The Crystal and Molecular Structure of

4-Phenyl-1,2-dithiolium Iodide

ASBJØRN HORDVIK and EINAR SLETTEN

Chemical Institute, University of Bergen, Bergen, Norway

The crystal and molecular structure of 4-phenyl-1,2-dithiolium iodide has been solved by Patterson projections along the b and c axes and refined by least squares methods using anisotropic temperature parameters. The refinement comprises the $h0l$, $hk0$, $hk1$, and $hk2$ reflections.

In the 1,2-dithiolium ring, which is planar within the experimental error, the bond lengths are $C-C = 1.40 \pm 0.03$ Å, $C-S = 1.67 \pm 0.02$ Å and $S-S = 2.028 \pm 0.010$ Å. This shows that there is pronounced conjugation in the ring, also extending over the sulphur-sulphur bond.

Average length of the $C-C$ bonds in the benzene ring is 1.38 Å, and the length of the $C-C$ bond connecting the two coplanar rings of the ion, is 1.45 ± 0.03 Å.

In the crystal, each iodide ion forms close contacts with four neighbouring sulphur atoms. Two of these close contacts, both 3.503 ± 0.008 Å, occur in an infinite $\cdots I \cdots S-S \cdots I \cdots S-S \cdots I \cdots$ chain which runs through the crystal in the b-axis direction, the $I \cdots S-S$ angle being $158.1 \pm 0.5°$ and the $S \cdots I \cdots S$ angle $136.2°$. This partial bonding between iodine and sulphur is probably established through a transfer of charge from the iodide ion to the p-orbitals of the sulphur atoms already engaged in the sulphur-sulphur σ-bond, or in M.O. language, to the antibonding sulphur-sulphur σ-orbital. The deviation from linearity of the $I \cdots S-S$ sequence probably indicates that the charge transfer is also directed towards the π-bonding system of the 4-phenyl-1,2-dithiolium ion.

The other two short iodine-sulphur distances, both 3.549 ± 0.008 Å, occur in a triangular arrangement were the iodide ion forms close contacts with both sulphur atoms of another disulphide group, thus interconnecting the infinite iodine-sulphur chains. Each triangular group lie in the plane of the corresponding 4-phenyl-1,2-dithiolium ion, the $S \cdots I \cdots S$ angle is $33.2 \pm 0.5°$ and the indicated bonding may be explained in terms of three-center two-electron bond.

Bergson[1] has by molecular orbital methods calculated π-bond orders for the different bonds of the unsubstituted 1,2-dithiolium ion. His values are, if one assumes a linear bond-length/bond-order relationship, in good agreement with the bond length found in the 1,2-dithiolium ring of 3-phenyl-1,2-dithiolium iodide.[2]

In order to secure more experimental evidence for the dimensions of the 1,2-dithiolium ring, the present investigation of 4-phenyl-1,2-dithiolium iodide has been carried out. It was also hoped that the structure analysis would reveal sulphur-iodine close contacts. Halogen-sulphur close contacts are found to occur in crystals of 3-phenyl-1,2-dithiolium iodide,[2] 3,5-diamino-1,2-dithiolium iodide,[3] thiuret hydroiodide,[4] hydrobromide,[5] and hydrochloride hemihydrate,[6] and might therefore also be present in crystals of 4-phenyl-1,2-dithiolium iodide.

EXPERIMENTAL

A sample of 4-phenyl-1,2-dithiolium iodide was generously supplied by Klingsberg.[7] Crystal data on the compound have been reported earlier.[8] It crystallizes from ethanol as orange needles and thin flakes elongated along c and with {100} predominant. The crystals are orthorhombic with the unit cell dimensions (redetermined): $a = 25.90$ Å, $b = 8.53$ Å and $c = 4.78$ Å. The experimental error is estimated to be within 0.5 %. There are four formula units per unit cell; density, calc. 1.93, found 1.93 g/cm³. The space group is *Pnma* (No. 62).

The intensities of the $hk0$, $hk1$, $hk2$, and $h0l$ reflections were estimated visually from Weissenberg photographs taken with CuKα radiation ($\mu = 346$ cm⁻¹). Small crystals of cross-section 0.08×0.03 mm were used in order to minimize absorption effects, and no absorption correction was applied. 589 of the 770 reflections obtainable with CuKα radiation were estimated. The intensities were corrected in the usual way to give sets of relative structure factors. Common reflections in $hk0$, $hk1$, $hk2$, and $h0l$ 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*,[9] 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 c and b-axes projections. The
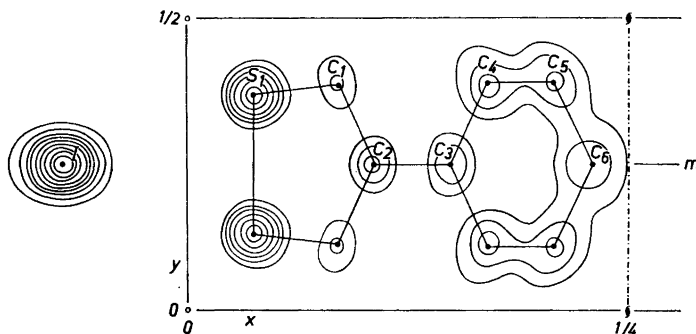

Fig. 1. Electron density projection of 4-phenyl-1,2-dithiolium iodide along the c-axis. Contour intervals for carbon 2e. Å⁻², for sulphur 4e. Å⁻² and iodide 10e. Å⁻². Lowest contour at 4e. Å⁻².

structure was thereafter refined by least squares methods on an IBM 1620[II] computer, using a program designed by Mair.[10] Weighting scheme No. 3, recommended by Mair, was used with $a = 64$ and $b = 40$.

The refinement comprised the $hk0$, $hk1$, $hk2$, and $h0l$ reflections, and was carried out with isotropic temperature factors until the shifts in sulphur and iodine parameters had become small. Thereafter the sulphur and iodine atoms were given anisotropic temperature parameters.

Hydrogen atoms are usually neglected in structure investigations of compounds containing an atom as heavy as iodine. However, the experience from the structure analysis of 3-phenyl-1,2-dithiolium iodide[2] was that more reasonable values were obtained for the carbon-carbon bond lengths after the hydrogen atoms had been accounted for. Therefore the positions of the hydrogen atoms in 4-phenyl-1,2-dithiolium iodide were calculated, taking $C-H = 1.1$ Å, and the scattering contribution of the hydrogen atoms were included in the structure factor calculation. Thereafter anisotropic temperature parameters were given to the carbon atoms, and in the last three least squares cycles also the hydrogen parameters were refined. Some low order reflections which were supposed to be affected by secondary extinction, were given zero weight in the refinement. Their F_o-values in Table 6 correspond to F_c-values from a previous cycle. Final value for the agreement factor $R = \sum ||F_o| - |F_c|| / \sum |F_o|$ is 0.083.

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

	x	y	z
I	−0.07112	0.25000	−0.59750
S_1	0.03760	0.36888	−0.19866
C_1	0.0862	0.3860	0.0281
C_2	0.1072	0.2500	0.1477
C_3	0.1491	0.2500	0.3498
C_4	0.1707	0.3908	0.4548
C_5	0.2099	0.3910	0.6499
C_6	0.2292	0.2500	0.7351
H_1	0.101	0.504	0.039
H_2	0.155	0.497	0.372
H_3	0.232	0.504	0.666
H_4	0.241	0.250	0.865

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_{12}	β_{23}	β_{13}
I	0.0019	0.0080	0.0379	0.0000	0.0000	−0.0025
S_1	0.0012	0.0082	0.0354	0.0010	−0.0014	−0.0011
C_1	0.0014	0.0112	0.0304	0.0007	0.0022	−0.0024
C_2	0.0006	0.0128	0.0667	0.0000	0.0000	0.0043
C_3	0.0009	0.0144	0.0430	0.0000	0.0000	0.0029
C_4	0.0016	0.0091	0.0397	−0.0017	−0.0003	−0.0019
C_5	0.0015	0.0153	0.0601	−0.0017	−0.0080	−0.0065
C_6	0.0012	0.0280	0.0630	0.0000	0.0000	−0.0026

Table 3. Bond lengths l and standard deviation in bond lengths $\sigma(l)$ in the 4-phenyl-1,2-dithiolium ion.

Bond	l (Å)	$\sigma(l)$ (Å)
S_1-S_2	2.028	0.010
S_1-C_1	1.67	0.02
C_1-C_2	1.40	0.03
C_2-C_3	1.45	0.03
C_3-C_4	1.42	0.03
C_4-C_5	1.36	0.03
C_5-C_6	1.37	0.03

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

	Angle (°)	σ (°)
$C_1-S_1-S_2$	95.0	0.5
$S_1-C_1-C_2$	119.0	1.0
$C_1-C_2-C_9$	112.0	1.6
$C_1-C_2-C_3$	124.0	1.6
$C_2-C_3-C_4$	122.0	1.6
$C_4-C_3-C_8$	116.0	1.6
$C_3-C_4-C_5$	122.1	1.8
$C_4-C_5-C_6$	118.4	1.8
$C_5-C_6-C_7$	122.8	1.8

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 *c*-axis projection, corresponding to the final state of refinement is shown in Fig. 1.

THE 4-PHENYL-1,2-DITHIOLIUM ION

Bond lengths and bond angles in the 4-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 4-phenyl-1,2-dithiolium ion lies across the crystallographic mirror plane *m* which passes through the crystal normal to the *b*-axis. The disulphide group is therefore planar and the 4-phenyl-1,2-dithiolium ion itself is nearly so. The equation for the least squares plane of the ion, excluding hydrogen atoms and with triple weight on the sulphur atoms is

$$-0.6728X + 0.7398Z + 1.3644 = 0$$

where X and Z are in Å units. The atoms of the 1,2-dithiolium ring, S_1, C_1, and C_2 lie 0.007, −0.038, and 0.019 Å, respectively, out of the plane, and the deviations from the plane for the atoms of the benzene ring, C_3, C_4, C_5, and C_6 are 0.003, −0.002, 0.024, and −0.030 Å, respectively. There is thus no significant deviation of the atoms from the least squares plane.
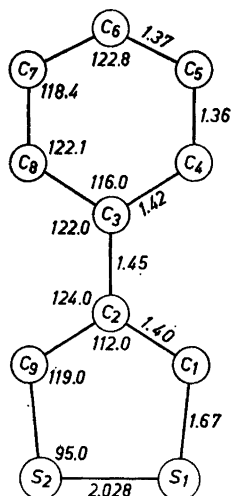
Fig. 2. Bond lengths (Å) and bond angles
(°) in the 4-phenyl-1,2-dithiolium ion.

The bond lengths in the 1,2-dithiolium ring as listed in Table 3, may be compared with those found for the equivalent bonds in the 1,2-dithiolium ring of 3-phenyl-1,2-dithiolium iodide,[2] and furthermore a comparison may be made with the results from Bergson's molecular orbital calculations on the unsubstituted 1,2-dithiolium ion.[1]

The bond lengths S—S = 2.028 ± 0.010 Å, S—C = 1.67 ± 0.02 Å, and C—C = 1.40 ± 0.03 Å found in the 1,2-dithiolium ring of 4-phenyl-1,2-dithiolium iodide, are all significantly shorter than single bonds, which shows that the 1,2-dithiolium ring is stabilized through π-orbital delocalization. In 3-dhenyl-1,2-dithiolium iodide the lengths of corresponding bonds are S—S = 2.00 ± 0.01 Å, S—C = 1.67 and 1.71 ± 0.03 Å, and C—C = 1.39 ± 0.04 Å. There is thus good agreement between the dimensions of the 1,2-dithiolium ring as found in the 3- and 4-phenyl substituted 1,2-dithiolium iodides.

The π-bond orders for the different bonds in the 1,2-dithiolium ring of 4-phenyl-1,2-dithiolium iodide have been estimated from the found bond lengths by assuming linear bond-order/bond-length relations. The π-bond orders zero and one are supposed to correspond to the bond lengths 2.10 and 1.89 Å,[11] respectively, for the sulphur-sulphur bond, and 1.79 and 1.61 Å,[11] respectively, for the sulphur-carbon bond. The value 2.10 Å is by one of the authors[12] proposed as a better value than the Pauling value 2.08 Å, for the length of a pure single bond between the two divalent sulphur atoms of a *cis* planar disulphide group, and 1.79 is the sum of the covalent radius 1.05 Å for divalent sulphur and 0.74 Å for a trigonal carbon atom. For carbon-carbon bonds a graph was used where bond length 1.51 Å corresponds to π-bond order zero and 1.34 to π-bond order one.

According to the above, the π-bond order of the sulphur-sulphur bond in 4-phenyl-1,2-dithiolium iodide is estimated to be 0.35, and the π-bond orders of the S—C and C—C bonds in the disulphide ring are estimated to be 0.67

and 0.65, respectively. These bond orders agree well with those calculated by Bergson [1] for the unsubstituted 1,2-dithiolium ion. Bergson's scheme No. I gives, in the same order as above, the π-bond orders 0.424, 0.691, and 0.653, respectively, and scheme No. II gives 0.355, 0.604, and 0.627.

The average length of the carbon bonds in the benzene ring, 1.38 Å, agrees within the limit of error with the length of the aromatic carbon-carbon bond. The length of the bond which connects the two rings, C_2—C_3 = 1.45 $\pm$ 0.03 Å, agrees with the length 1.466 Å proposed for a single bond between two sp^2-hybridized carbon atoms.[13] A bond length of 1.4943 $\pm$ 0.002 Å for the central bond in diphenyl has been found by Robertson [14] through an X-ray crystallographic investigation of the compound.

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 1.30 Å from the plane of the 4-phenyl-1,2-dithiolium ion, form close contacts with the sulphur atoms of the disulphide group in a bent I⋯S—S⋯I arrangement. The I⋯S distances are 3.503 $\pm$ 0.007 Å and the I⋯S—S angles are 158.1 $\pm$ 0.4°. Taking 4.00 Å as the sum of van der Waals radii [15] for iodine and sulphur, the iodine-sulphur distances of 3.50 Å indicate a weak bond. The analogy between this partial bonding and the bonding in polyhalide ions has been discussed elsewhere. [2] In 3-phenyl-1,2-dithiolium iodide a I⋯S—S arrangement occurs, probably because the steric requirements of the 3-phenyl group prevents a I⋯S—S⋯I arrangement as in 4-phenyl-1,2-dithiolium iodide. In 3-phenyl-1,2-dithiolium iodide the I⋯S—S sequence is almost linear, the corresponding angle being 178°, and since in this case the
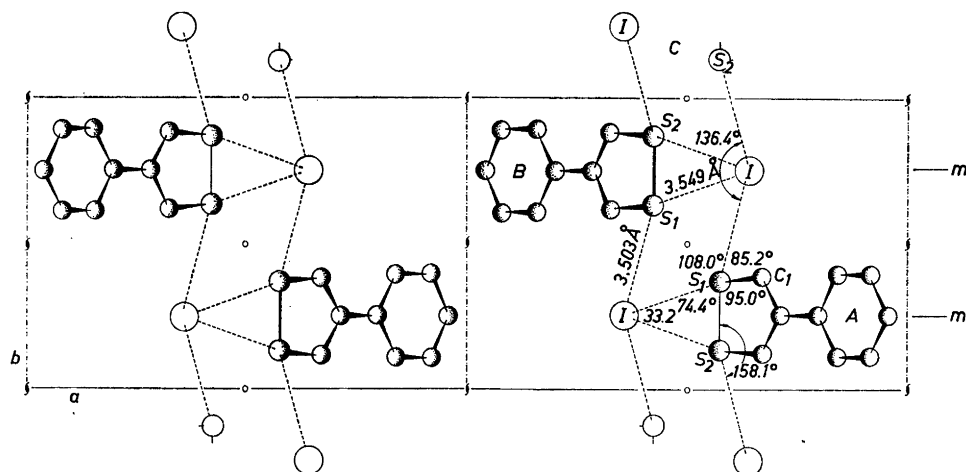
Fig. 3. The arrangement of ions in the unit cell as seen along the c-axis. Dashed lines indicate partial bonding between iodine and sulphur.

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

	Distance (Å)	σ (Å)
$I_A \cdots S_{1A}$	3.549	0.007
$I_B \cdots S_{1A}$	3.503	0.007

	Angle (°)	σ (°)
$S_{1A} \cdots I_A \cdots S_{2A}$	33.2	0.4
$I_A \cdots S_{1A} - S_{2A}$	74.4	0.4
$I_A \cdots S_{1A} \cdots I_B$	108.0	0.3
$I_B \cdots S_{1A} - C_{1A}$	85.2	1.0
$I_A \cdots S_{1B} - S_{2B}$	158.1	0.4
$S_{1A} \cdots I_B \cdots S_{2C}$	136.4	0.4

phenyl group is so far removed from the iodide ion one may assume that a linear I⋯S—S arrangement is the favourable one for the formation of the partial sulphur-iodine bond. This strongly indicates that the partial bonding is of the same type as in polyhalide ions. But iodine orbitals are large, and when a conjugated system is close to an iodide ion there may probably also be a transfer of charge to that system, as for instance in the present structure where the deviation from linearity of the I⋯S—S⋯I arrangement may reflect such a feature. The partial bonding between sulphur and iodine in the I⋯S—S⋯I arrangement in 4-phenyl-1,2-dithiolium iodide may thus be thought of as a transfer of charge from the iodide ion, to those p-orbitals of the sulphur atoms already engaged in the sulphur-sulphur σ-bond as well as to the π-bonding system of the cation.

Nearly linear X⋯S—S⋯X arrangements are also present in crystals of thiuret hydroiodide,[4] hydrobromide [5] and hydrochloride hemihydrate.[6] In the two former compounds the sulphur-halogen distances indicate partial bonding of σ-bond order about 0.23, while in the latter there is a weak sulphur-halogen contact of σ-bond order 0.10, on one side of the disulphide group only. Two different refinement procedures of the structure of thiuret hydroiodide [3,4] gave the bond lengths 2.083 ± 0.015 Å and 2.088 ± 0.012 Å, respectively, for the sulphur-sulphur bond; in thiuret hydrobromide the sulphur-sulphur bond length has been found to be 2.071 ± 0.009 Å.[5] In thiuret hydrochloride hemihydrate [6] the sulphur-sulphur bond, from a least squares refinement of the crystal structure is 2.063 ± 0.004 Å, and becomes 2.071 ± 0.004 Å when the libration of the thiuret ion has been accounted for. The uncorrected value, however, is probably relevant in a comparison with the sulphur-sulphur bond length in thiuret hydroiodide and hydrochloride because the latter values are also uncorrected.

It appears that the partial bonding between sulphur and halogen in the linear X⋯S—S⋯X arrangement is equally strong in thiuret hydroiodide and hydrobromide, and there is also very good agreement between the sulphur-sulphur bond lengths found in the two compounds. However, in thiuret hydrochloride the sulphur-sulphur bond is about 0.02 Å shorter and the partial sulphur-halogen bonding much weaker. This indicates that the partial sulphur-

Table 6. Observed and calculated *hk*0, *hk*1, *hk*2, and *h0l* structure factors for 4-phenyl-1,2-dithiolium iodide. The values given are ten times the absolute values. Reflections marked with asterisks were given zero weight in the refinement because of assumed secondary extinction.

h	k	l	F_o	F_c
4	0	0	63	-68
6	0	0	828	-824
8	0	0	946	-968
10	0	0	326	-344
12	0	0	148	164
14	0	0	236	260
16	0	0	96	-77
18	0	0	114	-132
20	0	0	264	-262
22	0	0	161	-153
24	0	0	77	87
26	0	0	219	211
28	0	0	215	236
30	0	0	111	116
32	0	0	<27	-22
0	2	0	1088	-1083
0	4	0	266	260
0	6	0	564	-608
0	8	0	541	635
0	10	0	186	-243
2	1	0	103	45
4	1	0	937	790
6	1	0	53	-28
8	1	0	499	-489
10	1	0	826	-894
12	1	0	500	-546
14	1	0	98	-108
16	1	0	498	475
18	1	0	625	563
20	1	0	270	271
22	1	0	<44	12
24	1	0	130	-126
26	1	0	100	-102
28	1	0	40	-36
30	1	0	<34	7
32	1	0	<26	32
2	2	0	679	-581
4	2	0	225	195
6	2	0	993	776
8	2	0	648	562
10	2	0	242	213
12	2	0	295	-313
14	2	0	447	-477
16	2	0	212	-237
18	2	0	<40	52
20	2	0	235	247
22	2	0	225	215
24	2	0	101	111
26	2	0	110	-131
28	2	0	141	-146
30	2	0	47	-63
2	3	0	997	-884
4	3	0	1063	-908
6	3	0	816	-715
8	3	0	126	126
10	3	0	663	615
12	3	0	310	315
14	3	0	<37	31
16	3	0	262	-269
18	3	0	181	-195
20	3	0	<44	-24
22	3	0	269	269
24	3	0	210	174
26	3	0	46	50
28	3	0	<41	17
30	3	0	88	-104
2	4	0	155	158
4	4	0	403	-356
6	4	0	707	-650
8	4	0	259	-266
10	4	0	<35	-29
12	4	0	516	479
14	4	0	663	622
16	4	0	409	410
18	4	0	<44	50
20	4	0	189	-176
22	4	0	303	-267
24	4	0	299	-245
26	4	0	<38	27
28	4	0	<33	34
30	4	0	<25	4
2	5	0	530	564
4	5	0	759	775
6	5	0	545	523
8	5	0	<38	-25
10	5	0	398	-371
12	5	0	255	-247
14	5	0	<43	-37
16	5	0	175	184
18	5	0	172	158
20	5	0	<50	-27
22	5	0	255	-223
24	5	0	156	-174
26	5	0	78	-84
28	5	0	<28	-1
2	6	0	216	-223
4	6	0	165	183
6	6	0	468	436
8	6	0	421	400
10	6	0	61	51
12	6	0	302	-273
14	6	0	398	-357
16	6	0	175	-176
18	6	0	<44	-1
20	6	0	132	144
22	6	0	152	157
24	6	0	<38	-46
26	6	0	<28	-43
2	7	0	162	-148
4	7	0	395	-367
6	7	0	70	-62
8	7	0	201	201
10	7	0	370	350
12	7	0	284	266
14	7	0	<44	34
16	7	0	221	-234
18	7	0	269	-285
20	7	0	96	-120
22	7	0	<37	-3
24	7	0	76	100
2	8	0	331	338
4	8	0	<45	-1
6	8	0	277	-276
8	8	0	391	-343
10	8	0	160	-149
12	8	0	<47	55
14	8	0	99	104
16	8	0	<49	6
18	8	0	70	-63
20	8	0	103	-120
2	9	0	125	144
4	9	0	153	165
6	9	0	<40	10
8	9	0	197	-206
10	9	0	279	-308
12	9	0	176	-198
14	9	0	<32	-2
16	9	0	152	173
18	9	0	155	206
2	10	0	162	-194
4	10	0	<32	19
6	10	0	154	188
8	10	0	124	157
10	10	0	52	73
12	10	0	47	-53
1	0	1	455	-464*
2	0	1	483	509*
3	0	1	242	239
4	0	1	671	758
5	0	1	96	86
6	0	1	788	936
7	0	1	467	507
8	0	1	<23	16
9	0	1	406	453
10	0	1	<55	5
11	0	1	72	-100
12	0	1	208	-246
13	0	1	407	-509
14	0	1	97	-100
15	0	1	374	-424
16	0	1	72	64
17	0	1	163	-165
18	0	1	<67	33
19	0	1	96	98
20	0	1	92	-89
21	0	1	309	283
22	0	1	214	-209
23	0	1	148	137
24	0	1	185	-168
25	0	1	<43	15
26	0	1	85	-62
27	0	1	61	-55
28	0	1	<38	2
29	0	1	81	-75
30	0	1	82	82
31	0	1	<29	5
32	0	1	104	110
0	1	1	208	-178
0	3	1	789	745
0	5	1	614	-583
0	7	1	157	152
0	9	1	69	-55
1	1	1	286	-247
2	1	1	191	-169
3	1	1	872	-981
4	1	1	504	551
5	1	1	632	-778
6	1	1	333	383
7	1	1	116	93
8	1	1	247	277
9	1	1	378	438
10	1	1	50	-41
11	1	1	339	410
12	1	1	405	-459
13	1	1	120	137
14	1	1	408	-423
15	1	1	143	-142
16	1	1	306	-302
17	1	1	286	-291
18	1	1	39	-38
19	1	1	136	-125
20	1	1	126	108
21	1	1	68	51
22	1	1	208	195
23	1	1	158	150
24	1	1	149	139
25	1	1	182	156
26	1	1	<51	29
27	1	1	49	32
28	1	1	<38	-24
29	1	1	35	-43
30	1	1	<77	19
1	2	1	675	612
2	2	1	362	-310
3	2	1	191	168
4	2	1	509	-468
5	2	1	454	-438
6	2	1	319	-311
7	2	1	548	-580
8	2	1	151	154
9	2	1	318	-350
10	2	1	313	320
11	2	1	93	99
12	2	1	281	286
13	2	1	389	415
14	2	1	<35	-16
15	2	1	325	348
16	2	1	146	-139
17	2	1	52	47
18	2	1	235	-230
19	2	1	174	-172
20	2	1	54	-46
21	2	1	192	-183
22	2	1	79	81
23	2	1	122	-102
24	2	1	114	93
25	2	1	<47	29
26	2	1	81	57
27	2	1	108	94
28	2	1	<37	15
29	2	1	54	51
30	2	1	<50	-11
31	2	1	<26	10
32	2	1	44	-52
1	3	1	425	349
2	3	1	530	472
3	3	1	465	423
4	3	1	<32	-24
5	3	1	347	320
6	3	1	308	-288
7	3	1	<33	36
8	3	1	400	-397
9	3	1	419	-431
10	3	1	168	-166
11	3	1	387	-410
12	3	1	71	-64
13	3	1	142	-165
14	3	1	139	142
15	3	1	99	94
16	3	1	49	31
17	3	1	229	252
18	3	1	70	-72
19	3	1	289	285
20	3	1	63	-52
21	3	1	68	57
22	3	1	129	-117
23	3	1	135	-125
24	3	1	<42	25
25	3	1	108	-99
26	3	1	106	99
27	3	1	100	-86
28	3	1	145	141
29	3	1	<31	23
30	3	1	45	51
31	3	1	62	77
1	4	1	649	-611
2	4	1	99	91
3	4	1	324	-283
4	4	1	154	152
5	4	1	449	404
6	4	1	109	-94
7	4	1	533	502
8	4	1	395	-370
9	4	1	328	311
10	4	1	491	-486
11	4	1	<36	-19
12	4	1	282	-295
13	4	1	315	-308
14	4	1	58	58
15	4	1	224	-237
16	4	1	216	212
17	4	1	<61	49
18	4	1	373	380
19	4	1	190	191
20	4	1	188	176
21	4	1	127	118
22	4	1	75	51
23	4	1	86	68
24	4	1	<76	-5
25	4	1	76	-78
26	4	1	45	-34
27	4	1	134	-117
28	4	1	<46	-35
29	4	1	54	-41
1	5	1	210	-194
2	5	1	444	-409
3	5	1	383	-374
4	5	1	<35	-8
5	5	1	291	-273
6	5	1	219	215
7	5	1	72	59
8	5	1	315	299
9	5	1	360	357
10	5	1	180	183
11	5	1	344	338
12	5	1	58	44
13	5	1	132	130
14	5	1	71	-54
15	5	1	94	-89
16	5	1	<53	11
17	5	1	239	-233
18	5	1	100	74
19	5	1	237	-216
20	5	1	79	75
21	5	1	70	-43
22	5	1	92	79
23	5	1	92	72
24	5	1	<37	-26

h	k	l	F_o	F_c
25	5	1	97	86
26	5	1	105	-102
27	5	1	72	56
28	5	1	122	-130
1	6	1	380	380
2	6	1	161	-165
3	6	1	65	60
4	6	1	230	-209
5	6	1	178	-164
6	6	1	131	-124
7	6	1	346	-330
8	6	1	166	164
9	6	1	254	-246
10	6	1	255	230
11	6	1	<48	36
12	6	1	214	195
13	6	1	231	231
14	6	1	<44	30
15	6	1	196	194
16	6	1	126	-129
17	6	1	<43	35
18	6	1	180	-155
19	6	1	100	-99
20	6	1	70	-76
21	6	1	165	-158
22	6	1	<37	14
23	6	1	78	-65
24	6	1	44	43
25	6	1	29	30
26	6	1	<25	20
1	7	1	116	112
2	7	1	89	92
3	7	1	401	398
4	7	1	152	-149
5	7	1	318	320
6	7	1	195	-184
7	7	1	58	-51
8	7	1	146	-140
9	7	1	235	-220
10	7	1	<44	-3
11	7	1	218	218
12	7	1	209	202
13	7	1	98	-85
14	7	1	197	188
15	7	1	96	85
16	7	1	132	129
17	7	1	179	167
18	7	1	<38	5
19	7	1	81	65
20	7	1	89	-86
21	7	1	<33	-20
22	7	1	116	-101
23	7	1	70	-69
24	7	1	66	-72
1	8	1	183	-188
2	8	1	196	191
3	8	1	<43	10
4	8	1	315	292
5	8	1	121	122
6	8	1	268	253
7	8	1	209	215
8	8	1	150	149
9	8	1	<47	42
10	8	1	<51	-43
11	8	1	60	-62
12	8	1	112	-89
13	8	1	225	-203
14	8	1	38	-40
15	8	1	185	-176
16	8	1	<35	22
17	8	1	78	-69
18	8	1	<32	9
19	8	1	62	58
20	8	1	<131	-38
1	9	1	102	-111
2	9	1	<39	-1
3	9	1	254	-247
4	9	1	120	114
5	9	1	204	-204
6	9	1	155	143
7	9	1	<37	-31
8	9	1	89	91
9	9	1	134	122
10	9	1	43	-36
11	9	1	137	142
12	9	1	162	-149
13	9	1	48	55

h	k	l	F_o	F_c
14	9	1	183	-183
15	9	1	43	-48
16	9	1	119	-125
17	9	1	81	-90
1	0	1	132	142
2	0	1	97	-104
3	0	1	34	47
4	0	1	137	-149
5	0	1	117	-136
6	0	1	89	-89
7	0	1	157	-168
8	0	1	<27	1
9	0	1	70	-78
10	0	1	74	79
11	0	1	37	38
1	0	2	274	-297 *
2	0	2	21	-27
3	0	2	442	-501
4	0	2	371	-371
5	0	2	445	-466
6	0	2	221	-243
7	0	2	325	303
8	0	2	178	-190
9	0	2	696	682
10	0	2	182	175
11	0	2	393	421
12	0	2	462	460
13	0	2	241	258
14	0	2	252	281
15	0	2	167	-204
16	0	2	138	159
17	0	2	325	-370
18	0	2	<48	1
19	0	2	309	-308
20	0	2	116	-120
21	0	2	124	-121
22	0	2	111	-86
23	0	2	90	81
24	0	2	<54	-28
25	0	2	115	93
26	0	2	73	-74
27	0	2	76	69
28	0	2	41	-43
29	0	2	<44	-10
30	0	2	32	-36
31	0	2	39	-42
0	2	2	129	-109
0	4	2	271	258
0	6	2	182	-182
0	8	2	<49	12
1	1	2	701	740
2	1	2	238	230
3	1	2	246	253
4	1	2	333	339
5	1	2	274	-291
6	1	2	294	298
7	1	2	387	-469
8	1	2	49	40
9	1	2	451	-532
10	1	2	71	53
11	1	2	41	-29
12	1	2	105	-115
13	1	2	301	302
14	1	2	<42	-38
15	1	2	239	236
16	1	2	<46	29
17	1	2	<47	35
18	1	2	<49	-2
19	1	2	197	-189
20	1	2	81	-62
21	1	2	210	-182
22	1	2	101	-79
23	1	2	108	-84
24	1	2	113	-120
25	1	2	69	61
26	1	2	56	-57
27	1	2	148	139
28	1	2	<49	37
29	1	2	105	95
30	1	2	47	63
1	2	2	294	250
2	2	2	169	-157
3	2	2	676	626
4	2	2	88	54
5	2	2	494	456
6	2	2	177	172

h	k	l	F_o	F_c
7	2	2	48	-32
8	2	2	183	187
9	2	2	390	-418
10	2	2	<37	6
11	2	2	392	-427
12	2	2	101	-108
13	2	2	154	-156
14	2	2	171	-146
15	2	2	79	90
16	2	2	83	-89
17	2	2	258	264
18	2	2	<52	53
19	2	2	257	240
20	2	2	69	67
21	2	2	<56	26
22	2	2	85	63
23	2	2	121	-109
24	2	2	<49	-13
25	2	2	156	-130
26	2	2	<55	-20
27	2	2	59	-60
28	2	2	<38	-29
29	2	2	<34	22
1	3	2	489	-432
2	3	2	275	-226
3	3	2	<40	-29
4	3	2	70	-68
5	3	2	348	327
6	3	2	101	83
7	3	2	543	547
8	3	2	245	237
9	3	2	243	235
10	3	2	279	292
11	3	2	88	-104
12	3	2	122	136
13	3	2	413	-443
14	3	2	122	-135
15	3	2	354	-421
16	3	2	121	-124
17	3	2	<58	-34
18	3	2	178	-174
19	3	2	107	109
20	3	2	71	-73
21	3	2	219	198
22	3	2	<50	9
23	3	2	148	129
24	3	2	<47	9
25	3	2	<45	4
26	3	2	<42	17
27	3	2	62	-50
28	3	2	<35	6
29	3	2	30	-34
1	4	2	253	-221
2	4	2	368	312
3	4	2	640	-617
4	4	2	147	123
5	4	2	516	-508
6	4	2	111	-109
7	4	2	137	-144
8	4	2	180	-178
9	4	2	196	197
10	4	2	147	-138
11	4	2	279	301
12	4	2	144	-146
13	4	2	96	80
14	4	2	<49	-16
15	4	2	<50	7
16	4	2	<51	-23
17	4	2	159	-155
18	4	2	94	-92
19	4	2	148	-132
20	4	2	51	-30
21	4	2	50	60
22	4	2	<48	-29
23	4	2	124	138
24	4	2	66	61
25	4	2	177	146
26	4	2	113	98
27	4	2	63	56
1	5	2	306	292
2	5	2	114	107
3	5	2	<44	1
4	5	2	<45	35
5	5	2	288	-288
6	5	2	102	-89
7	5	2	393	-389
8	5	2	215	-216
9	5	2	205	-206

h	k	l	F_o	F_c
10	5	2	227	-228
11	5	2	96	114
12	5	2	113	-121
13	5	2	360	388
14	5	2	84	61
15	5	2	332	338
16	5	2	125	123
17	5	2	95	82
18	5	2	151	157
19	5	2	106	-86
20	5	2	76	79
21	5	2	174	-161
22	5	2	<45	25
23	5	2	134	-111
24	5	2	<39	-4
25	5	2	<36	-19
26	5	2	<32	13
1	6	2	189	183
2	6	2	140	-120
3	6	2	403	394
4	6	2	<49	33
5	6	2	342	346
6	6	2	102	100
7	6	2	<50	13
8	6	2	130	178
9	6	2	247	-245
10	6	2	<51	25
11	6	2	<208	-219
12	6	2	75	-83
13	6	2	113	-119
14	6	2	<59	-54
15	6	2	79	80
16	6	2	<50	-4
17	6	2	197	170
18	6	2	<47	43
19	6	2	136	116
20	6	2	66	72
21	6	2	<41	2
22	6	2	<38	32
23	6	2	121	-103
24	6	2	<31	-28
25	6	2	90	-99
1	7	2	332	-327
2	7	2	99	-86
3	7	2	109	-97
4	7	2	144	-159
5	7	2	158	161
6	7	2	114	-114
7	7	2	251	246
8	7	2	<51	-4
9	7	2	260	252
10	7	2	<50	3
11	7	2	<50	-9
12	7	2	62	64
13	7	2	184	-175
14	7	2	<47	43
15	7	2	144	-140
16	7	2	<45	-30
17	7	2	43	-50
18	7	2	<41	-4
19	7	2	106	94
20	7	2	<36	19
21	7	2	106	102
22	7	2	28	25
23	7	2	39	50
1	8	2	119	-100
2	8	2	<49	-28
3	8	2	230	-213
4	8	2	108	-107
5	8	2	175	-159
6	8	2	99	-101
7	8	2	92	95
8	8	2	59	-60
9	8	2	269	251
10	8	2	88	68
11	8	2	204	208
12	8	2	171	175
13	8	2	90	98
14	8	2	131	131
15	8	2	83	-88
16	8	2	70	76
17	8	2	153	-168
18	8	2	<31	1
19	8	2	130	-145
1	9	2	244	262
2	9	2	95	104
3	9	2	99	96

h	k	l	F_O	F_C	h	k	l	F_O	F_C	h	k	l	F_O	F_C	h	k	l	F_O	F_C
4	9	2	119	131	1	0	3	48	−25	26	0	3	91	−84	22	0	4	135	134
5	9	2	90	−91	2	0	3	204	220	27	0	3	47	−59	23	0	4	86	104
6	9	2	107	101	3	0	3	158	−143	28	0	3	<33	−20	24	0	4	72	67
7	9	2	177	−196	4	0	3	410	370	1	0	4	113	−103	1	0	5	353	317
8	9	2	<38	38	5	0	3	147	−149	2	0	4	126	−104	2	0	5	<55	−13
9	9	2	146	−157	6	0	3	62	70	3	0	4	426	−367	3	0	5	136	135
10	9	2	<36	−5	7	0	3	219	−184	4	0	4	33	63	4	0	5	<55	17
11	9	2	<34	−20	8	0	3	341	−306	5	0	4	364	−329	5	0	5	88	−102
12	9	2	<32	−23	9	0	3	<53	44	6	0	4	217	185	6	0	5	<54	−34
13	9	2	81	88	10	0	3	442	−399	7	0	4	118	−98	7	0	5	221	−213
14	9	2	<27	3	11	0	3	108	117	8	0	4	197	178	8	0	5	<53	−10
15	9	2	77	88	12	0	3	304	−301	9	0	4	<59	25	9	0	5	133	−161
1	10	2	57	69	13	0	3	249	271	10	0	4	<59	40	10	0	5	<50	12
2	10	2	<29	−19	14	0	3	<58	−38	11	0	4	99	100	11	0	5	<49	−36
3	10	2	133	159	15	0	3	220	254	12	0	4	88	−88	12	0	5	<47	−20
4	10	2	<28	17	16	0	3	221	293	13	0	4	<69	43	14	0	5	<44	6
5	10	2	76	103	17	0	3	<59	33	14	0	4	176	−219	15	0	5	<41	40
6	10	2	44	65	18	0	3	247	283	15	0	4	57	−68	16	0	5	<38	10
7	10	2	<29	−19	19	0	3	<59	16	16	0	4	84	−130	17	0	5	<35	−28
0	0	2	<36	44	20	0	3	168	169	17	0	4	55	−53	1	0	6	33	43
0	0	4	241	−207	21	0	3	<57	−38	18	0	4	<53	−11	2	0	6	34	−41
0	0	6	47	−65	22	0	3	<55	−9	19	0	4	50	59	3	0	6	64	81
					23	0	3	79	−86	20	0	4	60	64	4	0	6	<29	28
					24	0	3	93	−94	21	0	4	96	112					
					25	0	3	62	−67										

halogen bonds in thiuret hydroiodide and hydrobromide affect the length of the sulphur-sulphur bond.

The different lengths which have been found for the sulphur-sulphur bond in 3-phenyl and 4-phenyl-1,2-dithiolium iodide, 2.00 ± 0.01 Å and 2.03 ± 0.02 Å, respectively, may be seen in relation to the above. The partial sulphur-iodine bonding in the I···S—S arrangement of the 3-phenyl compound corresponds to a σ-bond order of 0.39, and the partial sulphur-iodine bonding in the I···S—S···I arrangement of the 4-phenyl compound corresponds to σ-bond orders of 0.31. Since the sulphur-sulphur bond in 4-phenyl-1,2-dithiolium iodide is attacked from both sides, one may assume that it is relatively more affected than that in 3-phenyl-1,2-dithiolium iodide. Although the difference in sulphur-sulphur bond length is small, about 0.03 Å, and hardly significant, it is in the direction indicated by the above picture.

The iodide ion I_A, shown in Fig. 3 lies 0.49 Å from the plane of the cation and forms close contacts with both sulphur atoms of the disulphide group, the distances to S_1 and S_2 being 3.549 ± 0.007 Å. The angle $S_1I_AS_2$ is rather small, 33.2°, and it seems likely that the partial sulphur-iodine bonding in this triangular arrangement is 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. Similar three-center arrangements are present in crystals of 3-phenyl-1,2-dithiolium iodide,[2] thiuret hydroiodide,[4] hydrobromide [5] and hydrochloride hemihydrate.[6]

The arrangement of 4-phenyl-1,2-dithiolium ions and iodide ions in the unit cell is shown in Fig. 3. Infinite ···I···S—S···I···S—S···I··· chains, in which the S···I···S angle is 136° and the I···S—S angle is 158°, run through the crystal in the direction of the b-axis. Two and two of these chains are interconnected through the triangular S···I···S arrangement discussed above. There are very weak contacts across the glide plane n perpendicular to the a-axis. This probably accounts for the perfect cleavage of the crystals along the a plane.

The atoms I_A, I_B, S_{1A}, and C_{1A} lie nearly in the same plane, and S_{2A} lies 1.29 Å from this plane. The bond angles at S_{1A} are, $S_2S_1C_1 = 95.0°$, $C_1S_1I_B = 85.2°$, $I_BS_1I_A = 108.0°$ and $I_AS_1S_2 = 73.4°$, and there is thus a resemblance between the environment of S_1 in the present structure and the environment of divalent tellurium in square-planar complexes.[16]

REFERENCES

1. Bergson, G. *Arkiv Kemi* **19** (1962) 181.
2. Hordvik, A. and Kjøge, H. M. *Acta Chem. Scand.* **19** (1965) 935.
3. Hordvik, A. *Acta Chem. Scand.* **19** (1965) 1039.
4. Foss, O. and Tjomsland, O. *Acta Chem. Scand.* **12** (1958) 1799.
5. Hordvik, A. and Joys, S. *Acta Chem. Scand.* **19** (1965) 1539.
6. Hordvik, A. and Sletten (Sundsfjord), J. *Acta Chem. Scand.* **19** (1965) 753; **20** (1966) 1907.
7. Klingsberg, E. *J. Am. Chem. Soc.* **83** (1961) 2934.
8. Hordvik, A. *Acta Chem. Scand.* **17** (1963) 1809.
9. *International Tables for X-ray Crystallography*, Vol. III, The Kynoch Press, Birmingham 1962, p. 204.
10. Mair, G. A. *Structure Factor and Least Squares Programs for the IBM 1620*, Pure Chemistry Division, National Research Council, Ottawa, Canada 1963.
11. Abrahams, S. C. *Quart. Rev. (London)* **10** (1956) 407.
12. Hordvik, A. *Acta Chem. Scand.* **20** (1966) 1885.
13. Brown, M. G. *Trans. Faraday Soc.* **55** (1959) 694.
14. Robertson, G. B. *Nature* **191** (1961) 593.
15. Pauling, L. *The Nature of the Chemical Bond*. 3rd Ed., Cornell University Press, Ithaca, New York 1960.
16. Foss, O. and Marøy, K. *Acta Chem. Scand.* **20** (1966) 123, and work cited there.