

présence de la double liaison C(25)=C(26) fait que le groupe éthylénique est pratiquement plan, mais les atomes O(23) et O(30) s'écartent notablement de ce plan puisqu'ils en sont distants respectivement de 0,26 Å et -0,20 Å ce qui correspond à une rotation de 12,5° autour de C(25)-C(24).

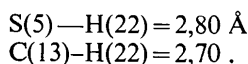
Interactions moléculaires-cohésion cristalline

La compacité de cette structure complexe est aussi élevée que celle du naphthalène ($C=0,70$). Une étude systématique des proximités atomiques permet de mettre en évidence deux directions d'enchaînement: parallèlement à [001] et à [100].

Enchaînement parallèle à [001]

Le motif cristallin est constitué d'un cation mopazine associé à un anion maléate par une liaison C-O⁻...H-N⁺. Mais d'autre part, nous observons des contacts entre les ions maléates superposés par l'intermédiaire des atomes O(29) et O(30) et des deux hydrogènes éthyléniques (Fig. 6).

Dans la même direction, les groupements méthoxyles assurent deux 'contacts' avec l'atome de soufre et le carbone C(3) (Fig. 7):

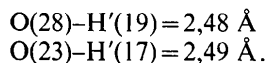


Enfin, notons la distance C(6)-C(6)=3,40 Å, proche de la distance graphitique entre deux cycles symétriques par rapport à un centre, mais la superposition est très imparfaite (Fig. 8).

Enchaînement parallèle à [100]

L'enchaînement principal est de nouveau réalisé au moyen des anions maléates. On constate sur la Fig. 9

que cet anion est en contact par les atomes O(23) et O(28) avec un méthyle et le méthylène en α de l'azote N⁺



Par ailleurs, on note O(28)-H''(17), 2,50 Å qui fait le pendant de la liaison hydrogène O⁻(23)-H...⁺N(18).

L'oxygène O(28) semble donc jouer un rôle donneur d'électrons comparable à celui de O(23).

Nous remarquons à nouveau, à propos de cette phénothiazine, que tout se passe comme si une partie de la charge positive de N⁺(18) était passée sur les méthyles terminaux. De même, une partie de cette charge semble se retrouver sur le carbone C(17) également en α de l'azote N⁺(18).

Références

- BELL, J. D., BLOUNT, J. F., BRISCOE, O. V. & FREEMAN, H. C. (1968). *Chem. Commun.* pp. 1656-1658.
 DARLOW, S. F. & COCHRAN, W. (1961). *Acta Cryst.* **14**, 1250-1257.
 ELLISON, R. D. & LEVY, H. A. (1965). *Acta Cryst.* **19**, 260-268.
 GOODWIN, T. H., PRZYBYLSKA, M. & ROBERTSON, J. M. (1959). *Acta Cryst.* **3**, 279-284.
 MARS AU, P. (1971). *Acta Cryst.* **B27**, 42-51.
 MARS AU, P. & BUSETTA, B. (1973). *Acta Cryst.* **B29**, 986-991.
 MARS AU, P. & CALAS, M. R. (1971). *Acta Cryst.* **B27**, 2058-2062.
 MARS AU, P. & CAM, Y. (1973). *Acta Cryst.* **B29**, 980-986.
 ROMERS, C. & HESPER, B. (1966). *Acta Cryst.* **20**, 162-169.
 VAN OIJEN, J. W. L. & ROMERS, C. (1966). *Acta Cryst.* **20**, 169-176.

Acta Cryst. (1973). **B29**, 998

The Crystal Structure of 3-Ethyl-5-[2'-(1',3'-dithiolanylidene)]rhodanine

BY HENRY R. LUSS AND DOUGLAS L. SMITH

Research Laboratories, Eastman Kodak Company, Rochester, New York 14650, U.S.A.

(Received 6 November 1972; accepted 19 January 1973)

The crystal structure of the merocyanine-like dye, 3-ethyl-5-[2'-(1',3'-dithiolanylidene)]rhodanine, C₈H₉NOS₄, has been determined from single-crystal X-ray intensity data collected with an automated diffractometer. The crystals are monoclinic, $P2_1/a$, with $a=21.230$ (5), $b=5.059$ (2), $c=10.305$ (3) Å, $\beta=95.78$ (1)°, and $Z=4$. The structure was solved by direct methods and refined by full-matrix least-squares calculations to $R_1=0.032$. Hydrogen atoms were located and refined. The puckered dithiolanylidene ring is disordered at the methylene groups with 90% of the molecules present in one conformation. The rhodanine ring is approximately planar, and there is some conjugation between the rings.

Introduction

Merocyanine dyes, neutral undissociated compounds which contain the characteristic amidic chromophore,

are well known as spectral sensitizers of photographic emulsions (Brooker, 1966). The crystal structures of the merocyanine dyes(I),(II) and (III) and the iodine complex of (I) have been determined by Van Meerssche and

co-workers (Germain, Paternotte, Piret & Van Meerssche, 1964; Germain, Piret, Van Meerssche & De Kerf, 1962, 1961; Bois d'Enghien-Peteau, Meunier-Piret & Van Meerssche, 1968) and represent the only crystal structure determinations reported for this class of dyes. These dyes all contain a 3-substituted rhodanine nucleus (IV), which is commonly used to furnish the carbonyl end of the amidic system. The crystal structure of rhodanine (IV, R=H), a much-studied dye in its own right, has also been determined (Van der Helm, Lessor & Merritt, 1962). Van Meerssche and coworkers have compared the molecular dimensions found in these structures to ascertain the extent of conjugation in the chromophore.

Yellow, long prismatic (*b*) crystals.
Monoclinic (Mo $K\alpha_1=0.70926 \text{ \AA}$)

$$\begin{array}{ll} a = 21.230 (5) \text{ \AA} & b = 5.059 (2) \\ c = 10.305 (3) & \beta = 95.78 (1)^\circ \end{array}$$

Volume of unit cell, $1101.1 (5) \text{ \AA}^3$.

Density calculated ($Z=4$) 1.589 g cm^{-3} ,
measured (flotation) 1.55 g cm^{-3} .

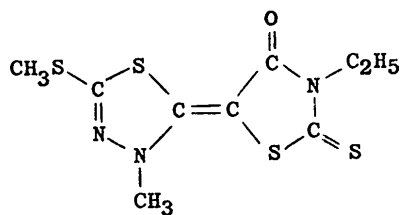
Linear absorption coefficient, $\mu = 8.0 \text{ cm}^{-1}$ (Mo $K\alpha$).

Total number of electrons per unit cell, $F(000) = 544$.

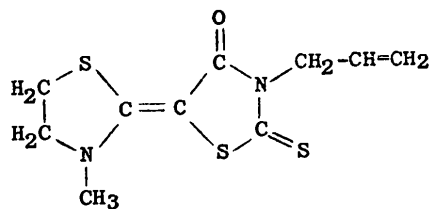
Absent spectra: $h0l$ for h odd, $0k0$ for k odd.

Space group, $P2_1/a$ (C_{2h}^5).

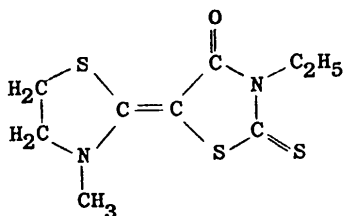
General positions: $\pm(x, y, z; \frac{1}{2} + x, \frac{1}{2} - y, z)$.



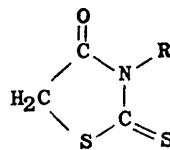
(I)



(II)

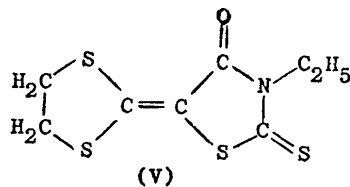


(III)



(IV)

We have determined the crystal structure of 3-ethyl-5-[2'-(1',3'-dithiolanylidene)]rhodanine (V), a merocyanine-like molecule in which the nitrogen in the amidic chromophore has been replaced by sulfur.



(V)

Crystal data

$C_8H_9NOS_4$ M.W. 263.42.
3-Ethyl-5-[2'-(1',3'-dithiolanylidene)]rhodanine or
2-thio-3-ethyl-5-[2'-(1',3'-dithiolanylidene)]thiazolidine-2,4-dione

Experimental

Single crystals grown from 2-propanol were supplied by A. P. Marchetti of the Kodak Research Laboratories. Space group extinctions and preliminary lattice dimensions were obtained from precession photographs. A small crystal, $0.14 \times 0.16 \times 0.58 \text{ mm}$, was cemented to a thin glass rod and used for intensity data collection on an automatic Picker four-circle goniostat at $25 \pm 2^\circ \text{C}$. To minimize the effect of multiple reflections (Zachariasen, 1965), the *b* axis was oriented 8.5° from the φ axis. Twenty reflections at moderately high Bragg angles (Mo $K\alpha$ radiation) were accurately centered through very narrow vertical and horizontal slits at a take-off angle of 0.5° . These observations were used as input to the computer program *PICK2* (Ibers, 1966), which refined the cell and orientation parameters by the method of least squares and generated the cards to control the goniostat.

Intensity data were collected with Zr-filtered Mo radiation at a 1.5° take-off angle. A scintillation detector was used, and the pulse-height analyzer was set for an approximately 90% window. All 2673 unique reflections for $2\theta < 56^\circ$ were measured by the θ - 2θ scan technique at a 2θ scan rate of $1.0^\circ \text{ min}^{-1}$. The scan range varied from 1.2° at low 2θ to 2.1° at high 2θ . Stationary-crystal stationary-counter background counts were taken for 20 sec at each end of the scan. For count rates above 11,000 c.p.s. brass attenuators were automatically inserted in the diffracted beam. To check electronic and crystal stability, the intensity of the 10,2,1 reflection was measured every 50th reflection. No systematic variation was observed for these standard intensities.

The background for a reflection was approximated by a straight line between the two measured background points. The intensities were corrected for background and for Lorentz and polarization effects and were reduced to structure amplitudes, $|F_o|$. Absorption corrections were not applied. The maximum error caused by absorption is estimated to be less than 2% of the intensity. Standard deviations $\sigma(I)$ were based on counting statistics and were corrected to $\sigma(F)$. 570 intensities were less than $2\sigma(I)$ and were considered unobserved. They were set equal to $2\sigma(I)$ and corrected to structure amplitudes, F_{lim} .

Determination and refinement of the structure

The observed structure factors were converted to normalized structure factor magnitudes, $|E_H|$ (Hauptman & Karle, 1953). The 285 E 's with $|E| \geq 1.60$ were phased by the multiple-solution computer program of Long (1965), modified by Tsai (1968), based on the reiterative application of Sayre's (1952) equation. An E map calculated from the most consistent set of phases yielded all 14 heavy atoms.

Refinement was by full-matrix least squares (Busing, Martin & Levy, 1962). The quantity minimized was $\sum w(F_o - F_c^*)^2$, where

$$F_c^* = KF_c \left\{ 1 + g \left[\frac{1 + \cos^4 2\theta}{(1 + \cos^2 2\theta) \sin 2\theta} \right] F_c^2 \right\}^{-1/2},$$

in which K is the scale factor, g is the extinction parameter (Zachariasen, 1963; Larson, 1967) and F_c is the usual calculated structure factor. Weights were defined as

$$w = [\sigma^2(F_o) + (rF_o)^2]^{-1},$$

where r was chosen to make the averages of $\sum w(F_o - F_c^*)^2$ approximately constant for groups of increasing F_o values (Cruickshank, 1965). Unobserved reflections were included in the refinement and agreement indices if $|F_c^*| > F_{\text{lim}}$. The usual agreement index was defined as $R_1 = \sum |F_o - F_c^*| / \sum |F_o|$ and the weighted agreement index as $R_2 = [\sum w(F_o - F_c^*)^2 / \sum wF_o^2]^{1/2}$. The atomic scattering factors were obtained from Stewart, Davidson & Simpson (1965) for hydrogen and *International Tables for X-ray Crystallography* (1962) for all other atoms. The anomalous scattering factors for sulfur ($\Delta f' = 0.110$, $\Delta f'' = 0.124$) (Cromer & Liberman, 1970) were applied. All computations were performed on an IBM 360/65 computer.

Three cycles of refinement with isotropic temperature factors and two with anisotropic temperature factors reduced R_2 to 0.076. The temperature factor for C(5) (see Fig. 1) diverged in the first two cycles but then converged as C(5) moved 0.74 Å from its initial position. A difference Fourier map revealed all 9 hydrogen atoms and an additional hydrogen-like peak near C(5). Refinement continued during which the heavy atoms were varied anisotropically and the hydrogen atoms isotropically. R_2 dropped to 0.045 as all parameters except the temperature factor for H(1) converged, although β_{22} for C(5) seemed abnormally high.

A new difference Fourier map was featureless except that the hydrogen-like peak near C(5) appeared again. Distances and angles calculated for the extra peak enabled us to formulate a disordered structure. In approximately 10% of the molecules, C(5) is located

Table 1. Final atomic parameters with estimated standard deviations in parentheses

The anisotropic thermal parameters are in the form $\exp[-0.25(h^2a^*^2B_{11} + \dots 2klb^*c^*B_{23})]$.

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> ₁₁	<i>B</i> ₂₂	<i>B</i> ₃₃	<i>B</i> ₁₂	<i>B</i> ₁₃	<i>B</i> ₂₃
S(1)	0.04454 (3)	-0.29256 (13)	0.38280 (6)	4.78 (4)	4.43 (3)	4.79 (3)	-0.80 (2)	0.68 (2)	1.53 (2)
S(2)	0.05179 (2)	0.05421 (11)	0.15294 (5)	3.09 (2)	3.88 (2)	3.56 (2)	-0.87 (2)	-0.07 (2)	0.67 (2)
S(3)	0.07248 (3)	0.40630 (11)	-0.09794 (5)	3.89 (2)	3.81 (2)	3.43 (2)	-1.12 (2)	-0.24 (2)	0.69 (2)
S(4)	0.18887 (2)	0.63405 (11)	0.03569 (6)	2.93 (2)	3.91 (2)	4.31 (3)	-0.82 (2)	0.33 (2)	0.42 (2)
O	0.20622 (7)	0.37813 (35)	0.29405 (15)	3.14 (5)	5.75 (8)	4.13 (7)	-1.23 (6)	-0.12 (5)	0.31 (6)
N	0.13744 (8)	0.05500 (34)	0.34641 (16)	2.89 (7)	3.41 (7)	3.28 (7)	0.24 (6)	0.06 (5)	0.41 (6)
C(1)	0.08135 (9)	-0.06648 (40)	0.30507 (19)	3.14 (7)	3.07 (8)	3.49 (8)	0.21 (7)	0.46 (6)	0.44 (7)
C(2)	0.15849 (9)	0.25050 (41)	0.26528 (19)	2.71 (7)	3.53 (9)	3.21 (8)	0.02 (7)	0.45 (6)	0.00 (7)
C(3)	0.11591 (9)	0.26805 (40)	0.14682 (19)	2.62 (7)	3.26 (8)	3.23 (8)	-0.33 (6)	0.37 (6)	0.10 (7)
C(4)	0.12519 (8)	0.42003 (38)	0.04257 (18)	2.62 (7)	2.79 (8)	3.28 (8)	-0.17 (6)	0.36 (6)	-0.16 (6)
C(5)	0.17581 (14)	0.68055 (81)	-0.14018 (30)	4.25 (14)	6.13 (22)	4.42 (15)	-1.30 (13)	0.61 (10)	1.57 (14)
C(6)	0.10721 (12)	0.66929 (56)	-0.18283 (25)	4.77 (11)	4.93 (12)	3.94 (11)	-1.20 (10)	0.20 (9)	1.22 (9)
C(7)	0.17367 (12)	-0.00331 (52)	0.47178 (23)	4.07 (11)	3.97 (11)	4.15 (10)	0.51 (8)	-0.54 (8)	0.85 (8)
C(8)	0.15402 (16)	0.16856 (61)	0.57916 (24)	6.64 (16)	5.18 (14)	3.12 (9)	0.44 (12)	-0.16 (10)	0.84 (9)

Table 1 (cont.)

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> *
C(5')	0.1577 (9)	0.8048 (42)	-0.1016 (19)	2.7 (3)
H(1)	0.1966 (22)	0.5285 (98)	-0.1826 (41)	9.8 (13)
H(2)	0.1950 (14)	0.8463 (64)	-0.1555 (28)	6.1 (7)
H(3)	0.0856 (14)	0.8566 (64)	-0.1523 (28)	5.6 (7)
H(4)	0.0980 (11)	0.6381 (48)	-0.2697 (24)	4.3 (5)
H(5)	0.1674 (12)	-0.1863 (52)	0.4863 (24)	4.5 (5)
H(6)	0.2212 (13)	0.0249 (52)	0.4571 (24)	5.6 (6)
H(7)	0.1832 (13)	0.1369 (57)	0.6650 (27)	6.2 (7)
H(8)	0.1070 (14)	0.1448 (58)	0.5880 (25)	6.0 (7)
H(9)	0.1605 (14)	0.3632 (64)	0.5553 (27)	6.6 (7)

* Isotropic Debye-Waller factor.

on the opposite side of the mean molecular plane. Any disorder in the position of C(6) could not be resolved in the electron density maps. As a result of the disorder in the C(5) position, the hydrogen atoms attached to both C(5) and C(6) must change location also. However, the shift in hydrogen positions occurs in such a way that the disordered H(1) moves to approximately the ordered H(2) position and the disordered H(3) moves to the ordered H(4) position. This leaves the H(2) and H(4) positions with full occupancy and the H(1) and H(3) positions with reduced occupancy corresponding to the reduced occupancy of C(5).

To continue the refinement, atom C(5) was assigned an occupancy factor which was subsequently refined. The occupancies of H(1) and H(3) were not refined but were reset after each cycle to equal the refined occupancy of C(5). A new atom, C(5'), with an isotropic temperature factor was introduced at the position of the extra peak and was assigned an occupancy equal to 1.0 minus the C(5) occupancy. The C(5') occupancy also was not refined but was reset after each cycle. All other atoms were given unit occupancies which were not refined. Three refinement cycles in which only the parameters of the seven atoms involved in the disorder were varied indicated the reasonableness of the model.

The largest structure factors were obviously affected by extinction, so the 266 largest *F*'s were used with unit weighting to refine *g*. Three further cycles of refinement in which all parameters except *g* were varied completed the refinement. The final agreement indices are $R_1=0.032$ and $R_2=0.040$ for 2102 observed reflections plus 64 unobserved reflections with $|F_c| > F_{lim}$. Of the unobserved reflections, none had $|F_c| > 1.7F_{lim}$. The standard deviation of an observation of unit weight was 1.32. The maximum parameter shift on the last cycle was 0.33σ . A final difference Fourier map

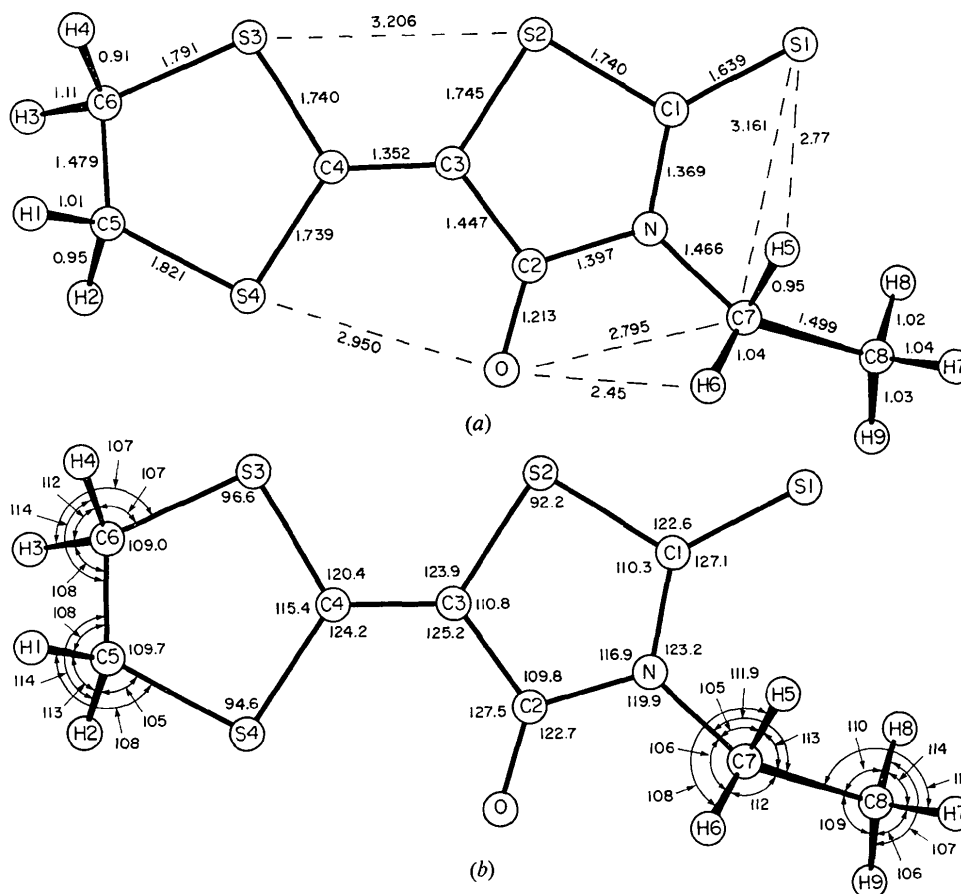


Fig. 1. Atomic labeling and (a) interatomic distances and (b) angles.

Table 2. Observed and calculated structure factors

The column headings are h, l, 10F_o/K, 10F_c*/K and 10σ(F_o)/K. An asterisk denotes unobserved reflections.

Table with multiple columns of numerical data representing structure factors and standard deviations for various reflections. The table is organized into several sections, with some columns containing asterisks to denote unobserved reflections. The data is presented in a grid-like format with varying column widths.

the dithiolanylidene and rhodanine rings. Consideration of the covalent radii for sulfur (Pauling, 1960), and for trigonal and tetrahedral carbon (Bastiansen & Trætterberg, 1962) leads to expected single-bond distances of 1.81 Å for S- sp^3 C and 1.78 Å for S- sp^2 C, and a double-bond distance of 1.61 Å for S- sp^2 C. The two S- sp^3 C bonds, whose difference of 0.03 Å should not be considered significant because of the disorder, average a normal 1.806 Å. The four S- sp^2 C bonds can be considered equal and average 1.741 Å, somewhat shorter than the expected single-bond value, whereas the S(1)-C(1) distance of 1.639 Å is somewhat longer than the double-bond distance. The bridge bond, C(3)-C(4), is slightly longer (1.352 Å) than the accepted double-bond distance of 1.335 Å (Sutton, 1965) and the adjacent C(2)-C(3) bond (1.447 Å) is shorter than the usual single-bond distance of 1.48 Å for trigonal carbons (Bastiansen & Trætterberg, 1962). The N-C(7) bond (1.466 Å) is comparable to the value 1.47 Å expected for unconjugated N-C single bonds (Sutton, 1965), whereas the N-C(1) and N-C(2) bonds are typical for conjugated N-C single bonds (Smith, 1969; Karle & Karle, 1967). The longer distance for N-C(2) (1.397 Å) compared to N-C(1) (1.369 Å) is probably due to the relatively

greater involvement in the conjugation of the C(2)-C(3) bond compared to the C(1)-S(2) bond. The C(2)-O distance (1.213 Å) agrees well with the 1.215 Å found in aldehydes and ketones (Sutton, 1965). The C(7)-C(8) bond (1.499 Å) is shorter than the normal sp^3 C- sp^3 C single-bond length of 1.534 Å (Bastiansen & Trætterberg, 1962), perhaps because of neglect of the thermal motion. The C(5)-C(6) bond (1.479 Å) is even shorter, possibly due to the disorder in this area of the molecule, but comparable with the 1.459 and 1.475 Å found by Lee & Goodacre (1971*a,b*) for a similarly situated bond in 1-chloro- and 1-phenyl-2,5-dithio-1-thiophosphorus(V) cyclopentane, respectively. The C-H distances average 1.01 Å, typical for structures determined by X-rays.

The angles at the sulfur atoms in the rings are slightly larger than 90°, as is generally observed (Chesick & Donohue, 1971). This causes the dithiolanylidene ring, with tetrahedral angles at C(5) and C(6), to be puckered, departing from planarity (C, Table 5) in the same manner as dye (II). The remainder of the molecule is also not planar. Atomic deviations from a mean plane through the molecule [excluding C(5), C(6), the ethyl group, and the hydrogen atoms] range up to 0.082 Å (A, Table 5). The five atoms of the

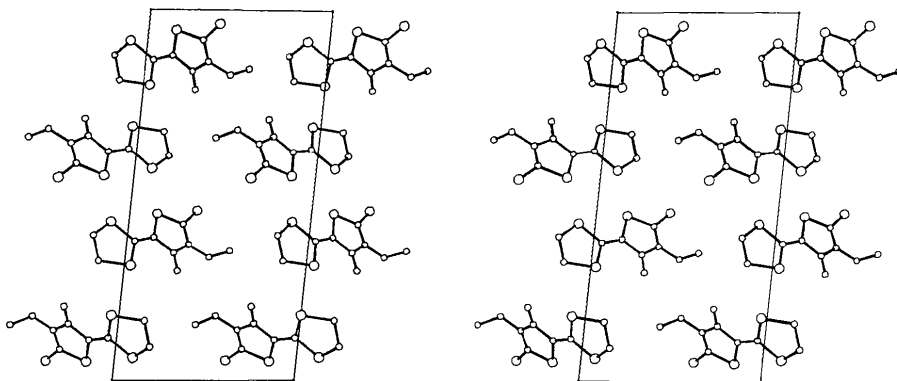


Fig. 2. Stereoscopic view of the molecular packing. The c axis is horizontal, left to right, a is vertical, top to bottom, and b points away from the viewer.

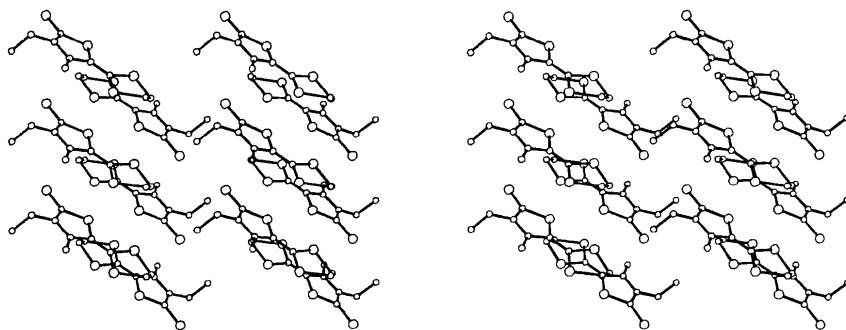


Fig. 3. Stereoscopic view of the molecular packing rotated 90° about c from Fig. 2. The c axis is horizontal left to right, b is vertical, bottom to top, and a is pointing away from the viewer. This picture shows two molecular sheets related by an inversion center.

rhodanine ring fit a plane (*B*, Table 5) to within 0.021 Å but O and C(4) deviate from this plane by 0.060 Å and -0.12 Å, respectively. These deviations from planarity and the apparent asymmetry in the angles at C(1), C(2), C(3), C(4), and N are caused by repulsions between the substituent groups. For example, S(2)···S(3) and S(4)···O are approximately 0.2 Å shorter than the sums of the van der Waals radii (1.7 Å for S, 1.4 Å for O). The atoms S(2) and S(3) fall on opposite sides of the mean molecular plane (*A*, Table 5), as do S(4) and O, and the angle C(3)-C(2)-O has opened up to 127.5°, which suggests repulsion. There is no evidence for S···S and S···O interactions of the type described by Klingsberg (1969) for the thiothiophene no-bond resonance compounds.

The molecular packing is shown stereoscopically (Johnson, 1965) in Figs. 2 and 3. The molecules are packed end to end and plane to plane in sheets parallel to (100). All molecules within a given sheet are translationally equivalent through the *b* and *c* axial repeats. The plane-to-plane stacking is along [010] with an interplanar spacing of 3.6 Å. The sheets are related in pairs by centers of inversion, so that end-to-end contact is alternatively along [011] for two sheets and then along [01 $\bar{1}$] for two sheets. For a pair of sheets related by a center of inversion, the molecules also line up edge to edge along their S(1), S(2), S(3) edges to form planar ribbons two molecules wide parallel to (41 $\bar{1}$) or ($\bar{4}$ 11). For all atoms, including C(5'), there are no intermolecular contacts shorter than would be expected from van der Waals radii.

References

- BASTIANSEN, O. & TRÆTTEBERG, M. (1962). *Tetrahedron* **17**, 147-154.
- BLOW, D. M. (1960). *Acta Cryst.* **13**, 168.
- BOIS D'ENGHIEN-PETEAU, M., MEUNIER-PIRET, J. & VAN MEERSSCHE, M. (1968). *J. Chim. Phys.* **65**, 1221-1225.
- BROOKER, L. G. S. (1966). *Theory of the Photographic Process*, Chap. 11, 3rd ed. Edited by C. E. K. MEES and T. H. JAMES. New York: Macmillan.
- BUSING, W. R., MARTIN, K. O. & LEVY, H. A. (1962). *ORFLS*. Report ORNL-TM-305, Oak Ridge National Laboratory, Tennessee.
- CHESICK, J. P. & DONOHUE, J. (1971). *Acta Cryst.* **B27**, 1441-1444.
- CROMER, D. T. & LIBERMAN, D. (1970). *J. Chem. Phys.* **53**, 1891-1898.
- CRUICKSHANK, D. W. J. (1965). In *Computing Methods in Crystallography*, chap. 14. Edited by J. S. ROLLETT, London: Pergamon Press.
- GERMAIN, G., PATERNOTTE, C., PIRET, P. & VAN MEERSSCHE, M. (1964). *J. Chim. Phys.* **61**, 1059-1069.
- GERMAIN, G., PIRET, P., VAN MEERSSCHE, M. & DE KERF, J. (1961). *Bull. Soc. Chim. Fr.* pp. 1407-1412.
- GERMAIN, G., PIRET, P., VAN MEERSSCHE, M. & DE KERF, J. (1962). *Acta Cryst.* **15**, 373-382.
- HAUPTMAN, H. & KARLE, J. (1953). *Solution of the Phase Problem. I. The Centrosymmetric Crystal*. Monograph No. 3, American Crystallographic Association.
- IBERS, J. A. (1966). Private communication.
- International Tables for X-ray Crystallography* (1962). Vol. III, pp. 202-203. Birmingham: Kynoch Press.
- JOHNSON, C. K. (1965). *ORTEP*. Report ORNL-3794 Revised, Oak Ridge National Laboratory, Oak Ridge, Tennessee.
- KARLE, J. & KARLE, I. L. (1967). *J. Amer. Chem. Soc.* **89**, 804-807.
- KLINGSBERG, E. (1969). *Quart. Rev.* **23**, 537-551.
- LARSON, A. C. (1967). *Acta Cryst.* **23**, 664-665.
- LEE, J. D. & GOODACRE, G. W. (1971a). *Acta Cryst.* **B27**, 1055-1061.
- LEE, J. D. & GOODACRE, G. W. (1971b). *Acta Cryst.* **B27**, 1841-1845.
- LONG, R. E. (1965). *A Program for Phase Determination by Iterative Application of Sayre's Equation*. Doctoral Dissertation (Part III). Univ. of California, Los Angeles.
- PAULING, L. (1960). *The Nature of the Chemical Bond*. 3rd ed. Ithaca: Cornell Univ. Press.
- SAYRE, D. (1952). *Acta Cryst.* **5**, 60-65.
- SCHOMAKER, V., WASER, J., MARSH, R. E. & BERGMAN, G. (1959). *Acta Cryst.* **12**, 600-604.
- SMITH, D. L. (1969). *Acta Cryst.* **B25**, 625-632.
- STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175-3187.
- SUTTON, L. E. (1965). *Interatomic Distances and Configuration in Molecules and Ions, Supplement*. Special Publication No. 18. London: The Chemical Society.
- TSAI, C. (1968). Private communication.
- VAN DER HELM, D., LESSOR, A. E. & MERRITT, L. L. (1962). *Acta Cryst.* **15**, 1227-1232.
- ZACHARIASEN, W. H. (1963). *Acta Cryst.* **16**, 1139-1144.
- ZACHARIASEN, W. H. (1965). *Acta Cryst.* **18**, 705-710.