

The Crystal and Molecular Structures of 3,5-Diphenyl-1,2-dithiolylum-4-olate, 3,5-Di(2-thienyl)-1,2-dithiolylum-4-olate and 3,5-Di(*t*-butyl)-1,2-dithiolylum-4-olate

ASBJØRN HORDVIK, KNUT JYNGE and INGE PEDERSEN

Department of Chemistry, Institute of Mathematical and Physical Sciences, University of Tromsø, Box 953, N-9001 Tromsø, Norway

The structures of the title compounds have been studied by X-ray crystallographic methods.

3,5-Diphenyl-1,2-dithiolylum-4-olate crystallizes in the orthorhombic space group $Pnma$ with $Z=4$ and unit cell dimensions $a=6.422(1)$ Å, $b=26.017(5)$ Å, and $c=7.164(2)$ Å. The structure was solved by means of Patterson maps and refined by least squares methods. The molecule lies across the mirror plane m , the 1,2-dithiolylum-4-olate part is nearly planar and the phenyl groups are twisted 28.2° about the respective connecting bonds.

3,5-Di(2-thienyl)-1,2-dithiolylum-4-olate crystallizes in the monoclinic space group $P2_1/c$ with $Z=4$ and unit cell dimensions $a=16.347(4)$ Å, $b=5.567(3)$ Å, $c=12.591(3)$ Å, and $\beta=100.96(18)^\circ$. The structure was solved by direct methods (MULTAN) and refined by least squares methods. The molecule is roughly planar and the thienyl sulfurs approach the olate oxygen at distances of 2.815(9) and 2.764(9) Å, respectively.

The dimensions of the 1,2-dithiolylum-4-olate moiety as found in the 3,5-diphenyl and in the 3,5-di(2-thienyl) derivatives, assuming symmetric disulfide ring, are, S–S=2.009(2) and 2.026(3) Å, S–C=1.710(4) and 1.715(6) Å, C–C=1.440(5) and 1.437(10) Å, and C–O=1.270(7) and 1.265(7) Å, respectively. The bond lengths have been corrected for libration.

3,5-Di(*t*-butyl)-1,2-dithiolylum-4-olate crystallizes in the monoclinic space group $P2_1/n$ with $Z=4$ and unit cell dimensions, $a=14.170(3)$ Å, $b=6.398(2)$ Å, $c=14.173(3)$ Å, and $\beta=93.34(2)^\circ$. The crystals are twinned in the ac face. A sharpened (E^2) Patterson map gave the S–S, S–C, and S–O vectors clearly and it showed that the methyl groups are in staggered positions relative to the olate oxygen. The molecules lie on twofold axes which run through the C–O bond and the midpoint of the S–S bond.

In crystals of the title compounds there are close contacts between the olate oxygen and the sulfur atoms of the disulfide group. These close contacts

occur in triangular arrangements $O \cdots \begin{array}{c} \text{S} \\ | \\ \text{S} \end{array}$ where

the $O \cdots S$ distances are found to be 2.87 Å for the 3,5-diphenyl derivative and 2.89 Å for the 3,5-di(2-thienyl) derivative.

The 1,2-dithiolylum ring (I) possesses a sextet of π -electrons and may therefore be regarded as a pseudoaromatic system.

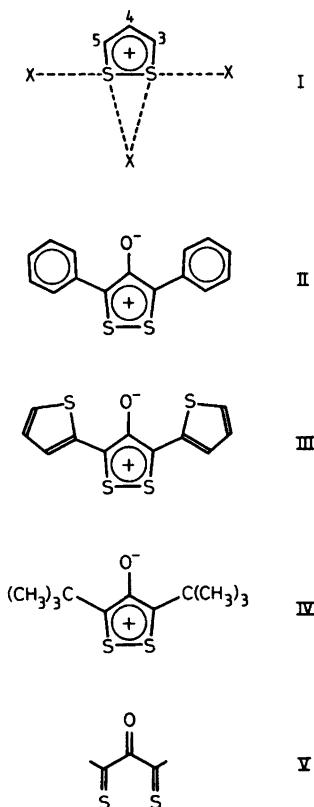
Structure investigations on 1,2-dithiolylum salts show that the five-membered disulfide ring is planar and that the conjugation in the ring also extends over the S–S bond. The S–S bond lengths in 4-phenyl-1,2-dithiolylum halides,^{1–3} for example, are found to be about 2.02 Å as compared with the value 2.10 Å for the S–S single bond length in a *cis* planar disulfide group.⁴

The halide ions (X), in crystals of the latter salts, participate in linear $X \cdots \begin{array}{c} | \\ \text{S} \\ | \\ \text{S} \\ | \\ \text{X} \end{array}$ arrangements and

triangular $X \cdots \begin{array}{c} \text{S} \\ | \\ \text{S} \end{array}$ arrangements where the $X \cdots S$

distances are 0.4–0.5 Å shorter than the corresponding van der Waals distances. The partial bonding between sulfur and halide ions in these arrangements may be described in terms of weak poly-centre bonds as discussed earlier.⁵

Polar forms of the present compounds (II, III and IV) are seen to contain the 1,2-dithiolylum



ring with a $-O^-$ group substituted in 4-position. A series of other polar forms may be thought of too, but the only non-polar alternative is V.

Structure V was still regarded as a possibility when we started our structure work on II some years ago. The results from that study⁶ showed that compound II, in fact, correctly may be described as a 1,2-dithiolium-4-olate, and structure studies of III and IV followed in order to verify the dimensions of this molecular system. Compound III was regarded to be of special interest due to possible intramolecular interaction between the olate oxygen and the thienyl sulfurs. Possible intermolecular $O \cdots S$ close contacts in the crystal structures was another point which interested us.

STRUCTURE ANALYSES

Samples of compounds II, III and IV were generously supplied by Barillier.⁷ Crystals from ethanol are dark red (II), dark purple (III), and light yellow (IV). The crystals of II and IV were readily

obtained, but crystallization of III seemed rather hopeless for a long time. However, a piece of solid material, which to our surprise gave relatively good diffraction, was eventually obtained by slow evaporation in a refrigerator over a period of three months. The crystals of IV are twinned, but in spite of that it has been possible to give a description of the structure. Although only rough molecular dimensions have been obtained for the latter, a brief account of this rather interesting crystallographic problem will be given.

Crystal data.

3,5-Diphenyl-1,2-dithiolium-4-olate (II)
 $C_{15}H_{10}OS_2$ F.W. = 270.363
 Space group $Pnma$
 $a = 6.422(1) \text{ \AA}$, $b = 26.017(5) \text{ \AA}$, $c = 7.164(2) \text{ \AA}$
 $V = 1196.97 \text{ \AA}^3$
 $D_c = 1.500 \text{ g/cm}^3$, $D_m(\text{flotation}) = 1.48 \text{ g/cm}^3$
 $Z = 4$
 $\mu = 4.16 \text{ cm}^{-1} (\text{MoK}\alpha)$
 Crystal size $0.3 \times 0.1 \times 0.3 \text{ mm}$
 $\theta_{\max} = 28^\circ$ $t = 20^\circ \text{ C}$
 No. of measured reflections 1483.
 724 reflections $> 4\sigma$ (I)
 $R = 0.048$

3,5-Di(2-thienyl)-1,2-dithiolium-4-olate (III)
 $C_{11}H_6OS_4$ F.W. = 282.407
 Space group $P2_1/c$
 $a = 16.347(4) \text{ \AA}$, $b = 5.567(3) \text{ \AA}$, $c = 12.591(3) \text{ \AA}$,
 $\beta = 100.96(18)^\circ$
 $V = 1124.93 \text{ \AA}^3$
 $D_c = 1.667 \text{ g/cm}^3$, $D_m(\text{flotation}) \sim 1.65 - 1.70 \text{ g/cm}^3$
 $Z = 4$
 $\mu = 7.84 \text{ cm}^{-1} (\text{MoK}\alpha)$
 Crystal size $0.015 \times 0.15 \times 0.5 \text{ mm}$
 $\theta_{\max} = 27^\circ$ $t = 20^\circ \text{ C}$
 No. of measured reflections 2542
 1176 reflections $> 4\sigma$ (I)
 $R = 0.050$

3,5-Di(*t*-butyl)-1,2-dithiolium-4-olate (IV)
 $C_{11}H_{18}OS_2$ F.W. = 230.38
 Space group $P2/n$
 $a = 14.170(3) \text{ \AA}$, $b = 6.398(2) \text{ \AA}$, $c = 14.173(3) \text{ \AA}$,
 $\beta = 93.34(2)^\circ$
 $V = 1282.74 \text{ \AA}^3$
 $D_c = 1.193 \text{ g/cm}^3$, $D_m(\text{flotation}) = 1.196 \text{ g/cm}^3$
 $\mu = 3.74 \text{ cm}^{-1} (\text{MoK}\alpha)$
 Crystal size $0.2 \times 0.4 \times 0.1 \text{ mm}$
 $\theta_{\max} = 28^\circ$ $t = 20^\circ \text{ C}$

No. of measured reflections 3206
 1852 reflections $> 2\sigma(I)$
 $R_{h0l} = 0.12$

The X-ray analyses were carried out on a computer controlled Enraf-Nonius CAD4 diffractometer using graphite monochromatized $\text{MoK}\alpha$ radiation ($\lambda = 0.71069 \text{ \AA}$). The unit cell dimensions were in each case determined from the 2θ values of 25 reflections measured in the θ -range $15\text{--}20^\circ$. A least squares procedure gave the cell dimensions quoted above.

The intensities of the reflections were measured by the $\omega - 2\theta$ scan technique. Two standard reflections were measured at regular intervals and their decrease in intensity during data collection were accounted for during data reduction. Lp corrections were applied and the intensity data for III were in addition corrected for absorption.⁸

Reflections for which $I > 4\sigma(I)$, where $\sigma(I)$ is based on counting statistics, were in the case of compounds II and III accepted as observed. For compound IV this threshold value was set to $2\sigma(I)$.

The scattering factors used for sulfur, oxygen and carbon in the structure factor calculations were those given by Cromer and Mann.⁹ For hydrogen, the scattering factor curve given by Stewart *et al.* was used.¹⁰

Structure solutions and refinements. The structure of II and IV were solved from Patterson maps and the structure of III was solved by means of direct methods (MULTAN).¹¹

Structure refinements were carried out by means of CRYLSQ of X-ray-76¹² using weights equal to σ_F^{-2} . All the calculations were performed on the UNIVAC 1110 of the University of Bergen.

Final atomic coordinates and temperature parameters for II and III are listed in Tables 1 and 2, respectively. The final structure factor lists are available on request.

The structure of compound IV. Oscillation and Weissenberg photographs strongly indicated that the crystals of IV were orthorhombic. Cell dimensions from diffractometer measurements were found to be $a = 6.401 \text{ \AA}$, $b = 19.447 \text{ \AA}$, and $c = 20.622 \text{ \AA}$, and the extinctions were hkl for $k+l=2n+1$ and $0kl$ for $k=n+1$. Consequently the space group should be either *Abm2* or *Abmm*.

However, a sharpened (E^2) three-dimensional Patterson map, calculated on the data collected for this orthorhombic cell, showed only one significant space group vector, namely that caused by glide plane b . Thus a monoclinic unit cell with $a = 6.401 \text{ \AA}$ as the unique axis seemed to be a better interpretation of the X-ray data, and the subsequent structure analysis confirmed this assumption.

Table 1. Fractional atomic coordinates for compound II with temperature parameters $U_{ij}(\text{\AA}^2)$ for sulfur, oxygen and carbon, and $U(\text{\AA}^2)$ for hydrogen. The expressions used are $\exp[-2\pi^2(h^2a^{*2}U_{11} + \dots + 2hka^*b^*U_{12} + \dots)]$ and $\exp[-8\pi^2U(\sin^2\theta/\lambda^2)]$, respectively. Standard deviations in parentheses.

Atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
S(1)	.21211(15)	.28855(5)	-.02489(17)	.0103(4)	.0304(5)	.0427(6)	-.0018(4)	.0021(5)	-.0012(5)
S(2)	.21211(15)	.21145(5)	-.02489(17)	.0103(4)	.0304(5)	.0427(6)	.0018(4)	.0021(5)	.0012(5)
C(3)	-.0509(6)	.2042(2)	-.0127(6)	.0103(15)	.0303(22)	.0280(20)	.0004(14)	.0026(15)	-.0017(17)
C(4)	-.1751(9)	.2500	-.0007(10)	.0133(25)	.0336(33)	.0369(36)	.0000	-.0005(23)	.0000
C(5)	-.0509(6)	.2958(2)	-.0127(6)	.0103(15)	.0303(22)	.0280(20)	-.0004(14)	.0026(15)	.0017(17)
O	-.3712(6)	.2500	.0130(9)	.0075(17)	.0370(27)	.0778(39)	.0000	.0033(23)	.0000
C(31)	-.1285(6)	.1514(2)	-.0119(6)	.0119(15)	.0304(21)	.0333(21)	-.0042(16)	-.0003(17)	.0017(18)
C(32)	-.3166(6)	.1390(2)	.0799(7)	.0111(18)	.0386(25)	.0360(23)	.0000(18)	.0023(16)	.0019(19)
C(33)	-.3850(7)	.0890(2)	.0883(7)	.0188(21)	.0433(28)	.0439(25)	-.0107(21)	.0048(20)	.0042(24)
C(34)	-.2732(8)	.0500(2)	.0064(8)	.0288(22)	.0352(24)	.0500(33)	-.0066(20)	.0025(23)	.0007(22)
C(35)	-.0879(8)	.0612(2)	-.0882(8)	.0299(22)	.0293(25)	.0470(28)	-.0041(20)	.0027(22)	-.0020(21)
C(36)	-.0180(7)	.1112(2)	-.0957(8)	.0216(19)	.0324(25)	.0368(22)	.0016(18)	.0035(19)	.0020(21)
Atom	x	y	z	U	Atom	x	y	z	U
H(32)	-.379(9)	.170(3)	.145(8)	.039(15)	H(35)	-.012(11)	.032(3)	-.147(9)	.061(20)
H(33)	-.511(9)	.083(2)	.161(8)	.036(15)	H(36)	.108(9)	.119(2)	-.172(7)	.035(14)
H(34)	-.317(8)	.013(2)	.014(7)	.026(12)					

Table 2. Fractional atomic coordinates and temperature parameters for compound III. The expressions used for U_{ij} and U are those given in the caption of Table 1. Standard deviation in parentheses.

Atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
S(1)	.80207(12)	.6652(4)	.98807(13)	.0594(16)	.0405(16)	.0174(12)	.0158(13)	.0072(9)	.0008(10)
S(2)	.71858(13)	.9359(4)	.95472(13)	.0572(15)	.0459(15)	.0231(12)	.0163(13)	.0117(10)	-.0014(11)
S(35)	.61789(14)	1.0274(4)	.61578(16)	.0736(17)	.0567(19)	.0375(13)	.0134(14)	.0015(11)	.0085(12)
S(55)	.85259(12)	.2979(4)	.70596(14)	.0538(16)	.0465(16)	.0309(13)	.0052(13)	.0125(10)	-.0037(11)
O	.74571(26)	.6871(9)	.67517(28)	.052(3)	.042(3)	.0145(21)	-.0007(29)	.0071(22)	.0033(24)
C(3)	.7063(4)	.9183(13)	.8171(5)	.021(4)	.031(5)	.021(3)	-.001(4)	.004(3)	-.001(4)
C(4)	.7524(4)	.7261(12)	.7748(5)	.033(4)	.025(5)	.022(4)	-.010(4)	.006(3)	.008(3)
C(5)	.8051(4)	.6002(14)	.8568(5)	.037(5)	.037(5)	.016(4)	-.007(4)	.006(3)	.004(4)
C(31)	.6512(4)	1.0771(15)	.7524(5)	.027(4)	.042(5)	.029(4)	-.007(4)	.003(4)	.016(4)
C(32)	.6148(5)	1.2879(15)	.7870(5)	.026(4)	.029(5)	.031(4)	-.007(4)	.001(4)	.006(5)
C(33)	.5603(6)	1.3866(16)	.6990(9)	.060(7)	.035(7)	.091(7)	.001(5)	.039(6)	.001(6)
C(34)	.5560(5)	1.2722(18)	.6062(7)	.049(6)	.056(7)	.062(7)	.006(6)	-.003(5)	.025(6)
C(51)	.8580(4)	.4039(13)	.8361(5)	.034(5)	.029(5)	.028(4)	-.009(4)	.010(4)	.008(4)
C(52)	.9153(5)	.2776(15)	.9083(5)	.056(5)	.050(6)	.032(4)	.013(5)	.018(4)	-.003(5)
C(53)	.9518(5)	.0954(15)	.8577(6)	.057(6)	.052(6)	.046(5)	.021(5)	.006(5)	.016(5)
C(54)	.9246(4)	.0843(14)	.7494(6)	.046(5)	.038(5)	.052(5)	.008(5)	.022(4)	-.001(5)

Atom	x	y	z	U	Atom	x	y	z	U
H(32)	.621(4)	1.316(13)	.846(4)	.03(2)	H(52)	.923(3)	.324(11)	.967(4)	.05(3)
H(33)	.530(5)	1.480(14)	.706(7)	.06(3)	H(53)	.989(3)	.021(9)	.889(4)	.03(2)
H(34)	.520(5)	1.287(14)	.546(5)	.05(3)	H(54)	.950(3)	-.041(11)	.703(4)	.05(3)

Dimensions and space group for the monoclinic cell are given above under *crystal data*. One notes from the values there that the lengths of the a and c axes are equal within the error. Possible twinning in the ac -plane may therefore give rise to reciprocal lattices which overlap exactly. Such a twinning is in fact found to be present for the crystals of IV, but a rough outline of the crystal and molecular structure can be given in spite of that.

A sharpened (E^2) Patterson map based on the "monoclinic" intensity data gave unambiguously the intramolecular S-S, S-O and S-C vectors which showed that the methyl groups nearest to the oxygen atom were in staggered positions relative to this atom. The Patterson map showed further that the molecules lie on twofold axes which run through the C-O bond and the midpoint of the S-S bond.

With molecules in these positions, and assuming the dimensions of the 1,2-dithiolylium-4-olate system and the interatomic S...O distances in IV to be equal to those in II (described below), the length of the b axis in IV may be estimated to be 6.45 Å as compared to the observed value of 6.398(2) Å.

A schematic view of the crystal structure as seen along the b axis is given in Fig. 1. The asymmetric unit consists of the two half molecules A and B;

(A) and (B) indicate their symmetry equivalents by twofold axis operation. One should note that the A-(A) and the B-(B) directions are symmetric with respect to the diagonals of the ac -plane. This is consistent with the extra symmetry observed for the intensities of the $h0l$ reflections; the intensities are symmetric about the diagonals in the $h0l$ section of the reciprocal lattice. As a consequence twinning in the ac -plane through a rotation of 180° about either ac -diagonal does not affect the relative intensities of the $h0l$ reflections.

Refinement of the structure was tried with isotropic temperature factors and hydrogens neglected.

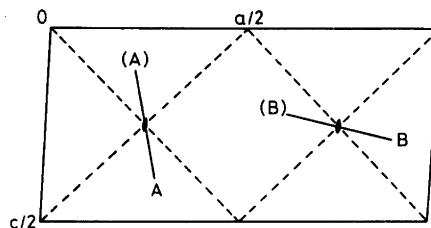


Fig. 1. A schematic view of the crystal structure of compound IV as seen along the b axis. See the text for further explanation.

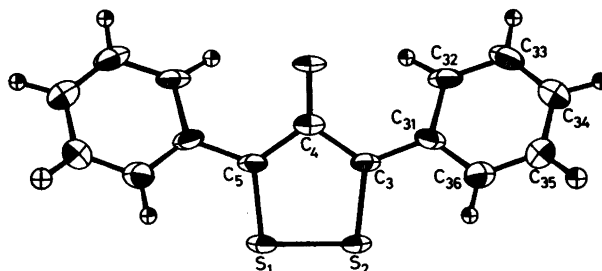


Fig. 2. The molecular structure of compound II with numbering of atoms.

Table 3. Fractional atomic x and z coordinates for compound IV.

Atom	Molecule A		Molecule B	
	x	z	x	z
S	.271	.320	.818	.269
C(1)	.271	.329	.827	.277
C(2)	.250	.250	.750	.250
C(3)	.301	.429	.930	.307
C(4)	.327	.500	.999	.329
C(5)	.389	.419	.917	.390
C(6)	.219	.464	.964	.222
O	.250	.250	.750	.250

The conventional R -factor came down to 0.12 for the $h0l$ reflections, but did not improve beyond 0.26 for the complete data set. The x and z coordinates corresponding to this stage of refinement are given in Table 3.

DISCUSSION

Compound II. The molecular structure of II as found in the present study is shown in Fig. 2. Bond lengths and angles are given in Table 4. The standard deviations given in Table 4 are based on the standard deviations in positional parameters

Table 4. Compound II. Bond lengths $l(ij)$ bond angles $\angle(ijk)$, and deviations Δ_i from least squares planes A and B, respectively. The deviations for atoms which are included in the least squares plane calculations are printed in italics. Bond lengths $l'(ij)$ have been corrected for libration. Standard deviations in parentheses.

Atoms i	j	k	Bonds $l(ij)$ Å	$l'(ij)$ Å	Angles $\angle(ijk)^\circ$	Deviations of atoms i from planes	
						Δ_i (A) Å	Δ_i (B) Å
S(1)	S(2)	C(3)	2.006(2)	2.009	96.4(2)	.006	
S(2)	C(3)	C(4)	1.702(4)	1.710	117.5(4)		
S(2)	C(3)	C(31)			116.3(3)	.006	
C(4)	C(3)	C(31)	1.437(5)	1.440	126.2(4)	.025	
C(5)	C(4)	C(3)			112.1(5)	-.018	
O	C(4)	C(3)	1.262(7)	1.270	123.9(3)	.030	
C(3)	C(31)	C(32)	1.461(6)		120.5(4)	-.018	
C(3)	C(31)	C(36)			121.9(4)		
C(36)	C(31)	C(32)	1.400(6)		117.6(4)		.000
C(31)	C(32)	C(33)	1.413(6)		120.6(4)	-.044	.006
C(32)	C(33)	C(34)	1.377(7)		120.8(5)		-.006
C(33)	C(34)	C(35)	1.373(7)		119.9(5)		.000
C(34)	C(35)	C(36)	1.400(6)		119.6(5)	.024	.005
C(35)	C(36)	C(31)	1.378(7)		121.5(5)		-.005

from the least squares refinement as listed in Table 1. The bond lengths of the disulfide ring and the C—O bond length have been corrected for libration.²²

It is realized that the standard deviations in bond lengths may be overestimated when based on standard deviations in positional parameters from least squares refinement. According to Hamilton and Abrahams¹³ a more realistic estimate of the standard deviations would probably be obtained by multiplying those given by a factor of two.

The molecule lies across the crystallographic mirror plane *m* which passes through the crystal normal to the *b*-axis. The disulfide group is therefore planar.

Least squares planes **A** for the atoms of the five-membered disulfide ring, and **B** for the atoms of the phenyl group, were calculated with equal weights. The equations for these planes are,

$$\mathbf{A} \quad 0.4237x + 7.1484z = -0.0940$$

$$\mathbf{B} \quad 3.2673x - 3.5612y + 6.0891z = -1.0371$$

with *x*, *y*, and *z* as fractional coordinates.

Deviations of atoms from least squares planes are given in Table 4. One sees from the values there that the phenyl group is planar within the error and that the 1,2-dithiolylium ring is nearly so. The oxygen atom and C(31) lie 0.030 and -0.044 Å, respectively, from the plane of the 1,2-dithiolylium ring. The twist about the C(3)—C(31) bond, taken as the angle between the normals of planes **A** and **B**, is 28.2°.

The bond lengths S(1)—S(2)=2.009(2) Å, S(2)—C(3)=1.710(4) Å, and C(3)—C(4)=1.440(5) Å in the 1,2-dithiolylium ring of compound II, *cf.* Table 4, may be compared with those in the 1,2-dithiolylium ring of 4-phenyl-1,2-dithiolylium thiocyanate^{5,14} and 4-phenyl-1,2-dithiolylium chloride monohydrate.^{3,5} They are, mentioned in the same order, S—S=2.004(5) and 2.021(4) Å, S—C=1.678(8) and

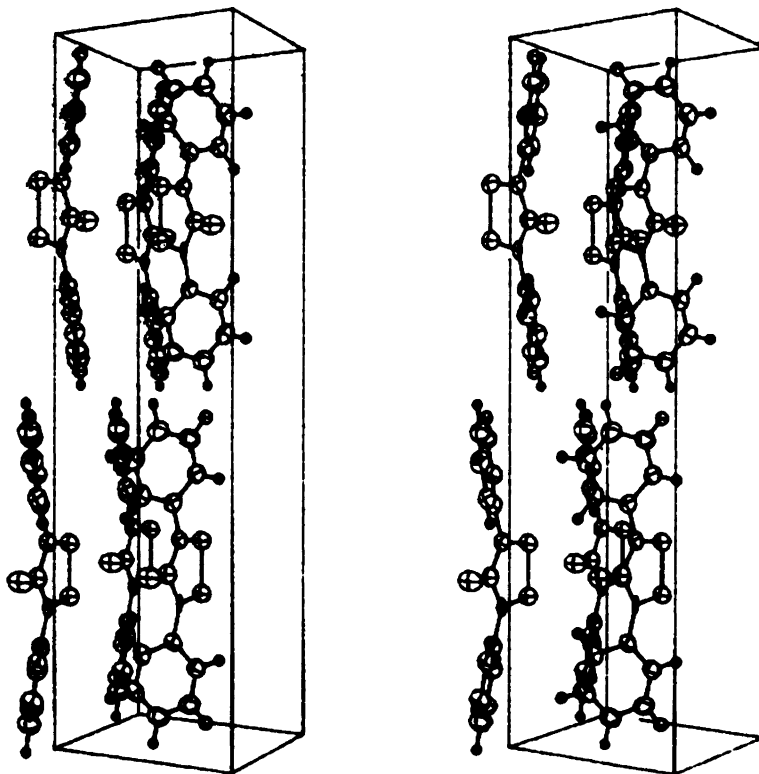


Fig. 3. An ORTEP²¹ stereoscopic view of the crystal structure of compound II in *c*-axis direction.

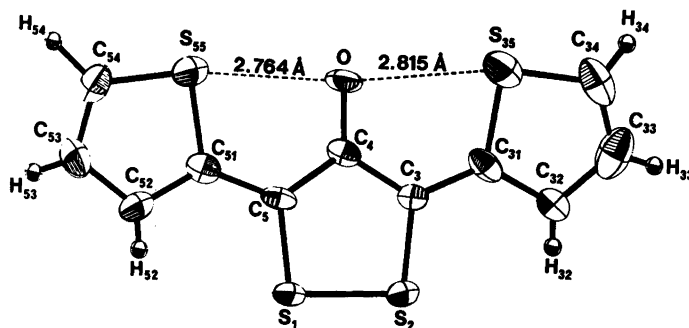


Fig. 4. The molecular structure of compound III with numbering of atoms.

1.673(11) Å, and C–C = 1.388(13) and 1.384(13) Å, respectively.

One notes that the latter S–C and C–C bonds are somewhat shorter than those in compound II. Such a difference might in fact be expected since the olate oxygen in II is strongly engaged in π -bonding with C(4), C(4)–O = 1.270(7) Å, and this is clearly at the expense of the π -bonding in the S–C–C–S part of the five-membered ring.

C(4) of the 4-phenyl-1,2-dithiolylium ion is much less engaged in π -bonding with an exocyclic atom.⁵ Thus, the connecting bond between C(4) and phenyl carbon is found to be 1.498(13) Å in the thiocyanate and 1.494(15) Å in the chloride monohydrate. These bond lengths agree with that of the central bond in diphenyl, 1.494(2) Å, as found by X-ray crystallographic methods.¹⁵

The dimensions of the phenyl groups in II are normal, *cf.* Table 4, and the C(3)–C(31) bond length of 1.461(6) Å show a small, although hardly significant deviation from the length of the central bond in diphenyl mentioned above.

The crystal structure of compound II, given in Fig. 3, shows that the oxygen atom approaches the sulfur atoms of a neighbouring molecule in a tri-

angular $\begin{array}{c} \cdot\cdot\cdot\text{S}- \\ \text{O}\cdot\cdot\cdot | \\ \cdot\cdot\cdot\text{S}- \end{array}$ arrangement where the S \cdots O dis-

tances are 2.870(5) Å; the oxygen atom lies 0.45 Å from the plane of the 1,2-dithiolylium ring of this molecule. It is interesting to note that this triangular arrangement is equivalent to those which occur between halide ions and disulfide groups in crystals of 1,2-dithiolylium halides (I).⁵

The mentioned S \cdots O distance of 2.870(5) Å is shorter than the sum of the van der Waals radii for

sulfur and oxygen. This sum becomes 3.25 Å if the radii given by Pauling,¹⁶ 1.85 Å for S and 1.40 for O, are used. It is believed, however, that the Pauling value for sulfur is somewhat too large, and values in the range 1.60–1.80 Å have been proposed by other authors.^{17–20} Even if the smallest of these values is used for sulfur the sum of the van der Waals radii remains larger than the above S \cdots O distance. Thus there seems to be partial bonding between oxygen and sulfur in the triangular

$\begin{array}{c} \cdot\cdot\cdot\text{S}- \\ \text{O}\cdot\cdot\cdot | \\ \cdot\cdot\cdot\text{S}- \end{array}$ arrangement, and this bonding may be

rationalized in terms of weak three-centre two-electron bonds, established through partial transfer of charge from a filled orbital on the oxygen atom into empty orbitals on the sulfur atoms.

Compound III. The molecular structure of III as found in the present study is shown in Fig. 4. Bond lengths and angles are given in Table 5. The standard deviations in bond lengths and angles are based on the standard deviations in atomic coordinates from the least squares calculations.

Rigid body analyses according to the method by Schomaker and Trueblood²² have been carried out for the 1,2-dithiolylium ring as well as for the entire molecule. The librational tensors arrived at were roughly the same and the differences between the two series of corrected bond lengths were negligible. The l' values in Table 5 have been corrected according to the librational tensor for the entire molecule. The libration is rather anisotropic with the axis of maximum libration (5.5°) running in the C(3)–C(5) direction.

Least squares planes for the atoms of the 1,2-dithiolylium ring A, and for the atoms of the

Table 5. Compound III. Bond lengths $l(ij)$, bond angles $\angle(ijk)$, and deviations Δ_i from least squares planes A, B, and C, respectively. The deviations for atoms which are included in the least squares plane calculations are printed in italics. Bond lengths $l(ij)$ have been corrected for libration. Standard deviations in parentheses.

Atoms			Bonds		Angles	Deviations of atoms i from planes		
i	j	k	$l(ij)$ Å	$l'(ij)$ Å	$\angle(ijk)^\circ$	Δ_i (A) Å	Δ_i (B) Å	Δ_i (C) Å
S(1)	S(2)	C(3)	2.023(3)	2.026	96.4(3)	-.009		
S(2)	C(3)	C(4)	1.709(6)	1.718	116.2(4)	-.006		
S(2)	C(3)	C(31)			119.3(5)			
C(4)	C(3)	C(31)			124.4(5)			
C(3)	C(4)	C(5)	1.463(10)	1.466	112.6(5)	.021	-.069	
O	C(4)	C(3)			122.6(5)	-.076	.364	.154
O	C(4)	C(5)	1.258(7)	1.265	124.3(6)			
C(4)	C(5)	S(1)			111.7(5)	-.032		
C(4)	C(5)	C(51)	1.403(8)	1.407	123.5(5)			
S(1)	C(5)	C(51)	1.702(6)	1.711	117.6(4)			
S(2)	S(1)	C(5)			95.7(3)			
C(5)	C(51)	C(52)			128.7(6)	.025		-.047
C(5)	C(51)	S(55)	1.448(10)	1.450	120.2(4)			
S(55)	C(51)	C(52)	1.729(7)	1.737	111.1(6)	-.213	.422	.005
C(51)	C(52)	C(53)	1.369(9)	1.373	111.7(6)	.008		-.008
C(52)	C(53)	C(54)	1.391(12)	1.394	114.1(7)	.134		.008
C(53)	C(54)	S(55)	1.353(10)	1.360	111.7(6)	.017		-.003
C(54)	S(55)	C(51)	1.689(8)	1.692	91.5(4)	-.170	.511	-.002
C(3)	C(31)	C(32)			126.9(6)			
C(3)	C(31)	S(35)	1.407(9)	1.411	121.5(6)			
S(35)	C(31)	C(32)	1.725(6)	1.735	111.5(5)	-.326	.007	-.031
C(31)	C(32)	C(33)	1.421(11)	1.424	108.8(7)	.027	-.011	
C(32)	C(33)	C(34)	1.396(12)	1.401	115.6(8)	.277	.011	
C(33)	C(34)	C(35)	1.321(14)	1.327	113.3(7)	.114	-.005	
C(34)	S(35)	C(31)	1.687(10)	1.689	90.8(4)	-.190	-.002	.095

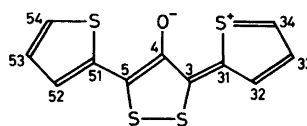
thienyl rings, B and C, respectively, cf. Fig. 4 and Table 5, were calculated with equal weights. The equations for these planes are,

$$\text{A } 12.4139x + 3.6220y - 1.7680z = 10.6281$$

$$\text{B } 13.1403x + 3.1067y - 4.4719z = 8.5495$$

$$\text{C } 12.4557x + 3.5261y - 3.4944z = 9.1977$$

with x , y and z as fractional coordinates. The angles between the planes A and B, A and C, and B and C are, 13.4, 8.0 and 6.4°, respectively. Deviations of atoms from least squares planes are given in Table 5. One sees from the values there that the three rings are planar within the error. Furthermore, from the Δ_i (C) values, S(35) lies close to plane C, $\Delta_{35} = -.031$ Å, and C(34) and O lie 0.095 and 0.154 Å, respectively, from this plane. The sequence C(34)–S(35)–O–S(55)–C(54) is thus almost planar.



IIIa

It is seen from the bond lengths in Table 5 that the bonds in the C(33)–C(32)–C(31)–C(3)–C(4)–C(5)–C(51)–C(52)–C(53) sequence are found to be alternating short and long, and it is therefore tempting to assume that the canonical form IIIa dominates the structure. However, the rather short C(33)–C(34) bond 1.327(14) Å, is inconsistent with this assumption, and the standard deviations in bond lengths hardly permit a conclusion to be made on this point.

The average structure, given in Fig. 5, is probably a more appropriate basis for a discussion because

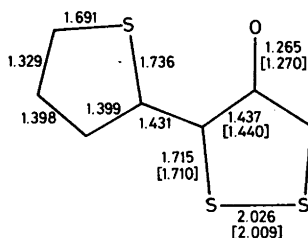
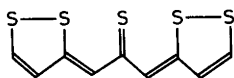


Fig. 5. The average structure of compound III. The average of bond lengths for equivalent bonds in the two halves of the molecule are given. The values in brackets refer to compound II.

none of the found lengths deviate significantly from this structure. The bond lengths in the 1,2-dithiolylium-4-olate part of the average structure agree with those found for this molecular moiety in compound III, given in brackets in Fig. 5. The dimensions of the thienyl group agree with reported values.²³⁻²⁵

The thienyl sulfurs approach the olate oxygen at distances shorter than the corresponding van der Waals distance; $S(35)\cdots O = 2.815(9)$ Å and $S(55)\cdots O = 2.764(9)$ Å. The $C(34)-S-O-S-C(54)$ sequence is roughly linear, *cf.* Fig. 4, and the structure resembles that of a polysulfur system (VI).



VI

This system has been studied by Sletten^{26,27} who shows that partial bonding occurs in the central

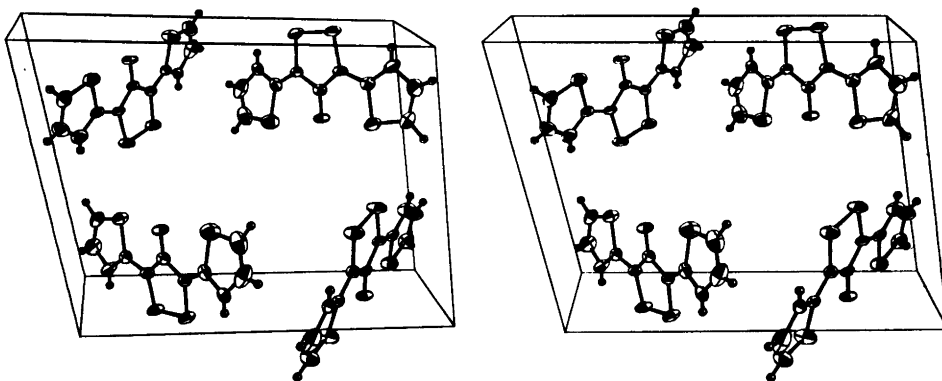


Fig. 6. A stereoscopic view of the crystal structure of compound III in *b*-axis direction.

part of this sulfur chain, and that the central sulfur atom carries excess negative charge.

Weak bonding between olate oxygen and thienyl sulfur may therefore also occur in the present compound, and the fact that the molecule has a configuration with a roughly linear $C(34)-S-O-S-C(54)$ sequence supports this assumption.

In crystals of III there are close contacts between the olate oxygen and a neighbouring disulfide group.

The close contacts occur in a triangular $O\cdots S-S$ arrangement where the $O\cdots S$ distances are 2.89 Å.

The planes of the two molecules in question are almost perpendicular to each other, *cf.* Fig. 6, and the angle between the $C-O$ bond and the direction from the olate oxygen to the midpoint of the adjacent $S-S$ bond is 160° . This implies that the environment of the olate oxygen may be regarded as being roughly square planar.

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