Table 3. *Distances* (Å) *and angles* (°) *for the possible* H *bonds*

O*W*···N(3^{i})	2·892 (4)	N(3^{i})–O*W*–N(3^{ii})	107·82 (9)
O*W*···N(3^{ii})	3·005 (5)	N(3^{i})–O*W*–O(1)	123·5 (1)
O*W*···O(1)	2·762 (4)	N(3^{i})–O*W*–O(2^{iii})	151·9 (1)
O*W*···O(2^{iii})	2·863 (4)	N(3^{ii})–O*W*–O(1)	103·3 (1)
		N(3^{ii})–O*W*–O(2^{iii})	82·0 (1)
		O(1)–O*W*–O(2^{iii})	77·34 (9)

Symmetry operation: (i) $1+x, y, z$; (ii) $1-x, \frac{1}{2}+y, 1-z$; (iii) $1-x, \frac{1}{2}+y, 2-z$.

The elemental analysis indicated that half a mole of water was present for one mole of the compound, while the least-squares refinements have resulted in $m = 0{\cdot}862$ (8). It is well known that the structural role of a solvent is merely to occupy space in the crystal lattice or to stabilize the compound by forming weak H bonds. Examination around the water molecule reveals that it is surrounded by four N or O atoms with which hydrogen bonds could be formed. Distances and angles of these interactions are shown in Table 3.

The authors are grateful to Drs George M. Brown and W. R. Busing of the Chemistry Division of ORNL for the use of their diffractometer. CHW is particularly indebted to Dr C. R. Richmond, Associate Director of ORNL, for the arrangement of financial support.

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Acta Cryst. (1989). C**45**, 119–121

6-Chloro-1,2-benzodithiole-3-thione

BY GABRIELE BOCELLI

Centro di Studio per la Strutturistica Diffrattometrica del CNR, Viale delle Scienze, 43100 *Parma, Italy*

AND CORRADO RIZZOLI

Istituto di Strutturistica Chimica, Università di Parma, Viale delle Scienze, 43100 *Parma, Italy*

(*Received* 5 *May* 1988; *accepted* 22 *August* 1988)

Abstract. $C_7H_3ClS_3$, $M_r = 218{\cdot}7$, monoclinic, $P2_1/a$, $a = 14{\cdot}427$ (3), $b = 14{\cdot}695$ (3), $c = 3{\cdot}891$ (2) Å, $\beta = 90{\cdot}67$ (3)°, $V = 824{\cdot}9$ (5) Å^3, $Z = 4$, $D_x = 1{\cdot}76$ g cm^{-3}, λ(Cu $K\alpha$) = 1·5418 Å, $\mu = 105{\cdot}7$ cm^{-1}, $F(000) = 440$, room temperature, $R = 0{\cdot}049$ ($wR = 0{\cdot}052$) for 1073 observed reflections [$I > 2\sigma(I)$]. The benzodithiole skeleton is practically planar and the thione bond is clearly double.

Introduction. The title compound, which is the starting material of condensation reactions with amines, was structurally analyzed to help understand the relationship between the biological properties and structure of its derivatives.

Experimental. Red crystal approximately 0·43 × 0·51 × 0·58 mm, from methanol solution, Siemens AED single-crystal diffractometer with an IBM PS/2 M30 computer, Cu $K\alpha$ radiation, cell parameters from least-squares treatment of setting angles of 21 reflections ($19 \leq \theta \leq 44$°), one standard reflection monitored every 50 counts showed no more than 0·3%

Table 1. *Positional* (× 10⁴ *for* Cl, S *and* C *atoms*, × 10³ *for* H *atoms*) *and equivalent isotropic thermal parameters* (Å² × 10⁴; *Hamilton*, 1959) *with their e.s.d.'s in parentheses*

	x	*y*	*z*	U_{eq}
Cl	4676 (1)	3882 (1)	−1141 (4)	599 (4)
S1	1830 (1)	2000 (1)	4419 (4)	492 (4)
S2	1911 (1)	621 (1)	5371 (3)	499 (4)
S3	3449 (1)	−603 (1)	3973 (5)	677 (6)
C1	3015 (3)	432 (3)	3845 (12)	436 (13)
C2	3458 (3)	1257 (3)	2587 (11)	368 (12)
C3	4356 (3)	1281 (3)	1245 (13)	424 (13)
C4	4724 (3)	2073 (3)	114 (13)	454 (14)
C5	4189 (3)	2871 (3)	299 (11)	411 (13)
C6	3310 (3)	2879 (3)	1586 (13)	452 (15)
C7	2933 (3)	2066 (3)	2765 (11)	381 (11)
H3	471 (4)	70 (3)	107 (13)	
H4	531 (4)	213 (4)	−95 (16)	
H6	292 (4)	343 (3)	180 (12)	

Table 2. *Bond distances* (Å) *and angles* (°)

Cl—C5	1·739 (5)	C2—C3	1·403 (6)
S1—S2	2·063 (2)	C2—C7	1·412 (6)
S1—C7	1·726 (5)	C3—C4	1·355 (6)
S2—C1	1·729 (5)	C4—C5	1·406 (6)
S3—C1	1·645 (5)	C5—C6	1·369 (6)
C1—C2	1·458 (6)	C6—C7	1·393 (6)
S2—S1—C7	94·1 (2)	C3—C4—C5	118·8 (4)
S1—S2—C1	98·4 (2)	Cl—C5—C4	118·2 (3)
S2—C1—S3	119·3 (3)	C4—C5—C6	122·5 (4)
S3—C1—C2	127·6 (3)	Cl—C5—C6	119·3 (3)
S2—C1—C2	113·0 (3)	C5—C6—C7	118·7 (4)
C1—C2—C7	116·5 (4)	C2—C7—C6	119·6 (4)
C1—C2—C3	123·8 (4)	S1—C7—C6	122·4 (3)
C3—C2—C7	119·7 (4)	S1—C7—C2	117·9 (3)
C2—C3—C4	120·6 (4)		

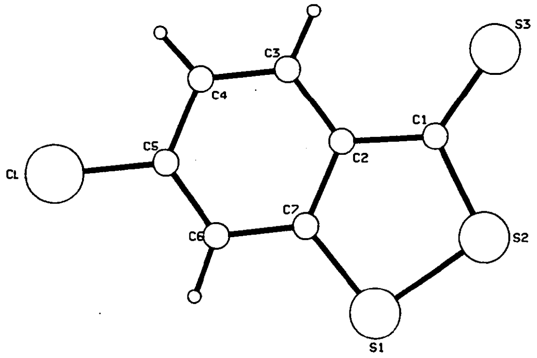

Fig. 1. Atom-numbering scheme of 6-chloro-1,2-benzodithiole-3-thione.

intensity variation throughout the data collection procedure, 1567 unique reflections ($R_{\text{int}} = 0{\cdot}016$) were collected in the $3 \leq \theta \leq 70°$ range, $-17 \leq h \leq 17$, $0 \leq k \leq 17$, $0 \leq l \leq 4$, intensities were evaluated with a modified version (Belletti, Cantoni & Pasquinelli, 1988) of the Lehmann & Larsen (1974) procedure, the data were corrected for Lorentz and polarization effects but not for absorption. The structure was solved by direct methods and refined by full-matrix least squares with *SHELX76* (Sheldrick, 1976). At the end of anisotropic refinement ($R = 0{\cdot}051$) the H atoms were located in a ΔF map and refined isotropically. 112 parameters refined, $\sum w(\Delta F)^2$ minimized, $R = 0{\cdot}049$, $wR = 0{\cdot}052$ with $w = 0{\cdot}6265/(\sigma^2 F + 0{\cdot}0172F^2)$, max. shift/e.s.d. $= 0{\cdot}11$ for the heavy atoms, final ΔF map shows $\Delta\rho_{\max} = 0{\cdot}71$ e Å^{-3}. Atomic scattering factors from *SHELX76*.

All the calculations were performed on an IBM PS/2 M80 computer using the *CRYSRULER* package (Rizzoli, Sangermano, Calestani & Andreetti, 1987).

Discussion. Table 1 contains the positional parameters of the molecule which is illustrated in Fig. 1.* Bond distances and angles are given in Table 2.

The molecule as a whole is practically planar with the dihedral angle formed by the mean benzene and dithiole ring planes [which are planar to within 0·002 (5) and 0·012 (5) Å respectively] being only 0·3 (1)°. In detail this last ring is a little deformed with the C7 and C1 atoms 0·014 (4) and 0·017 (5) Å out of plane with respect to the mean plane of the remaining atoms. Bond distances and angles of the heterocyclic ring agree very well with those reported for the 3*H*-1,2-dithiole-3-thione (Wei, 1983, 1985) and 1,3,2-dithiazole-4-thione (Oakley, Koenig & Cordes, 1987) derivatives. The thione bond length [S3—C1 = 1·645 (5) Å] is a little larger with respect to the value reported by Pauling (1960) for a double C=S bond length (1·61 Å). The C1—C2 single bond is shorter than the normal value because of its partial double-bond character. The C—Cl distance [1·739 (5) Å] agrees very well with the value reported by Domenicano, Vaciago & Coulson (1975) [1·7404 (11) Å]. The inductive and resonance effects of the Cl atom determine a deformation of the benzene ring from D_{6h} geometry with an enlargement of the internal angle at Cl with respect to the adjacent ones.

The molecules are held together in the crystal by van der Waals forces.

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* Lists of structure factors and of anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51345 (6 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Acta Cryst. (1989). C**45**, 121–123

Structure of *cyclo*-Tetrakis(*p*-phenylenesulfide)

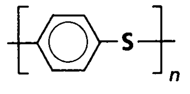
BY I. A. ZAMAEV, I. V. RAZUMOVSKAYA, V. E. SHKLOVER,* YU. T. STRUCHKOV, A. V. ASTANKOV, V. I. NEDEL'KIN, V. A. SERGEEV AND YU. E. OVCHINNIKOV

Nesmeyanov Institute of the Organoelement Compounds of the USSR Academy of Sciences, 28 Vavilov St, Moscow B-334, USSR

(*Received 4 January* 1988; *accepted* 25 *July* 1988)

Abstract. 2,7,12,17-Tetrathiapentacyclo[16.2.2.$0^{3,6}$.$0^{8,11}$.$0^{13,16}$]octadecane, $C_{24}H_{16}S_4$, $M_r = 432\cdot6$, monoclinic, $P2_1/c$, $a = 11\cdot326\ (1)$, $b = 19\cdot011\ (2)$, $c = 10\cdot507\ (1)$ Å, $\beta = 115\cdot076\ (4)°$, $V = 2049\cdot3\ (3)$ Å^3, $Z = 4$, $D_x = 1\cdot40$, $D_m = 1\cdot39$ Mg m^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 0\cdot46$ mm^{-1}, $F(000) = 896$, $T = 293$ K, $R = 0\cdot035$ for 2870 reflections. Four S atoms form a very flattened tetrahedron; the dihedral angle between two SSS triangles is 16·0 (2)°. The S—C bond lengths are 1·776–1·792 (3) Å, C—S—C bond angles 98·4–99·0 (1)°. There is one intermolecular S···S contact of 3·497 (2) Å.

Introduction. As part of structural investigations of organic and organoelement polymer precursors we carried out an X-ray study of the macrocyclic poly(*p*-phenylenesulfides) (I), (III) and (IV). The structure of the pentamer (II) was studied earlier (Kaplan, Reents, Hill & Day, 1982).



$n = 4$ (I)
$n = 5$ (II)
$n = 6$ (III)
$n = 8$ (IV)

Our purpose is to investigate (*a*) the influence of cyclization and ring enlargement on the geometry of diphenylenesulfide moieties; (*b*) the conformational flexibility of *cyclo*-poly(*p*-phenylenesulfides); (*c*) the topology of channels formed in crystals of macrocyclic *p*-phenylenesulfides, *e.g.* (III) and (IV). Macrocyclic *cyclo*-poly(*p*-phenylenesulfides) are interesting also because of their potential ability to form metal complexes of different types, *e.g.* the donor–acceptor complexes with participation of the S atoms of the η-arene complexes *via* the benzene π systems. In this work the data of an X-ray study of (I) are reported.

Experimental. Colourless irregular-shaped crystal. Unit-cell parameters from 24 reflections ($28 \leq 2\theta \leq 32°$). 3984 reflections measured ($-15 \leq h \leq 15$, $0 \leq k \leq 24$, $0 \leq l \leq 15$). Hilger & Watts diffractometer (graphite monochromator, $\theta/2\theta$ scan, $2\theta_{\max} = 60°$). No significant variation in intensities of two standard reflections (002 and 400) measured after every 100 reflections. No absorption or secondary-extinction corrections. Structure solved by direct methods (*MULTAN*; Germain, Main & Woolfson, 1971) revealing all non-hydrogen atoms and refined by block-diagonal least squares with anisotropic thermal parameters for non-hydrogen atoms using 2870 reflections with $I > 2\sigma$ and minimizing $\sum w(|F_o| - |F_c|)^2$; $w = [\sigma^2(F_o) + kF_o^2]^{-1}$. Scattering factors from *International Tables for X-ray Crystallography* (1974). Positions of H atoms are calculated and refined isotropically. Final $R = 0\cdot035$, $wR = 0\cdot028$, $S = 2\cdot1$, max. $(\Delta/\sigma) = 0\cdot5$, final electron density fluctuations $\pm0\cdot4$ e Å^{-3}. All calculations carried out with an Eclipse S/200 computer using the *INEXTL* programs (Gerr, Yanovsky & Struchkov, 1983).

Discussion. Positional and thermal atomic parameters are given in Table 1,† and the atom numbering in Fig. 1, wherein the structure of a molecule of (I) is shown. Bond lengths and bond angles are listed in Table 2.

The S(1), S(2), S(3) and S(4) atoms form a very flattened tetrahedron: the deviations from their mean plane *A* are −0·279, 0·330, −0·305 and 0·340 (1) Å respectively. The dihedral angle between the S(1)-

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* Author to whom correspondence should be addressed.

† Tables of structure factors, anisotropic thermal parameters, H-atom coordinates, and bond lengths and bond angles involving H atoms have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51272 (25 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

0108-2701/89/010121-03$03.00