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4-Benzyl-5-ethylthio-3*H*-1,2-dithiole-3-thione

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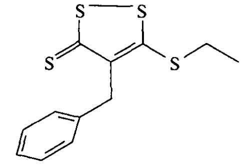
Abstract

The title compound, $C_{12}H_{12}S_4$, crystallizes in $P\bar{1}$ with two independent molecules in the asymmetric unit labelled (*A*) and (*B*). In both molecules, the phenyl and 3*H*-1,2-dithiole-3-thione rings are almost perpendicular to each other, the main difference being the position of the ethyl group which lies in the same plane as the heterocyclic ring in (*A*) but points outwards in (*B*). The crystal packing is governed by short S···S interactions.

Comment

Drugs containing 3*H*-1,2-dithiole-3-thione have found important chemotherapeutic applications (Landis, 1965; Pedersen, 1982, 1995). An example is oltipraz [4-methyl-5-(2-pyrazinyl)-3*H*-1,2-dithiole-3-thione] which has an anti-schistosomal activity (Bueding, Nolan & Leroy, 1982) and has recently been studied as a quimioprotector (Kensler *et al.*, 1992). It has also been suggested that this compound inhibits the replication of human immunodeficiency virus type-1 (HIV-1) (Prochaska, Yeh, Baron & Polsky, 1993). Other dithiolethione derivatives have been found active as fungicides, bacteriostatics, anti-cancer drugs, radioprotectors and also as corrosion inhibitors (Landis, 1965; Pedersen, 1982, 1995).

Despite the variety of applications of this family of compounds, little is known about their solid state structures and only a handful of X-ray crystallographic studies have been reported so far, from the pioneering structural work on the subject, on 4-methyl-3*H*-1,2-dithiole-3-thione, (1) (Jeffrey & Shiono, 1959) and (2) (Wei, 1985); 5-(*p*-methoxyphenyl)-3*H*-1,2-dithiole-3-thione, (3) (Wang, Lin & Wei, 1985); 4-methyl-5-[2-(2-pyrazinyl)vinyl]-3*H*-1,2-dithiole-3-thione, (4) (Wei, 1987); two isomers of phenyl-3*H*-1,2-dithiole-3-thione, (5*a*) and (5*b*) (Wei, 1986), and oltipraz, (6) (Wei, 1983). Recently, we have reported a new method for the synthesis of 5-alkylthio derivatives (Aimar & de Rossi, 1996) and we are now studying their potential biological activity. In order to correlate chemotherapeutic properties with structure, we have started a long-aim project regarding the crystal structure determination of new 3*H*-1,2-dithiole-3-thione derivatives, of which the title compound, (7), is a part.



(7)

Compound (7) crystallizes in $P\bar{1}$ with two independent molecules in the asymmetric unit, labelled (*A*) and (*B*) (Fig. 1). Interatomic distances and angles are very

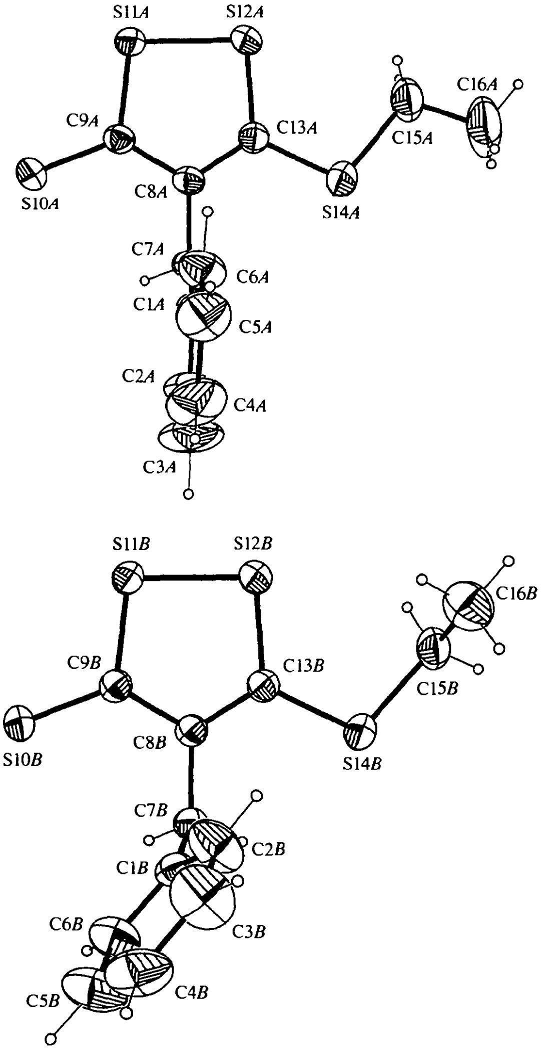


Fig. 1. The structure of the two independent molecules of (7) with atom labels. Displacement ellipsoids are drawn at the 40% probability level.

similar in both molecules, the main structural difference being found in the relative conformation of the ethylthio group (see below).

A detailed analysis of the closely related structures (2)–(6) [compound (1) has been disregarded because of the low quality of the data] reveals the existence of a few 'structural invariants' characterizing the heterocycle, and a comparison with the present results corroborates the fact, *viz.* S11—S12 [(7): 2.048 (1); (2)–(6): 2.047–2.050 Å], C9—S10 [(7): 1.665 (2); (2)–(6): 1.655–1.669 Å] or the fact that the endocyclic angle subtended at S11 is invariably larger than the one at S12. There are some other characteristics which depend on the character of the atoms or groups attached to C13. Thus, in (2) and (5*a*), where this site is occupied by hydrogen, there is a noticeable shortening of the C—S bond [1.693 (7) and 1.701 (2) Å, respectively, against the range 1.731 (2)–1.762 (2) Å in those compounds where this site is occupied by a heavier atom]. The present structure clearly fits among the latter, with two pairs of almost equivalent endocyclic C—S bonds in the range 1.732 (4)–1.738 (4) Å.

The two independent five-membered rings 1,2-dithiole-3-thione (I) in (7) are planar, the maximum deviations being 0.016 (4) (C9*A* in I*A*) and 0.011 (4) Å (C9*B* in I*B*). These values are comparable with those found in (2), (3) and (4) [typically 0.010 (6) Å], and smaller than the maximum deviations present in the more deformed (5) and (6) [typically 0.04 (1) Å]. The phenyl rings, (II), in (7) are planar as well, with maximum departures of 0.020 (8) (C4*A* in II*A*) and 0.020 (7) Å (C2*B* in II*B*). Through the unrestricted rotation around C7—C8 and C7—C1 the two independent molecules find similar conformations which minimize steric hindrance by positioning the planar groups almost perpendicular to each other in (*A*) [I*A*–II*A* 83.31 (14)°] and slightly less so in (*B*) [I*B*–II*B* 75.82 (14)°]. This is also evidenced by the large torsion angles C1—C7—C8—C9 and C1—C7—C8—C13 [−96.2 (4) and 85.3 (4)° for (*A*); −82.3 (4) and 98.9 (4)° for (*B*)].

The ethylthio groups afford the most significant differences between the two otherwise very similar molecules: in molecule (*A*), the $-SCH_2CH_3$ unit lies almost in the same plane as the planar heterocycle [C13*A*—S14*A*—C15*A*—C16*A* 174.0 (5) and S12*A*—C13*A*—S14*A*—C15*A* −2.4 (5)°], whereas in (*B*), on the other hand, this planar configuration is precluded by the intermolecular steric hindrance between the benzyl and the ethyl groups from neighbouring molecules, which forces the terminal C15*B*—C16*B* bond to point outwards [C13*B*—S14*B*—C15*B*—C16*B* 87.1 (4) and S12*B*—C13*B*—S14*B*—C15*B* −1.7 (5)°]. Most of the relevant residual electron density peaks in the structure (extreme values are 0.85 and −0.41 e Å^3) appear around the ethylthio group in (*B*).

Packing appears to be governed by S···S interactions. The relevant S···S non-bonding contacts involved are S10*A*···S11*B* 3.519 (1), S10*A*···S12*B* 3.458 (1), S11*A*···S10*B*(1 + *x*, *y*, *z*) 3.518 (1), S11*A*···S12*B* 3.569 (1), S12*A*···S10*B*(1 + *x*, *y*, *z*) 3.434 (1) and S12*A*···S11*B*(1 + *x*, *y*, *z*) 3.638 (1) Å, which, even if longer than those reported in some related structures [*viz.* 3.374 (1) and 3.363 (1) Å in (5*a*) and (5*b*)], are nontheless shorter than the sum of the van der Waals radii (3.7 Å), and contribute to the formation of chains along the **a** direction. These chains, in turn, are held together by van der Waals interactions. The solid-state packing with S···S intermolecular distances shorter than the sum of van der Waals radii appears to be a characteristic of compounds containing the dithiolethione ring. This effect has been observed in many of the members in the family, (2), (5), (6), (7), as well as in other compounds containing S atoms in the ring (Lu, Keshavarz-K, Srdanov, Jacobson & Wudl, 1989).

Experimental

4-Benzyl-5-ethylthio-3*H*-1,2-dithiole-3-thione was prepared as reported elsewhere (Aimar & de Rossi, 1996). Yellow crystals suitable for X-ray diffraction were obtained by slow evaporation of the solvent (15 d approximately) from a dichloromethane–isoctane solution.

Crystal data

$C_{12}H_{12}S_4$
$M_r = 284.45$
Triclinic
$P\bar{1}$
$a = 9.5433\,(5)$ Å
$b = 11.0572\,(7)$ Å
$c = 13.0444\,(5)$ Å
$\alpha = 78.840\,(4)°$
$\beta = 89.737\,(4)°$
$\gamma = 89.700\,(4)°$
$V = 1350.42\,(12)$ Å^3
$Z = 4$
$D_x = 1.399$ Mg m^{-3}
D_m not measured

Cu $K\alpha$ radiation
$\lambda = 1.54184$ Å
Cell parameters from 25 reflections
$\theta = 10$–$30°$
$\mu = 6.21$ mm^{-1}
$T = 293\,(2)$ K
Prismatic
0.35 × 0.25 × 0.15 mm
Yellow

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: numerical by integration (*SHELX*76; Sheldrick, 1976)
$T_{min} = 0.16$, $T_{max} = 0.37$
5137 measured reflections
4305 independent reflections

3777 reflections with $I > 2\sigma(I)$
$R_{int} = 0.027$
$\theta_{max} = 65°$
$h = -11 \rightarrow 11$
$k = -12 \rightarrow 12$
$l = 0 \rightarrow 15$
2 standard reflections every 98 reflections intensity decay: <2%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.049$
$wR(F^2) = 0.137$
$S = 1.120$

$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.85$ e Å^{-3}
$\Delta\rho_{min} = -0.41$ e Å^{-3}
Extinction correction: none

4305 reflections
289 parameters
H atoms riding (see text)
$w = 1/[\sigma^2(F_o^2) + (0.0575P)^2 + 1.5671P]$
where $P = (F_o^2 + 2F_c^2)/3$

Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

C9*A*– S10*A*	1.664 (4)	C9*B*—S10*B*	1.666 (4)
C9*A*—S11*A*	1.735 (4)	C9*B*—S11*B*	1.738 (4)
C13*A*—S14*A*	1.726 (4)	C13*B*—S12*B*	1.734 (4)
C13*A*—S12*A*	1.732 (4)	C13*B*—S14*B*	1.736 (4)
C15*A*—S14*A*	1.805 (5)	C15*B*—S14*B*	1.801 (5)
S11*A*—S12*A*	2.0486 (14)	S11*B*—S12*B*	2.0479 (14)
C9*A*—S11*A*—S12*A*	97.25 (14)	C9*B*—S11*B*—S12*B*	96.71 (13)
C13*A*—S12*A*—S11*A*	93.61 (13)	C13*B*—S12*B*—S11*B*	93.99 (13)
C13*A*—S14*A*—C15*A*	104.7 (2)	C13*B*—S14*B*—C15*B*	105.5 (2)

Owing to technical reasons beyond our control, we were forced to measure a slightly restricted data set (up to 65° in θ instead of the usual 67°). In spite of this drawback, a very adequate ratio of reflections to parameters ($\sim$15) was attained, and refinement on F^2 using the whole data set led to reasonable R factors, as well as satisfactory s.u. values for parameters involving non-H atoms. H atoms were placed at idealized positions and allowed to ride with isotropic displacement factors 1.25 times larger than those of their hosts.

Data collection: *CAD*-4-*PC* (Enraf–Nonius, 1993). Cell refinement: *CAD*-4-*PC*. Data reduction: *MolEN* (Fair, 1990). Program(s) used to solve structure: *XS* in *SHELXTL/PC* (Sheldrick, 1991). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *XP* in *SHELXTL/PC*. Software used to prepare material for publication: *CIFTAB* (Sheldrick, 1993), *PARST* (Nardelli, 1983) and *CSD* (Allen, Kennard & Taylor, 1983).

Data collection was performed at the Laboratorio Nacional de Difracción (LANADI), La Plata, Argentina.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: AB1441). Services for accessing these data are described at the back of the journal.

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Four 9-Alkylthiophenanthrenes at 193 K (Alkyl = Methyl, Ethyl, Propyl and Butyl)

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Abstract

Four 9-alkylthiophenanthrenes, namely, 9-methylthiophenanthrene, $C_{15}H_{12}S$, (1), 9-ethylthiophenanthrene, $C_{16}H_{14}S$, (2), 9-propylthiophenanthrene, $C_{17}H_{16}S$, (3) and 9-butylthiophenanthrene, $C_{18}H_{18}S$, (4), have been characterized by X-ray analysis. Compound (1) crystallizes in space group $P2_1$ with two molecules, and the other three compounds, in a novel display of isostructurality, in space group $P2_1/c$, with one molecule per asymmetric unit.

Comment

Some 9-alkylthiophenanthrenes were recently required as starting materials in connection with our studies of the preparation of new hemithiodithioacetals and their reactions (Kansikas, Leskelä, Sipilä & Hase, 1995; Kansikas, Sipilä & Hase, 1996).

After crystallization, the title compounds (2), (3) and (4) were found to appear as colorless plates, and compound (1) as light brown rods or yellow needles. Melting points were determined in open capillary tubes with an electrothermal apparatus and are uncorrected. Thin yellow needles of (1) have a melting point of 367 K, but the thicker light brown cystals used in the structure determination have a melting point of

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