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Crystal and Molecular Structures of Two Dithieno-[1,4]-dithiins, C₈H₄S₄

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Abstract

The structures of two isomeric dithieno-[1,4]-dithiins, $C_8H_4S_4$, dithieno[3,4-*b*;3′,4′-*e*]-*p*-dithiin (I) and dithieno[2,3-*b*;3′,2′-*e*]-*p*-dithiin (II), have been determined. Both compounds crystallize in space group $P2_1/c$ with $Z = 4$; $a = 14.093$ (2), $b = 8.118$ (2), $c = 8.061$ (2) Å, $\beta = 98.06$ (2)° for (I), $a = 11.672$ (2), $b = 6.152$ (2), $c = 13.607$ (3) Å, $\beta = 110.63$ (2)° for (II). Refinement of (I) and (II) with respectively 2308 and 2532 independent reflections gave $R_w(|F|) = 0.057$ and 0.073, $R(|F|) = 0.051$ and 0.063 respectively. Both molecules are folded along the S–S axis of the [1,4]-dithiin ring. The dihedral angle is 136.2° for (I) and 130.3° for (II). The molecular symmetry is *mm* for (I) and *m* for (II).

Introduction

Compounds containing the [1,4]-dithiin moiety have aroused much interest during the last 25 years. X-ray diffraction studies of the parent compound (V) (Howell, Curtis & Lipscomb, 1954; Parham, Wynberg, Hasek, Howell, Curtis & Lipscomb, 1954) and of thianthrene

(VI) (Rowe & Post, 1956, 1958; Lynton & Cox, 1956) proved the non-planarity of these molecules, which had been proposed earlier on the basis of dipole measurements in solution. Since the isolation of two members of the group of dithieno-[1,4]-dithiins (I–IV) in 1969 (Voronkov & Pereferkovich, 1969; Janssen & Bos, 1969) the synthesis and chemical and physical properties of these compounds have been studied in the Department of Organic Chemistry of this University
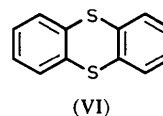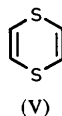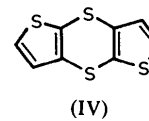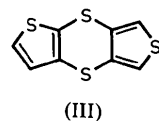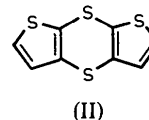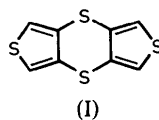
(I)   (II)

(III)   (IV)

(V)   (VI)

(Kooistra, 1977). For the interpretation of the observed properties, which depend on the interaction between the π systems of the two thiophene rings of a molecule, knowledge of the detailed geometry of the molecules was desirable. For an X-ray study, dithieno[3,4-b;3',4'-e]-[1,4]-dithiin (I) and dithieno[2,3-b;3',2'-e]-[1,4]-dithiin (II) were chosen.

Experimental

Colourless crystals of (I) and (II) were grown by recrystallization from tetrachloromethane and a mixture of hexane, ligroin and benzene respectively. Approximate dimensions of the crystals used were 0·2 × 0·45 × 0·45 mm for (I) and 0·3 × 0·45 × 0·4 mm for (II). The cell constants given in Table 1 were determined from zero-layer-line Weissenberg photographs about the three axes, calibrated with NaCl reflection spots [λ(Cu $K\alpha_1$) = 1·54051, λ(Cu $K\alpha_2$) = 1·54434 Å, a(NaCl, 293 K) = 5·6400 Å]. The intensities were measured on an automated Nonius diffractometer with Zr-filtered Mo radiation, and the θ–2θ scan technique. Reference reflections were collected at regular intervals. For (I) 2497 and for (II) 3436 independent reflections with $I > 0$ were measured. Corrections were made for Lorentz and polarization effects, for absorption (Busing & Levy, 1957) and for changes in the intensity of the primary beam. In the structure determination for (I), 2308 reflections and, for (II), 2532 reflections with $|F_o| > 3\sigma_c(|F_o|)$ were taken into account, σ_c being the standard deviation based on counting statistics and on errors in the attenuation factors (when used).

The structures were solved with MULTAN (Germain, Main & Woolfson, 1971) and by difference maps. In the final stages of the least-squares refinement H atoms were constrained at geometrically reasonable positions with C–H $\simeq$ 1·08 Å. Anisotropic thermal parameters were used for the non-hydrogen atoms and isotropic parameters for H. For (I) an isotropic extinction parameter was refined. The scattering factors for C and S were taken from Cromer & Mann (1968)

and that for H from Stewart, Davidson & Simpson (1965). The weighting schemes were $w(I) = [\sigma_c^2(F_o) + 0.0003|F_o|^2]^{-1}$ and $w(II) = [\sigma_c^2(F_o) + 0.0004|F_o|^2 + 0.4 \sin \theta]^{-1}$. Final values of $R_w(|F|) = [\sum w(\Delta F)^2/ \sum wF_o^2]^{1/2}$ were 0·057 for (I) and 0·073 for (II), both based on all reflections with $|F_o| > 3\sigma_c(|F_o|)$; $R = 0.051$ and 0·063 respectively. The final coordinates are listed in Tables 2 and 3.* For the computations the XRAY system (1975) was used.

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* Lists of structure factors and anisotropic temperature parameters for (I) and (II) have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34214 (24 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Final coordinates* ($\times 10^4$) *for* (I)

For numbering see Fig. 1. E.s.d.'s in units of the last decimal place are given in parentheses.

	x	y	z
S(1)	3354 (1)	3375 (1)	3628 (1)
C(2)	2267 (2)	2520 (3)	2670 (3)
C(3)	2084 (2)	881 (4)	2594 (4)
S(4)	936 (1)	483 (1)	1672 (1)
C(5)	701 (2)	2538 (3)	1314 (4)
C(6)	1467 (2)	3470 (3)	1924 (3)
S(7)	1467 (1)	5642 (1)	1895 (1)
C(8)	2654 (2)	5996 (3)	1529 (3)
C(9)	2917 (2)	7268 (3)	599 (3)
S(10)	4132 (1)	7303 (1)	581 (1)
C(11)	4296 (2)	5575 (3)	1799 (3)
C(12)	3453 (2)	5014 (3)	2229 (3)
H(13)	2573	−119	2964
H(14)	−13	2889	760
H(15)	2461	8221	−13
H(16)	4996	5015	2060

Table 3. *Final coordinates* ($\times 10^4$) *for* (II)

For numbering see Fig. 2. E.s.d.'s in units of the last decimal place are given in parentheses.

	x	y	z
S(1)	1397 (1)	5942 (2)	4347 (1)
C(2)	2885 (3)	5231 (5)	5159 (2)
S(3)	3788 (1)	6871 (2)	6142 (1)
C(4)	4921 (3)	4991 (8)	6510 (3)
C(5)	4696 (3)	3149 (6)	5913 (2)
C(6)	3461 (3)	3340 (5)	5103 (2)
S(7)	2780 (1)	1349 (1)	4141 (1)
C(8)	2037 (3)	3070 (5)	3067 (2)
C(9)	1981 (3)	2639 (6)	1985 (2)
C(10)	1382 (3)	4288 (8)	1361 (3)
S(11)	927 (1)	6319 (2)	1991 (1)
C(12)	1502 (3)	4970 (5)	3175 (2)
H(13)	5776	5196	7176
H(14)	5325	1783	6012
H(15)	2362	1216	1733
H(16)	1214	4316	521

Table 1. *Crystal data of* (I) *and* (II)

E.s.d.'s as calculated by the least-squares program are given in parentheses.

	(I)	(II)	(I) + (II)
a	= 14·093 (2)	11·672 (2) Å	$C_8H_4S_4$
b	= 8·118 (2)	6·152 (2)	MW 228·38
c	= 8·061 (2)	13·607 (3)	Space group $P2_1/c$
β	= 98·06 (2)	110·63 (2)°	$Z = 4$
V	= 913·1	914·4 Å^3	μ(Mo $K\alpha$) = 0·935 mm^{-1}
D_c	= 1·63	1·66 Mg m^{-3}	

Discussion

Figs. 1 and 2 give the structural formulae with the numbering scheme. The packing is shown in Figs. 3 and 4. Comparison of these figures and of the cell constants (Table 1) shows that the modes of packing of (I) and (II) are completely different. On the other hand, the crystal structures of (II) and thianthrene (Lynton & Cox, 1956) are isomorphous. Intermolecular distances shorter than the sum of the relevant van der Waals radii are not present.

Geometric data of the molecules are given in Figs. 1 and 2 and in Tables 4 and 5. The [1,4]-dithiin rings in the two dithieno-[1,4]-dithiins have a boat conformation, analogous to their conformation in thianthrene and in [1,4]-dithiin. One can consider (I) and (II) as being constructed out of two planar moieties, each containing one thiophene ring and the two S atoms of the dithiin ring. The deviations from the respective best least-squares planes are <0·05 Å (Tables 4 and 5). To a good approximation the symmetry of the molecules in the crystal is mm for (I) and m for (II).

The dihedral angles [136·2 for (I) and 130·3° for (II)] and the bond angles in the dithiin ring are interdependent. With the observed values for S—C—C (Figs. 1 and 2) the rings would have been planar for C—S—C 112·4 in (I) and 113·0° in (II). Due to the presence of the lone pairs of electrons on S the angles C—S—C have a tendency to become 90°, however. The C—S—C angles of 99·2 and 99·7 in (I) and 96·8 and 99·2° in (II) are similar to those in thianthrene (100°), [1,4]-dithiin (101°) and [1,4]-dithiane (99°; Marsh, 1955). C—S—C angles in these cyclic compounds are smaller,

however, than the C—S—C angles in acyclic compounds of type R—S—R', e.g. 103·3° in di-o-tolyl sulphide (Sacerdoti, Bertolasi & Gilli, 1976) and 104·1° in 4-dimethylaminophenyl phenyl sulphide (Bandoli, Clemente, Tondello & Dordoni, 1974). This difference is presumably due to the fact that the repulsion between the ligands in the cyclic compound is, among other

Table 4. *Geometric data for* (I)

Normal equations of the least-squares planes are given in the orthonormal system X, Y, Z with X, Y and Z parallel to **a**, **b** and **c***.

(*a*) Least-squares planes

Plane (*A*)   S(1), C(2), C(3), S(4), C(5), C(6), S(7)
$-0.4681X - 0.0401Y + 0.8828Z = 0.3042$

Plane (*B*)   S(1), S(7), C(8), C(9), S(10), C(11), C(12)
$0.0146X - 0.6017Y + 0.7986Z = -0.9022$

(*b*) Deviations from planes in 10^{-3} Å with numbers of atoms in brackets

Plane (*A*): 16[1], −20[2], −11[3], 35[4], −14[5], −26[6], 21[7], −1027[8], −1864[9], −2677[10], −1919[11], −1055[12], −85[13], +48[14], −1995[15], −2202[16].

Plane (*B*): 42[1], −1007[2], −1860[3], −2664[4], −1893[5], −1034[6], 8[7], −27[8], 9[9], 39[10], −27[11], −45[12], −2103[13], −2088[14], 76[15], −120[16].

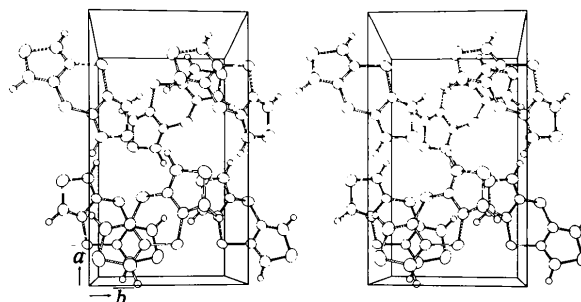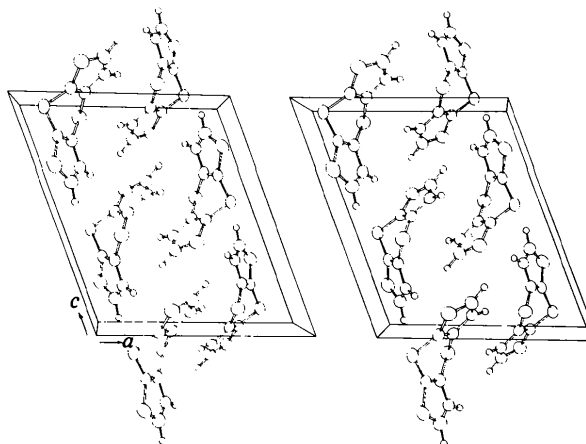(*c*) Dihedral angle

Angle between planes (*A*) and (*B*): 136·2°.
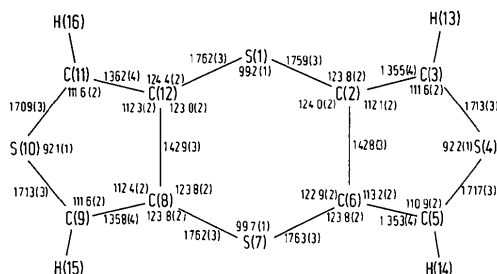
Fig. 3. Compound (I). Stereoscopic view along c of the packing.

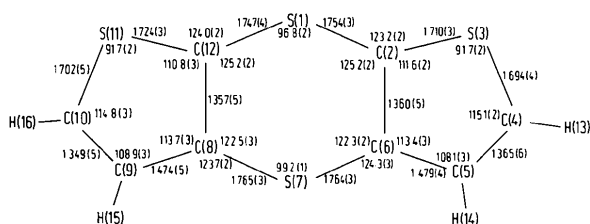Fig. 1. Structural formula of (I) with numbering scheme, bond lengths (Å) and angles (°).

Fig. 2. Structural formula of (II) with numbering scheme, bond lengths (Å) and angles (°).

Fig. 4. Compound (II). Stereoscopic view along b of the packing.

Table 5. *Geometric data for* (II)

See caption of Table 4.

(a) Least-squares planes

Plane (A) S(1), C(2), S(3), C(4), C(5), C(6), S(7)
$-0\cdot6470X - 0\cdot4337Y + 0\cdot6272Z = 2\cdot1530$

Plane (B) S(1), S(7), C(8), C(9), C(10), S(11), C(12)
$0\cdot8545X + 0\cdot4852Y + 0\cdot1857Z = 2\cdot4327$

(b) Deviations from planes in 10^{-3} Å with numbers of atoms in brackets

Plane (A): 27[1], −6[2], −36[3], 18[4], 18[5], 1[6], −21[7], −1109[8], −2151[9], −2831[10], −2331[11], −1093[12], 56[13], 17[14], −2339[15], −3644[16].

Plane (B): −19[1], 1113[2], 2333[3], 2838[4], 2166[5], 1132[6], 26[7], −16[8], −14[9], −10[10], 33[11], −1[12], 3636[13], 2369[14], −14[15], −24[16].

(c) Dihedral angle

Angle between planes (A) and (B): 130·3°.

things, balanced by the bending of two C—S—C angles rather than one as in the acyclic compounds.

The C—S distances of 1·747–1·765 Å in the [1,4]-dithiin rings of (I) and (II) lie close to the values usually observed for C(sp^2)—S distances, e.g. 1·76 Å in thianthrene and 1·776 Å in di-o-tolyl sulphide.

In (I) where the symmetries of the dithiin and thiophene rings match with the total molecular symmetry, the geometry of the thiophene moieties [apart from the bonds of type C(2)—C(3) which are 0·013 Å shorter on average] is equal to that of thiophene itself (Bak, Christensen, Hansen-Nygaard & Rastrup-Andersen, 1961). In (II) the symmetries of the dithiin and the thiophene rings do not match, which gives distortion of the rings. In (II) S(5)—C(6) and S(1)—C(2) are elongated relative to S(5)—C(4) and S(7)—C(6) respectively. Further, C(2)—C(3) is considerably larger than the 1·423 Å of the corresponding bond in thiophene, and the values of the angles S(3)—C(4)—C(5) and C(4)—C(5)—C(6) are

different from the thiophene values. We tentatively ascribe these deformations to steric repulsion effects.

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