved slightly after the introduction of hydrogen, and dropped to the final value 0.10 when the carbon atoms had been treated anisotropically. From the fifth least squares cycle, when anisotropic temperature factors were introduced for iodine and sulphur, and throughout the entire refinement process, only negligible coordinate shifts, which did not accumulate in specific directions, occurred for iodine and sulphur. Applications of anisotropic temperature parameters to the carbon atoms seemingly led to more reasonable $C-C$ bond lengths than did the application of isotropic temperature parameters.

Final coordinates and temperature parameters are given in Tables 1 and 2, respectively. The observed and calculated structure factors are listed in Table 6. A Fourier map of the b -axis projection, corresponding to the final state of refinement is shown in Fig. 1.

THE 3-PHENYL-1,2-DITHIOLIUM ION

Bond lengths and angles in the 3-phenyl-1,2-dithiolium ion together with their standard deviations are listed in Tables 3 and 4 and shown in Fig. 2. The values correspond to the coordinates in Table 1.

The 1,2-dithiolium ring is approximately planar and the equation for the least

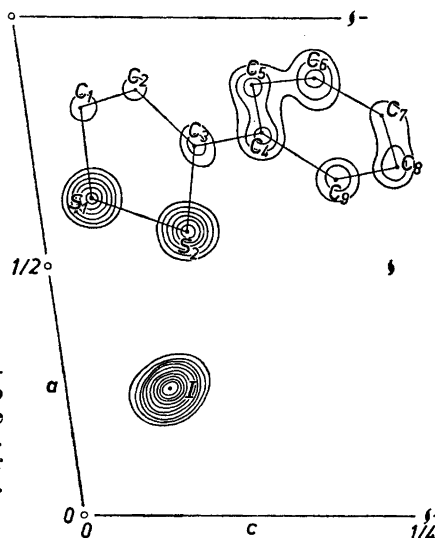


Fig. 1. Electron density projection of 3-phenyl-1,2-dithiolium iodide along the b axis, showing one asymmetric unit. Plane group $p2$ and origin in center of symmetry. Contour intervals for carbon $2e \cdot \text{\AA}^{-2}$, for sulphur $4e \cdot \text{\AA}^{-2}$ and for iodide $10e \cdot \text{\AA}^{-2}$. Lowest contour at $6e \cdot \text{\AA}^{-2}$.

Table 1. Final atomic coordinates in fractions of corresponding cell edges.

	<i>x</i>	<i>y</i>	<i>z</i>
I	0.7474	0.5490	-0.0763
S ₁	0.6376	0.2307	0.0394
S ₂	0.5712	0.0342	0.1064
C ₁	0.8189	0.0955	0.0422
C ₂	0.8612	-0.0869	0.0843
C ₃	0.7417	-0.1428	0.1194
C ₄	0.7668	-0.2953	0.1697
C ₅	0.8652	-0.5097	0.1704
C ₆	0.8814	-0.6773	0.2159
C ₇	0.8031	-0.6377	0.2626
C ₈	0.6989	-0.4344	0.2651
C ₉	0.6769	-0.2616	0.2192
H ₁	0.900	0.167	0.010
H ₂	0.955	-0.167	0.090
H ₃	0.925	-0.533	0.133
H ₄	0.963	-0.850	0.217
H ₅	0.815	-0.767	0.300
H ₆	0.635	-0.413	0.302
H ₇	0.600	-0.107	0.221

Table 2. Final temperature parameters β_{ij} . The expression used is $\exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + hk\beta_{12} + kl\beta_{23} + hl\beta_{13})]$.

	β_{11}	β_{22}	β_{33}	β_{23}	β_{13}	β_{12}
I	0.0156	0.0336	0.0025	-0.0065	0.0045	-0.0177
S ₁	0.0141	0.0171	0.0016	-0.0016	0.0010	-0.0082
S ₂	0.0123	0.0273	0.0019	-0.0032	0.0018	-0.0084
C ₁	0.0156	0.0190	0.0026	0.0052	0.0060	-0.0154
C ₂	0.0198	0.0239	0.0012	-0.0030	0.0031	-0.0029
C ₃	0.0083	0.0409	0.0019	0.0083	0.0022	-0.0051
C ₄	0.0132	0.0460	0.0015	0.0017	0.0005	-0.0079
C ₅	0.0140	0.0252	0.0028	0.0056	0.0032	-0.0009
C ₆	0.0188	0.0655	0.0012	0.0026	-0.0015	0.0273
C ₇	0.0137	0.0416	0.0023	-0.0029	-0.0020	0.0057
C ₈	0.0165	0.0571	0.0018	-0.0034	0.0015	0.0483
C ₉	0.0128	0.0317	0.0017	-0.0026	0.0021	-0.0169

For the hydrogen atoms a temperature factor $\exp[-B(\sin^2 \theta / \lambda^2)]$ was used, with $B = 4.0 \text{ \AA}^2$.

squares plane of the ring atoms, with sulphur given three times the weight of carbon, and $c \sin \beta$ chosen as the third orthogonal axis is

$$0.3175 X + 0.6771 Y + 0.6677 Z = 3.0845$$

where X , Y , and Z are in \AA units. S_1 and S_2 are -0.005 \AA and 0.007 \AA , respectively, out of this plane, and the deviations from the plane for C_1 , C_2 , and C_3 are 0.005 \AA , 0.015 \AA , and -0.026 \AA , respectively. There is thus no significant deviation of atoms from the least squares plane.

The least squares plane of the benzene ring:

$$0.7147 X + 0.5160 Y + 0.4720 Z = 5.0668$$

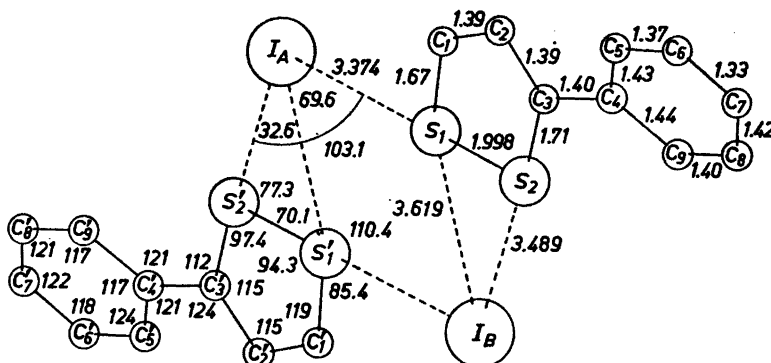


Fig. 2. Bond lengths (Å) and bond angles ($^{\circ}$) in the 3-phenyl-1,2-dithiolium ion together with atomic distances (Å) and angles ($^{\circ}$) in the environment of the disulphide group.

is rotated 27° relatively to the plane of the 1,2-dithiolium ring, and the C_3-C_4 bond lies approximately in the intersection of the two planes.

The bond lengths in the 1,2-dithiolium ring as listed in Table 3, may be compared with the results of Bergson's³ molecular orbital calculations on the unsubstituted 1,2-dithiolium ion. Bergson's calculations show that the unsubstituted ion should be symmetric. The dithiolium ring in 3-phenyl-1,2-dithiolium iodide, may be expected to be slightly unsymmetric due to the electronegative 3-substituent, which might cause a change in the C_2-C_3 and S_2-C_3 bonds in relation to the corresponding bonds in the unsubstituted ion. The S_2-C_3 bond (1.71 Å) has been found longer than the S_1-C_1 bond (1.67 Å), and although the difference is hardly significant, it indicates a slightly unsymmetric ring.

The bond lengths $S_1-S_2 = 2.00 \pm 0.01$ Å, $S_1-C_1 = 1.67 \pm 0.03$ Å, $S_2-C_3 = 1.71 \pm 0.03$ Å, $C_1-C_2 = 1.39 \pm 0.04$ Å and $C_2-C_3 = 1.39 \pm 0.03$ Å, found for the 1,2-dithiolium ring, are all significantly shorter than single bonds, and it may be concluded that the 1,2-dithiolium ring is stabilized

Table 3. Bond lengths l and standard deviation in bond length $\sigma(l)$ in the 3-phenyl-1,2-dithiolium ion.

Bond	$l(\text{Å})$	$\sigma(l)$ (Å)
S_1-S_2	1.998	0.010
S_1-C_1	1.67	0.03
S_2-C_3	1.71	0.03
C_1-C_2	1.39	0.05
C_2-C_3	1.39	0.04
C_3-C_4	1.40	0.04
C_4-C_5	1.43	0.05
C_5-C_6	1.37	0.05
C_6-C_7	1.33	0.04
C_7-C_8	1.42	0.05
C_8-C_9	1.40	0.05
C_9-C_4	1.44	0.03

Table 4. Bond angles and standard deviation in bond angles in the 3-phenyl-1,2 dithiolium ion.

	Angle (°)	Standard deviation (°)
C ₁ -S ₁ -S ₂	94.3	1.1
S ₁ -S ₂ -C ₃	97.4	1.0
S ₁ -C ₁ -C ₂	119	2
C ₁ -C ₂ -C ₃	115	3
C ₂ -C ₃ -S ₂	115	3
C ₂ -C ₃ -C ₄	124	3
S ₂ -C ₃ -C ₄	120	2
C ₃ -C ₄ -C ₅	121	2
C ₃ -C ₄ -C ₉	121	3
C ₅ -C ₄ -C ₉	117	3
C ₄ -C ₅ -C ₆	124	3
C ₅ -C ₆ -C ₇	118	4
C ₆ -C ₇ -C ₈	122	3
C ₇ -C ₈ -C ₉	121	2
C ₈ -C ₉ -C ₄	117	3

through π -orbital delocalization. Assuming linear bond-order/bond-length relations, and using the accepted values for the lengths of sulphur-sulphur, carbon-sulphur and carbon-carbon single and double bonds, one arrives at a π -bond order of 0.39 for the sulphur-sulphur bond of 2.00 Å, a π -bond order of 0.61 for the average length 1.69 Å of the carbon-sulphur bonds, and a π -bond order of 0.72 for the carbon-carbon bond lengths of 1.39 Å. These estimated bond orders agree with those calculated by Bergson.³ Bergson's scheme No. I gave, in the same order as above, the π -bond orders 0.424, 0.691, and 0.653, respectively, and scheme No. II gave 0.355, 0.604, and 0.627.

The average length of the carbon-carbon bonds in the benzene ring, 1.40 Å, agrees with the length of the aromatic carbon-carbon bond. The length of the bond which connects the two rings, C₃-C₄ = 1.40 ± 0.04 Å, is not significantly shorter than the length 1.466 Å for a single bond between two sp^2 hybridized carbon atoms.¹⁰ A bond length of 1.48 Å has been found by Bastiansen¹¹ for the connecting bond in diphenyl.

THE ENVIRONMENT OF THE DISULPHIDE GROUP

The environment of the disulphide group is shown in Fig. 3, and the corresponding interatomic distances and angles are listed in Table 5. Two iodide ions, both near to the plane of the dithiolium ring, form close contacts with sulphur. The I_A...S₁ distance is 3.374 ± 0.007 Å and the angle I_AS₁S₂ is 178° ± 0.4°. Taking 4.00 Å as the sum of van der Waal's radii¹² for iodine and sulphur, the iodine-sulphur distance of 3.37 Å indicates a weak bond.



The sulphur atoms in a disulphide group, S-S, are electronically equivalent to the atoms in a chlorine molecule, and one may assume that the bonding between sulphur and iodide ion is of the same type as in a linear trihalide ion, S₁ being the central atom in this case. It is found by Foss and coworkers

Table 5. Atomic distances and angles with reference to the environment of the disulphide with standard deviations.

	Distance (Å)	Standard deviation (Å)
$I_A \cdots S_1$	3.374	0.007
$I_B \cdots S_1$	3.619	0.008
$I_B \cdots S_2$	3.489	0.008

	Angle (°)	Standard deviation (°)
$S_1 I_A S_1'$	69.6	0.5
$S_1 I_A S_2'$	103.1	0.5
$S_1 I_A S_2'$	32.6	0.5
$I_A S_2' S_1'$	77.3	0.5
$I_A S_1' I_B$	110.4	0.4
$S_2' S_1' I_A$	70.1	0.5
$C_1' S_1' I_B$	85.4	1.0

through a series of structure investigations of divalent tellurium complexes,^{13,14} that tellurium is able to form σ -bonds, of bond orders less than one, in opposite directions. That divalent selenium also can do so is shown by Foss and Hauge through a structure investigation of potassium triselenocyanate.¹⁵ The analogy between the linear triselenocyanate ion and a linear trihalide ion is evident. From the existence of trithiocyanates one may assume that also sulphur is able to form σ -bonds in opposite directions. The trithiocyanates, however, are rather unstable compounds, and the sulphur-sulphur bonds in trithiocyanates are probably weaker than the selenium-selenium bonds in triselenocyanates, in accordance with the relative stabilities of triiodide, tribromide and trichloride ions.¹⁶ A stable linear trisulphur system exists in thio-thioptene,¹⁷ in which the sulphur atoms are built into a resonance-stabilized ring system. Further evidence for divalent sulphur's ability to form σ -bonds in opposite directions derives from the structure investigation of 2,5-dimethyl-



dithio-furoptene.¹⁸ The linear $I_A \cdots S_1 - S_2$ system, found in the present investigation, may according to the above, be described as analogous to a linear trihalide ion, and the bond between iodine and sulphur as established through partial transfer of charge from the iodide ion to the p -orbital on S_1 already engaged in the σ -bond between S_1 and S_2 , at the expense of this bond. The iodine-sulphur distance of 3.37 Å corresponds to a σ -bond order of 0.04 if a linear relationship bond-order/bond-length is assumed. The oxygen-sulphur bonding in 2,5-dimethyl-dithio-furoptene, for which a σ -bond order of 0.55 is given,¹⁸ has probably a small effect on the adjacent sulphur-sulphur bond for which a σ -bond order of 0.95 is reported. Since the length of the sulphur-sulphur bond in 3-phenyl-1,2-dithiolium iodide has been found to agree with the calculated value for this bond length for an isolated 1,2-dithiolium ion, one may conclude that if the $I_A \cdots S$ bonding has affected the neighbouring oppositely directed sulphur-sulphur bond, it has done so to a very small degree.

H	K	L	F0	FC	H	K	L	F0	FC	H	K	L	F0	FC	H	K	L	F0	FC						
-	6	2	5	211	181	7	2	12	< 45	-	31	8	2	3	111	-	124	-	8	2	20	105	-	133	
-	6	2	6	399	344	7	2	13	57	76	8	2	4	< 49	-	46	9	2	1	46	-	50			
-	6	2	7	71	-	7	2	14	37	-	27	8	2	5	53	-	57	9	2	2	94	-	114		
-	6	2	8	282	263	7	2	15	35	18	8	2	6	52	-	69	9	2	3	39	-	45			
-	6	2	9	157	139	7	2	16	< 30	13	8	2	7	45	-	20	9	2	4	106	-	150			
-	6	2	10	51	-	7	2	17	100	-	106	8	2	8	< 43	-	42	9	2	5	36	-	12		
-	6	2	11	18*	-	7	2	18	95	-	110	8	2	9	< 41	-	58	9	2	6	34	-	9		
-	6	2	12	80	-	7	2	19	54	-	1	8	2	10	< 39	-	45	9	2	7	32	-	40		
-	6	2	13	80	-	7	2	20	279	-	264	8	2	11	36	28	88	117	9	2	8	28	56		
-	6	2	14	150	-	7	2	21	138	112	8	2	12	40	40	56	85	-	9	2	9	32	58		
-	6	2	15	66	62	-	7	2	22	90	100	-	8	2	13	111	-	102	-	9	2	1	< 43	52	
-	6	2	16	65	-	7	2	23	85	73	-	8	2	14	52	-	23	-	9	2	2	< 124	138		
-	6	2	17	121	121	-	7	2	24	68	68	-	8	2	15	145	-	144	-	9	2	3	< 43	8	
-	6	2	18	< 49	23	-	7	2	25	227	207	-	8	2	16	4	-	4	-	9	2	4	< 126	144	
-	6	2	19	< 47	18	-	7	2	26	89	-	8	2	17	86	-	79	-	9	2	5	< 43	64		
-	6	2	20	100	88	-	7	2	27	83	94	-	8	2	18	146	-	144	-	9	2	6	< 48	64	
-	6	2	21	61	-	7	2	28	142	-	140	-	8	2	19	103	89	-	9	2	7	79	-	110	
-	6	2	22	47	35	-	7	2	29	78	84	-	8	2	20	122	125	-	9	2	8	< 42	-	9	
-	6	2	23	59	-	7	2	30	163	-	186	-	8	2	21	49	32	-	9	2	9	51	-	62	
-	6	2	24	40	-	7	2	31	46	15	-	8	2	22	48	62	-	9	2	10	44	-	63		
7	2	1	163	140	-	7	2	32	88	95	-	8	2	23	132	136	-	9	2	11	42	49	-	54	
7	2	2	246	245	-	7	2	33	36	37	-	8	2	24	46	-	11	-	9	2	12	35	-	54	
7	2	3	60	51	-	7	2	34	85	91	-	8	2	25	183	210	-	9	2	13	67	-	111		
7	2	4	116	132	-	7	2	35	88	96	-	8	2	26	80	93	-	9	2	14	32	-	32		
7	2	5	51	63	-	7	2	36	16	35	-	8	2	27	62	71	-	9	2	15	29	-	43		
7	2	6	< 53	29	-	7	2	37	69	-	52	-	8	2	28	62	-	9	2	16	38	-	58		
7	2	7	137	148	-	7	2	38	69	-	52	-	8	2	29	47	-	9	2	17	< 13	-	23		
7	2	8	76	95	-	7	2	39	30	30	-	8	2	30	29	-	23	-							
7	2	9	68	76	-																				
7	2	10	82	104	-																				
7	2	11	< 47	30	-																				

The iodide ion I_B , shown on Fig. 2, is related to I_A by a center of symmetry. I_B lies 0.3 Å from the plane of the dithiolium ring and forms close contacts with both sulphur atoms of the disulphide group, the distances to S_1 and S_2

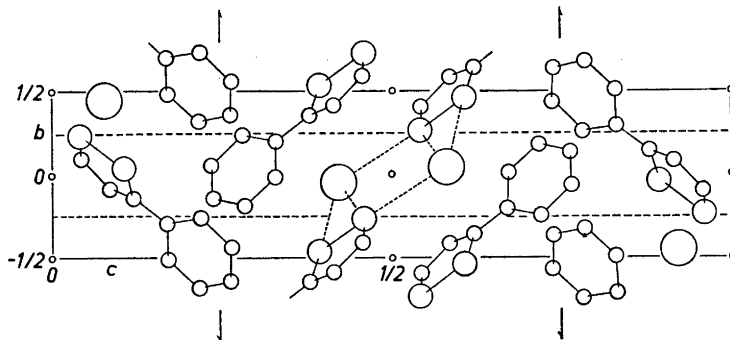


Fig. 3. The arrangement of ions in the unit cell as seen along the a axis. Dashed lines indicate bonding between iodine and sulphur.

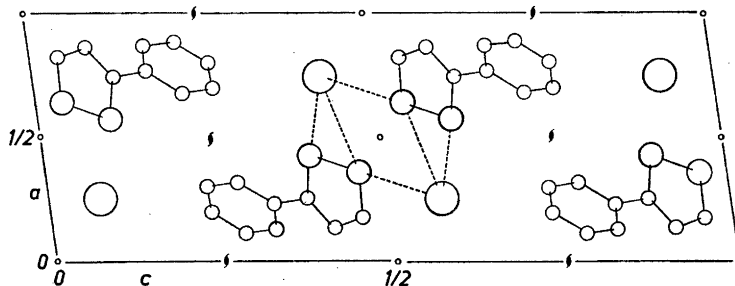


Fig. 4. The arrangement of ions in the unit cell as seen along the b axis. The bonding between iodine and sulphur is indicated by dashed lines.

being 3.63 Å and 3.49 Å, respectively. The angle $S_1I_B S_2$ is rather small, 32.6° , and it seems likely that weak iodine-sulphur bonds are established through overlap of one filled orbital of the iodide ion with two orbitals of the sulphur atoms, one from each. Since both sulphur atoms form weak bonds with iodine, one may assume that electrons are partially transferred from the iodide ion to the sulphur atoms, *e.g.* to those *p*-orbitals of the sulphur atoms already engaged in the sulphur-carbon σ -bonds, with weak three-center two-electron bonds as result. Assuming the iodide ion to be sp^3 hybridized, one should, according to the valence angles, $S_1I_B S_2$ (103.1°) and $S_1I_B S_1$ (69.6°), expect the $I_B \cdots S_2$ overlap to be greater than the $I_B \cdots S_1$ overlap. It is found in agreement with this that the $I_B \cdots S_2$ distance is significantly shorter than the $I_B \cdots S_1$ distance.

The sulphur atom S_1 lies approximately in the same plane as I_A , I_B , S_2 , and C_1 to which it is bound. The bond angles are, $S_2 S_1 C_1 = 94.3^\circ$, $C_1 S_1 I_A = 85.4^\circ$, $I_A S_1 I_B = 110.4^\circ$ and $I_B S_1 S_2 = 70.1^\circ$, and there is accordingly a striking resemblance between the environment of S_1 in the present structure and the environment of divalent tellurium in square planar complexes.

The arrangement of 3-phenyl-1,2-dithiolium ions and iodide ions in the unit cell is shown in Figs. 3 and 4. The 3-phenyl-1,2-dithiolium iodide units are arranged in pairs across a center of symmetry. Between pairs there are only van der Waal's contacts.

Acknowledgements. The authors wish to express their thanks to Dr. E. Klingsberg of the American Cyanamid Company for a sample of 3-phenyl-1,2-dithiolium iodide, and to Professor Olav Foss for many helpful discussions.

REFERENCES

1. Hordvik, A. *To be published.*
2. Foss, O. and Tjomsland, O. *Acta Chem. Scand.* **12** (1958) 1799.
3. Bergson, G. *Arkiv Kemi* **19** (1962) 181.
4. Hordvik, A. *Acta Chem. Scand.* **15** (1961) 1186; **17** (1963) 2575.
5. Hordvik, A. *Acta Chem. Scand.* **14** (1960) 1218; and *to be published.*
6. Klingsberg, E. *J. Am. Chem. Soc.* **83** (1961) 2934.
7. Hordvik, A. *Acta Chem. Scand.* **17** (1963) 1809.
8. *International Tables for X-ray Crystallography*, Vol. III, The Kynoch Press, Birmingham 1962, p. 204.
9. Mair, G. A. *Structure Factor and Least Squares Programs for the IBM 1620*, Pure Chemistry Division, National Research Council, Ottawa, Canada 1963.
10. Brown, M.G. *Trans. Faraday Soc.* **55** (1959) 694.
11. Bastiansen, O. *Acta Chem. Scand.* **3** (1949) 408.
12. Pauling, L. *The Nature of the Chemical Bond*, 3rd Ed., Cornell University Press, Ithaca, New York 1960.
13. Foss, O. *Acta Chem. Scand.* **16** (1962) 779.
14. Foss, O., Husebye, S. and Marøy, K. *Acta Chem. Scand.* **17** (1963) 1806.
15. Foss, O. and Hauge, S. *Acta Chem. Scand.* **17** (1963) 1807.
16. Wiebenga, E. H., Havinga, E. E. and Boswijk, K.H. *Advan. Inorg. Chem. Radiochem.* **3** (1961) 133.
17. Bezzi, S., Mammi, M. and Garbuglio, C. *Nature* **182** (1958) 247.
18. Mammi, M., Bardi, R., Traverso, G. and Bezzi, S. *Nature* **192** (1961) 1282.

Received February 1, 1965.

Acta Chem. Scand. **19** (1965) No. 4