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

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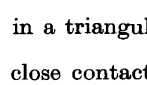
An X-ray structure study of 4-phenyl-1,2-dithiolium chloride monohydrate has been carried out. The crystals belong to the space group *Pnma*, with unit cell dimensions: $a = 26.00$ Å, $b = 9.366$ Å, and $c = 4.781$ Å. There are four formula units per unit cell.

The structure was solved from Patterson and Fourier projections and the atomic parameters were refined by least squares methods. The refinement comprises the $hk0 - hk3$ 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 = 1.384 ± 0.013 Å, C – S = 1.673 ± 0.011 Å, and S – S = 2.021 ± 0.004 Å.

The C – C bond connecting the 1,2-dithiolium ring and the benzene ring is 1.494 ± 0.013 Å, and reckoned from this bond the C – C bonds in the benzene ring are: 1.386 ± 0.016 Å, 1.390 ± 0.017 Å, and 1.376 ± 0.020 Å, respectively.

In the crystal, each chloride ion forms close contacts with four neighbouring sulphur atoms. Two of these close contacts, both 3.231 ± 0.004 Å, occur in · · · Cl · · · S – S · · · Cl · · · S – S · · · Cl · · · chains which run through the crystal in the *b*-axis direction, the Cl · · · S – S angle being 169.1 ± 0.3°, and the S · · · Cl · · · S angle 158.3 ± 0.3°. The other two short chlorine – sulphur distances, both 3.187 ± 0.004 Å, occur in a triangular  Cl arrangement where the chloride ion forms close contacts with both sulphur atoms of a disulphide group, thus interconnecting the chlorine-sulphur chains into pairs. The S · · · Cl · · · S angle in the triangular arrangement is 37.0 ± 0.2°.

The water molecule forms hydrogen bonds to two chloride ions; the O · · · Cl distances are 3.140 and 3.107 ± 0.021 Å, respectively, and the Cl · · · O · · · Cl angle is 99.9 ± 0.5°.

X-Ray structure studies of 4-phenyl-1,2-dithiolium iodide [1] and 4-phenyl-1,2-dithiolium bromide [2] have shown that in crystals of these salts there

is partial bonding between the halide ions and the sulphur atoms of the disulphide group. The partial bonding occurs in nearly linear X · · · S–S · · ·X arrangements and in triangular X(···S–)(···S–) arrangements. The linear arrangements may be established through transfer of charge from the halide ions into the antibonding S–S σ-orbital, and the triangular arrangements may be established through overlap of one filled orbital of the halide ion with two orbitals of the sulphur atoms, one from each.

The X · · · S distances in the X · · · S–S · · · X arrangements of 4-phenyl-1,2-dithiolium iodide and 4-phenyl-1,2-dithiolium bromide are about 0.50 Å shorter than the corresponding van der Waals distances,[3] and the sulphur–sulphur bonds in the two compounds are 2.028 ± 0.010 Å and 2.008 ± 0.008 Å, respectively.

In crystals of 4-phenyl-1,2-dithiolium thiocyanate,[4] isomorphous with those of the iodide and bromide, it is the nitrogen atom of the thiocyanate ion that approaches the disulphide group in a linear and a triangular arrangement. The N · · · S distances in the N · · · S–S · · · N sequence, 3.386 ± 0.008 Å, when compared with the corresponding van der Waals distance of 3.35 Å, show that there is no partial bonding between nitrogen and sulphur in this arrangement. Thus the sulphur–sulphur bond in 4-phenyl-1,2-dithiolium thiocyanate is not subject to interaction with external atoms, and this may explain why the sulphur–sulphur bond there, 2.004 ± 0.005 Å, is somewhat shorter than the sulphur–sulphur bonds in the iodide and the bromide.

The present structure study of 4-phenyl-1,2-dithiolium chloride monohydrate was carried out mainly in order to find how the chloride ions interact with the disulphide group, but also in order to obtain further experimental evidence for the dimensions of the 4-phenyl-1,2-dithiolium ion.

EXPERIMENTAL

A sample of 4-phenyl-1,2-dithiolium chloride monohydrate was generously supplied by Klingsberg.[5] Crystal data on the compound have been reported earlier.[6] It crystallizes from water as colourless needles and thin flakes elongated along *c* and with {100} predominant. The crystals are orthorhombic, space groups *Pnma*.

Unit cell dimensions were redetermined from high order reflections on *hk*0 and *h0l* Weissenberg photographs, where sodium chloride powder lines had been superimposed for reference ($a_{NaCl} = 5.6394$ Å). A least squares procedure on 59 measured 2θ-values gave: $a = 25.995(5)$ Å, $b = 8.365(3)$ Å, and $c = 4.781(3)$ Å.

Four formula units per unit cell give a calculated density of 1.487 g/cm³ as compared with the density, 1.46 g/cm³, found by flotation.

The intensities of the *hk*0 – *hk*3 and *h0l* reflections were estimated visually from Weissenberg photographs taken with Ni-filtered Cu$K\alpha$ radiation ($\mu = 64.74$ cm^{-1}). *h0l* reflections from the zero layer about *b* were used for scaling only. The intensity data comprise 876 *hk*0 – *hk*3 reflections, including 269 unobserved.

Lp corrections and absorption corrections were applied, the latter according to a procedure by Coppens *et al.*[7] The intensity crystal was bounded by faces perpendicular to *a*, *b*, and *c*, with dimensions 0.005, 0.11, and 0.50 mm in the respective directions. A grid of $4 \times 8 \times 24$ points was used.

The calculated structure factors in Table 5 are based on the atomic scattering curves for chloride ion, sulphur, oxygen, carbon, and hydrogen, given in the *International Tables*.[8]

The computer programs used were made available by the Weizmann Institute of Science, Rehovot, Israel, and modified for the IBM 360/50 H computer at this University by Dr. Dove Rabinovich.

STRUCTURE DETERMINATION

The structure of 4-phenyl-1,2-dithiolium chloride monohydrate was solved in the *c*-axis projection. Approximate x and y coordinates for the chloride ion and the sulphur atom of the asymmetric unit were found from the Patterson *c*-projection. The positions of the carbon atoms were estimated by taking into account that 4-phenyl-1,2-dithiolium chloride monohydrate is isomorphous with 4-phenyl-1,2-dithiolium bromide and iodide;[1,2] the structures of the latter were already known. A subsequent Fourier map revealed the position of the water oxygen, and the atomic z coordinates were thereafter estimated from the Patterson *b*-projection.

The structure was refined by a full-matrix least squares procedure which minimizes the function

$$r = \sum W(|F_o| - K|F_c|)^2$$

with $W = [(Ka_1)^2 + (a_2F_o)^2/4W_o]^{-1}$. W_o in the weighting scheme is an individual weight which is estimated from the assumed reliability of the intensity measurement. The constants a_1 and a_2 were in the present case set equal to 1.0. Unobserved reflections with $K|F_c|$ greater than $F_o^{\text{threshold}}$ were included in the refinement with $F_o = F_o^{\text{threshold}}$. The refinement comprises the $hk0 - hk3$ reflections, and was carried out with anisotropic temperature factors for all atoms, except the hydrogens which were given constant isotropic temperature factors. The positions of the water hydrogens were kept constant during the refinement.

Suspiciously high temperature factor for the water oxygen as well as a too low Fourier peak for this atom made us believe that some of the water

Table 1. Atomic coordinates in fractions of corresponding cell edges. The standard deviations given in parentheses refer to the last digits of respective values.

Atom	x	y	z
Cl	−0.05302 (15)	0.25000 (0)	−0.6585 (10)
S(1)	0.03611 (8)	0.12921 (29)	−0.2526 (6)
C(1)	0.08379 (37)	0.1115 (12)	−0.0198 (24)
C(2)	0.10444 (47)	0.2500 (0)	0.0917 (35)
C(3)	0.14720 (53)	0.2500 (0)	0.3005 (35)
C(4)	0.16708 (50)	0.1073 (17)	0.4003 (32)
C(5)	0.20653 (54)	0.1071 (24)	0.5968 (38)
C(6)	0.22757 (76)	0.2500 (0)	0.6815 (43)
O	−0.13036 (63)	0.2500 (0)	−0.1631 (45)
H(1)	0.0954	0.0013	0.043
H(2)	0.1513	0.0006	0.327
H(3)	0.2250	0.0007	0.674
H(4)	0.2503	0.2500	0.836
H(5)	−0.1055	0.2500	0.000
H(6)	−0.1055	0.2500	−0.326

positions were unoccupied. The occupancy factor of the water oxygen was therefore refined, and the final value of this factor is 0.79 ± 0.03. With 79 % of the water positions filled, the calculated density of the compound becomes 1.464 g/cm^3 in close agreement with the experimental value 1.46 g/cm^3.

Corrections for secondary extinction according to the formula of Lipson [9] were carried out after the refinement had converged. There were no significant atomic parameter shifts in the subsequent, final refinement cycle. The conventional R factor, including unobserved reflections, did not improve beyond 0.099.

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 5.

Table 2. Components of atomic vibration tensors $\mathbf{U}^r$ in Å^2, referred to crystallographic axes. Isotropic temperature factors $\exp[-8\pi^2 U(\sin^2\theta/\lambda^2)]$ with $U = 0.068$ Å^2 were used for the hydrogen atoms.

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{23}	U_{13}
Cl	0.0656	0.0384	0.0692	0.0000	0.0000	−0.0309
S(1)	0.0453	0.0424	0.0404	−0.0130	0.0054	−0.0096
C(1)	0.0489	0.0623	0.0436	0.0093	0.0099	−0.0082
C(2)	0.0325	0.0566	0.0415	0.0000	0.0000	−0.0003
C(3)	0.0411	0.0889	0.0384	0.0000	0.0000	−0.0042
C(4)	0.0890	0.1185	0.0539	0.0491	−0.0343	−0.0351
C(5)	0.0965	0.1659	0.0688	0.0737	−0.0373	−0.0455
C(6)	0.0575	0.2246	0.0528	0.0000	0.0000	−0.0195
O	0.0938	0.0903	0.1539	0.0000	0.0000	0.0407

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)	2.021	0.004
S(1) − C(1)	1.673	0.011
C(1) − C(2)	1.384	0.013
C(2) − C(3)	1.494	0.015
C(3) − C(4)	1.386	0.016
C(4) − C(5)	1.390	0.017
C(5) − C(6)	1.376	0.020

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)	95.1	0.4
S(1) − C(1) − C(2)	118.0	0.8
C(1) − C(2) − C(9)	113.7	1.2
C(1) − C(2) − C(3)	123.1	0.7
C(2) − C(3) − C(4)	120.5	0.8
C(4) − C(3) − C(8)	119.0	1.4
C(3) − C(4) − C(5)	120.6	1.2
C(4) − C(5) − C(6)	119.4	1.5
C(5) − C(6) − C(7)	120.7	1.5

Table 5. Observed and calculated structure factors for 4-phenyl-1,2-dithiolium chloride monohydrate. The values given are ten times the absolute values. Unobserved reflections are marked with a minus sign in front of F_o.

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)	H	K	L	F(O)	F(C)
4	0	0	203	214	8	6	0	161	181	18	1	1	330	-322	22	4	1	241	248	12	8	1	-45	14
6	0	0	156	-151	10	6	0	162	135	19	1	1	-45	23	23	4	1	-46	-2	13	8	1	-44	22
8	0	0	638	-697	12	6	0	-62	41	20	1	1	235	-248	24	4	1	211	226	14	8	1	71	-82
10	0	0	726	-773	14	6	0	95	-62	21	1	1	70	-64	25	4	1	-42	-1	15	8	1	-41	-32
12	0	0	588	-710	16	6	0	120	-61	22	1	1	58	28	26	4	1	102	119	16	8	1	107	-128
14	0	0	399	-428	18	6	0	132	-109	23	1	1	67	-64	27	4	1	-36	21	17	8	1	85	-61
16	0	0	627	-558	20	6	0	102	-129	24	1	1	156	165	28	4	1	-33	2	18	8	1	115	-140
18	0	0	115	-59	22	6	0	-53	-8	25	1	1	-46	-10	29	4	1	61	79	19	8	1	39	-46
20	0	0	92	75	24	6	0	-46	19	26	1	1	177	188	1	5	1	-37	-43	20	8	1	84	-112
22	0	0	196	177	26	6	0	-37	38	27	1	1	-43	-3	2	5	1	598	-558	1	9	1	-43	-27
24	0	0	228	196	2	7	0	115	88	28	1	1	111	133	3	5	1	88	-86	2	9	1	85	77
26	0	0	159	168	4	7	0	-60	-4	29	1	1	-37	13	4	5	1	302	-262	3	9	1	53	-63
28	0	0	141	129	6	7	0	-61	26	30	1	1	108	141	5	5	1	174	-160	4	9	1	84	87
30	0	0	86	66	8	7	0	-62	39	31	1	1	37	32	6	5	1	-40	7	5	9	1	52	-54
32	0	0	-36	21	10	7	0	108	86	32	1	1	53	78	7	5	1	111	-68	6	9	1	59	68
0	4	0	312	-306	12	7	0	189	174	1	2	1	111	137	8	5	1	273	223	7	9	1	-41	-24
0	6	0	333	-374	14	7	0	190	180	2	2	1	84	31	9	5	1	-43	33	8	9	1	-41	38
0	8	0	478	522	16	7	0	-61	35	3	2	1	261	288	10	5	1	439	377	9	9	1	-40	4
0	10	0	120	-130	18	7	0	99	-112	4	2	1	382	-422	11	5	1	-45	21	10	9	1	-39	-24
4	1	0	223	238	20	7	0	112	-117	5	2	1	-25	-4	12	5	1	461	365	11	9	1	-38	15
6	1	0	451	-494	22	7	0	120	-142	6	2	1	635	-583	13	5	1	114	75	12	9	1	72	-77
8	1	0	103	-66	24	7	0	82	-108	7	2	1	271	-277	14	5	1	317	266	13	9	1	-35	19
10	1	0	345	-365	2	8	0	332	353	8	2	1	138	-138	15	5	1	141	129	14	9	1	89	-107
12	1	0	387	-420	4	8	0	175	128	9	2	1	220	-219	16	5	1	253	222	15	9	1	-30	31
14	1	0	562	-567	6	8	0	-61	-39	10	2	1	57	53	17	5	1	106	90	16	9	1	92	-119
16	1	0	-52	14	8	8	0	174	-163	11	2	1	146	-141	18	5	1	61	30	1	10	1	42	39
18	1	0	357	336	10	8	0	243	-232	12	2	1	198	187	19	5	1	77	-63	2	10	1	51	-43
20	1	0	299	296	12	8	0	240	-235	13	2	1	103	80	20	5	1	98	-101	3	10	1	-33	26
22	1	0	334	303	14	8	0	207	-193	14	2	1	119	98	21	5	1	66	-67	4	10	1	70	-91
24	1	0	260	245	16	8	0	137	-131	15	2	1	81	65	22	5	1	64	-65	5	10	1	-32	-15
26	1	0	146	149	18	8	0	-47	-22	16	2	1	268	221	23	5	1	53	-53	6	10	1	77	-104
28	1	0	-53	-26	20	8	0	-39	35	17	2	1	110	95	24	5	1	70	-68	7	10	1	-30	-46
30	1	0	66	-109	2	9	0	-57	-15	18	2	1	-45	33	25	5	1	-38	-28	8	10	1	59	-72
32	1	0	61	-101	4	9	0	-56	-21	19	2	1	-46	15	26	5	1	73	-82	3	0	2	186	-175
2	2	0	351	-413	6	9	0	68	-54	20	2	1	58	-35	27	5	1	-31	33	4	0	2	552	-606
4	2	0	65	54	8	9	0	107	-90	21	2	1	-47	35	28	5	1	61	-86	5	0	2	524	-570
6	2	0	267	279	10	9	0	132	-136	22	2	1	-48	-9	1	6	1	97	72	6	0	2	356	-345
8	2	0	-37	2	12	9	0	125	-139	23	2	1	-47	27	2	6	1	-43	-10	7	0	2	41	32
10	2	0	429	449	14	9	0	75	-85	24	2	1	87	-78	3	6	1	68	45	8	0	2	76	67
12	2	0	375	351	16	9	0	-38	13	25	2	1	-45	-29	4	6	1	129	-122	9	0	2	50	57
14	2	0	-50	35	2	10	0	79	-102	26	2	1	69	-65	5	6	1	100	77	10	0	2	628	653
16	2	0	76	-84	4	10	0	-45	-36	27	2	1	-42	-24	6	6	1	191	-171	11	0	2	192	-184
18	2	0	222	-195	6	10	0	-43	18	28	2	1	-39	-15	7	6	1	68	-38	12	0	2	716	720
20	2	0	131	-135	8	10	0	-40	53	29	2	1	51	-54	8	6	1	-46	17	13	0	2	371	391
22	2	0	137	-111	10	10	0	63	65	30	2	1	-32	36	9	6	1	177	-151	14	0	2	498	513
24	2	0	125	99	3	0	1	289	301	31	2	1	-28	-22	10	6	1	129	93	15	0	2	193	216
26	2	0	-57	52	4	0	1	1388	1242	1	3	1	196	191	11	6	1	101	-97	16	0	2	245	258
28	2	0	-52	3	5	0	1	950	-891	2	3	1	667	758	12	6	1	117	90	17	0	2	95	99
30	2	0	-44	27	6	0	1	2053	1887	3	3	1	-27	0	13	6	1	-49	-21	18	0	2	132	133
32	2	0	-32	16	7	0	1	95	96	4	3	1	291	330	14	6	1	148	129	19	0	2	-55	15
2	3	0	755	-674	8	0	1	844	502	5	3	1	72	75	15	6	1	-49	34	20	0	2	-56	-17
4	3	0	601	-725	9	0	1	410	404	6	3	1	63	-47	16	6	1	70	58	21	0	2	119	-114
6	3	0	880	-947	10	0	1	611	624	7	3	1	301	290	17	6	1	-49	48	22	0	2	162	-143
8	3	0	515	-567	11	0	1	402	413	8	3	1	370	-395	18	6	1	-48	-10	23	0	2	108	-121
10	3	0	-45	-34	12	0	1	80	73	9	3	1	-38	-4	19	6	1	66	70	24	0	2	106	-94
12	3	0	-49	32	13	0	1	-36	30	10	3	1	380	-364	20	6	1	-45	-38	25	0	2	-52	-47
14	3	0	273	255	14	0	1	219	-243	11	3	1	-37	20	21	6	1	-42	18	26	0	2	191	-190
16	3	0	176	142	15	0	1	84	-62	12	3	1	523	-465	22	6	1	49	-63	27	0	2	-47	-22
18	3	0	274	213	16	0	1	325	-341	13	3	1	112	-97	23	6	1	-37	-19	28	0	2	149	-155
20	3	0	199	172	17	0	1	165	-173	14	3	1	333	-281	24	6	1	42	-68	29	0	2	-39	9
22	3	0	243	229	18	0	1	367	-377	15	3	1	252	-201	25	6	1	-31	-2	30	0	2	84	-101
24	3	0	-60	33	19	0	1	192	-219	16	3	1	222	-198	26	6	1	33	-61	0	2	2	351	353
26	3	0	127	-132	20	0	1	354	-338	17	3	1	201	-179	1	7	1	-46	29	0	8	2	170	174
28	3	0	-49	-3	21	0	1	-46	10	18	3	1	100	-83	2	7	1	57	-51	0	6	2	-53	-15
30	3	0	-40	-9	22	0	1	247	-243	19	3	1	79	53	3	7	1	146	152	0	8	2	224	-240
2	4	0	302	-313	23	0	1	-47	21	20	3	1	215	187	4	7	1	91	-97	1	1	2	302	365
4	4	0	425	-436	24	0	1	129	-119	21	3	1	196	181	5	7	1	137	131	2	1	2	-21	-1
6	4	0	248	-242	25	0	1	-46	26	22	3	1	79	75	6	7	1	67	-59	3	1	2	52	58
8	4	0	248	210	26	0	1	-45	4	23	3	1	-47	33	7	7	1	48	-29	4	1	2	108	108
10	4	0	-49	-44	27	0	1	-43	53	24	3	1	76	64	8	7	1	68	-67	5	1	2	79	-87
12	4	0	167	126	28	0	1	-41	38	25	3	1	-44	33	9	7	1	68	-69	6	1	2	359	367
14	4	0	422	376	29	0	1	-38	9	26	3	1	89	91	10	7	1	-48	-29	7	1	2	119	101
16	4	0	502	470	30	0	1	-34	30	27	3	1	-40	-42	11	7	1	59	-47	8	1	2	491	500
18	4	0	370	359	31	0	1	-31	-5	28	3	1	84	87	12	7	1	84	85	9	1	2	498	-476
20	4	0	241	233	32	0	1	53	81	29	3	1	-33	-31	13	7	1	-48	-18	10	1	2	370	358
22	4	0	-61	-8	0	1	1	292	358	30	3	1	-29	26	14	7	1	101	100	11	1	2	153	-146
24	4	0	266	-294	0	3	1	785	844	1	4	1	155	-148	15	7	1	-47	-24	12	1	2	101	92
26	4	0	205	-169	0	5	1	586	-605	2	4	1	248	-266	16	7	1	120	125	13	1	2	47	30
28	4	0	148	-162	0	7	1	57	-25	3	4	1	247	-245	17	7	1	-45	0	14	1	2	54	81
30	4	0	90	-117	0	9	1	72	62	4	4	1	251	-252	18	7	1	123	108	15	1	2	107	101
2	5	0	361	358	1	1	1	168	190	5	4	1	153	152	19	7	1	-41	2	16	1	2	98	-66
4	5	0	576	591	2	1	1	128	132	6	4	1	187	-179	20	7	1	61	84	17	1	2	100	104
6	5	0	687	648	3	1	1	635	-706	7	4	1	184	188	21	7	1	-36	18	18	1	2	175	-181
8	5	0	464	445	4	1	1	587	608	8	4	1	394	-377	22	7	1	-33	0	19	1	2	-55	29
10	5	0	265	209	5	1	1	467	-493	9	4	1	176	160	23	7	1	-29	43	20	1	2	238	-207
12	5	0	-58	-18	6	1	1	-28	40	10	4	1	512	-478	24	7	1	42	-68	21	1	2	-56	34
14	5	0	240	-193	7	1	1	170	146	11	4	1	58	40	1	8	1	-47	-33	22	1	2	178	-137
16	5	0	246	-210	8	1	1	247	246	12	4	1	325	-290	2	8	1	150	138	23	1	2	-55	26
18	5	0	195	-159	9	1	1	224	217	13	4	1	150	-109	3	8	1	-47	-42	24	1	2	195	-164
20	5	0	198	-175	10	1	1	52	50	14	4	1	113	-87	4	8	1	275	310	25	1	2	-52	-49
22	5	0	201	-189	11	1	1	97	88	15	4	1	101	-79	5	8	1	47	-50	26	1	2	144	-140
24	5	0	-54	7	12	1	1	409	-403	16	4	1	-48	-38	6	8	1	350	357	27	1	2	57	-75
26	5	0	-46	30	13	1	1	63	-53	17	4	1	-49	-7	7	8	1	-47	37	28	1	2	-43	-10
28	5	0	-37	0	14	1	1	269	-277	18	4	1	316	280	8	8	1	237	254	29	1	2	47	-57
2	6	0	123	-108	15	1	1	122	105	19	4	1	69	58	9	8	1	81	95	30	1	2	-34	36
4	6	0	138	122	16	1	1	361	-331	20	4	1	321	299	10	8	1	146	150	1	2	2	183	196
6	6	0	135	107	17	1	1	-42	6	21	4	1	68	-60	11	8	1	76	85	2	2	2	84	90

Table 5. Continued.

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)	H	K	L	F(O)	F(C)
3	2	2	322	349	22	4	2	-53	-8	1	8	2	-54	-81	19	1	3	-61	38	17	4	3	88	71
4	2	2	-30	2	23	4	2	72	-86	2	8	2	216	-215	20	1	3	66	58	18	4	3	129	-94
5	2	2	212	235	24	4	2	59	53	3	8	2	106	-110	21	1	3	103	107	19	4	3	97	90
6	2	2	-34	17	25	4	2	-45	-32	4	8	2	176	-157	22	1	3	-58	3	20	4	3	169	-151
7	2	2	-36	23	26	4	2	108	124	5	8	2	106	-118	23	1	3	-55	46	21	4	3	-54	38
8	2	2	43	-51	27	4	2	-37	16	6	8	2	89	-77	24	1	3	-53	-25	22	4	3	160	-144
9	2	2	70	87	28	4	2	120	156	7	8	2	65	-42	25	1	3	-49	39	23	4	3	57	-56
10	2	2	212	-194	1	5	2	151	158	8	8	2	65	60	26	1	3	78	-70	24	4	3	122	-119
11	2	2	96	-102	2	5	2	156	-167	9	8	2	-52	-10	27	1	3	-41	-24	1	5	3	-57	38
12	2	2	111	-100	3	5	2	97	87	10	8	2	188	195	1	2	3	148	-150	2	5	3	211	216
13	2	2	157	-139	4	5	2	319	-337	11	8	2	-50	25	2	2	3	-36	6	3	5	3	146	142
14	2	2	-51	11	5	5	2	-49	-30	12	8	2	198	214	3	2	3	87	-77	4	5	3	177	176
15	2	2	167	-149	6	5	2	328	-355	13	8	2	59	90	4	2	3	-39	33	5	5	3	154	150
16	2	2	66	-46	7	5	2	81	-65	14	8	2	149	172	5	2	3	41	-23	6	5	3	140	131
17	2	2	162	-127	8	5	2	353	-361	15	8	2	71	75	6	2	3	-43	24	7	5	3	104	90
18	2	2	-56	3	9	5	2	208	-182	16	8	2	93	111	7	2	3	103	92	8	5	3	68	-51
19	2	2	94	79	10	5	2	278	-240	17	8	2	52	52	8	2	3	90	-66	9	5	3	-62	-41
20	2	2	-57	44	11	5	2	240	-209	1	9	2	58	71	9	2	3	172	168	10	5	3	192	-176
21	2	2	65	67	12	5	2	190	-174	2	9	2	58	43	10	2	3	98	84	11	5	3	83	-76
22	2	2	69	59	13	5	2	-58	16	3	9	2	-47	43	11	2	3	186	183	12	5	3	220	-184
23	2	2	106	99	14	5	2	115	96	4	9	2	66	70	12	2	3	151	131	13	5	3	79	-63
24	2	2	-53	37	15	5	2	116	109	5	9	2	-46	12	13	2	3	-60	-14	14	5	3	244	-205
25	2	2	62	52	16	5	2	218	189	6	9	2	103	104	14	2	3	-61	2	15	5	3	150	-116
26	2	2	-48	31	17	5	2	-59	58	7	9	2	-44	-39	15	2	3	-62	-6	16	5	3	171	-160
27	2	2	-45	4	18	5	2	210	176	8	9	2	114	122	16	2	3	-62	-38	17	5	3	72	-76
28	2	2	-41	-18	19	5	2	119	96	9	9	2	52	-76	17	2	3	99	-82	18	5	3	169	-148
29	2	2	-36	-32	20	5	2	162	153	10	9	2	80	82	18	2	3	76	-63	19	5	3	-54	-9
30	2	2	38	-37	21	5	2	-52	51	11	9	2	48	-59	19	2	3	131	-111	20	5	3	-51	-35
1	3	2	193	-211	22	5	2	127	118	12	9	2	51	46	20	2	3	74	-57	21	5	3	-47	29
2	3	2	46	53	23	5	2	-46	32	13	9	2	-33	-19	21	2	3	98	-88	22	5	3	61	62
3	3	2	135	-139	24	5	2	90	81	3	0	3	-28	-2	22	2	3	-57	-30	1	6	3	151	-150
4	3	2	379	404	25	5	2	-38	-10	4	0	3	228	-388	23	2	3	-58	-3	2	6	3	-61	-20
5	3	2	53	-56	26	5	2	-34	13	5	0	3	-36	-3	24	2	3	-51	-3	3	6	3	96	-76
6	3	2	372	396	1	6	2	75	71	6	0	3	322	-389	25	2	3	-47	40	4	6	3	96	-60
7	3	2	158	160	2	6	2	-53	-13	7	0	3	300	-288	26	2	3	-43	1	5	6	3	-61	-3
8	3	2	407	420	3	6	2	161	148	8	0	3	528	-563	27	2	3	-38	25	6	6	3	119	-72
9	3	2	208	199	4	6	2	-54	6	9	0	3	225	-242	1	3	3	69	-69	7	6	3	131	91
10	3	2	311	334	5	6	2	183	165	10	0	3	308	-315	2	3	3	222	-213	8	6	3	-62	-17
11	3	2	263	252	6	6	2	-55	3	11	0	3	98	-99	3	3	3	226	-232	9	6	3	131	113
12	3	2	195	188	7	6	2	69	81	12	0	3	242	-254	4	3	3	153	-149	10	6	3	-62	8
13	3	2	116	125	8	6	2	-56	2	12	0	3	-56	23	5	3	3	271	-262	11	6	3	121	98
14	3	2	195	-204	9	6	2	-57	8	14	0	3	109	-83	6	3	3	252	-251	12	6	3	-61	27
15	3	2	234	-240	10	6	2	-57	-56	15	0	3	-55	2	7	3	3	150	-156	13	6	3	-60	24
16	3	2	261	-271	11	6	2	-58	16	16	0	3	291	315	8	3	3	-53	20	14	6	3	-60	32
17	3	2	-57	-31	12	6	2	-58	-53	17	0	3	-61	53	9	3	3	137	118	15	6	3	-58	-12
18	3	2	181	-167	13	6	2	114	-106	18	0	3	237	239	10	3	3	294	306	16	6	3	-55	-46
19	3	2	95	-97	14	6	2	-58	20	19	0	3	87	70	11	3	3	72	68	17	6	3	-52	-18
20	3	2	176	-163	15	6	2	142	-131	20	0	3	250	246	12	3	3	148	140	18	6	3	-49	-15
21	3	2	120	-100	16	6	2	-57	45	21	0	3	154	147	13	3	3	76	56	19	6	3	-46	-41
22	3	2	117	-93	17	6	2	-55	-37	22	0	3	234	233	14	3	3	241	236	20	6	3	-42	21
23	3	2	-53	-10	18	6	2	-53	50	23	0	3	68	78	15	3	3	155	148	1	7	3	-60	15
24	3	2	63	-55	19	6	2	-51	-1	24	0	3	152	137	16	3	3	226	197	2	7	3	146	119
25	3	2	-48	11	20	6	2	-48	51	25	0	3	-50	33	17	3	3	77	59	3	7	3	-60	-22
26	3	2	-45	-26	21	6	2	-45	58	26	0	3	65	70	18	3	3	135	103	4	7	3	84	52
27	3	2	-42	42	22	6	2	-42	42	27	0	3	-41	-20	19	3	3	-61	41	5	7	3	84	-67
28	3	2	-37	-5	23	6	2	-38	58	28	0	3	-36	-20	20	3	3	-59	45	6	7	3	-59	15
29	3	2	-32	37	24	6	2	-33	-12	0	1	3	349	-411	21	3	3	-57	-12	7	7	3	88	-51
1	4	2	161	-159	1	7	2	130	-112	0	3	3	217	-204	22	3	3	-54	-61	8	7	3	65	-41
2	4	2	383	391	2	7	2	-56	15	0	5	3	258	213	23	3	3	-51	-24	9	7	3	-58	-17
3	4	2	270	-271	3	7	2	-56	-24	0	7	3	178	189	24	3	3	104	-107	10	7	3	111	-76
4	4	2	320	318	4	7	2	-56	-28	1	1	3	112	-130	25	3	3	75	-92	11	7	3	-56	16
5	4	2	139	-126	5	7	2	-56	18	2	1	3	325	-369	26	3	3	86	-121	12	7	3	82	-69
6	4	2	171	163	6	7	2	98	-93	3	1	3	82	96	1	4	3	80	57	13	7	3	66	61
7	4	2	73	-67	7	7	2	-57	42	4	1	3	137	-140	2	4	3	155	161	14	7	3	116	-105
8	4	2	-47	-21	8	7	2	164	-154	5	1	3	196	208	3	4	3	96	81	15	7	3	93	82
9	4	2	-48	6	9	7	2	164	181	6	1	3	-40	-36	4	4	3	269	258	16	7	3	-85	-43
10	4	2	165	-168	10	7	2	163	-127	7	1	3	139	139	5	4	3	71	61	1	8	3	114	112
11	4	2	105	106	11	7	2	63	63	8	1	3	104	100	6	4	3	332	334	2	8	3	85	-74
12	4	2	361	-327	12	7	2	-56	-43	9	1	3	61	52	7	4	3	-56	-15	3	8	3	-53	38
13	4	2	-55	-6	13	7	2	-55	-31	10	1	3	178	190	8	4	3	437	459	4	8	3	121	-124
14	4	2	490	-480	14	7	2	-54	-6	11	1	3	-53	-7	9	4	3	102	-86	5	8	3	-53	-20
15	4	2	152	140	15	7	2	-53	-41	12	1	3	176	178	10	4	3	158	149	6	8	3	136	-145
16	4	2	238	-207	16	7	2	-51	23	13	1	3	86	-95	11	4	3	182	-181	7	8	3	62	-68
17	4	2	72	66	17	7	2	54	-66	14	1	3	285	316	12	4	3	77	37	8	8	3	137	-156
18	4	2	175	-148	18	7	2	51	48	15	1	3	157	-155	13	4	3	-64	-17	9	8	3	60	-58
19	4	2	100	-67	19	7	2	-42	-30	16	1	3	138	142	14	4	3	-65	-12	10	8	3	128	-128
20	4	2	69	-61	20	7	2	48	63	17	1	3	81	-76	15	4	3	-65	21	11	8	3	51	-58
21	4	2	-55	-35	21	7	2	-35	-19	18	1	3	-62	0	16	4	3	145	-125	12	8	3	74	-97
																				13	8	3	-39	-11

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

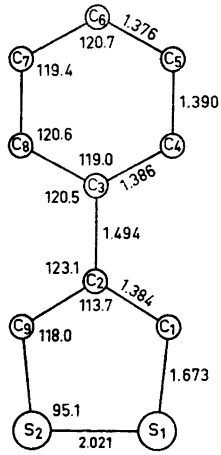


Fig. 1. Bond lengths (Å) and bond angles (°) in the 4-phenyl-1,2-dithiolium ion.

so. The equation for the least squares plane of the ion, excluding hydrogen atoms and with weights inversely proportional to standard deviations in atomic coordinates is

$$-0.6736X + 0.7391Z + 1.5235 = 0$$

where X and Z are in Å units. The atoms of the 1,2-dithiolium ring, S(1), C(1), and C(2), lie −0.001, −0.014, and 0.018 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 0.008, 0.012, 0.015, and −0.054 Å, respectively.

From table 3 and Fig. 1 the bonds in the 1,2-dithiolium ring of the present structure are: S−S = 2.021 ± 0.004 Å, S(1)−C(1) = 1.673 ± 0.011 Å, and C(1)−C(2) = 1.384 ± 0.013 Å. The connection bond C(2)−C(3) is 1.494 ± 0.015 Å, and the bonds in the benzene ring are: C(3)−C(4) = 1.386 ± 0.016 Å, C(4)−C(5) = 1.390 ± 0.017 Å, and C(5)−C(6) = 1.376 ± 0.020 Å. These bond lengths may be compared with those found for the 1,2-dithiolium ion in the thiocyanate salt.[4] They are, reckoned in the same order as above, S−S = 2.004 ± 0.005 Å, S(1)−C(1) = 1.678 ± 0.008 Å, C(1)−C(2) = 1.388 ± 0.013 Å, C(2)−C(3) = 1.498 ± 0.013 Å, C(3)−C(4) = 1.396 ± 0.013 Å, C(4)−C(5) = 1.388 ± 0.013 Å, and C(5)−C(6) = 1.391 ± 0.013 Å. One notes that the lengths of the C−S bonds and the lengths of the corresponding C−C bonds from the two structure studies agree within one standard deviation. The difference in S−S bond lengths, however, is somewhat greater. It represents 3.4σ (σ = ± 0.005 Å), and may be real as discussed below.

The crystal structure. The *c*-projection of the crystal structure of 4-phenyl-1,2-dithiolium chloride monohydrate is shown in Fig. 2. Intermolecular atomic distances and angles are given in the figure.

Three chloride ions approach the disulphide group to form close contacts with the sulphur atoms. This gives rise to roughly linear $\cdots Cl \cdots \begin{matrix} | \\ S \end{matrix} - \begin{matrix} | \\ S \end{matrix} \cdots Cl \cdots \begin{matrix} | \\ S \end{matrix} - \begin{matrix} | \\ S \end{matrix} \cdots Cl \cdots$ chains, which run through the crystal in the *b*-axis

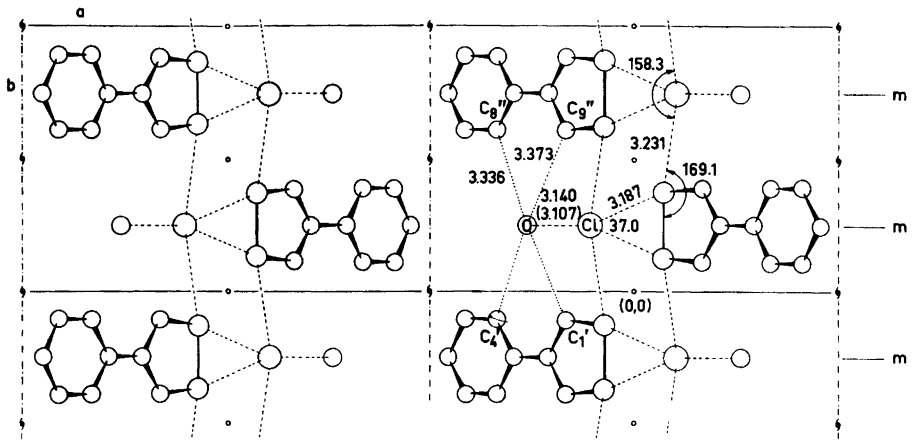


Fig. 2. The crystal structure of 4-phenyl-1,2-dithiolium chloride monohydrate as seen along the *c*-axis. Interatomic distances (Å) and angles (°) are given.

direction, and also to triangular $\begin{matrix} -S \cdot \\ | \quad \vdots \\ -S \cdot \end{matrix}$ Cl arrangements, interconnecting the chains into pairs (*cf.* Fig. 2). The Cl · · · S–S and S · · · Cl · · · S angles in the chains are $169.1 \pm 0.3°$ and $158.3 \pm 0.3°$, respectively, and the S · · · Cl · · · S angles in the triangular arrangements are $37.0 \pm 0.2°$.

The Cl · · · S close contacts of 3.231 ± 0.004 Å in the linear arrangements, 0.42 Å shorter than the corresponding van der Waals contact,[3] are compatible with the equivalent close contacts in 4-phenyl-1,2-dithiolium iodide and 4-phenyl-1,2-dithiolium bromide.[1,2] The sulphur–sulphur bond in the present structure, therefore, may be affected from interaction between the sulphur atoms and chloride ions. This may explain why the S–S bond here is found to be somewhat longer than the S–S bond in the thiocyanate salt.[4]

From Fig. 2 it is seen that the chlorine-sulphur distances in the triangular arrangements are 3.187 ± 0.004 Å and thus 0.46 Å shorter than the corresponding van der Waals contact. The halogen–sulphur distances in the triangular arrangements of the iodide and the bromide are 0.45 and 0.49 Å shorter, respectively, than the corresponding van der Waals contacts.[1,2]

The water molecule lies in the mirror plane *m* and forms hydrogen bonds to two chloride ions. The O · · · Cl distances are 3.140 and 3.107 ± 0.021 Å, respectively, and the Cl · · · O · · · Cl angle is $99.9 \pm 0.5°$. Furthermore, the water oxygen accepts four weaker hydrogen bonds from C(1)′, C(4)′, C(8)″ and C(9)″ (*cf.* Fig. 2). The C(1)′ · · · O and C(9)″ · · · O distances are 3.373 ± 0.013 Å with the C–H · · · O angles 174°, and the C(4)′ · · · O and the C(8)″ · · · O distances are 3.336 ± 0.017 Å with the C–H · · · O angles 171°.

There are only weak contacts across the diagonal glide plane *n*.

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