

The Crystal and Molecular Structure of 3,5-Diacetamido-1,2-dithiolium Bromide

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The crystal and molecular structure of 3,5-diacetamido-1,2-dithiolium bromide has been determined, and refined by least squares methods using anisotropic temperature parameters. The refinement comprises the $h0l$, $h1l$, $h2l$, and $hk0$ reflections, and the final atomic coordinates of the 3,5-diacetamido-1,2-dithiolium ion have been corrected for the rigid-body libration of the ion.

The C—C bonds in the 1,2-dithiolium ring are 1.367 ± 0.017 Å and 1.393 ± 0.016 Å, the C—S bonds are 1.743 and 1.746 ± 0.011 Å, and the S—S bond is 2.080 ± 0.005 Å. The 1,2-dithiolium ring is planar within the experimental error, and the bond lengths show that the ring is stabilized through π -orbital delocalization. The nitrogen substituents lie in the plane of the ring; the acetyl groups are slightly bent out of this plane.

Adjacent to the cyclic C—C bond of length 1.393 Å, there is a C—N bond of length 1.339 ± 0.016 Å, while the lengths of the other C—N bonds in the ion are 1.380 ± 0.015 Å, 1.378 ± 0.018 Å, and 1.406 ± 0.017 Å, respectively.

For the acetyl groups the C—O bond lengths are found to be 1.200 ± 0.017 Å and 1.225 ± 0.015 Å, and the C—C bond lengths 1.513 ± 0.019 Å and 1.528 ± 0.021 Å, respectively.

There are close contacts between the carbonyl oxygens and the sulphur atoms of the disulphide group, the O...S distances being 2.515 ± 0.011 Å and 2.571 ± 0.010 Å, respectively. The oxygen atom which is engaged in the latter of these two close contacts, also forms a weaker contact, 3.113 ± 0.010 Å, with a sulphur atom of a symmetry-related ion.

If the partial bonding between oxygen and sulphur in the linear O...S—S...O arrangement has affected the length of the sulphur-sulphur bond, it has done so only to a very small degree.

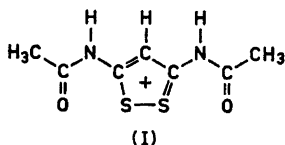
In the crystal, the 3,5-diacetamido-1,2-dithiolium ions are arranged in pairs about twofold axes, through N—H...Br...H—N hydrogen bonding, the N...Br distances are 3.241 and 3.270 ± 0.009 Å, and the N...Br...N angle is $92.0 \pm 1.0^\circ$.

In thio-thiophthene¹ a linear trisulphur system S—S—S occurs in which the two sulphur-sulphur bonds have equal lengths (2.36 Å). These bonds are longer than single bonds² (2.10 Å) which shows that one of the sulphur-

sulphur bonds is formed at the expense of the other. A nearly linear S—S...O arrangement is present in 2,5-dimethyl-dithiofurophthene,³ an isologue of thio-thiophthene. The σ -bond order of the partial sulphur-oxygen bond (2.41 Å) in this compound is reported to be 0.55; the bonding seems to have a small effect on the sulphur-sulphur bond (2.12 Å) for which a σ -bond order of 0.95 is reported.

Close contacts between sulphur and oxygen has also been found in the methyl ester of *o*-nitrobenzenesulphenic acid⁴ and 2-benzoylimino-3-methylthiazolid-5-one.⁵ In the former compound there is a linear O—S...O arrangement where the S...O distance is 2.44 Å and in the latter there is a nearly linear C—S...O arrangement with a S...O distance of 2.66 Å.

Structure investigations of unsaturated five-membered cyclic disulphides, in which *both* sulphur atoms form partial bonds with external atoms or ions in a linear arrangement X...S—S...X, may contribute to the understanding of the character of this kind of partial bonding. The degree to which the partial bonding affects the sulphur-sulphur bond may be more detectable when the bond is attacked from both sides. A structure investigation of the 3,5-diacetamido-1,2-dithiolium ion (I) is of interest in this respect.



EXPERIMENTAL

Crystal data on 3,5-diacetamido-1,2-dithiolium bromide have been reported earlier.⁶ The salt crystallizes from water as light yellow needles elongated along the *b* axis. The crystals are monoclinic, with unit cell dimensions (redetermined): $a = 24.46$ Å, $b = 4.85$ Å, $c = 21.08$ Å, $\beta = 113.4^\circ$. The experimental error is estimated to be within 0.2%. There are eight formula units per unit cell; density, calc. 1.71, found 1.71 g/cm³. The space group is *C*2/*c* (No. 15).

The intensities of the $h0l$, $h1l$, $h2l$, and $hk0$ reflections were estimated visually from Weissenberg photographs taken with $\text{CuK}\alpha$ radiation ($\mu = 48.2$ cm⁻¹). Small crystals of cross-section 0.05×0.04 mm were used in order to minimize absorption effects, and no absorption correction was applied. 1206 of the 1481 reflections obtainable with $\text{CuK}\alpha$ radiation were estimated, with a range of intensities of 15 000 to 3. The intensities were corrected in the usual way to give sets of relative structure factors. Common reflections in $h0l$, $h1l$, $h2l$, and $hk0$ were used to put all the reflections on the same scale.

The calculated structure factors in Table 11 are based on the atomic scattering curves for sulphur, oxygen, nitrogen, carbon, hydrogen and bromide ion given in the *International Tables*,⁷ the first set of the listed scattering factors for carbon being used.

DETERMINATION OF THE STRUCTURE

Coordinates for the bromide ion and the sulphur atoms were found from Patterson projections, and the positions of the carbon, nitrogen and oxygen atoms were estimated on the basis of the known *b* projection of the isomorphous 3,5-diacetamido-1,2-dithiolium iodide.⁸ The structure was thereafter refined by least squares methods on an IBM 1620^{II} computer, using a

program designed by Mair.⁹ Weighting scheme No. 3, recommended by Mair, was used with $a = 20$ and $b = 12.5$. The refinement comprises the $h0l$, $h1l$, $h2l$, and $hk0$ reflections, and was carried out with isotropic temperature factors at first. $R = \sum ||F_o| - |F_c|| / \sum |F_o|$ dropped to 0.14 during this part of the refinement. Then anisotropic temperature factors were applied to bromine and sulphur and the refinement continued until R stopped at 0.09. A difference map of the b -axis projection was calculated in order to find the positions of the methyl hydrogens. Maxima near the methyl carbon atoms gave fairly good indication of the hydrogen positions, and the other three hydrogen atoms in the ion could also be placed by reference to the difference map. The scattering contribution from the hydrogen atoms were now included in the structure factor calculations, but the hydrogen positions were not refined until the carbon, nitrogen and oxygen positions had been refined with anisotropic temperature factors. The temperature factors of the hydrogen atoms, taken as $\exp[-4(\sin^2\theta/\lambda^2)]$, were kept fixed, and during the refinement of the hydrogen positions the atomic parameters of the other atoms were also kept fixed. Furthermore, in the weighting scheme, a change was made to $a = 40$ and $b = 25$ in order to put more weight on low order reflections when refining the hydrogen positions. Eventually all atomic parameter, except B for the hydrogens, were refined simultaneously and R dropped to the final value 0.076.

Some low order reflections, supposed to be affected by secondary extinction, were excluded from the least squares refinement. These reflections,

Table 1. Final atomic coordinates from the least squares refinement.

Atom	x	y	z
Br	-0.10176	0.0087	0.15754
S ₁	0.02261	0.8118	0.07051
S ₂	0.10787	0.8129	0.14787
C ₁	-0.0021	0.5458	0.1076
C ₂	0.0366	0.4384	0.1687
C ₃	0.0941	0.5450	0.1943
C ₄	-0.1012	0.5791	0.0171
C ₅	-0.1633	0.4630	-0.0062
C ₆	0.1928	0.5879	0.2819
C ₇	0.2334	0.4584	0.3503
N ₁	-0.0601	0.4569	0.0757
N ₂	0.1370	0.4582	0.2532
O ₁	-0.0866	0.7604	-0.0135
O ₂	0.2040	0.7754	0.2523
H ₁	-0.074	0.264	0.095
H ₂	0.117	0.294	0.275
H ₃	0.025	0.229	0.194
H ₄	-0.160	0.285	0.037
H ₅	-0.176	0.443	-0.040
H ₆	-0.194	0.672	-0.010
H ₇	0.215	0.427	0.370
H ₈	0.232	0.628	0.386
H ₉	0.276	0.507	0.365

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

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{23}	U_{13}
B _r	0.0863	0.0489	0.0717	-0.0071	-0.0045	0.0530
S ₁	0.0437	0.0308	0.0425	-0.0022	0.0078	0.0193
S ₂	0.0401	0.0360	0.0472	-0.0024	0.0056	0.0220
C ₁	0.0439	0.0293	0.0374	-0.0018	-0.0020	0.0238
C ₂	0.0426	0.0150	0.0393	0.0020	0.0014	0.0194
C ₃	0.0480	0.0000	0.0438	0.0041	0.0040	0.0256
C ₄	0.0516	0.0470	0.0400	0.0047	0.0031	0.0142
C ₅	0.0416	0.0991	0.0637	-0.0033	0.0040	0.0059
C ₆	0.0391	0.0726	0.0489	0.0076	-0.0034	0.0211
C ₇	0.0465	0.0879	0.0514	0.0051	0.0051	0.0151
N ₁	0.0406	0.0148	0.0527	-0.0007	0.0023	0.0211
N ₂	0.0403	0.0378	0.0470	-0.0017	-0.0022	0.0185
O ₁	0.0595	0.0374	0.0474	0.0079	0.0140	0.0173
O ₂	0.0467	0.0640	0.0715	-0.0044	0.0003	0.0307

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

marked with asterisks in Table 11, were included in the final structure factor calculations with F_o equal to F_c from a previous cycle.

Atomic coordinates and components of atomic vibration tensors U^r are given in Tables 1 and 2. The observed and calculated structure factors are listed in Table 11.

Thermal analysis. Due to the pronounced conjugation in the 3,5-diacetamido-1,2-dithiolium ion it appears reasonable to assume that the ion is rigid, and the atomic positions should therefore be corrected for the rigid-body libration of the ion. The rigid-body parameters were found according to a method by Hirshfeld,¹⁰ and the corrections in atomic positions were carried out according to Cruickshank's procedure.¹¹

The computer program used in the rigid-body calculations, referred to below, is written in FORTRAN II by Hirshfeld, and the calculations were carried out on the IBM 1620¹².

An orthogonal molecular coordinate system L , M , N , was chosen such that L and M are in the plane of the 3,5-diacetamido-1,2-dithiolium ion and N is perpendicular to this plane. The origin is in an approximate centre of gravity and the directions of L , M , and N are the directions of the principal

Table 3. Origin, and direction cosines of the axes L , M , N of the molecular coordinate system, referred to crystal axes.

	a	b	c
L	0.6953	0.0029	0.3835
M	0.4906	0.7288	-0.6332
N	0.5251	-0.6847	-0.6723

Origin at $x = 0.0515$, $y = 0.6437$, $z = 0.3174$.

Table 4. Atomic coordinates in Å units in the coordinate system L, M, N ; (a) final coordinates from the least squares refinement, (b) the latter values corrected for rigid-body libration.

Atom	(a)			(b)		
	L (Å)	M (Å)	N (Å)	L (Å)	M (Å)	N (Å)
S ₁	-1.0305	1.1406	0.0186	-1.0321	1.1476	0.0192
S ₂	1.0448	1.1350	0.0139	1.0479	1.1427	0.0154
C ₁	-1.1551	-0.5909	0.0593	-1.1576	-0.5909	0.0607
C ₂	-0.0038	-1.3209	0.0479	-0.0039	-1.3235	0.0500
C ₃	1.1820	-0.5977	0.0677	1.1848	-0.5969	0.0701
C ₄	-3.5705	-0.4547	-0.0416	-3.5787	-0.4550	-0.0416
C ₅	-4.8180	-1.2989	-0.1235	-4.8294	-1.3031	-0.1240
C ₆	3.5689	-0.4308	-0.0483	3.5774	-0.4285	-0.0453
C ₇	4.8118	-1.3130	-0.0642	4.8228	-1.3138	-0.0605
N ₁	-2.4006	-1.1763	0.0604	-2.4063	-1.1792	0.0615
N ₂	2.3871	-1.1747	0.0740	2.3926	-1.1759	0.0772
O ₁	-3.5681	0.7689	-0.0234	-3.5758	0.7735	-0.0237
O ₂	3.5236	0.7621	-0.1063	3.5323	0.7692	-0.1040

Table 5. Components of atomic vibration tensors V^r in Å² as found by the least squares refinement (exp) and as calculated from the rigid-body parameters (RB).

Atom	V_{LL}	V_{MM}	V_{NN}	V_{LM}	V_{MN}	V_{LN}
S ₁ (exp)	0.0447	0.0253	0.0449	0.0008	0.0037	-0.0013
(RB)	0.0497	0.0253	0.0409	0.0033	0.0043	-0.0022
S ₂ (exp)	0.0451	0.0293	0.0443	-0.0035	0.0003	-0.0044
(RB)	0.0496	0.0264	0.0458	-0.0046	0.0007	-0.0015
C ₁ (exp)	0.0467	0.0289	0.0277	-0.0016	-0.0009	0.0015
(RB)	0.0431	0.0260	0.0240	-0.0002	0.0071	-0.0028
C ₂ (exp)	0.0435	0.0247	0.0256	0.0016	0.0102	-0.0011
(RB)	0.0444	0.0236	0.0228	0.0000	0.0097	-0.0035
C ₃ (exp)	0.0514	0.0148	0.0186	0.0026	0.0166	-0.0039
(RB)	0.0431	0.0276	0.0240	0.0000	0.0062	-0.0054
C ₄ (exp)	0.0456	0.0488	0.0479	0.0087	0.0014	0.0022
(RB)	0.0430	0.0506	0.0514	0.0008	-0.0005	-0.0015
C ₅ (exp)	0.0386	0.0839	0.0959	-0.0037	-0.0095	-0.0029
(RB)	0.0439	0.0741	0.0841	-0.0075	-0.0098	0.0018
C ₆ (exp)	0.0443	0.0667	0.0460	-0.0012	-0.0155	-0.0077
(RB)	0.0430	0.0534	0.0525	-0.0015	-0.0035	-0.0066
C ₇ (exp)	0.0452	0.0721	0.0725	0.0040	-0.0155	-0.0045
(RB)	0.0441	0.0773	0.0736	0.0076	-0.0063	-0.0099
N ₁ (exp)	0.0458	0.0261	0.0336	-0.0047	0.0149	-0.0055
(RB)	0.0440	0.0353	0.0380	-0.0033	0.0048	-0.0001
N ₂ (exp)	0.0430	0.0411	0.0397	-0.0042	0.0027	-0.0013
(RB)	0.0440	0.0381	0.0335	0.0033	0.0054	-0.0074
O ₁ (exp)	0.0534	0.0387	0.0558	0.0139	0.0094	-0.0023
(RB)	0.0471	0.0505	0.0577	0.0104	0.0003	-0.0032
O ₂ (exp)	0.0587	0.0550	0.0616	-0.0131	-0.0058	-0.0092
(RB)	0.0471	0.0521	0.0700	-0.0114	-0.0087	-0.0015

axes of inertia. The direction cosines of L , M , and N with respect to the crystallographic axes are given in Table 3 together with the coordinates of the origin.

Table 6. Final rigid-body translation parameters T_{ij} and libration parameters ω_{ij} .

	LL	MM	NN	LM	MN	LN
T (\AA^2)	0.04266	0.02236	0.02063	-0.00028	0.00807	-0.00416
ω (rad^2)	0.005889	0.002424	0.002265	-0.000712	0.000744	-0.000832

Coordinates and vibration tensors of the atoms in the 3,5-diacetamido-1,2-dithiolium ion (except hydrogen), were transformed to the molecular coordinate system, and the transformed values are given in Tables 4a and 5.

The temperature parameters of the sulphur atoms were given triple weight in the calculations of the rigid-body parameters, and the final values of the translation and libration parameters are given in Table 6. Components of atomic vibration tensors as calculated from the rigid-body parameters are listed in Table 5. Principal components of the rigid-body vibrations and their direction cosines with respect to molecular axes, together with the coordinates of the libration centre, are given in Table 7. The corrected atomic coordinates are listed in Table 4b.

The amplitudes of translational motion in directions of the principal axes are, according to the values in Table 7, 0.11, 0.17, and 0.21 \AA and the amplitudes of libration about the principal axes are 2.2, 3.0, and 4.5°, respectively. The libration centre lies 0.42 \AA out of the L , M plane, on the same side of the plane as the atoms of the acetyl groups, and 0.72 \AA off the molecular N axis in direction towards C_2 . Maximum libration occurs about an axis through the libration centre roughly parallel to the molecular L axis.

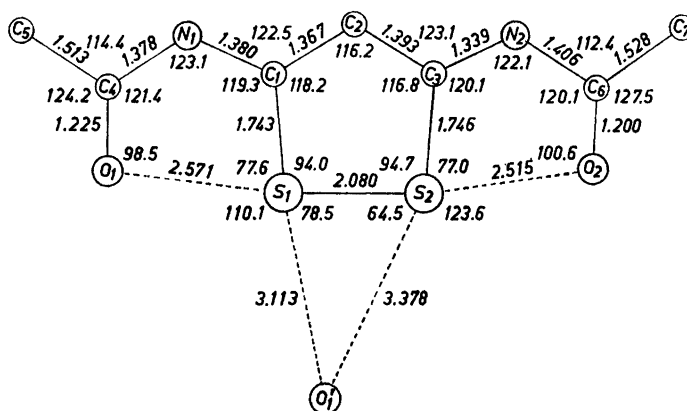


Fig. 1. Bond lengths (\AA) and bond angles ($^\circ$) in the 3,5-diacetamido-1,2-dithiolium ion, together with atomic distances and angles in the environment of the disulphide group.

DISCUSSION

Bond lengths as calculated from the coordinates in Table 4b, are listed in Table 8 and shown in Fig. 1. An assumed 0.1 % standard deviation in cell dimensions has been included in the listed standard deviations in bond lengths. The bond angles, listed in Table 9 and shown on Fig. 1, are based on the coordinates in Table 4a. The difference between the latter bond angles and those calculated from the corrected coordinates in Table 4b were negligible.

Table 7. Principal components of rigid-body vibrations, with direction cosines, and coordinates of libration centre, referred to molecular axes.

	<i>L</i>	<i>M</i>	<i>N</i>
$T_1^2 = 0.0435 \text{ \AA}^2$	-0.9734	0.0926	0.2091
$T_2^2 = 0.0289$	-0.2059	-0.7529	-0.6250
$T_3^2 = 0.0130$	-0.0995	0.6515	-0.7520
$\omega_1^2 = 0.0062 \text{ (rad}^2\text{)}$	-0.9457	0.2213	0.2378
$\omega_2^2 = 0.0027$	-0.3223	-0.7306	-0.6018
$\omega_3^2 = 0.0015$	-0.0405	0.6458	-0.7623

Libration centre at $L = 0.051$, $M = -0.717$, $N = -0.424$

Table 8. Bond lengths (*l*) and standard deviation in bond lengths $\sigma(l)$ in the 3,5-diacetamido-1,2-dithiolium ion, values in parentheses are without correction for rigid-body libration.

Bond	<i>l</i> (Å)	$\sigma(l)$ (Å)
S ₁ -S ₂	2.080 (2.075)	0.005
S ₁ -C ₁	1.743 (1.737)	0.011
S ₂ -C ₃	1.746 (1.739)	0.011
C ₁ -C ₂	1.367 (1.363)	0.017
C ₂ -C ₂	1.393 (1.389)	0.016
C ₁ -N ₁	1.380 (1.376)	0.015
C ₄ -N ₁	1.378 (1.378)	0.018
C ₄ -O ₁	1.225 (1.224)	0.015
C ₄ -C ₅	1.513 (1.509)	0.019
C ₃ -N ₂	1.339 (1.336)	0.016
C ₆ -N ₂	1.406 (1.402)	0.017
C ₆ -O ₂	1.200 (1.195)	0.017
C ₆ -C ₇	1.528 (1.524)	0.021

Table 9. Bond angles and standard deviation in bond angles in the 3,5-diacetamido-1,2-dithiolium ion.

	Angle(°)	σ (°)
C ₁ -S ₁ -S ₂	94.0	0.5
S ₁ -S ₂ -C ₃	94.7	0.5
S ₁ -C ₁ -C ₂	118.2	0.9
C ₁ -C ₂ -C ₃	116.2	1.0
C ₂ -C ₃ -S ₂	116.8	0.9
S ₁ -C ₁ -N ₁	119.3	0.9
C ₂ -C ₁ -N ₁	122.5	1.0
C ₁ -N ₁ -C ₄	123.1	1.0
C ₅ -C ₄ -N ₁	114.4	1.1
C ₅ -C ₄ -O ₁	124.2	1.3
N ₁ -C ₄ -O ₁	121.4	1.2
S ₂ -C ₃ -N ₂	120.1	0.9
C ₂ -C ₃ -N ₂	123.1	1.0
C ₃ -N ₂ -C ₆	122.1	1.0
C ₇ -C ₆ -N ₂	112.4	1.1
C ₇ -C ₆ -O ₂	127.5	1.3
N ₂ -C ₆ -O ₂	120.1	1.3

Table 10. Atomic distances and angles with reference to the environment of the disulphide group, together with the respective standard deviations in atomic distances and angles.

	Distance (Å)	σ (Å)
$S_1 \cdots O_1$	2.571	0.010
$S_2 \cdots O_2$	2.515	0.011
$S_1 \cdots O_1'$	3.113	0.010
$S_2 \cdots O_1'$	3.378	0.011
	Angle (°)	σ (°)
$O_1 \cdots S_1 \cdots O_1'$	110.1	0.8
$O_1' \cdots S_1 - S_2$	78.5	0.5
$O_1 \cdots S_1 - C_1$	77.6	0.9
$O_1' \cdots S_2 - S_1$	64.5	0.5
$O_1' \cdots S_2 \cdots O_2$	123.6	1.0
$O_2 \cdots S_2 - C_3$	77.0	0.9
$C_4 - O_1 \cdots S_1$	98.5	1.0
$C_6 - O_2 \cdots S_2$	100.6	0.9

The 1,2-dithiolium ring of the 3,5-diacetamido-1,2-dithiolium ion is approximately planar. The least squares plane of the ring, with sulphur given three times the weight of carbon, and $c \sin \beta$ chosen as the third orthogonal axis, is

$$0.5347 X - 0.6704 Y - 0.5142 Z = - 3.3621$$

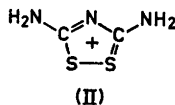
where X , Y , and Z are in Å units. S_1 and S_2 are -0.001 and 0.003 Å, respectively, out of this plane, the deviations from the plane for C_1 , C_2 , and C_3 are -0.008 , 0.018 , and -0.018 Å, respectively. The nitrogen atoms lie close to the plane of the 1,2-dithiolium ring, the deviation being 0.001 Å for N_1 and -0.012 Å for N_2 . For the exocyclic carbon atoms C_4 and C_6 , bonded to the nitrogens, the deviations are 0.091 and 0.094 Å, respectively, and for the methyl carbons C_5 and C_7 the deviations are 0.190 and 0.153 Å. The carbon atoms of the acetyl groups are thus symmetrically bent out of the plane of the dithiolium ring, but the deviations of the carbonyl oxygens O_1 and O_2 from the plane of the dithiolium ring, 0.048 and 0.130 Å, respectively, are slightly unsymmetric.

The bond lengths in the 1,2-dithiolium ring of the 3,5-diacetamido-1,2-dithiolium ion as listed in Table 8, may now be compared with the bond lengths found in the 1,2-dithiolium ring of other compounds containing this ring system. The results from the structure investigations of 3- and 4-phenyl-1,2-dithiolium iodide^{12,13} and 3,5-diamino-1,2-dithiolium iodide¹⁴ are of interest in this respect. The structure of the latter compound is known in one projection only, but this gives the length of the sulphur-sulphur bond which lies across a crystallographic mirror plane parallel to the projection axis.

The bonds $C_1 - C_2 = 1.367 \pm 0.017$, $C_2 - C_3 = 1.393 \pm 0.018$ Å, $S_1 - C_1 = 1.743 \pm 0.011$ Å, and $S_2 - C_3 = 1.746 \pm 0.011$ Å in the dithiolium ring of the present structure are significantly shorter than single bonds. The carbon-sulphur bonds, however, are longer than in 4- and 3-phenyl-1,2-dithiolium

H	K	L	F0	FC	H	K	L	F0	FC	H	K	L	F0	FC	H	K	L	F0	FC
12	4	0	8.41	3.44	22	4	0	3.44	0.95	7	5	0	7.73	- 0.25	17	5	0	3.65	2.68
14	4	0	8.10	- 5.78						9	5	0	14.30	15.24					
16	4	0	7.54	- 5.50	1	5	0	23.38	22.25	11	5	0	6.89	7.88	0	6	0	7.69	8.57
18	4	0	6.72	2.39	3	5	0	8.08	- 1.41	13	5	0	8.79	- 9.82	2	6	0	5.05	3.90
20	4	0	5.54	4.34	5	5	0	13.76	- 10.92	15	5	0	9.13	- 10.59	4	6	0	4.79	4.76
															6	6	0	4.30	2.74

iodide where the carbon-sulphur bonds are found to be $1.67 \pm 0.02 \text{ \AA}$ and $1.69 \pm 0.03 \text{ \AA}$, respectively. Also the sulphur-sulphur bond in 3,5-diacetamido-1,2-dithiolium bromide is longer, $\text{S-S} = 2.080 \pm 0.005 \text{ \AA}$, than the sulphur-sulphur bonds, $2.028 \pm 0.010 \text{ \AA}$ and $1.998 \pm 0.010 \text{ \AA}$, respectively, in 4- and 3-phenyl-1,2-dithiolium iodide. Accordingly one may conclude that the conjugation in the dithiolium ring of the 3,5-diacetamido-1,2-dithiolium ion is less pronounced than in the dithiolium rings of 3- and 4-phenyl-1,2-dithiolium ions. This is probably due to the nitrogens in 3 and 5 positions, which according to the carbon-nitrogen bond lengths, $\text{C}_1\text{-N}_1 = 1.380 \pm 0.015 \text{ \AA}$ and $\text{C}_3\text{-N}_2 = 1.339 \pm 0.016 \text{ \AA}$, strongly engage in π -bonding with ring carbons, at the expense of the conjugation in the disulphide group. In agreement with this, the sulphur-sulphur bond length in 3,5-diamino-1,2-dithiolium iodide¹⁴ is found to be $2.08 \pm 0.02 \text{ \AA}$. In the thiuret ion (II),¹⁵⁻¹⁷ which contains a ring analogous to the 1,2-dithiolium ring,



one finds that the conjugation in the carbon-sulphur part of the ion is less pronounced than in the nitrogen-carbon part. Thus in thiuret hydrochloride hemihydrate,¹⁷ the sulphur-sulphur bond is $2.071 \pm 0.004 \text{ \AA}$, the carbon-sulphur bonds are $1.765 \pm 0.007 \text{ \AA}$, the cyclic carbon-nitrogen bonds $1.346 \pm 0.010 \text{ \AA}$ and the exocyclic carbon-nitrogen bonds $1.309 \pm 0.010 \text{ \AA}$.

The acetamido nitrogen-carbon bonds, $\text{N}_1\text{-C}_4 = 1.378 \pm 0.018 \text{ \AA}$ and $\text{N}_2\text{-C}_6 = 1.406 \pm 0.017 \text{ \AA}$ in 3,5-diacetamido-1,2-dithiolium bromide, are shortened through π -bonding, and the carbon-oxygen bonds, $\text{C}_4\text{-O}_1 = 1.225 \pm 0.017 \text{ \AA}$ and $\text{C}_6\text{-O}_2 = 1.200 \pm 0.017 \text{ \AA}$, seem to be close to pure double bonds. Values ranging from 1.17 \AA to 1.20 \AA are suggested for the length of a carbon-oxygen double bond.¹⁸ The carbon-carbon bonds in the acetyl group of the present structure are $\text{C}_4\text{-C}_5 = 1.513 \pm 0.019 \text{ \AA}$ and $\text{C}_6\text{-C}_7 = 1.528 \pm 0.021 \text{ \AA}$, which agrees with the expected value, 1.504 \AA ,¹⁹ for a $\text{C}(sp^3)\text{-C}(sp^2)$ bond.

There are close contacts between oxygen and sulphur in the 3,5-diacetamido-1,2-dithiolium ion, the atomic distances being $\text{S}_1\cdots\text{O}_1 = 2.571 \pm 0.010 \text{ \AA}$ and $\text{S}_2\cdots\text{O}_2 = 2.515 \pm 0.011 \text{ \AA}$. Taking the sum of covalent radii for sulphur and oxygen as 1.71 \AA and the sum of their van der Waals radii as 3.25 \AA , and assuming a linear bond-order/bond-length relationship, the above close contacts correspond to σ -bond orders of 0.44 and 0.47, respectively. The close contacts occur in a linear $\text{O}\cdots\text{S}\text{-S}\cdots\text{O}$ arrangement. The partial bonding between oxygen and sulphur seems to affect the sulphur-sulphur bond only

to a very small degree. This may be concluded from a comparison of the sulphur-sulphur bond length, 2.080 ± 0.005 Å, in the present structure with the sulphur-sulphur bond length 2.071 ± 0.004 Å, in thiuret hydrochloride hemihydrate. In the latter compound there is a linear $\text{Cl}\cdots\text{S}-\text{S}\cdots\text{Cl}$ arrangement in which there is one weak sulphur-chlorine contact of σ -bond order 0.10. It should be noted, however, that the conjugation in the disulphide group of the 3,5-diacetamido-1,2-dithiolium ion, judging from the C—S bond lengths, 1.745 ± 0.011 Å, probably is somewhat more pronounced than the conjugation in the disulphide group of the thiuret ion, where the C—S bonds are 1.765 ± 0.007 Å. This probably means that an unaffected sulphur-sulphur bond in the 3,5-diacetamido-1,2-dithiolium ion should be *shorter* than the sulphur-sulphur bond in the thiuret ion.

O_1 which takes part in the oxygen-sulphur close contact of 2.57 Å, forms a weaker contact 3.113 ± 0.011 Å, with a sulphur atom of a symmetry-related ion. This probably accounts for the indicated asymmetry of the 3,5-diacetamido-1,2-dithiolium ion. The right-hand side of the ion in Fig. 1 shows similarities with the 2,5-dimethyl-dithiofurophthene molecule³ (III). It should be noted that the

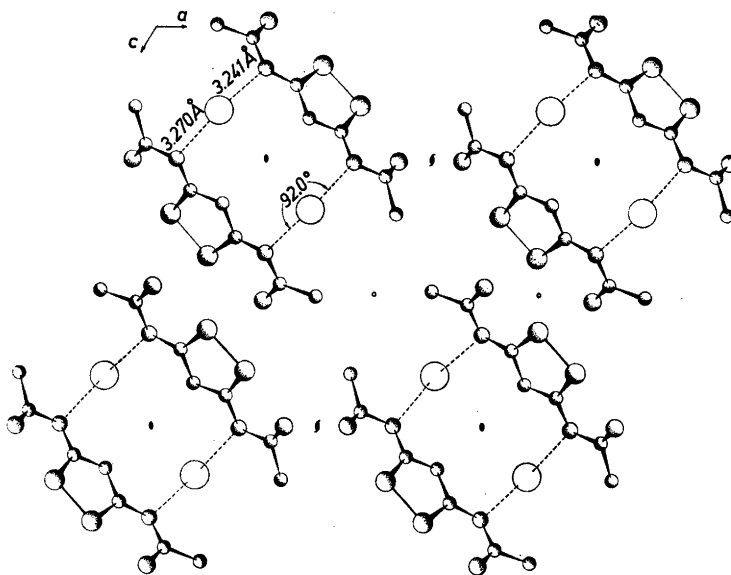
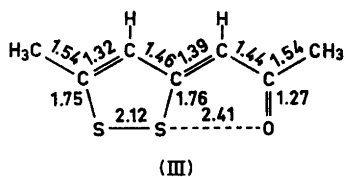


Fig. 2. The arrangement of ions in the unit cell as seen along the b axis.

tendency towards localized double bond for the C_1-C_2 and C_3-N_2 bonds of the present structure also occur for corresponding bonds in the carbon chain of dithiofurophthene. The oxygen-sulphur distance in the latter compound is shorter, 2.41 Å, than in the 3,5-diacetamido-1,2-dithiolium ion, and the sulphur-sulphur bond longer.

$S_1, S_2, C_1, O_1,$ and O_1' lie nearly in the same plane. The least squares plane of these atoms, with sulphur given three times the weight of carbon and oxygen, passes 0.016 Å from S_1 , 0.024 Å from S_2 , - 0.100 Å from C_1 , 0.038 Å from O_1 , and 0.058 Å from O_1' . The bond angles at S_1 are $O_1S_1C_1 = 77.6 \pm 0.5^\circ$, $C_1S_1S_2 = 94.0 \pm 0.4^\circ$, $S_2S_1O_1' = 78.5 \pm 0.5^\circ$, and $O_1'S_1O_1 = 110.1 \pm 0.5^\circ$, and there is accordingly a striking resemblance between the environment of S_1 in the present structure and the environment of divalent tellurium in square planar complexes.²⁰

In the crystal, the 3,5-diacetamido-1,2-dithiolium ions are arranged in pairs about twofold axes through $N-H \cdots Br \cdots H-N$ hydrogen bonding. The $N \cdots Br$ distances are 3.241 and 3.270 ± 0.009 Å, and the $N \cdots Br \cdots N$ angle is $92.0 \pm 1.0^\circ$. The arrangement of ions in the unit cell is shown in Fig. 2.

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