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4-[(Methoxyglycyl)carbonyl]tetrathiafulvalene

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The title compound, $C_{10}H_9NO_3S_4$, has a nearly planar tetrathiafulvalene–amide moiety and an ester group normal to it. Molecules in the crystal structure are linked by S···O interactions and N—H···O hydrogen bonds.

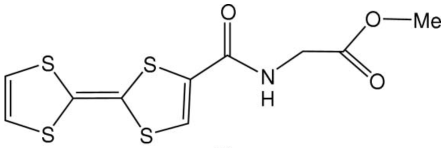
Key indicators

Single-crystal X-ray study
T = 120 K
Mean σ(C–C) = 0.002 Å
R factor = 0.028
wR factor = 0.075
Data-to-parameter ratio = 17.3

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

Comment

The chemistry of tetrathiafulvalene (TTF) and its derivatives has been at the forefront of research in the field of organic conductors for over 30 years (Bendikov *et al.*, 2004). As the physical properties displayed by these materials depend on the intermolecular architecture, tetrathiafulvalene derivatives bearing substituents which can participate in hydrogen bonding have been actively investigated as an approach to improving the dimensionality of intermolecular interactions in their charge-transfer complexes (Fourmigué & Batail, 2004). Derivatives bearing functionalities such as alcohols, amides, thioamides, amines, and carboxylic and nucleic acids have all been studied. Booth *et al.* (1998) investigated the incorporation of TTF-bearing amino acids into a polypeptide backbone with the aim of controlling the spatial arrangements of the TTF units. In the present paper, we report the crystal structure of tetrathiafulvalene bearing a pendant glycine methyl ester chain to investigate potential hydrogen bonding in the neutral state which may, possibly, be manifested in charge-transfer complexes and radical ion salts.



(I)

In the title molecule, (I) (Fig. 1), the TTF-amide moiety is nearly planar, except for a small folding along the S1···S2 vector [6.8 (1)°] and a twist around the C2—C7 bond

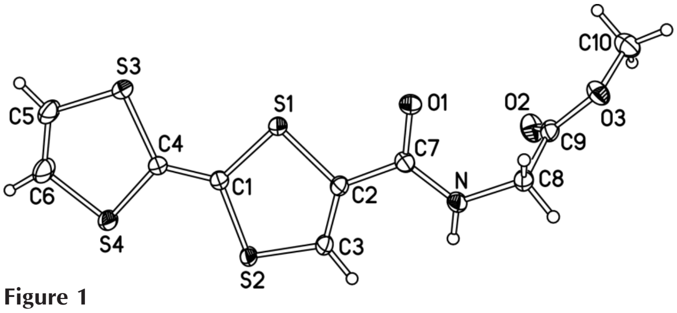


Figure 1
The molecular structure of (I), showing atomic displacement ellipsoids drawn at the 50% probability level.

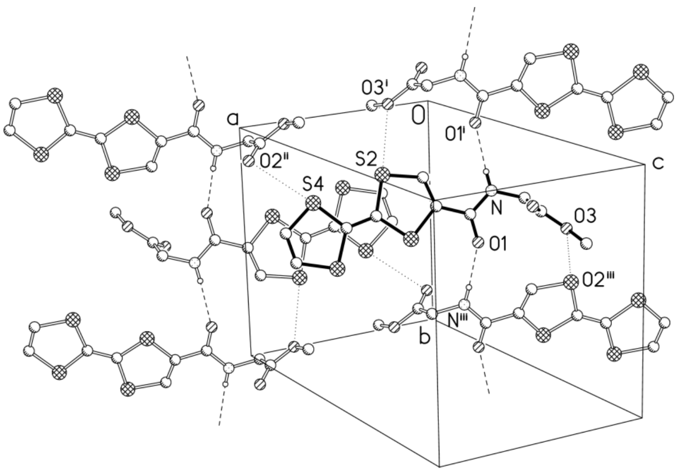


Figure 2
The crystal packing of (I), showing hydrogen bonds (dashed) and short S···O contacts (dotted lines) [symmetry codes: (i) $-x$, $y-\frac{1}{2}$, $\frac{1}{2}-z$; (ii) $x+1$, $\frac{1}{2}-y$, $z-\frac{1}{2}$; (iii) $-x$, $y+\frac{1}{2}$, $\frac{1}{2}-z$].

[8.5 (1)°]. The planar ester moiety, however, is inclined to the plane of the adjacent amido group by 86.1 (1)°. Such a conformation hinders the formation of a continuous stacking motif, although molecules do form centrosymmetric face-to-face dimers with a longitudinal offset, so that a dithiole ring of one molecule overlaps with the central C1═C4 bond of another. The mean planes of the two TTF moieties within the dimer are strictly parallel, with an interplanar separation of 3.48 (1) Å. Bond distances in (I) are similar to those in the two previously studied amide derivatives of TTF (Batsanov *et al.*, 1994, 1995). In particular, the bond distances S1—C2 [1.759 (1) Å] and S2—C3 [1.728 (1) Å] differ substantially, due to π-conjugation with the amide C7═O1 bond.

In the crystal structure, intermolecular N—H···O hydrogen bonds (Table 2) link the molecules into infinite chains, parallel to the *b* axis. The chains are further linked into a three-dimensional motif (Fig. 2) by intermolecular S···O contacts [S2···O3^{i} = 3.055 (1) Å and S4···O2^{ii} = 3.243 (1) Å; symmetry codes: (i) $-x$, $y-\frac{1}{2}$, $\frac{1}{2}-z$; (ii) $x+1$, $\frac{1}{2}-y$, $z-\frac{1}{2}$], which are substantially shorter than the sum of van der Waals radii of S and O (3.39 Å) according to Rowland & Taylor (1996).

Experimental

Dry triethylamine (0.63 ml, 4.53 mol) was added to a solution of glycine methyl ester hydrochloride, $MeO_2CCH_2NH_3^{+}\cdot Cl^{-}$ (0.21 g, 1.66 mmol), in dry dichloromethane (20 ml) and the solution was stirred for 30 min at room temperature under dry nitrogen. A solution of 4-fluorocarbonyltetrathiafulvalene (0.38 g, 1.52 mmol) (Cooke *et al.*, 1999) in dry dichloromethane (20 ml) was added and stirring continued overnight. The organics were washed with water (3 × 25 ml), dried over $MgSO_4$ and evaporated. Column chromatography of the residue, eluting initially with dichloromethane to remove trace impurities, and subsequently ethyl acetate afforded (I) (0.42, yield 87%) as a red crystalline solid, *m*/*z* (LC–MS) 318.9 (M^{+}, 100%); ^{1}H NMR ($CDCl_3$): δ 8.96 (1H, *t*, *J* 5.8), 7.57 (1H, *s*), 6.75 (2H, *s*), 3.91 (2H, *d*, *J* 5.8), 3.65 (3H, *s*); IR (KBr) (cm^{-1}): 3324, 3034, 1741, 1613, 1543, 1213. A crystal of X-ray quality was grown by slow evaporation of an ethyl acetate solution (m.p. 325–327 K).

Crystal data

$C_{10}H_9NO_3S_4$
$M_r = 319.42$
Monoclinic, $P2_1/c$
$a = 8.9306$ (11) Å
$b = 10.0106$ (12) Å
$c = 14.4694$ (17) Å
$\beta = 94.02$ (1)°
$V = 1290.4$ (3) Å^3
$Z = 4$

$D_x = 1.644$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 896 reflections
$\theta = 12.1$–26.4°
$\mu = 0.73$ mm^{-1}
$T = 120$ (2) K
Plate, red
0.24 × 0.23 × 0.08 mm

Data collection

Bruker SMART 1K CCD area-detector diffractometer
ω scans
Absorption correction: by integration (*XPREP* in *SHELXTL*; Bruker, 2001)
$T_{min} = 0.825$, $T_{max} = 0.945$
15591 measured reflections

3448 independent reflections
2992 reflections with $I > 2\sigma(I)$
$R_{int} = 0.040$
$\theta_{max} = 29.1$°
$h = -12 \rightarrow 12$
$k = -13 \rightarrow 13$
$l = -19 \rightarrow 19$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.028$
$wR(F^2) = 0.075$
$S = 1.04$
3448 reflections
199 parameters
All H-atom parameters refined

$w = 1/[\sigma^2(F_o^2) + (0.041P)^2 + 0.4425P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.44$ e Å^{-3}
$\Delta\rho_{min} = -0.30$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

S1—C1	1.7562 (14)	O3—C9	1.3359 (16)
S1—C2	1.7590 (14)	O3—C10	1.4524 (18)
S2—C3	1.7281 (14)	N—C7	1.3405 (18)
S2—C1	1.7644 (14)	N—C8	1.4463 (17)
S3—C5	1.7430 (16)	C1—C4	1.3465 (19)
S3—C4	1.7603 (14)	C2—C3	1.3402 (19)
S4—C6	1.7302 (16)	C2—C7	1.4818 (18)
S4—C4	1.7560 (14)	C5—C6	1.325 (2)
O1—C7	1.2413 (16)	C8—C9	1.521 (2)
O2—C9	1.2012 (18)		
C1—S1—C2	94.33 (6)	C7—C2—S1	114.68 (9)
C3—S2—C1	94.93 (7)	C2—C3—S2	118.05 (11)
C5—S3—C4	94.76 (7)	S4—C4—S3	114.33 (7)
C6—S4—C4	94.91 (7)	C6—C5—S3	117.56 (12)
C9—O3—C10	117.19 (12)	C5—C6—S4	118.41 (12)
C7—N—C8	119.19 (12)	O1—C7—N	122.00 (12)
S1—C1—S2	114.66 (7)	O1—C7—C2	119.67 (12)
C3—C2—C7	127.85 (12)	N—C7—C2	118.32 (12)
C3—C2—S1	117.44 (10)		
C3—C2—C7—N	7.7 (2)	N—C8—C9—O3	156.57 (11)
C2—C7—N—C8	−179.08 (12)	C8—C9—O3—C10	179.65 (12)
C7—N—C8—C9	−76.58 (16)		

Table 2
Hydrogen-bonding geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N—H1N···O1^{i}	0.84 (2)	2.13 (2)	2.9688 (15)	177.0 (19)

Symmetry code: (i) $-x$, $y-\frac{1}{2}$, $\frac{1}{2}-z$.

All H atoms were located in a difference Fourier map and refined freely in an isotropic approximation, bond distances Csp^3—H = 0.91 (2)–0.97 (2) Å and Csp^2—H = 0.86 (2)–0.94 (3) Å.

Data collection: *SMART* (Bruker, 1998); cell refinement: *SMART*; data reduction: *SAINT* (Bruker, 2001); program(s) used to solve

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structure: *SHELXTL* (Bruker, 2001); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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