sheets almost parallel to the [410] direction connected by van der Waals interactions. The intramolecular distance O(1)···O(9) has a value of 3·109 (4) Å, a little too long for a hydrogen bond.

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# Structure of 3*H*-1,2-Dithiole-3-thione*

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**Abstract.** $C_3H_2S_3$, $M_r = 134{\cdot}241$, tetragonal, $P4_2/mbc$, $a = b = 10{\cdot}654$ (3), $c = 9{\cdot}304$ (3) Å, $V = 1056{\cdot}1$ Å$^3$, $Z = 8$, $D_m = 1{\cdot}66$ (2), $D_x = 1{\cdot}688$ g cm$^{-3}$, $\lambda(\text{Mo } K\alpha_1) = 0{\cdot}7093$ Å, $\mu = 11{\cdot}85$ cm$^{-1}$, $F(000) = 544$, $T = 296$ (1) K. Final $R(F) = 0{\cdot}049$ for 571 unique nonzero reflections. The two H atoms were located and their positional parameters refined. Molecules are nearly planar, to within 0·004 (2) Å (H atoms excluded), and the plane normal of the five-membered ring makes an angle of 91·2 (1)° with the $z$ axis. The disordered-crystal model successfully utilized in the refinement assumes a random distribution of each molecule in the two orientations related to each other by a crystallographic mirror plane.

**Introduction.** To understand the relationship between chemotherapeutic properties and structure, Bueding, Dolan & Leroy (1982) have studied the anti-schistosomidal effects on mice of several drugs, including the drug oltipraz, the structure of which was reported from this laboratory (Wei, 1983), and its analogs. Because of their structural similarities a detailed comparison of these compounds affords considerable stereochemical insight concerning the chemotherapeutic value, and one of our systematic investigations on 5-(*p*-methoxyphenyl)-3*H*-1,2-dithiole-3-thione has been reported (Wang, Lin & Wei, 1985).

In most cases drugs of this class contain 3*H*-1,2-dithiole-3-thione as a building unit, and it is considered by Bueding *et al.* (1982) as a necessary unit to make these drugs function. Investigation of the structure of this basic fragment is clearly desirable in view of its important role. A similar structure, that of 4-methyl-1,2-dithia-4-cyclopentene-3-thione, has previously been reported in detail by Jeffrey & Shiono (1959).

**Experimental.** Orange crystals having leek-like smell grown from an ethyl acetate solution. Crystal density determined by flotation in mixtures of bromobenzene and 2-bromobutyric acid. A crystal with approximate dimensions 0·66 × 0·24 × 0·22 mm mounted on a Picker four-circle diffractometer with **c** approximately parallel to the $\varphi$ axis of the diffractometer; lattice parameters refined by least-squares method from angle measurements of 10 strong reflections in $2\theta$ range 41–50° (Busing, Ellison, Levy, King & Roseberry, 1968); systematic absences $0kl$, $k = 2n + 1$ (or $h0l$, $h = 2n + 1$) and $hhl$, $l = 2n + 1$, consistent with $P4_2bc$ or $P4_2/mbc$. Intensity data collected by $\theta$–$2\theta$ step scans in $2\theta$ range 1–55° ($0 \le h \le 13$, $0 \le k \le 9$, $0 \le l \le 12$; $h \ge k$). All 646 unique reflections including 571 nonzero and 75 zero intensities used for final least-squares refinement. Absorption corrections calculated analytically by the method of Busing & Levy (1957); transmission range 0·765–0·788. No extinction corrections applied. Maximum mosaic spread of crystal used estimated to be 0·8°.

Interpretation of a Patterson map inconclusive. Structure solved instead with *MULTAN* (Germain, Main & Woolfson, 1971), which gave positions of all non-H atoms except C(5). Centrosymmetric space

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group $P4_2/mbc$ chosen on basis of intensity statistics.* By iterated least-squares refinements [*ORXLS*4 (Busing, Martin & Levy, 1962)] and difference-Fourier syntheses [*ORFFP*3 (Levy, 1977)] all atoms eventually located. Scattering factors those of Cromer & Waber (1974); anomalous-scattering corrections for S ($f' = 0{\cdot}110, f'' = 0{\cdot}124$) from Cromer (1974).

There was an ambiguity in choosing the correct crystal model. Application of *MULTAN* indicated that both S(3) and C(3) were located on the mirror plane passing through $z = 0$. The centrosymmetric space group assigned, however, does not require that any atom be constrained to the mirror plane. Least-squares refinements were carried out for several different models including (*a*) neither S(3) nor C(3) on the mirror plane, (*b*) only S(3) on the mirror plane, (*c*) only C(3) on the mirror plane and (*d*) both S(3) and C(3) on the mirror plane. Weights ($w$) used in the refinements were reciprocals of $\sigma^2(F_o^2) + (0{\cdot}04F_o^2)^2$. The measures obtained for these cases are shown below.

|  | $R(F)$ | $R(F^2)$ | $wR(F^2)$ | $S$ |
|---|---|---|---|---|
| (*a*) | 0·058 | 0·061 | 0·077 | 1·011 |
| (*b*) | 0·059 | 0·061 | 0·077 | 1·018 |
| (*c*) | 0·059 | 0·060 | 0·077 | 1·016 |
| (*d*) | 0·059 | 0·060 | 0·078 | 1·025 |

The four models, which have very similar values for $wR(F^2)$, are equally good representations of the structure. However, when atom C(3) was not constrained to the mirror plane [models (*a*) and (*b*)], its $\beta_{33}$ becomes much too small compared with the corresponding values of other non-H atoms, and when only atom C(3) was constrained to the mirror plane [model (*c*)], S(3) refines to a position only 0·04 (2) Å from this plane. With both atoms S(3) and C(3) constrained to the mirror plane, C(3) appears to have reasonable temperature factors, and for this rather arbitrary reason model (*d*) is selected for representation in this paper.†

In final cycle of refinement for model (*d*), $\Delta/\sigma$ for non-H atoms $<0{\cdot}046$; maximum $\Delta$ in positional parameters for H atoms $0{\cdot}074\sigma$. With only 571 unique nonzero reflections, $R(F) = 0{\cdot}049$; final difference-Fourier map showed maximum $\Delta\rho$ 0·35 e Å$^{-3}$.

**Discussion.** Atomic coordinates and isotropic temperature factors are listed in Table 1.*

The crystal structure of the title compound is made up of discrete units such as the one shown in Fig. 1(*a*), in which molecular parameters calculated by the program *ORFFE*4 (Busing, Martin & Levy, 1964) are also given. All figures were prepared with the program *ORTEP*II (Johnson, 1976). The closest intermolecular contact (excluding mirror-related molecules) between non-H atoms is 3·288 (2) Å for S(1)···S(3); the closest such contact between non-H and H atoms is 2·97 (5) Å for S(3)···H(5).

Table 1. *Positional and isotropic thermal parameters*

The e.s.d.'s are given in parentheses in this table and in the text. The digits in parentheses correspond to the least-significant digits of the parameters. The equivalent isotropic temperature factors for C and S atoms were calculated from the corresponding anisotropic thermal parameters and unit-cell parameters by the relation $B_{eq} = \frac{4}{3}(\beta_{11}a^2 + \beta_{22}b^2 + \beta_{33}c^2)$ (Hamilton, 1959).

|  | $x$ | $y$ | $z$ | $B_{eq}$(Å$^2$) |
|---|---|---|---|---|
| S(1) | 0·1927 (2) | 0·5206 (2) | 0·1117 (2) | 5·40 (6) |
| S(2) | 0·3295 (2) | 0·3968 (2) | 0·1745 (2) | 5·70 (4) |
| S(3) | 0·4935 (1) | 0·2465 (1) | 0 | 5·64 (2) |
| C(3) | 0·3765 (3) | 0·3506 (2) | 0 | 4·47 (7) |
| C(4) | 0·3066 (6) | 0·4107 (6) | −0·1036 (7) | 6·1 (2) |
| C(5) | 0·2179 (8) | 0·4931 (8) | −0·0652 (7) | 5·4 (2) |
| H(4) | 0·297 (6) | 0·373 (6) | −0·166 (8) | 6·0* |
| H(5) | 0·148 (5) | 0·537 (5) | −0·135 (6) | 6·0* |

* Not adjusted in the least-squares refinement.

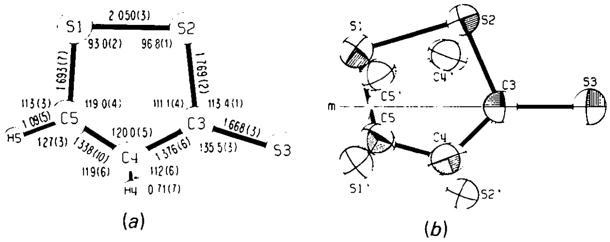

Fig. 1. (*a*) Numbering scheme, bond lengths (Å), and bond angles (°) for the molecule. (*b*) Two alternative orientations of the molecule above and below the crystallographic mirror plane; for the sake of clarity, H atoms are not shown.

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* Prior to the use of *MULTAN*, the application of *NORMAL* (part of *MULTAN*) revealed that the statistical averages of $|E^2 - 1|$ and $|E|$ were 0·989 and 0·780, corresponding to those for a centrosymmetric crystal [theoretical values for centrosymmetric 0·968 and 0·798 and for noncentrosymmetric 0·736 and 0·886, respectively (Karle, Dragonette & Brenner, 1965)].

† To confirm further the correctness of the centrosymmetric space group chosen, an attempt was made to refine the structure in the noncentrosymmetric space group $P4_2bc$, but the refinement diverged and gave nonpositive-definite temperature factors for all C atoms and atom S(3). The possibility that the structure consists of up and down domains (twinning mirror plane normal to the $c$ axis) in the noncentrosymmetric space group can be ruled out, because such an arrangement would still be expected to show an acentric intensity distribution (contrary to that observed). This is because the observed intensity for each reflection from the twin composite would be the sum of the intensities for a pair of $hkl$ and $\bar{h}\bar{k}\bar{l}$ (or $hkl$ and $hk\bar{l}$) reflections [for examples, see Wei (1969), Uchtman & Dahl (1969), Pratt, Coyle & Ibers (1971)], and $|F(hk\bar{l})| = |F(\bar{h}\bar{k}\bar{l})| = |F(hk\bar{l})|$ for the noncentrosymmetric space group $P4_2bc$.

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42357 (4 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

The crystal structure is disordered in that half of the units in the crystal are related to the other half by the crystallographic mirror plane passing through $z = 0$. With S(3) and C(3) atoms constrained to the mirror plane, the other atoms are required to take alternative positions with 50% occupancy on opposite sides of the mirror plane, as shown in Fig. 1(*b*). Other similar cases of disorder about crystallographic mirror planes have been reported for $Co_3(CO)_{10}BH_2N(C_2H_5)_3$ (Klanberg, Askew & Guggenberger, 1968) and $[Co_3(CO)_9C]$-($\mu_3$-SCS)$[Co_3(CO)_7S]$ (Wei, 1984).

Because of the disorder the molecular parameters and anisotropic thermal parameters are not as precise as might otherwise be expected. As in the case of oltipraz (Wei, 1983), the heterocyclic five-membered ring system is similar to that of 4-methyl-1,2-dithia-4-cyclopentene-3-thione (Jeffrey & Shiono, 1959). A pronounced double-bond character is indicated by the bond length of 1·338 (10) Å for C(4)—C(5). The thione bond length, 1·668 (3) Å, is in agreement with that of one of the two independent molecules for oltipraz [1·670 (2) Å]. Similarly, the S(1)—S(2) bond length of 2·050 (3) Å agrees with those for oltipraz within two e.s.d.'s. The two endocyclic S(1)—C(5) and S(2)—C(3) bonds are different by 0·076 (7) Å, a phenomenon also observed but to a lesser degree for other molecules with similar environments. Presumably this difference can be attributed to different $\pi$ character arising from interaction between *d* orbitals of the S atoms and the *p* orbitals of the adjacent C atoms. Despite this difference in S—C bond lengths, which could in part be attributed to the disorder, the overall bond lengths and angles are in close agreement with those found for oltipraz.

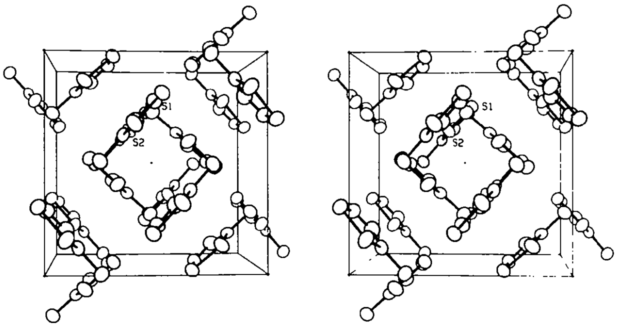

Fig. 2. A stereoscopic pair showing the unit-cell packing viewed down **c**. The axial system is right-handed. For the sake of clarity, mirror-related half molecules as well as H atoms are omitted, and only S(1) and S(2) atoms of the reference half molecule are labeled. The origin of the unit cell is in the upper left, rear corner.

The five-membered ring is planar to within 0·004 (2) Å, the r.m.s. deviation of the fitted atoms being 0·003 (2) Å. Shown in Fig. 2 is the [001] projection of the unit cell (mirror-related half molecules excluded for the sake of clarity). The molecular ring plane lies in a plane approximately perpendicular to the *ab* plane. The angle between the plane normal for the ring and the *z* axis of the unit cell is 91·2 (1)°.

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