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4a,6,7,8a-Tetrahydro[1,3]dithiolo[4′,5′:5,6]-[1,4]dithiino[2,3-*b*][1,4]dioxine-2-thione. A Precursor for the Preparation of New Donor Molecules and Derived Conducting Cation Radical Salts

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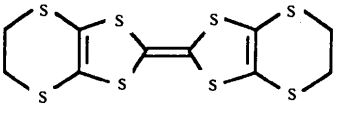
Abstract

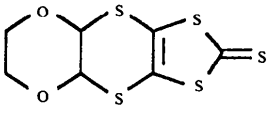
The title molecule ($C_7H_6O_2S_5$) contains three side-by-side five- or six-membered sulfur- or oxygen-containing rings. Due to the saturated character of the external oxygen-containing ring, the title molecule is severely bent with a dihedral angle of 97° along the S—S axis of the central ring.

Comment

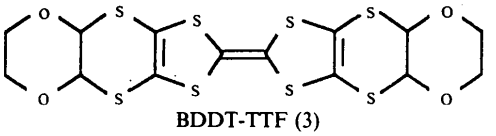
Since the discovery of superconductivity in bis(ethylenedithio)tetrathiafulvalene (BEDT-TTF) salts (Williams *et al.*, 1991), much work has been devoted to the synthesis of new π-donor molecules derived from BEDT-TTF, (1). The title molecule (2) has been used for the preparation of one such new organic donor, 4,5;4′,5′-bis(1,4-dioxane-2,3-diyldithio)tetrathiafulvalene, hereafter abbreviated as BDDT-TTF, (3) (Kotov, Faulmann, Cassoux & Yagubskii, 1994).



BEDT-TTF (or ET) (1)



(2)



BDDT-TTF (3)

The BDDT-TTF donor molecule, which can be used for the preparation of conducting cation radical salts, is of special interest due to (i) the retention of the essential electronic structural features and solubility of the BEDT-TTF parent molecule, together with (ii) the increase in the number of peripheral heteroatoms (which may result in additional side-by-side inter-cation interactions), and (iii) the non-coplanarity of the 1,4-dioxane rings with respect to the central BEDT-TTF molecular framework (which should hinder the formation of dense face-to-face stacked packing).

The planarity of the C_3S_5 fragment of (2), in contrast with the rest of the molecule, and the angle of 97.1 (1)° between this fragment and the rest of the molecule, is clearly shown in Fig. 1. The largest deviation in the C_3S_5 plane is less than 0.03 Å (S3). Although the four C atoms (C4–C7) of the dioxane ring also form a plane (deviation less than 0.015 Å), the C_4O_2 ring adopts a chair conformation with the two O atoms at 0.578 (6) (O1) and −0.645 (5) Å (O2) from the mean plane of the C atoms. In the C_5S_5 moiety the intramolecular distances are comparable to those found in 5,6-dihydro-5,6-dimethyl-1,3-dithiolo[4,5-*b*][1,4]dithiine-2-thione, $C_7H_8S_5$ (it should be noted, however, that the structure of $C_7H_8S_5$ was solved by equalizing chemically equivalent intramolecular distances) (Wallis & Dunitz, 1988).

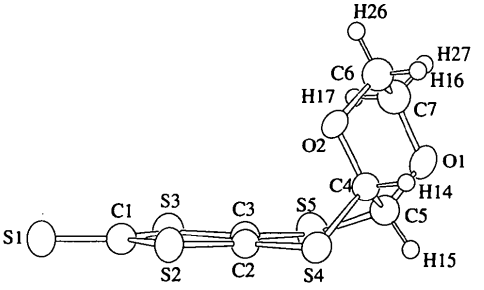


Fig. 1. Molecular structure of the title compound. Non-H atoms are represented as 50% probability displacement ellipsoids.

The dihedral angles between the S2—C2—S4 and C2—S4—C4 planes, and the S3—C3—S5 and C3—S5—C5 planes, are very large (*ca* 139 and 160°, respectively). In spite of this distortion from planarity, molecules of (2) stack along the [010] direction (Fig. 2). When considering only the planar C_3S_5 fragment, the distances between two adjacent planes is quite short (3.58 Å). However, as the stacking direction is not perpendicular to the C_3S_5 fragment, there are no S···S contacts shorter than the sum of

the van der Waals radii. The shortest intrastack distances between two S atoms are 3.83 (S3···S5′) and 3.86 Å (S3···S1′).

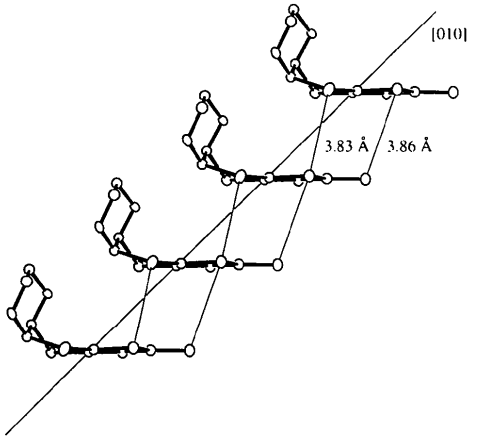


Fig. 2 Stacking of the title molecule along the *b* axis.

Experimental

The title compound (2) was synthesized by cycloaddition of 1,4-dioxine to oligomeric 1,3-dithiole-2,4,5-trithione $(C_3S_5)_x$ (Neiland, Kacens & Kreicberga, 1989*a*,*b*) in 1,4-dioxane at 363 K (Kotov, Faulmann, Cassoux & Yagubskii, 1994).

Crystal data

$C_7H_6O_2S_5$
M_r = 282.4
Monoclinic
$P2_1$
a = 9.631 (2) Å
b = 5.491 (1) Å
c = 9.895 (1) Å
β = 92.04 (1)°
V = 522.9 (2) Å^3
Z = 2
D_x = 1.79 Mg m^{-3}
Mo $K\alpha$ radiation
λ = 0.71069 Å
Cell parameters from 25 reflections
θ = 4.5–19.5°
μ = 1.03 mm^{-1}
T = 293 K
Needle
0.40 × 0.10 × 0.10 mm
Orange–yellow

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: empirical (North, Phillips & Mathews, 1968)
T_{min} = 0.71, T_{max} = 0.99
1121 measured reflections
1033 independent reflections
821 observed reflections [$I \geq 3\sigma(I)$]
R_{int} = 0.0683
θ_{max} = 25°
h = 0 → 11
k = 0 → 6
l = −11 → 11
3 standard reflections
frequency: 120 min
intensity variation: 0.2%

Refinement

Refinement on F
R = 0.039
wR = 0.045
S = 0.89
821 reflections
91 parameters
H-atom parameters not refined
$w = 1/\sigma^2(F)$
$(\Delta/\sigma)_{max}$ = 0.1
$\Delta\rho_{max}$ = 0.60 e Å^{-3}
$\Delta\rho_{min}$ = −0.37 e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. *Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters* (Å^2)

B_{iso} for C atoms; $B_{eq} = (4/3)\Sigma_i\Sigma_j\beta_{ij}\mathbf{a}_i.\mathbf{a}_j$ for others.

	x	y	z	B_{iso}/B_{eq}
S1	1.1150 (2)	0.6286 (6)	0.2646 (2)	3.94 (5)
C1	0.9967 (9)	0.419 (2)	0.2414 (8)	3.1 (2)
S2	0.9116 (2)	0.360	0.0886 (2)	3.20 (4)
S3	0.9417 (2)	0.2310 (5)	0.3703 (2)	3.50 (4)
C2	0.8109 (8)	0.119 (2)	0.1425 (7)	2.6 (1)
C3	0.8228 (8)	0.062 (2)	0.2718 (8)	2.8 (2)
S4	0.6945 (2)	−0.0189 (5)	0.0254 (2)	3.02 (4)
S5	0.7367 (2)	−0.1712 (5)	0.3573 (3)	4.25 (5)
C4	0.5521 (8)	−0.057 (2)	0.1348 (7)	2.6 (1)
C5	0.5810 (8)	−0.240 (2)	0.2486 (8)	2.9 (2)
O1	0.4668 (6)	−0.265 (1)	0.3305 (5)	3.2 (1)
O2	0.5075 (5)	0.166 (1)	0.1857 (5)	2.7 (1)
C6	0.3856 (8)	0.134 (2)	0.2627 (8)	3.3 (2)
C7	0.4163 (9)	−0.038 (2)	0.3775 (9)	3.7 (2)

Table 2. *Selected geometric parameters* (Å, °)

S1—C1	1.630 (9)	S4—C4	1.790 (8)
C1—S2	1.725 (8)	S5—C5	1.853 (8)
C1—S3	1.737 (9)	C4—C5	1.53 (1)
S2—C2	1.735 (9)	C4—O2	1.40 (1)
S3—C3	1.744 (9)	C5—O1	1.397 (9)
C2—C3	1.32 (1)	O1—C7	1.42 (1)
C2—S4	1.756 (8)	O2—C6	1.43 (1)
C3—S5	1.759 (9)	C6—C7	1.50 (1)
S1—C1—S2	124.3 (5)	C3—S5—C5	104.8 (4)
S1—C1—S3	123.1 (5)	S4—C4—C5	113.6 (6)
S2—C1—S3	112.6 (5)	S4—C4—O2	111.4 (6)
C1—S2—C2	97.3 (4)	C5—C4—O2	111.2 (6)
C1—S3—C3	96.7 (4)	S5—C5—C4	114.7 (6)
S2—C2—C3	116.7 (7)	S5—C5—O1	108.7 (5)
S2—C2—S4	118.5 (5)	C4—C5—O1	111.6 (7)
C3—C2—S4	124.7 (7)	C5—O1—C7	112.7 (7)
S3—C3—C2	116.6 (7)	C4—O2—C6	110.4 (7)
S3—C3—S5	115.5 (5)	O1—C7—C6	111.4 (7)
C2—C3—S5	127.9 (7)	O2—C6—C7	109.8 (7)
C2—S4—C4	97.9 (4)		

Data collection and cell refinement: *CAD-4 Express* (Enraf–Nonius, 1992). Programs used to solve structure: *SHELXS*86 (Sheldrick, 1985) and *MolEN* (Fair, 1990). Program used to refine structure: *MolEN*. Program used to produce the molecular graphics: *ORTEP*II (Johnson, 1976).

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: PA1109). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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4,6,7,8,9,9a-Hexahydro-11*H*-pyrido-[1,2-*a*]thieno[2,3-*e*][1,3]diazepin-11(10*H*)-one

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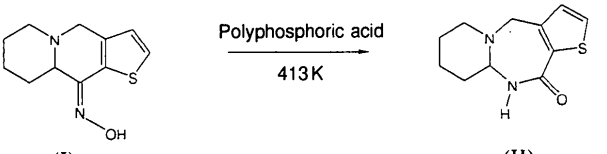
Abstract

The title molecule ($C_{11}H_{14}N_2OS$) consists of a seven-membered diazepine ring fused to a five-membered thiophene ring and a six-membered piperidine ring. The thiophene ring is planar while the diazepine moiety adopts a half-chair conformation; the *cis*-fused piperidine ring possesses a chair conformation. The least-squares plane of the thiophene and the diazepine rings makes an angle of about 102° with the best plane of the piperidine moiety.

Comment

The reported anticonvulsant, anxiolytic, muscle-relaxant and central nervous system activity of fused tricyclic thienodiazepines (Bauer, Langbein & Weber, 1975; Weber, Bauer, Dannenberg & Kuhn, 1974; Hunkeler & Kyburz, 1981) stimulated the search in our laboratory for other heterocycles incorporating this ring system. The Beckmann rearrangement of 10-(hydroxyimino)-6,7,8,9,9a,10-hexahydro-4*H*-thieno[2,3-*b*]quinolizine (I) with polyphosphoric acid at 413 K led to the title compound (II) (Marchalín & Decroix, 1994).



(I) (II)

The structure of (II) was inferred from exhaustive ^1H and ^{13}C NMR studies. To confirm that the *E* configuration of the starting oxime (I) was retained and to obtain detailed stereochemistry of the new tricyclic heterocycle, the X-ray diffraction study of (II) was undertaken.

The X-ray analysis shows that the molecule consists of a seven-membered diazepine ring fused to a five-membered thiophene ring and a six-membered piperidine ring. The thiophene ring is planar, while the

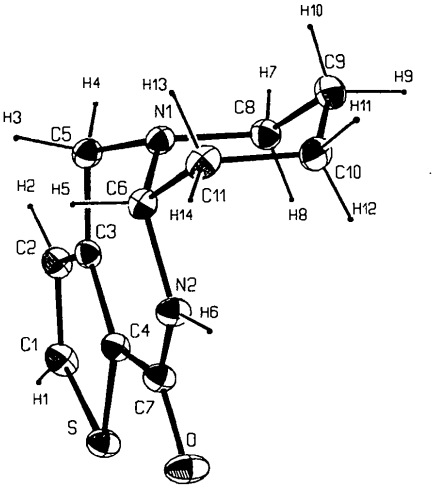


Fig. 1. The molecular structure of the title compound, with displacement ellipsoids given at 30% probability for non-H atoms.

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