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An unsymmetrical tetrathiafulvalene with a fused 1,2,5-thiadiazole ring and an ethylenedioxy group

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Key indicators

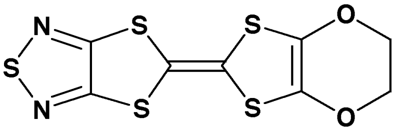
Single-crystal X-ray study
T = 296 K
Mean σ(C–C) = 0.017 Å
R factor = 0.063
wR factor = 0.174
Data-to-parameter ratio = 8.5

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

In the crystal structure of the title compound, 4,5-ethylenedioxy[1,2,5]thiadiazolotetrathiafulvalene, $C_8H_4N_2O_2S_5$, a large number of short intermolecular S···S contacts are observed. The molecules stack along the *c* axis in a face-to-face fashion.

Comment

In recent years tetrathiafulvalene (TTF) derivatives with a fused 1,2,5-thiadiazole ring have received much attention as component molecules for organic conducting solids (Tomura *et al.*, 1993; Underhill *et al.*, 1993; Naito *et al.*, 1996; Tomura & Yamashita, 1997). Intermolecular interactions caused by S···N and S···S heteroatom contacts may increase the dimensionality in the solid state (Yamashita & Tomura, 1998). The title unsymmetrical TTF derivative, (I), contains a fused 1,2,5-thiadiazole ring and an ethylenedioxy group. Two superconductors based on bis(ethylenedioxy)tetrathiafulvalene (BEDO-TTF) are known to date (Beno *et al.*, 1990; Kahlich *et al.*, 1991). We report here the molecular and crystal structure of (I).



(I)

Compound (I) crystallizes in the space group *Pna*2₁. Its molecular structure is shown in Fig. 1 and selected geometric parameters are given in Table 1. The molecule of (I) is bent slightly at the central C1═C4 bond. The dihedral angle between the two least-squares planes (S1/S2/S5/N1/N2/C1/C2/C3 and S3/S4/O1/O2/C4/C5/C6) is 12.4 (4)°. The maximum and r.m.s. deviations of fitted atoms from the least-squares plane for all non-H atoms are 0.49 (1) for C8 and 0.20 Å, respectively. The geometric parameters of the 1,2,5-thiadiazole ring in (I) are almost the same as those of 3,4-diphenyl-1,2,5-thiadiazole (Mellini & Merlino, 1976).

Fig. 2 shows the packing of (I), viewed along the *c* axis. A large number of short intermolecular S···S contacts within the sum of the van der Waals radii (Pauling, 1960) are observed (Table 2), but no short heteroatom contacts involving the N and O atoms exist in the crystal. Two types of dimers are formed *via* the short S···S contacts. One is composed of two parallel molecules and the other is formed by a T-shaped molecular arrangement. The molecules stack along the *c* axis, where the distance between the molecular planes is 3.59 (1) Å.

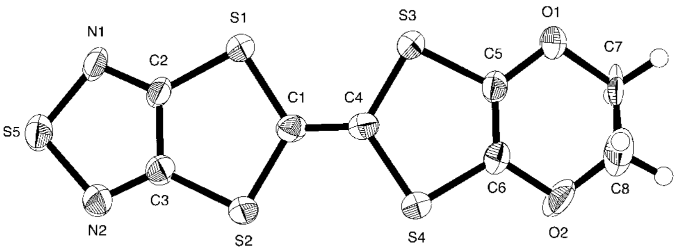


Figure 1
Molecular structure of (I), with the atomic numbering scheme. Displacement ellipsoids for non-H atoms are drawn at the 50% probability level..

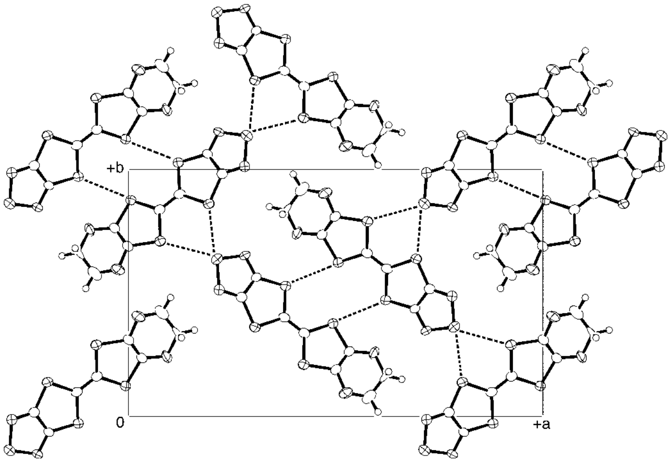


Figure 2
Packing diagram of (I), viewed along the *c* axis. Dashed lines indicate the short intermolecular S· · ·S contacts.

TTF derivatives with a fused 1,2,5-thiadiazole ring tend to stack in a head-to-tail fashion (Tomura & Yamashita, 2001). In the stacking of (I), however, the molecules overlap face-to-face with each other.

Experimental

The title compound was synthesized according to the literature method of Tomura & Yamashita (1997). Orange crystals of (I) suitable for X-ray analysis were grown from a toluene solution.

Crystal data

$C_8H_4N_2O_2S_5$
$M_r = 320.43$
Orthorhombic, $Pna2_1$
$a = 21.7363$ (10) Å
$b = 12.9552$ (6) Å
$c = 3.9938$ (5) Å
$V = 1124.65$ (16) Å^3
$Z = 4$
$D_x = 1.892$ Mg m^{-3}

Cu $K\alpha$ radiation
Cell parameters from 18 reflections
$\theta = 14.1$–$42.7°$
$\mu = 9.43$ mm^{-1}
$T = 296$ (2) K
Needle, orange
0.40 × 0.04 × 0.02 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
ω–2θ scans
Absorption correction: ψ scan (North *et al.*, 1968)
$T_{\min} = 0.116$, $T_{\max} = 0.834$
1303 measured reflections
1303 independent reflections

791 reflections with $I > 2\sigma(I)$
$\theta_{\max} = 74.2°$
$h = -27 \rightarrow 0$
$k = 0 \rightarrow 16$
$l = -4 \rightarrow 0$
3 standard reflections frequency: 120 min intensity decay: 0.4%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.063$
$wR(F^2) = 0.174$
$S = 1.05$
1303 reflections
154 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0859P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.61$ e Å^{-3}
$\Delta\rho_{\min} = -0.87$ e Å^{-3}
Absolute structure: (Flack, 1983); 0 Friedel pairs
Flack parameter = 0.03 (10)

Table 1
Selected geometric parameters (Å, °).

S1—C2	1.726 (11)	O1—C5	1.369 (12)
S1—C1	1.796 (12)	O1—C7	1.468 (19)
S2—C3	1.740 (12)	O2—C6	1.363 (12)
S2—C1	1.758 (12)	O2—C8	1.453 (14)
S3—C5	1.751 (11)	N1—C2	1.317 (14)
S3—C4	1.765 (12)	N2—C3	1.281 (12)
S4—C6	1.754 (11)	C1—C4	1.322 (14)
S4—C4	1.759 (12)	C2—C3	1.444 (16)
S5—N1	1.653 (9)	C5—C6	1.323 (16)
S5—N2	1.662 (10)	C7—C8	1.400 (18)
C2—S1—C1	94.1 (6)	C3—C2—S1	117.7 (9)
C3—S2—C1	95.1 (5)	N2—C3—C2	115.2 (10)
C5—S3—C4	93.7 (5)	C2—C3—S2	116.2 (8)
C6—S4—C4	93.6 (6)	S4—C4—S3	115.6 (6)
N1—S5—N2	98.8 (5)	C6—C5—O1	124.8 (10)
C5—O1—C7	107.3 (11)	C6—C5—S3	118.2 (8)
C6—O2—C8	108.6 (9)	C5—C6—O2	124.9 (10)
C2—N1—S5	106.0 (8)	C5—C6—S4	118.3 (8)
C3—N2—S5	106.4 (8)	C8—C7—O1	110.6 (12)
S2—C1—S1	116.1 (6)	C7—C8—O2	112.3 (11)
N1—C2—C3	113.6 (10)		

Table 2
Short intermolecular S· · ·S contacts (Å).

S1· · ·S5$^{\text{i}}$	3.541 (5)	S4· · ·S2$^{\text{iv}}$	3.519 (5)
S1· · ·S5$^{\text{ii}}$	3.547 (5)	S5· · ·S1$^{\text{v}}$	3.541 (5)
S2· · ·S4$^{\text{iii}}$	3.519 (5)	S5· · ·S1$^{\text{vi}}$	3.547 (5)
S3· · ·S5$^{\text{i}}$	3.610 (5)	S5· · ·S3$^{\text{v}}$	3.610 (5)

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

All H atoms were placed in geometrically calculated positions and refined using a riding model, with C—H set to 0.97 Å. The short C7—C8 bond length [1.40 (2) Å] may be due to positional disorder of the C7 and C8 atoms. This type of disorder is often observed in TTF derivatives with an ethylenedithio or ethylenedioxy group.

Data collection: *CAD*-4 *EXPRESS Software* (Enraf–Nonius, 1992); cell refinement: *CAD*-4 *EXPRESS Software*; data reduction: *teXsan* (Molecular Structure Corporation/Rigaku Corporation, 2000); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*III (Burnett & Johnson, 1996); software used to prepare material for publication: *SHELXL*97.

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