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

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An X-ray structure study of 4-phenyl-1,2-dithiolium thiocyanate has been carried out. The crystals belong to the space group *Pnma*, with unit cell dimensions: $a=25.41$ Å, $b=8.644$ Å, and $c=4.755$ Å. There are four formula per unit cell.

The structure was solved from Patterson and Fourier projections, and the atomic parameters were refined by least squares methods using anisotropic temperature factors. The refinement comprises the $hk0$-$hk3$ and $h0l$ reflections.

The 4-phenyl-1,2-dithiolium ion is planar within the error and lies across a crystallographic mirror plane passing through the central carbon atoms and the midpoint of the S–S bond.

There is pronounced conjugation in the 1,2-dithiolium ring, also extending over the sulphur-sulphur bond; the bond lengths in the ring are, C–C=1.388±0.013 Å, C–S=1.678±0.008 Å, and S–S=2.004±0.005 Å.

The C–C bond connecting the 1,2-dithiolium ring and the benzene ring is 1.498±0.013 Å, and reckoned from this bond the C–C bonds in the benzene ring are, 1.396, 1.388, and 1.391±0.013 Å, respectively.

The dimensions of the thiocyanate ion are, C–N=1.179±0.013 Å, C–S=1.598±0.008 Å, and N–C–S=177.6±0.4°.

In the crystal, the nitrogen atom of the thiocyanate ion approaches the two sulphur atoms of the disulphide group in a triangular arrangement, at N···S distances of 2.871±0.008 Å. The partial bonding between nitrogen and sulphur in this arrangement may be rationalized as involving weak triangular three-center two-electron bonds.

X-Ray structure analyses of 4-phenyl-1,2-dithiolium halides [1-3] have shown that partial bonding occurs in these salts between the halide ions and the sulphur atoms of the disulphide group. The found, nearly linear X···S–S···X arrangements may be envisaged as established through transfer of charge from the halide ions into the antibonding S–S σ-orbital. The halide ions, furthermore, approach the disulphide group of a neighbouring 4-phenyl-1,2-dithiolium ion, equidistant to the two sulphur atoms of the disulphide group and near the plane of the group, in a triangular three-center arrangement.

The present structure analysis of 4-phenyl-1,2-dithiolium thiocyanate was undertaken in order to find how the nitrogen and sulphur of the thiocyanate ion interact with the disulphide group.

EXPERIMENTAL

A sample of 4-phenyl-1,2-dithiolium thiocyanate was generously supplied by Klingsberg.[4] Crystal data on the compound have been reported earlier.[5] It crystallizes from water as brownish needles and thin flakes elongated along the c axis. The crystals are orthorhombic, *Pnma*, and the unit cell dimensions are, $a = 25.41$ Å, $b = 8.644$ Å, and $c = 4.755$ Å, to within 0.2 %. There are four formula units in the unit cell; density, calc. 1.46, found 1.47 g/cm^3.

The intensities of the $hk0$-$hk3$ and $h0l$ reflections were estimated visually from Weissenberg photographs taken with Cu$K\alpha$ radiation. Small crystals of cross-section 0.1 × 0.05 mm were used in order to minimize absorption effects, and no absorption correction was applied. 779 reflections were observed and measured. The intensities were corrected in the usual way to give sets of relative structure factors. Common reflections in $hk0$-$hk3$ 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, nitrogen, carbon, and hydrogen which are given in the *International Tables*,[6] the first set of the listed scattering factors for carbon being used.

DETERMINATION OF THE STRUCTURE

The structure of 4-phenyl-1,2-dithiolium thiocyanate was first solved in the c-axis projection. Approximate x and y coordinates for the sulphur atoms were found from the Patterson c-projection, and the positions of the carbon atoms in the 4-phenyl-1,2-dithiolium ion were estimated by taking into account that 4-phenyl-1,2-dithiolium thiocyanate is isomorphous with the 4-phenyl-1,2-dithiolium halides;[1-3] the structures of the latter were already known. From the subsequent Fourier map the nitrogen and carbon atoms of the thiocyanate ion could be located, and the atomic z-coordinates were thereafter estimated from the Patterson b-projection.

The structure was refined by least squares methods on an IBM 1620II computer using a program designed by Mair.[7] Weigthing scheme No. 3, recommended by Mair, was used, with $a = 12$ and $b = 7.5$. The refinement comprises the $hk0$-$hk3$ and $hk0$ reflections, and was carried out with anisotropic temperature factors for all atoms except the hydrogens which were given isotropic temperature factors. Final value for the agreement factor $R = \sum||F_o| - |F_c||/\sum|F_o|$ is 0.10.

Atomic coordinates and components of atomic vibration tensors are given in Tables 1 and 2, respectively. The observed and calculated structure factors are listed in Table 6. Six low order reflections, supposed to be affected by secondary extinction, were exluded from the least squares refinement. These reflections, marked with asterisks in Table 6, were included in the final structure factor calculations with $F_o = F_c$.

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

	x	y	z
S_1	−0.14270	0.25000	−0.87448
S_2	0.03410	0.13411	−0.24427
C_1	0.08285	0.11615	−0.00850
C_2	0.10533	0.25000	0.09885
C_3	0.14895	0.25000	0.31082
C_4	0.16911	0.11039	0.41193
C_5	0.20898	0.11128	0.61151
C_6	0.22910	0.25000	0.71353
C_7	−0.08533	0.25000	−0.73694
N	−0.04383	0.25000	−0.62587
H_1	0.096	0.002	0.062
H_2	0.155	0.003	0.371
H_3	0.223	0.013	0.660
H_4	0.258	0.250	0.848

DISCUSSION

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. 1. 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 the hydrogen atoms and with triple weight on the sulphur atoms, is

$$-0.6745\,X+0.7398\,Z+1.4476=0$$

where X and Z are in Å units. The atoms of the 1,2-dithiolium ring, S_2, C_1, and C_2 lie 0.005, −0.005, 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

Table 2. Components of atomic vibration tensors U^r in Å², referred to crystallographic axes.

	U_{11}	U_{22}	U_{33}	U_{12}	U_{23}	U_{13}
S_1	0.0589	0.0417	0.0970	0.0000	0.0000	−0.0326
S_2	0.0432	0.0466	0.0483	−0.0016	−0.0067	−0.0115
C_1	0.0553	0.0399	0.0301	0.0021	−0.0054	−0.0084
C_2	0.0340	0.0362	0.0323	0.0000	0.0000	0.0047
C_3	0.0356	0.0408	0.0268	0.0000	0.0000	0.0023
C_4	0.0448	0.0443	0.0514	0.0049	0.0004	−0.0050
C_5	0.0461	0.0577	0.0557	0.0098	0.0093	−0.0098
C_6	0.0370	0.0760	0.0331	0.0000	0.0000	0.0020
C_7	0.0592	0.0444	0.0664	0.0000	0.0000	0.0018
N	0.0631	0.1087	0.0752	0.0000	0.0000	−0.0249

Isotropic temperature factors exp $[-B\,(\sin^2\theta/\lambda^2)]$ were used for the hydrogen atoms with B equal to 4.0, 4.1, 5.7, and 4.0 for H_1, H_2, H_3, and H_4, respectively.

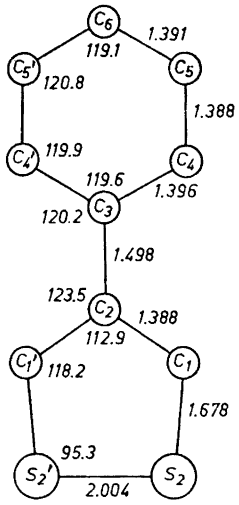

Fig. 1. Bond lengths (Å) and bond angles (°) in the 4-phenyl-1,2-dithiolium ion.

are −0.019, −0.009, −0.007, and 0.020 Å, respectively. There is thus no significant deviation of the atoms from the least squares plane.

From Table 3 the bonds in the 1,2-dithiolium ring of the present structure are, S—S = 2.004±0.005 Å, S—C = 1.678±0.008 Å, and C—C = 1.388± 0.013 Å. These bonds are significantly shorter than single bonds, and hence the ring is stabilized through π-orbital delocalization.

The lengths of the different bonds in the 1,2-dithiolium ring from the structure studies of 4-phenyl-1,2-dithiolium iodide,[1] bromide,[2] and chloride

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

	l (Å)	$\sigma(l)$ (Å)
4-Phenyl-1,2-dithiolium ion.		
S_2-S_2'	2.004	0.005
S_2-C_1	1.678	0.008
C_1-C_2	1.388	0.013
C_2-C_3	1.498	0.013
C_3-C_4	1.396	0.013
C_4-C_5	1.388	0.013
C_5-C_6	1.391	0.013
H_1-C_1	1.09	0.1
H_2-C_4	1.02	0.1
H_3-C_5	0.95	0.1
H_4-C_6	0.97	0.1
Thiocyanate ion.		
S_1-C_7	1.598	0.008
C_7-N	1.179	0.012

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

4-Phenyl-1,2-dithiolium ion.		
$C_1-S_2-S_2'$	95.3°	0.3°
$S_2-C_1-C_2$	118.2	0.4
$C_1-C_2-C_3$	123.5	0.6
$C_1-C_2-C_1'$	112.9	0.6
$C_2-C_3-C_4$	120.2	0.6
$C_4-C_3-C_4'$	119.6	0.6
$C_3-C_4-C_5$	119.9	0.6
$C_4-C_5-C_6$	120.8	0.6
$C_5-C_6-C_5'$	119.1	0.6
Thiocyanate ion.		
S_1-C_7-N	177.6	0.4

monohydrate [3] are listed in Table 5. From the values given there, and weights inversely proportional to the respective standard deviations, the average lengths of the different bonds are, S—S = 2.019 Å, C—S = 1.680 Å, and C—C = 1.38 Å. These bond lengths may now be compared with those given above for the 1,2-dithiolium ring of the present structure. The C—C and C—S bonds agree well, but the difference in the S—S bond lengths, 3.0 standard deviations, may be real. This is discussed below in connection with the environment of the disulphide group.

Table 5. S—S, C—S and C—C bond lengths in the 1,2-dithiolium ring from the structure studies of 4-phenyl-1,2-dithiolium iodide,[1] bromide,[2] and chloride monohydrate.[3]

Compound	S—S (Å)	C—S (Å)	C—C (Å)
4-Phenyl-1,2-dithiolium iodide	2.028 ±0.010	1.67 ±0.02	1.40 ±0.03
» » bromide	2.008 ±0.008	1.695 ±0.011	1.37 ±0.02
» » chloride·H_2O	2.021 ±0.006	1.673 ±0.009	1.384 ±0.012

Further, from Table 3, the bond which connects the 1,2-dithiolium ring and the benzene ring, C_2-C_3, is 1.498±0.013 Å. This bond length agrees with that of 1.4934±0.002 Å found for the central bond in biphenyl through an X-ray crystallographic investigation of the compound.[8] From the structure studies of 4-phenyl-1,2-dithiolium iodide, bromide, and chloride monohydrate the values 1.45±0.03 Å, 1.47±0.02 Å, and 1.479±0.013 Å, respectively, have been found for the length of the central C—C bond. A bond length of 1.466 Å has been proposed for a single bond between two sp^2-hybridized carbon atoms.[9]

The bond lengths in the benzene ring of the present structure, $C_3-C_4 = 1.396\pm0.013$ Å, $C_4-C_5 = 1.388\pm0.013$ Å, and $C_5-C_6 = 1.391\pm0.013$ Å, agree with the accepted value, 1.397 Å, for the aromatic C—C bond, and

Table 6. Observed and calculated *hk*0-*hk*3 and *h*0*l* structure factors for 4-phenyl-1,2-dithiolium thiocyanate, based on four asymmetric units. Reflections marked with asterisks were excluded from the refinement because of assumed secondary extinction.

H	K	L	F_o	F_c
2	0	0	*28.96	28.96
4	0	0	9.11	6.59
6	0	0	13.88	11.97
8	0	0	14.63	12.54
10	0	0	33.35	32.40
12	0	0	22.92	21.56
14	0	0	13.16	11.23
16	0	0	41.52	45.04
18	0	0	21.70	22.26
20	0	0	3.21	2.77
22	0	0	5.60	5.40
24	0	0	6.28	6.74
26	0	0	7.14	7.74
28	0	0	11.02	13.05
30	0	0	4.87	6.77
32	0	0	< 0.91	0.15
2	1	0	25.57	28.40
4	1	0	8.23	7.89
6	1	0	*52.04	52.04
8	1	0	0.93	0.80
10	1	0	16.25	16.15
12	1	0	26.89	24.48
14	1	0	21.35	15.27
16	1	0	18.80	15.11
18	1	0	10.79	8.36
20	1	0	1.69	0.47
22	1	0	18.45	16.31
24	1	0	12.99	12.29
26	1	0	3.85	3.85
28	1	0	3.70	3.13
30	1	0	< 1.26	0.13
32	1	0	2.86	3.10
0	2	0	*63.80	63.80
2	2	0	9.28	7.93
4	2	0	21.18	21.54
6	2	0	< 0.93	1.59
8	2	0	17.16	17.33
10	2	0	20.23	23.03
12	2	0	8.58	7.73
14	2	0	5.67	6.10
16	2	0	10.84	10.10
18	2	0	10.29	8.94
20	2	0	7.60	6.71
22	2	0	7.51	7.42
24	2	0	8.67	7.84
26	2	0	3.87	3.31
28	2	0	4.63	4.56
30	2	0	< 1.20	0.42
32	2	0	< 0.72	1.98
2	3	0	48.20	51.64
4	3	0	14.66	13.48
6	3	0	27.65	27.40
8	3	0	26.51	27.90
10	3	0	4.33	4.22
12	3	0	< 1.36	0.67
14	3	0	2.56	3.17
16	3	0	10.13	10.74
18	3	0	12.64	12.93
20	3	0	14.43	13.95
22	3	0	16.32	15.03
24	3	0	2.47	1.80
26	3	0	< 1.59	0.63
28	3	0	2.37	3.35
30	3	0	4.28	4.60
0	4	0	16.48	15.06
2	4	0	25.60	24.77
4	4	0	34.11	36.39
6	4	0	7.86	6.03
8	4	0	27.04	26.75
10	4	0	5.87	6.21
12	4	0	10.31	11.89
14	4	0	22.66	25.36
16	4	0	13.17	14.43
18	4	0	6.22	5.99
20	4	0	13.35	15.06
22	4	0	6.28	6.65
24	4	0	17.31	16.77
26	4	0	2.74	2.61
28	4	0	3.88	4.23
30	4	0	5.87	6.52
2	5	0	27.21	25.67
4	5	0	19.62	17.85
6	5	0	20.20	18.75
8	5	0	25.34	27.07
10	5	0	12.63	13.00
12	5	0	2.43	2.16
14	5	0	2.24	2.24
16	5	0	5.59	6.39
18	5	0	8.58	10.41
20	5	0	13.32	15.72
22	5	0	11.95	12.63
24	5	0	3.39	3.58
26	5	0	2.90	3.24
28	5	0	1.64	2.17
0	6	0	24.98	23.43
2	6	0	11.03	10.74
4	6	0	18.68	18.52
6	6	0	< 1.61	1.41
8	6	0	5.22	4.74
10	6	0	4.79	4.22
12	6	0	4.16	5.11
14	6	0	10.22	12.27
16	6	0	< 1.76	1.88
18	6	0	< 1.73	0.94
20	6	0	5.22	5.84
22	6	0	2.51	2.68
24	6	0	2.71	3.07
26	6	0	< 1.04	1.22
2	7	0	5.41	5.09
4	7	0	2.43	1.97
6	7	0	14.33	13.03
8	7	0	2.77	3.25
10	7	0	< 1.76	0.70
12	7	0	8.14	8.15
14	7	0	4.09	4.78
16	7	0	5.47	6.51
18	7	0	2.39	2.82
20	7	0	2.05	2.83
22	7	0	5.52	6.19
24	7	0	3.38	3.58
0	8	0	38.15	34.11
2	8	0	9.82	7.76
4	8	0	3.05	3.00
6	8	0	4.57	4.04
8	8	0	< 5.54	0.06
10	8	0	8.41	8.52
12	8	0	5.14	5.37
14	8	0	2.11	2.54
16	8	0	10.32	12.78
18	8	0	7.25	8.06
20	8	0	< 1.14	0.68
22	8	0	2.06	2.16
2	9	0	< 1.66	0.81
4	9	0	8.85	8.41
6	9	0	11.04	11.20
8	9	0	4.63	4.17
10	9	0	5.57	6.34
12	9	0	5.78	7.57
14	9	0	2.14	2.20
16	9	0	4.91	5.68
18	9	0	2.55	3.13
0	10	0	9.21	8.33
2	10	0	3.90	3.96
4	10	0	2.20	2.22
6	10	0	1.69	2.00
8	10	0	4.74	4.52
10	10	0	4.37	5.10
12	10	0	3.30	3.84
14	10	0	< 0.71	0.49
2	11	0	4.06	5.40
4	11	0	< 0.70	0.46
1	0	1	16.12	14.96
2	0	1	*36.30	36.30
3	0	1	8.40	9.74
4	0	1	*39.76	39.76
5	0	1	*48.29	48.29
6	0	1	*62.58	62.58
7	0	1	7.31	8.76
8	0	1	21.57	26.90
9	0	1	11.46	11.98
10	0	1	*45.53	45.53
11	0	1	7.22	6.07
12	0	1	3.70	3.12
13	0	1	6.28	6.57
14	0	1	2.82	2.42
15	0	1	7.44	6.82
16	0	1	4.73	3.63
17	0	1	10.76	9.54
18	0	1	18.97	18.12
19	0	1	11.42	10.98
20	0	1	23.97	23.78
21	0	1	8.23	7.09
22	0	1	15.65	14.88
23	0	1	3.61	3.35
24	0	1	10.95	9.77
25	0	1	4.23	3.79
26	0	1	7.99	6.85
27	0	1	4.01	3.47
28	0	1	< 1.57	1.19
29	0	1	< 1.44	0.19
30	0	1	2.46	1.83
31	0	1	< 1.09	0.25
32	0	1	2.02	2.25
0	1	1	3.24	3.00
1	1	1	21.90	21.31
2	1	1	15.47	16.89
3	1	1	22.82	23.06
4	1	1	51.01	62.72
5	1	1	25.78	33.26
6	1	1	7.37	7.42
7	1	1	11.18	11.46
8	1	1	5.97	6.71
9	1	1	14.72	15.40
10	1	1	3.48	3.19
11	1	1	5.64	5.55
12	1	1	22.20	24.75
13	1	1	13.05	13.00
14	1	1	21.07	22.32
15	1	1	6.75	7.01
16	1	1	11.35	10.64
17	1	1	1.67	1.80
18	1	1	5.04	4.66
19	1	1	< 1.80	0.66
20	1	1	13.49	12.86
21	1	1	< 1.88	0.51
22	1	1	2.67	2.23
23	1	1	3.08	2.62
24	1	1	8.08	6.65
25	1	1	< 1.82	1.69
26	1	1	6.09	5.48
27	1	1	3.72	3.48
28	1	1	2.37	2.52
29	1	1	< 1.41	0.50
30	1	1	7.72	7.64
31	1	1	1.36	1.49
32	1	1	< 0.74	5.10
1	2	1	6.59	5.53
2	2	1	19.44	19.24
3	2	1	20.84	21.57
4	2	1	8.63	6.85
5	2	1	4.85	4.16
6	2	1	8.24	6.69
7	2	1	15.04	14.82
8	2	1	10.72	9.23
9	2	1	5.21	4.94
10	2	1	5.39	5.63
11	2	1	3.79	3.15
12	2	1	8.63	8.99
13	2	1	< 1.49	2.15
14	2	1	5.74	5.24
15	2	1	5.28	4.79
16	2	1	2.90	2.46
17	2	1	4.37	3.70
18	2	1	1.37	1.84
19	2	1	< 1.83	0.28
20	2	1	9.95	8.79
21	2	1	2.17	1.85
22	2	1	2.67	1.98
23	2	1	2.47	1.63
24	2	1	< 1.84	0.97
25	2	1	4.85	4.26
26	2	1	< 1.71	0.89
27	2	1	< 1.62	0.01
28	2	1	< 1.49	0.79
29	2	1	3.50	3.49
30	2	1	< 1.18	0.06
31	2	1	0.95	0.75
0	3	1	56.08	50.01
1	3	1	3.73	2.26
2	3	1	28.05	25.51
3	3	1	14.55	13.64
4	3	1	5.87	5.66
5	3	1	5.89	6.13
6	3	1	8.80	8.35
7	3	1	11.25	10.21
8	3	1	< 1.32	0.20
9	3	1	9.91	9.60
10	3	1	12.81	13.06
11	3	1	8.68	8.42
12	3	1	18.46	18.75
13	3	1	5.95	5.69
14	3	1	1.89	1.78
15	3	1	11.28	11.41
16	3	1	16.92	17.54
17	3	1	11.61	11.90
18	3	1	16.52	16.61
19	3	1	7.86	7.34
20	3	1	7.56	7.00
21	3	1	6.47	5.50
22	3	1	< 1.88	0.29
23	3	1	5.01	4.58
24	3	1	< 1.80	0.94
25	3	1	4.46	4.08
26	3	1	5.08	4.38
27	3	1	1.52	0.84
28	3	1	8.27	8.41
29	3	1	1.74	1.11
30	3	1	< 1.03	0.60
1	4	1	2.15	1.36
2	4	1	4.41	2.61
3	4	1	23.94	22.18
4	4	1	21.84	21.04
5	4	1	8.68	7.02
6	4	1	27.16	27.23
7	4	1	12.92	12.24
8	4	1	18.03	16.66
9	4	1	2.64	1.94
10	4	1	19.33	20.72
11	4	1	4.93	5.05
12	4	1	18.87	19.11
13	4	1	2.78	2.32
14	4	1	2.67	2.59
15	4	1	2.73	2.42
16	4	1	4.09	4.23
17	4	1	< 1.85	0.73
18	4	1	12.36	12.66
19	4	1	7.34	6.09
20	4	1	6.18	5.85
21	4	1	< 1.87	0.09
22	4	1	11.18	10.83
23	4	1	< 1.78	0.26
24	4	1	11.47	10.95
25	4	1	4.85	4.50
26	4	1	5.57	5.14
27	4	1	1.36	1.34
28	4	1	3.07	2.64
29	4	1	4.43	5.21
30	4	1	< 0.69	1.09
0	5	1	37.98	38.78
1	5	1	5.42	4.24
2	5	1	25.26	23.00
3	5	1	5.63	4.29
4	5	1	< 1.55	0.67
5	5	1	8.40	7.82
6	5	1	10.28	9.85
7	5	1	2.65	1.86
8	5	1	< 1.65	0.27
9	5	1	8.40	6.88
10	5	1	15.19	14.52
11	5	1	5.46	4.97
12	5	1	14.79	14.70
13	5	1	5.03	4.88
14	5	1	7.62	7.61
15	5	1	7.25	8.18
16	5	1	15.99	17.86
17	5	1	6.65	7.04
18	5	1	13.82	14.70
19	5	1	4.56	4.55
20	5	1	1.84	2.12
21	5	1	< 1.80	2.64
22	5	1	< 1.73	0.39
23	5	1	2.69	2.28
24	5	1	< 1.55	1.22
25	5	1	2.04	1.61
26	5	1	5.07	4.89
27	5	1	< 1.14	0.17
28	5	1	7.25	8.16
1	6	1	5.24	4.57
2	6	1	4.55	3.15
3	6	1	4.46	2.95
4	6	1	5.50	5.14
5	6	1	8.36	8.08
6	6	1	5.40	5.33
7	6	1	5.93	5.44
8	6	1	5.99	5.85
9	6	1	2.78	2.31
10	6	1	2.37	2.02
11	6	1	3.88	2.95
12	6	1	8.34	8.50

Table 6. Continued.

H	K	L	F_o	F_c
13	6	1	< 1.88	1.37
14	6	1	< 1.88	0.48
15	6	1	3.27	2.78
16	6	1	5.53	5.62
17	6	1	2.83	2.80
18	6	1	< 1.87	1.08
19	6	1	2.51	2.45
20	6	1	1.97	1.29
21	6	1	4.01	3.68
22	6	1	3.69	3.39
23	6	1	< 1.44	0.63
24	6	1	3.14	3.33
25	6	1	2.25	2.42
26	6	1	1.71	1.68
27	6	1	< 0.67	1.99
0	7	1	4.41	4.20
1	7	1	8.66	7.06
2	7	1	4.80	3.42
3	7	1	6.37	5.89
4	7	1	16.99	15.13
5	7	1	11.93	10.99
6	7	1	3.91	4.00
7	7	1	5.66	5.05
8	7	1	4.08	3.27
9	7	1	6.75	6.42
10	7	1	3.45	3.46
11	7	1	2.44	2.23
12	7	1	7.37	7.71
13	7	1	5.69	5.79
14	7	1	6.28	6.00
15	7	1	2.07	2.13
16	7	1	1.75	0.97
17	7	1	< 1.71	0.00
18	7	1	< 1.64	0.06
19	7	1	< 1.57	0.11
20	7	1	3.92	3.60
21	7	1	1.59	1.09
22	7	1	< 1.26	0.87
23	7	1	1.12	1.06
24	7	1	3.02	3.10
25	7	1	< 0.56	1.69
1	8	1	6.26	5.27
2	8	1	9.38	8.08
3	8	1	< 1.88	0.62
4	8	1	9.34	7.89
5	8	1	7.73	7.19
6	8	1	11.31	10.58
7	8	1	2.39	2.31
8	8	1	9.69	8.98
9	8	1	1.82	2.00
10	8	1	9.48	10.21
11	8	1	< 1.77	0.51
12	8	1	< 1.73	0.70
13	8	1	1.68	1.53
14	8	1	1.64	1.32
15	8	1	2.04	1.76
16	8	1	1.51	1.74
17	8	1	3.53	3.69
18	8	1	5.11	5.52
19	8	1	3.13	3.06
20	8	1	7.22	7.62
21	8	1	2.15	2.62
22	8	1	< 0.70	4.94
0	9	1	3.74	3.08
1	9	1	2.64	1.96
2	9	1	8.22	7.91
3	9	1	< 1.71	0.48
4	9	1	11.72	11.69
5	9	1	4.68	3.94
6	9	1	< 1.66	0.31
7	9	1	< 1.64	0.80
8	9	1	2.95	2.88
9	9	1	4.18	4.19
10	9	1	1.53	1.60
11	9	1	1.92	2.07
12	9	1	5.50	6.51
13	9	1	3.62	3.66
14	9	1	7.76	8.84
15	9	1	1.71	1.46
16	9	1	3.74	4.18
17	9	1	1.26	1.45
18	9	1	1.38	1.65
1	10	1	2.11	1.65
2	10	1	3.80	3.96
3	10	1	4.15	4.41
4	10	1	2.44	2.75
5	10	1	< 1.31	0.61
6	10	1	2.22	2.99
7	10	1	3.13	2.99
8	10	1	4.40	5.11
9	10	1	< 1.14	0.35
10	10	1	1.97	2.33
11	10	1	1.41	1.28
12	10	1	< 0.89	0.30
13	10	1	< 0.73	0.18
0	0	2	*30.78	30.78
1	0	2	< 6.12	6.30
2	0	2	25.01	25.01
3	0	2	7.35	8.45
4	0	2	*31.26	31.26
5	0	2	*34.88	34.88
6	0	2	12.68	14.16
7	0	2	10.17	10.06
8	0	2	1.90	2.99
9	0	2	17.65	20.04
10	0	2	21.16	22.54
11	0	2	18.52	19.80
12	0	2	22.83	23.77
13	0	2	5.72	5.32
14	0	2	20.11	20.00
15	0	2	9.12	8.85
16	0	2	22.02	21.29
17	0	2	9.01	8.23
18	0	2	14.38	12.19
19	0	2	3.97	2.68
20	0	2	3.69	2.72
21	0	2	1.93	2.86
22	0	2	< 1.92	0.20
23	0	2	3.92	2.92
24	0	2	< 1.83	0.78
25	0	2	3.66	2.94
26	0	2	12.37	11.16
27	0	2	3.78	3.35
28	0	2	8.23	7.02
29	0	2	< 1.23	1.09
30	0	2	5.79	5.41
31	0	2	< 0.60	1.34
1	1	2	< 0.88	1.08
2	1	2	< 0.92	0.54
3	1	2	16.70	16.80
4	1	2	8.15	7.72
5	1	2	4.90	4.88
6	1	2	19.78	22.87
7	1	2	< 1.22	1.46
8	1	2	23.04	28.19
9	1	2	14.97	15.49
10	1	2	24.85	29.76
11	1	2	9.43	9.25
12	1	2	3.33	2.68
13	1	2	4.55	3.92
14	1	2	4.51	3.99
15	1	2	9.33	8.80
16	1	2	7.79	6.75
17	1	2	5.20	4.93
18	1	2	5.84	5.18
19	1	2	2.69	2.34
20	1	2	11.10	10.51
21	1	2	6.00	5.42
22	1	2	6.63	5.77
23	1	2	3.25	2.15
24	1	2	7.87	6.48
25	1	2	4.72	4.09
26	1	2	6.98	6.45
27	1	2	2.91	2.20
28	1	2	2.87	2.23
29	1	2	2.96	2.74
0	2	2	19.41	18.11
1	2	2	8.11	7.73
2	2	2	1.82	0.67
3	2	2	3.75	2.06
4	2	2	2.65	1.67
5	2	2	18.84	18.61
6	2	2	2.43	1.04
7	2	2	1.32	0.61
8	2	2	2.10	1.46
9	2	2	10.19	10.16
10	2	2	5.31	4.52
11	2	2	7.05	6.96
12	2	2	4.16	4.28
13	2	2	10.24	9.69
14	2	2	< 1.71	1.74
15	2	2	11.39	10.78
16	2	2	8.83	8.74
17	2	2	8.84	8.32
18	2	2	4.25	2.67
19	2	2	7.46	6.68
20	2	2	< 1.93	0.50
21	2	2	2.22	1.30
22	2	2	< 1.89	0.23
23	2	2	3.54	3.28
24	2	2	< 1.78	0.71
25	2	2	1.68	1.28
26	2	2	4.49	4.18
27	2	2	2.37	2.39
28	2	2	< 1.30	0.13
29	2	2	2.50	1.71
1	3	2	9.76	8.65
2	3	2	3.48	2.05
3	3	2	13.98	12.80
4	3	2	9.51	15.70
5	3	2	8.17	7.11
6	3	2	5.21	12.19
7	3	2	16.71	16.27
8	3	2	15.52	15.13
9	3	2	2.68	1.70
10	3	2	11.30	10.65
11	3	2	< 1.66	0.22
12	3	2	10.93	12.24
13	3	2	5.92	5.69
14	3	2	< 1.80	1.73
15	3	2	5.32	5.05
16	3	2	4.73	4.17
17	3	2	< 1.90	0.68
18	3	2	9.11	8.31
19	3	2	4.73	4.66
20	3	2	6.38	5.51
21	3	2	2.89	1.95
22	3	2	4.77	3.97
23	3	2	2.91	1.78
24	3	2	6.68	6.21
25	3	2	4.99	4.90
26	3	2	4.45	3.78
27	3	2	< 1.34	1.09
28	3	2	< 1.16	0.94
29	3	2	2.42	2.52
0	4	2	6.61	5.59
1	4	2	6.68	6.10
2	4	2	24.49	23.08
3	4	2	6.36	4.97
4	4	2	19.54	18.15
5	4	2	12.65	11.44
6	4	2	11.55	10.59
7	4	2	2.29	2.09
8	4	2	2.88	1.57
9	4	2	7.01	6.72
10	4	2	9.84	9.28
11	4	2	2.90	2.86
12	4	2	21.89	24.87
13	4	2	15.72	16.72
14	4	2	18.80	20.81
15	4	2	9.60	9.26
16	4	2	7.70	6.55
17	4	2	6.11	5.71
18	4	2	8.33	7.47
19	4	2	8.27	7.99
20	4	2	3.25	2.65
21	4	2	4.35	3.36
22	4	2	< 1.75	0.75
23	4	2	2.90	2.98
24	4	2	2.41	2.16
25	4	2	< 1.45	0.08
26	4	2	2.52	2.46
27	4	2	1.32	0.90
28	4	2	6.43	6.77
1	5	2	7.65	5.89
2	5	2	5.98	4.91
3	5	2	9.38	8.49
4	5	2	18.30	15.14
5	5	2	4.61	4.01
6	5	2	17.85	15.72
7	5	2	9.29	8.46
8	5	2	16.05	15.35
9	5	2	< 1.84	2.26
10	5	2	10.53	10.77
11	5	2	< 1.88	1.39
12	5	2	11.70	11.41
13	5	2	2.93	3.02
14	5	2	< 1.93	1.27
15	5	2	< 1.93	0.20
16	5	2	3.51	3.47
17	5	2	1.90	1.80
18	5	2	8.94	8.74
19	5	2	2.98	2.95
20	5	2	7.31	6.47
21	5	2	2.19	1.85
22	5	2	7.08	6.99
23	5	2	3.13	2.51
24	5	2	6.72	7.06
25	5	2	3.64	3.96
26	5	2	3.96	3.71
27	5	2	< 0.77	0.48
0	6	2	4.90	4.30
1	6	2	5.25	4.94
2	6	2	7.04	6.39
3	6	2	2.84	2.40
4	6	2	3.90	3.16
5	6	2	11.77	10.49
6	6	2	3.27	1.49
7	6	2	3.80	3.27
8	6	2	< 1.91	1.40
9	6	2	9.22	8.98
10	6	2	< 1.93	0.12
11	6	2	8.28	7.27
12	6	2	5.34	5.28
13	6	2	4.30	3.16
14	6	2	5.27	5.43
15	6	2	4.85	4.37
16	6	2	< 1.84	1.19
17	6	2	2.54	2.23
18	6	2	1.74	2.14
19	6	2	3.73	3.34
20	6	2	3.29	2.72
21	6	2	< 1.48	1.39
22	6	2	< 1.37	0.71
23	6	2	2.37	2.06
24	6	2	2.70	2.58
25	6	2	< 0.83	0.59
1	7	2	< 1.93	1.16
2	7	2	2.73	2.67
3	7	2	7.23	5.80
4	7	2	< 1.93	0.13
5	7	2	2.22	2.39
6	7	2	4.16	3.94
7	7	2	< 1.92	0.67
8	7	2	8.14	7.81
9	7	2	6.23	6.22
10	7	2	9.78	9.22
11	7	2	5.06	4.55
12	7	2	< 1.84	0.35
13	7	2	< 1.80	1.10
14	7	2	3.82	3.71
15	7	2	5.05	5.57
16	7	2	2.52	2.48
17	7	2	3.29	3.14
18	7	2	< 1.49	0.92
19	7	2	1.62	1.68
20	7	2	3.08	2.68
21	7	2	2.41	2.89
22	7	2	< 0.98	0.20
23	7	2	< 0.70	1.62
0	8	2	9.56	8.38
1	8	2	3.87	3.54
2	8	2	8.45	6.97
3	8	2	3.38	2.77
4	8	2	8.32	7.34
5	8	2	7.40	7.03
6	8	2	4.57	4.33
7	8	2	4.28	3.69
8	8	2	< 1.76	0.18
9	8	2	6.36	6.56
10	8	2	6.54	6.63
11	8	2	4.81	4.55
12	8	2	6.86	7.14
13	8	2	< 1.56	0.08
14	8	2	5.85	5.98
15	8	2	3.17	3.28
16	8	2	6.45	6.88
17	8	2	2.36	2.59
18	8	2	3.86	3.80
19	8	2	2.22	2.13
20	8	2	< 0.69	0.15
1	9	2	1.85	1.97
2	9	2	2.92	2.54
3	9	2	4.20	3.74
4	9	2	4.16	3.61
5	9	2	< 1.55	1.89
6	9	2	6.54	7.22
7	9	2	2.86	2.46
8	9	2	7.67	8.46
9	9	2	< 1.41	0.85
10	9	2	6.67	7.69
11	9	2	2.69	2.55
12	9	2	1.88	1.88
13	9	2	1.14	0.86
14	9	2	< 1.04	0.42
15	9	2	< 0.90	0.70
16	9	2	< 0.67	1.49
0	10	2	6.23	6.54
1	10	2	< 1.15	1.66
2	10	2	2.55	2.65
3	10	2	1.13	0.27
4	10	2	1.41	1.29
5	10	2	2.54	2.76
6	10	2	< 1.01	0.65
7	10	2	0.96	0.01
8	10	2	1.34	1.47
9	10	2	< 0.77	2.36
1	0	3	< 8.41	6.48
2	0	3	10.20	10.50
3	0	3	3.30	2.56
4	0	3	16.06	18.56
5	0	3	2.41	1.79
6	0	3	16.82	19.82
7	0	3	13.10	15.11
8	0	3	16.22	17.43
9	0	3	1.71	0.65
10	0	3	8.05	7.49
11	0	3	3.20	2.59
12	0	3	15.84	16.64
13	0	3	4.27	3.87
14	0	3	11.07	11.67
15	0	3	< 2.06	0.30
16	0	3	16.64	15.48

Table 6. Continued.

H	K	L		F_o	F_c
17	0	3	<	2.17	0.38
18	0	3		6.29	4.37
19	0	3	<	2.12	0.10
20	0	3		8.99	7.39
21	0	3	<	2.04	1.01
22	0	3		12.08	11.33
23	0	3		7.63	5.73
24	0	3		10.31	10.10
25	0	3		5.36	4.79
26	0	3		4.10	3.96
27	0	3	<	1.28 -	0.68
28	0	3		1.42	1.57
0	1	3		27.76 -	27.15
1	1	3		13.37 -	12.06
2	1	3		16.66 -	14.72
3	1	3		1.31 -	1.23
4	1	3		6.07 -	5.61
5	1	3		8.49	8.00
6	1	3		9.20 -	8.45
7	1	3		2.26 -	2.03
8	1	3		2.55 -	2.71
9	1	3	<	1.75	0.54
10	1	3		13.64	14.44
11	1	3		8.75	8.71
12	1	3		11.33	12.84
13	1	3		6.72	5.77
14	1	3		15.60	15.44
15	1	3		9.57 -	8.82
16	1	3		10.09	8.49
17	1	3	<	2.13	0.02
18	1	3		4.94	4.33
19	1	3		5.05	4.32
20	1	3		4.51	4.12
21	1	3	<	2.03 -	1.13
22	1	3		3.39 -	3.60
23	1	3		3.57 -	3.02
24	1	3	<	1.75	0.39
25	1	3		1.86	0.98
26	1	3		4.02 -	3.13
27	1	3		2.04 -	1.95
28	1	3		4.91 -	5.52
1	2	3	<	1.47 -	0.08
2	2	3		1.49 -	1.96
3	2	3		5.21 -	4.24
4	2	3		6.95	4.56
5	2	3		2.94 -	2.77
6	2	3		7.21	6.26
7	2	3		4.55	3.97
8	2	3		9.76 -	10.24
9	2	3	<	1.84 -	0.25
10	2	3	<	1.89	0.92
11	2	3		2.24	2.07
12	2	3		7.65	7.15
13	2	3	<	2.03	1.49
14	2	3		4.81	4.78
15	2	3		3.22	2.99
16	2	3		5.08 -	4.61
17	2	3		3.01 -	2.07
18	2	3	<	2.12 -	0.39
19	2	3		2.09	0.94
20	2	3	<	2.05	1.71
21	2	3	<	1.99	0.47
22	2	3		2.20 -	1.37
23	2	3		2.08 -	1.81
24	2	3		3.22 -	3.18
25	2	3		1.76 -	1.61
26	2	3		1.35 -	0.24
27	2	3		1.13	0.07
28	2	3		0.68	0.19
0	3	3		6.35 -	3.72
1	3	3		2.94	2.04
2	3	3		15.19 -	12.26
3	3	3		4.69 -	3.37
4	3	3		7.55 -	6.37
5	3	3		9.56 -	8.89
6	3	3		8.71 -	7.76
7	3	3		4.32	3.61
8	3	3		7.96	7.55
9	3	3		12.22	13.34
10	3	3		8.24	7.24
11	3	3		4.24 -	2.72
12	3	3		2.06 -	2.73
13	3	3		2.42 -	2.32
14	3	3		10.91	12.06
15	3	3		4.77	4.49
16	3	3		6.65	6.70
17	3	3	<	2.11 -	0.91
18	3	3		4.01	3.10
19	3	3	<	2.04 -	1.73
20	3	3		6.07	5.02
21	3	3		2.90	2.15
22	3	3		1.80	1.95
23	3	3		3.91	3.54
24	3	3		5.39 -	4.81
25	3	3		5.44 -	5.49
26	3	3		4.02 -	4.15
27	3	3	<	0.83 -	1.89
1	4	3	<	1.91 -	2.69
2	4	3		10.54	9.30
3	4	3		6.94	5.46
4	4	3		9.47	8.32
5	4	3		5.90	5.58
6	4	3		10.97	10.76
7	4	3		4.02	3.47
8	4	3		28.12	29.98
9	4	3	<	2.06	0.75
10	4	3		9.75	9.85
11	4	3		4.03 -	3.82
12	4	3		3.25	2.59
13	4	3		3.48 -	3.42
14	4	3	<	2.13 -	0.92
15	4	3		5.06 -	4.68
16	4	3		3.63 -	2.94
17	4	3		2.66	2.38
18	4	3		5.45 -	4.43
19	4	3		1.94 -	1.96
20	4	3		9.52 -	10.19
21	4	3		1.75 -	1.98
22	4	3		7.56 -	7.77
23	4	3		1.94 -	1.93
24	4	3		4.66 -	4.17
25	4	3	<	1.13 -	1.06
26	4	3	<	0.74 -	3.63
0	5	3		10.04	7.42
1	5	3		3.37 -	2.84
2	5	3		15.32	12.98
3	5	3		2.68	1.61
4	5	3		10.95	10.37
5	5	3		7.65	6.77
6	5	3		6.08	5.45
7	5	3		2.44 -	2.09
8	5	3		6.50 -	6.20
9	5	3		7.99 -	8.03
10	5	3		6.29 -	5.58
11	5	3		3.01	2.60
12	5	3		4.91 -	4.20
13	5	3	<	2.11	1.21
14	5	3		10.78 -	11.00
15	5	3		5.28 -	4.71
16	5	3		8.00 -	8.25
17	5	3	<	1.93 -	0.80
18	5	3		7.38 -	5.81
19	5	3	<	1.77	1.30
20	5	3		4.52 -	3.90
21	5	3		2.52 -	1.98
22	5	3		1.80 -	2.07
23	5	3		2.33 -	2.49
24	5	3		4.03	4.27
1	6	3	<	2.13	0.10
2	6	3		2.76 -	2.21
3	6	3	<	2.13 -	0.82
4	6	3	<	2.13 -	1.00
5	6	3	<	2.13 -	0.27
6	6	3		3.48 -	2.99
7	6	3		3.68	3.40
8	6	3		7.92 -	7.86
9	6	3	<	2.10 -	0.99
10	6	3		6.71 -	6.61
11	6	3	<	2.05 -	2.02
12	6	3	<	2.02	1.61
13	6	3	<	1.98 -	1.10
14	6	3		3.35	3.51
15	6	3	<	1.87	0.09
16	6	3		4.52 -	4.62
17	6	3	<	1.71 -	0.63
18	6	3		2.63	2.60
19	6	3		1.49	1.30
20	6	3		3.68	3.88
21	6	3	<	1.18	1.07
0	7	3		8.37	7.65
1	7	3		5.48	5.56
2	7	3		3.37	2.75
3	7	3	<	2.05	1.21
4	7	3	<	2.04 -	1.43
5	7	3		4.07 -	3.85
6	7	3		4.80	3.58
7	7	3	<	2.00 -	1.43
8	7	3	<	1.97	1.61
9	7	3	<	1.93 -	1.35
10	7	3		5.37 -	5.14
11	7	3		4.54 -	4.66
12	7	3		1.79 -	2.06
13	7	3		2.64 -	2.32
14	7	3		4.89 -	5.02
15	7	3		4.54	5.02
16	7	3		1.46 -	1.23
17	7	3	<	1.35	1.05
18	7	3	<	1.21	0.28
19	7	3		1.75 -	2.14
1	8	3	<	1.83	0.46
2	8	3		3.48 -	2.90
3	8	3	<	1.81 -	0.86
4	8	3		6.63 -	6.26
5	8	3	<	1.77 -	1.38
6	8	3		6.97 -	7.32
7	8	3		4.06 -	4.58
8	8	3		4.51 -	4.91
9	8	3	<	1.62	0.38
10	8	3		2.20 -	2.46
11	8	3		1.48	1.97
12	8	3		5.21 -	6.02
13	8	3	<	1.31	1.86
14	8	3		2.50 -	2.73
15	8	3	<	1.04	0.90
16	8	3	<	0.81	5.58
0	9	3		7.15 -	7.86
1	9	3		1.60 -	2.59
2	9	3		4.24 -	4.81
3	9	3	<	1.36 -	0.41
4	9	3		2.31 -	2.71
5	9	3		1.99	2.23
6	9	3		1.92 -	2.11
7	9	3	<	1.20 -	0.11
8	9	3	<	1.13 -	1.06
9	9	3	<	1.03 -	1.20
10	9	3	<	0.89	3.00
0	0	4		11.33	9.85
1	0	4	<	5.35	0.55
2	0	4		21.91	19.05
3	0	4	<	5.37 -	2.23
4	0	4	<	12.06	11.58
5	0	4	<	5.41	0.50
6	0	4	<	5.43 -	5.77
7	0	4	<	5.43 -	1.53
8	0	4	<	5.45 -	4.10
9	0	4	<	5.45 -	3.80
10	0	4		5.43 -	4.17
11	0	4	<	5.43 -	3.30
12	0	4		5.41 -	3.13
13	0	4	<	5.36 -	0.02
14	0	4		10.22 -	10.43
15	0	4	<	5.20 -	4.10
16	0	4		7.16 -	9.28
17	0	4	<	4.92 -	0.14
18	0	4		7.08 -	9.23
19	0	4	<	4.52	2.53
20	0	4		4.75 -	7.55
21	0	4	<	3.97 -	4.78
22	0	4	<	3.62	1.95
23	0	4	<	3.22	0.71
24	0	4	<	2.65	3.98
1	0	5	<	5.07	2.92
2	0	5	<	5.05	3.62
3	0	5	<	5.03	2.59
4	0	5		7.05	9.07
5	0	5	<	4.96	3.24
6	0	5		5.99	7.97
7	0	5	<	4.83 -	3.85
8	0	5	<	4.76	5.48

the average value of the C—H bond lengths, 1.04 Å, seems quite normal for such bonds when determined by X-ray methods.

The thiocyanate ion. The lengths of the C—S and the C—N bond in the thiocyanate ion were found to be 1.598±0.008 Å and 1.179±0.013 Å, respectively, and the N—C—S angle 177.6±0.4°. There is thus a slight, but significant deviation from linearity. From the C—S and C—N bond lengths, the C—S bond is a double bond and the C—N bond almost a triple bond; the accepted lengths for a C—S double and a C—N triple bond are 1.61 Å and 1.15 Å, respectively.[10,11] In ammonium thiocyanate[12] the thiocyanate ion was found to be linear with C—S = 1.58±0.02 Å and C—N = 1.24±0.02 Å.

The environment of the disulphide group. It is the nitrogen atom of the thiocyanate ion that approaches the disulphide groups in the crystals of 4-phenyl-1,2-dithiolium thiocyanate, *cf.* Fig. 2. It does so in linear N···S—S···N and triangular S···N···S arrangements equivalent to the X···S—S···X

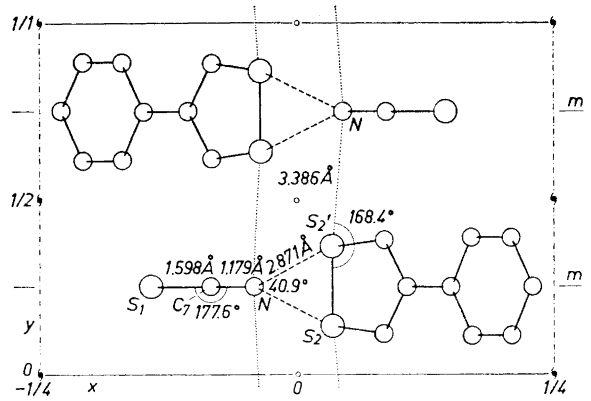

Fig. 2. The arrangement of ions in the unit cell as seen along the *c*-axis.

and S···X···S arrangements present in crystals of the 4-phenyl-1,2-dithiolium halides. The N···S—S and S—S···N angles in the linear arrangements are 168.4±0.4°, and the S···N···S angle in the triangular arrangements, where the nitrogen atom approaches both sulphur atoms of the disulphide group, is 40.9±0.4°.

The N···S distances in the N···S—S···N arrangements, 3.386±0.008 Å, are close to the corresponding van der Waals distance, 3.35 Å, and the sulphur-sulphur bond, therefore, is not subject to interaction with external atoms. This may explain why the sulphur-sulphur bond in the thiocyanate, 2.004± 0.005 Å, is found to be somewhat shorter than the sulphur-sulphur bonds in the halides (*cf.* Table 5) where halogen-sulphur close contacts occur in the X···S—S···X arrangements. One notes from Table 5 that the longest S—S bond, 2.028±0.010 Å, is found in the iodide. This, in fact, might be anticipated if one takes the electronegativities of the halogens into account and assumes that the partial bonding between halogen and sulphur is established through transfer of charge from the halide ions into the antibonding sulphur-sulphur σ-orbital.

The N···S distances in the triangular S···N···S arrangements are 0.48 Å shorter than the corresponding van der Waals distance. Thus they indicate weak bonds. The thiocyanate ion in mirror plane *m* (*cf.* Fig. 2) forms an angle of 162° with the plane of the 4-phenyl-1,2-dithiolium ion, and the nitrogen atom lies in the latter plane. Since the nitrogen atom forms weak bonds with both sulphur of the disulphide group, one may assume that electrons are partially transferred from the nitrogen atom, *e.g.* from a filled *sp*-orbital, to the sulphur atoms, *e.g.* to those *p*-orbitals of the sulphur atoms already engaged in the sulphur-carbon σ-bond, with weak three-centre two-electron bonds as result.

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REFERENCES

1. Hordvik, A. and Sletten, E. *Acta Chem. Scand.* **20** (1966) 1874.
2. Hordvik, A. and Baxter, R. M. *Acta Chem. Scand.* **23** (1969) 1082.
3. Grundtvig, F. and Hordvik, A. *Acta Chem. Scand. To be published.*
4. Klingsberg, E. *J. Am. Chem. Soc.* **83** (1961) 2934.
5. Hordvik, A., Sletten, E. and Sletten, J. *Acta Chem. Scand.* **20** (1966) 1172.
6. *International Tables for X-ray Crystallography*, Kynoch Press, Birmingham 1962, Vol III, p. 204.
7. Mair, G. A. *Structure Factor and Least Squares Programs for the IBM 1620*, Pure Chemistry Division, National Research Council, Ottawa, Canada 1963.
8. Robertson, G. B. *Nature* **191** (1961) 593.
9. Brown, M. G. *Trans. Faraday Soc.* **55** (1959) 694.
10. Abrahams, S. C. *Quart. Rev. (London)* **10** (1956) 407.
11. Pauling, L. *The Nature of the Chemical Bond*, 3rd. Ed., Cornell University Press, Ithaca, New York 1960.
12. Zvonkova, Z. and Zhdanov, G. *Zh. Fiz. Khim.* **23** (1949) 1495.

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