Acta Cryst. (1988). C**44**, 1037–1039

A Pseudo-centrosymmetric Chiral Crystal Structure: (5*S*,6*S*)-5,6-Dihydro-5,6-dimethyl-1,3-dithiolo[4,5-*b*][1,4]dithiin-2-thione

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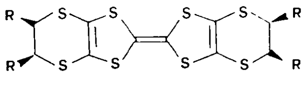
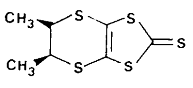
(*Received* 14 *September* 1987; *accepted* 4 *February* 1988)

Abstract. $C_7H_8S_5$, $M_r = 252{\cdot}45$, monoclinic, $P2_1$, $a = 13{\cdot}315\ (5)$, $b = 6{\cdot}051\ (1)$, $c = 13{\cdot}869\ (4)$ Å, $\beta = 106{\cdot}40\ (2)°$, $V = 1071{\cdot}95$ Å^3, $Z = 4$, $D_x = 1{\cdot}57$ Mg m^{-3}, Mo $K\alpha$ radiation, $\lambda = 0{\cdot}7107$ Å, $\mu = 9{\cdot}39$ cm^{-1}, $F(000) = 520$, $T = 293$ K, $R = 0{\cdot}036$ for 1782 observed reflections. Problems associated with full-matrix least-squares refinement of a pseudo-centrosymmetric chiral crystal structure were overcome by constraining chemically equivalent intramolecular distances to be equal. The six-membered rings adopt conformations in which five atoms lie nearly in a plane with one (methine C) 0·7 Å out of this plane.

Introduction. Centrosymmetric atomic arrangements cannot be refined in non-centrosymmetric space groups because the least-squares normal-equations matrix becomes singular (Ermer & Dunitz, 1970). For structures which have nearly centrosymmetric atomic arrangements, least-squares refinement often produces unreasonable molecular geometries and atomic displacement parameters. Most of the literature on this subject has been concerned with the problem of identifying the *correct* space group, *e.g.* $P1$ or $P\bar{1}$, $P2$ or $P2/m$, when more than one is compatible with the space-group absences and available chemical information (Marsh, 1986). In the course of our work on organic conductors (Wallis, Karrer & Dunitz, 1986; Karrer, Wallis, Dunitz, Hilti, Mayer, Bürkle & Pfeiffer, 1987), we encountered a related but distinct problem. X-ray diffraction of compounds such as $(1)_2PF_6$ and $(1)_3(ClO_4)_2$ led to centrosymmetric structures in space group $P\bar{1}$. However, there was no doubt here that the substances were actually chiral. As expected, it was not possible to refine these pseudo-centrosymmetric structures adequately by unconstrained least-squares methods in space group $P1$ or to determine their absolute configurations. We therefore turned to crystals of (3), from which (1) had been synthesized by treatment with triethylphosphite, with the aim of determining accurate structural parameters and the absolute configuration. Unfortunately for our purpose, this crystal turned out also to have a pseudo-centrosymmetric structure in space group $P2_1$ (pseudo $P2_1/n$, $Z = 4$).



(1) R = CH_3
(2) R = H



(3)

Experimental. Crystals of (3) grown by slow evaporation of an ether/pentane solution; m.p. 350–351 K, $(\alpha)_D^{25} = -360°$ ($c = 1{\cdot}35$ in $CHCl_3$); Enraf–Nonius CAD-4 diffractometer; Mo $K\alpha$ radiation, graphite monochromator; ω scan; crystal dimensions $0{\cdot}3 \times 0{\cdot}2 \times 0{\cdot}15$ mm, unit-cell dimensions by least-squares fit to setting angles of 16 automatically centred reflections with $9 < \theta < 17°$. Room-temperature measurement, no absorption correction, max. $(\sin\theta)/\lambda$ in intensity measurements 0·64 Å^{-1}, two standard reflections monitored, 2686 reflections measured, 2553 unique, $R_{\rm int} = 0{\cdot}02$, 1782 counted as observed [$I > 3\sigma(I)$], index range h −17/17, k 0/7, l 0/17. $h0l$ reflections very weak for $h + l$ = odd: pseudo n-glide plane. Structure solved in $P2_1$ (*SHELXS*86), y coordinate of S(2*A*) fixed during refinements, some missing C atoms found in electron-density difference map. Further refinement, including anisotropic Gaussian displacement parameters (ADP's) for C and S, gave results with wildly inconsistent bond lengths and angles, as well as unreasonable values of anisotropic displacement parameters.

Apart from the outer dimethylated C_2 bridges, the coordinates of the two symmetry-independent molecules happen to be related within close limits by the operation $x, y, z \rightarrow 0{\cdot}5-x, 0{\cdot}45-y, 0{\cdot}5-z$. Pairs of centrosymmetrically related bond distances were, typically, one too long, the other too short, their average being fairly reasonable for the type of bond in question. This kind of behaviour can be expected for pseudo-centrosymmetric structures because the magnitudes of the structure factors are relatively insensitive to small departures from centrosymmetry. Each set of *chemically equivalent* intramolecular interatomic distances in the central portions of the molecules was

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0108-2701/88/061037-03$03.00

Table 1. *Constraints applied to groups of chemically equivalent intramolecular distances*

Intramolecular distances for molecules *A* and *B*	Refined value of constrained distance (Å) (with e.s.d. in parentheses)
S(1)–C(1)	1·636 (8)
S(2)–C(1), S(3)–C(1)	1·727 (8)
S(2)–C(2), S(3)–C(3)	1·743 (5)
C(2)–C(3)	1·339 (8)
C(2)–S(4), C(3)–S(5)	1·742 (5)
S(1)–S(2), S(1)–S(3)	2·969 (8)
S(1)–S(4), S(1)–S(5)	5·805 (5)
S(2)–S(3)	2·866 (7)
S(2)–S(4), S(3)–S(5)	2·954 (5)
S(4)–S(5)	3·487 (7)
S(2)–S(5), S(3)–S(4)	4·326 (5)

therefore constrained using *SHELX*76 to a single (refinable) parameter (Table 1). Full-matrix least-squares analyses incorporating these constraints then led to more acceptable results.

H-atom positions were recalculated after each refinement cycle; isotropic displacement parameters, one value for methine H and another for methyl H atoms were refined. With $w = [\sigma^2(F)]^{-1}$ and constraints as described above (Table 1), the model converged to $R = 0{\cdot}036$, $wR = 0{\cdot}035$. Max. Δ/σ in final cycle for positional parameters: S 0·07, C 0·11; for displacement parameters S 0·06, C 0·17, H isotropic, 0·05. Max. and min. residual electron density in final difference Fourier synthesis 0·29, $-0{\cdot}36$ e Å^{-3}. Computer programs: *SHELXS*86 (Sheldrick, 1986), *SHELX*76 (Sheldrick, 1976), molecular illustrations with *ORTEP* (Johnson, 1976). Atomic scattering factors for S, C from Cromer & Mann (1968), for H from Stewart, Davidson & Simpson (1965).

Because of the nearly centrosymmetric arrangement of the S atoms and of the resulting small calculated differences between Bijvoet pairs, our aim of determining the absolute configuration of (1) by X-ray analysis of (3) was abandoned. In the diagrams, the molecules are depicted as having the (*S,S*) configuration, as suggested by the preparation (Wallis, Karrer & Dunitz, 1986).

Discussion. The atom-numbering scheme is shown in Fig. 1. Final positional and equivalent isotropic displacement parameters U_{eq} are given in Table 2,* unconstrained bond distances and angles in Table 3(*a*), (*b*) and bond angles in constrained regions in Table 3 (*c*). A stereoview showing the nearly centrosymmetric crystal structure with its pseudo *n*-glide is given (Fig. 2); pairs of pseudosymmetrically related molecules, lying almost face to face, are packed in layers perpendicular to the *b* axis. The pattern of C—S bond lengths is similar to that in (2) and its radical-cation salts (Kobayashi, Kato, Mori, Kobayashi, Sasaki, Saito & Inokuchi, 1983; Kobayashi, Kobayashi, Sasaki, Saito & Inokuchi, 1986); data for other 5,6-dihydro-1,3-dithiolo[4,5-*b*][1,4]dithiin-2-thiones are not available. The conformations of the two independent molecules are similar: in the six-membered rings, the two C(sp^3) atoms are displaced to opposite sides of the best plane through the other four atoms, one displacement being much greater than the other [C(5*A*), +0·58; C(4*A*), −0·21; C(4*B*), −0·67; C(5*B*), +0·15 Å]; the two larger displacements are both away from the pseudo-inversion centre between the molecules. The methyl substituents occupy pseudo-equatorial positions and lie fairly close to the molecular plane (deviations of methyl C atoms from the best plane through the five S atoms lie in the range 0·29 to 0·70 Å). The conformations around the

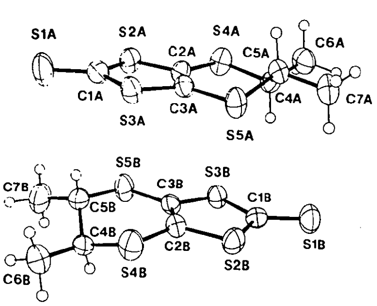

Fig. 1. Pair of pseudo-centrosymmetrically related molecules *A* and *B* with atom-numbering scheme; thermal ellipsoids drawn at the 50% probability level.

Table 2. *Fractional atomic coordinates with e.s.d.'s in parentheses and equivalent isotropic displacement parameters* (Å^2)

$$U_{eq} = \tfrac{1}{3}\textstyle\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i . \mathbf{a}_j.$$

	x	*y*	*z*	U_{eq}
S(1*A*)	1·1004 (1)	0·1728 (6)	−0·7450 (1)	0·080
S(2*A*)	0·9828 (1)	0·0548	−0·5990 (1)	0·055
S(3*A*)	0·9195 (1)	0·4347 (6)	−0·7255 (1)	0·051
S(4*A*)	0·8239 (1)	0·0997 (5)	−0·4902 (1)	0·058
S(5*A*)	0·7385 (1)	0·5486 (5)	−0·6503 (1)	0·055
C(1*A*)	1·0072 (4)	0·218 (1)	−0·6923 (4)	0·050
C(2*A*)	0·8745 (3)	0·198 (1)	−0·5847 (4)	0·039
C(3*A*)	0·8439 (4)	0·373 (1)	−0·6451 (4)	0·041
C(4*A*)	0·7057 (4)	0·261 (1)	−0·5046 (4)	0·042
C(5*A*)	0·7163 (4)	0·505 (1)	−0·5277 (4)	0·043
C(6*A*)	0·6804 (4)	0·226 (2)	−0·4049 (4)	0·066
C(7*A*)	0·6162 (4)	0·634 (1)	−0·5342 (4)	0·061
S(1*B*)	0·4131 (1)	0·2571 (6)	−0·7466 (1)	0·074
S(2*B*)	0·5232 (1)	0·3930 (3)	−0·8967 (1)	0·057
S(3*B*)	0·5941 (1)	0·0096 (5)	−0·7757 (1)	0·054
S(4*B*)	0·6800 (1)	0·3646 (6)	−1·0108 (1)	0·067
S(5*B*)	0·7707 (1)	−0·0915 (5)	−0·8577 (1)	0·069
C(1*B*)	0·5050 (4)	0·225 (1)	−0·8029 (4)	0·046
C(2*B*)	0·6319 (4)	0·260 (1)	−0·9160 (4)	0·047
C(3*B*)	0·6660 (4)	0·082 (1)	−0·8584 (4)	0·041
C(4*B*)	0·7474 (4)	0·127 (1)	−1·0423 (4)	0·049
C(5*B*)	0·8291 (4)	0·034 (1)	−0·9483 (4)	0·052
C(6*B*)	0·7972 (4)	0·210 (2)	−1·1206 (4)	0·072
C(7*B*)	0·8965 (5)	−0·146 (2)	−0·9746 (5)	0·083

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* Lists of structure factors, anisotropic temperature factors and calculated H-atom positions have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44754 (12 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 3. *Molecular geometry for* (3), *e.s.d.'s in parentheses*

(*a*) Unconstrained bond lengths (Å)

	Molecule *A*	Molecule *B*
S(4)–C(4)	1·815 (6)	1·813 (6)
S(5)–C(5)	1·826 (5)	1·819 (6)
C(4)–C(5)	1·523 (8)	1·549 (7)
C(4)–C(6)	1·527 (7)	1·509 (7)
C(5)–C(7)	1·526 (7)	1·520 (9)

(*b*) Unconstrained bond angles (°)

	Molecule *A*	Molecule *B*
C(2)–S(4)–C(4)	103·9 (3)	101·9 (3)
C(3)–S(5)–C(5)	102·2 (2)	104·0 (3)
S(4)–C(4)–C(5)	114·5 (4)	111·3 (4)
S(4)–C(4)–C(6)	103·4 (4)	105·0 (6)
C(5)–C(4)–C(6)	112·4 (6)	112·3 (5)
S(5)–C(5)–C(4)	112·7 (4)	113·5 (4)
S(5)–C(5)–C(7)	103·8 (4)	105·3 (5)
C(4)–C(5)–C(7)	112·2 (5)	112·3 (5)

(*c*) Averaged values for endocyclic bond angles in the constrained section of molecules *A* and *B* (°)

C(1)–S(2)–C(2), C(1)–S(3)–C(3)	97·9
S(2)–C(2)–C(3), S(3)–C(3)–C(2)	116·0
S(4)–C(2)–C(3), S(5)–C(3)–C(2)	128·0

(*d*) Intra-annular torsion angles (τ) for the six-membered rings (°) (e.s.d.'s are less than 1°)

C(2*A*)–C(3*A*)	−3·1	C(3*B*)–C(2*B*)	2·4
C(3*A*)–S(5*A*)	21·0	C(2*B*)–S(4*B*)	20·7
S(5*A*)–C(5*A*)	−51·7	S(4*B*)–C(4*B*)	−54·9
C(5*A*)–C(4*A*)	66·0	C(4*B*)–C(5*B*)	68·2
C(4*A*)–S(4*A*)	−40·8	C(5*B*)–S(5*B*)	−39·1
S(4*A*)–C(2*A*)	8·9	S(5*B*)–C(3*B*)	3·4

C(4)–C(5) bonds are staggered (CH_3–C–C–CH_3, −59·8 and −55·1°; S–C–C–S, 66·0 and 68·2°); torsion angles in the six-membered rings are given in Table 3(*d*). There are only two short intermolecular S···S contacts, both between a pair of pseudo-centrosymmetrically related molecules in adjacent layers: S(5*A*)···S(3*B*, *x*, 1+*y*, *z*), 3·55 and S(3*A*)···S(5*B*, *x*, 1+*y*, *z*), 3·67 Å.

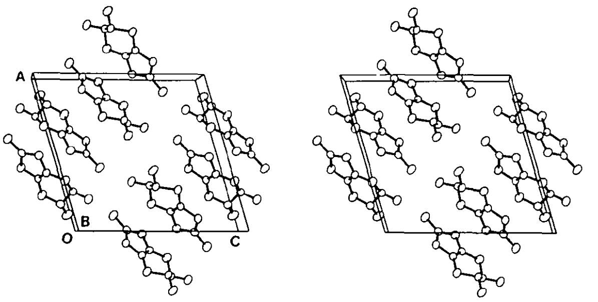

Fig. 2. Stereoview of the crystal packing of (3), H atoms omitted.

This work was supported by the Swiss National Science Foundation.

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Acta Cryst. (1988). C**44**, 1039–1041

Structure of 2-Methoxy-*N*-(4-nitrobenzylidene)-5-pyridylamine. II. Non-centrosymmetric Modification

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(*Received* 14 *December* 1987; *accepted* 17 *February* 1988)

Abstract. $C_{13}H_{11}N_3O_3$, $M_r = 257·2$, monoclinic, $P2_1$, $a = 3·8566\ (5)$, $b = 19·542\ (4)$, $c = 8·066\ (1)$ Å, $\beta = 89·37\ (1)°$, $V = 607·9\ (6)$ Å^3, $Z = 2$, $D_x = 1·40$, $D_m = 1·39$ g cm^{-3}, $\lambda(\mathrm{Cu}\ K\alpha) = 1·5418$ Å, $\mu = 7·62$ cm^{-1}, $F(000) = 268$, $R = 0·0493$ for 1116 observed reflections. The molecule is not planar. The dihedral angle between the phenyl and the pyridyl rings is 35·7 (2)°. The conformation of the molecule differs from that of the centrosymmetric modification [Moustakali-Mavridis, Terzis & Hadjoudis (1987). *Acta Cryst.* C**43**, 1793–1795] but bond distances and angles are very similar, the highest deviations being observed in the bond lengths of the 'bridge' atoms connecting the two ring systems.

0108-2701/88/061039-03$03.00