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6-(4-Methoxyphenyl)thieno[2,3-*d*][1,3]dithiole-2-thione at 150K

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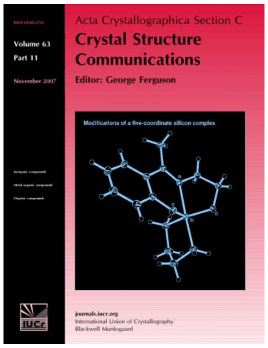

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Sato, M., Nakano, T. & Mukaida, K. I. (1995). *Liq. Cryst.* **18**, 645–649.
Sheldrick, G. M. (1994). *SHELXTL*. Version 5. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
Siemens (1995). *SMART and SAINT Area-Detector Control and Integration Software*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
Tsunekawa, T., Gotoh, J., Mataki, H., Kondoh, T., Fukuda, S. & Iwamoto, M. (1990). *Nonlinear Opt. Prop. Org. Mater.* **3**, 272–284.
Zamir, S., Bernstein, J., Ioffe, A., Brunvoll, J., Kolonits, M. & Hargittai, I. (1994). *J. Chem. Soc. Perkin Trans. 2*, pp. 895–900.

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6-(4-Methoxyphenyl)thieno[2,3-*d*][1,3]-dithiole-2-thione at 150 K

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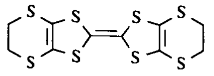
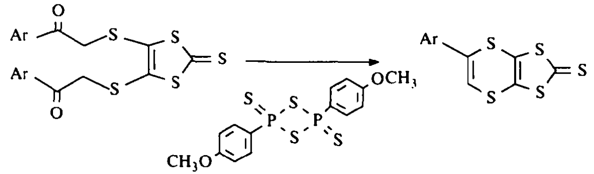
Abstract

The structure determination at 150 K of 6-(4-methoxyphenyl)thieno[2,3-*d*][1,3]dithiole-2-thione, $C_{12}H_8OS_4$, which was obtained from a novel rearrangement reaction, is the first measurement of this heterocyclic system. The bond lengths in the thiophene ring are not perturbed significantly by the fusion of the second ring; however, there is a degree of asymmetry in the bond lengths of the dithiole ring.

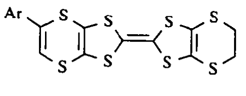
Comment

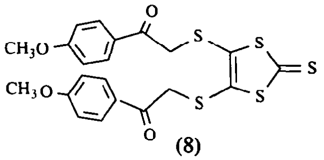
Since many radical cation salts of bis(ethylenedithio)-tetrathiafulvalene, (1), show electrical conductivity, and in some cases superconductivity (Williams *et al.*, 1985), we have been exploring synthetic routes to new derivatives of (1) (Ozturk, Rice & Wallis, 1995). Recently, it was discovered that reactions of 4,5-bis(benzoylmethylthio)-1,3-dithiolethione, (2), and 4,5-bis(4-nitrobenzoylmethylthio)-1,3-dithiolethione, (3), with Lawesson's reagent, (4), provide an efficient route to the 1,3-dithiolo[1,4]dithiin-2-thiones (5) and (6) (Ozturk, 1996); the former has been converted subsequently to the tetrathiafulvalene derivative (7), a precursor for the preparation of organic metals. In contrast, reaction with Lawesson's reagent of the corresponding bis(4-methoxybenzoyl) derivative, (8), gave a material (58%) containing one less S atom than (5) or (6) according to chemical analysis and mass spectral data. To determine the structure of this substance unambiguously, the crystal structure was determined at 150 K.


(1)



(2) $Ar = C_6H_5$-
(3) $Ar = 4\text{-}NO_2\text{-}C_6H_4$-
(4)
(5) $Ar = C_6H_5$-
(6) $Ar = 4\text{-}NO_3\text{-}C_6H_4$-


(7) $Ar = C_6H_5$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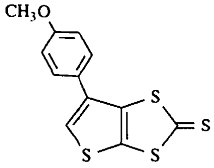
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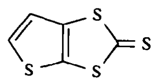
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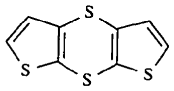
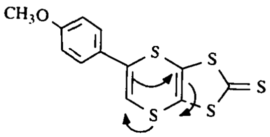

(11)


(12)

The substance was identified as the thieno[2,3-*d*][1,3]dithiole derivative (9). The molecular structure is shown in Fig. 1. No structure determinations of molecules containing this heterocyclic system have been reported, indeed only the preparation of the unsubstituted thione, (10), has been recorded (Engler, Patel, Andersen, Schumaker & Fukushima, 1978; Santalo *et al.*, 1991). The fused heterocycle is almost planar; the best planes of the two five-membered rings lie at just 4.2 (1)°. The bond lengths in the thiophene ring are very similar to those for an isolated thiophene ring (Allen *et al.*, 1987), showing the shortest bonds from C to S in the molecule [S4—C2 1.716 (4), S4—C3 1.713 (4) Å] and C—C bonds in the range 1.362 (5)–1.433 (5) Å. There is a marked asymmetry in the dithiole ring; the bonds to ring atom S1 are longer than those to ring atom S3 [S1—C1 1.751 (4) and S1—C5 1.748 (4) Å *cf.* S3—C1 1.737 (4) and S3—C2 1.730 (4) Å]. Similar general trends are found in the molecular structure of the dithieno[1,4]dithiin, (11) (Hiemstra & Kiers, 1979). The best plane through the substituted benzene ring lies at 30.0 (1)° to the best plane through the heterocyclic system. The aryl substituent is prevented from attaining coplanarity with the heterocyclic system by two short

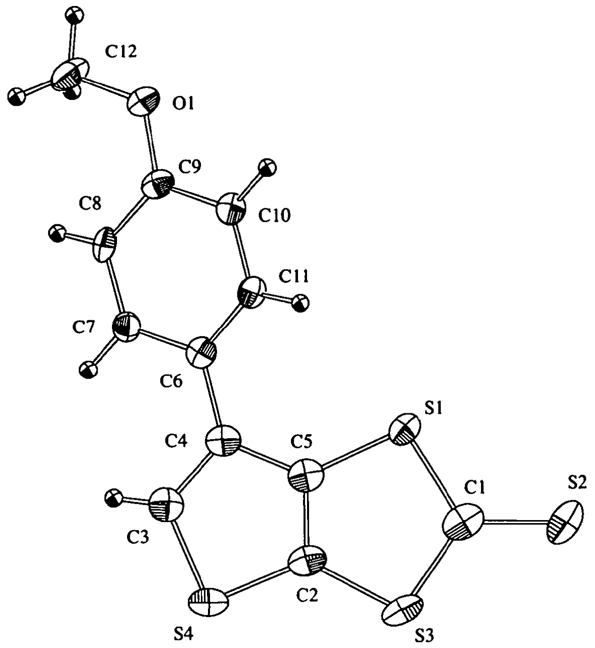


Fig. 1. Molecular structure of (9) (Zsolnai & Pritzkow, 1996) with displacement ellipsoids at the 50% probability level.

contacts involving *ortho* H atoms: H11···S1 [2.78 (3) Å] and H7···H3 [2.29 (5) Å]. The molecule may have been formed from the 1,3-dithiolo[1,4]dithiin (12) by an electrocyclic reaction followed by elimination of an S atom.

In the crystal, the molecules are packed in layers related by the translation [001]. There is an S···O contact of 3.109 (3) Å between the methoxy O atom and the S4 atom of a molecule related by a 2_1 axis. The S4···O vector lies at an angle of 165.1 (3)° to the S4—C2 bond in accord with the general observation of an electron-rich atom approaching a S atom along the line of one of the S—C bonds (Rosenfield, Parthasarathy & Dunitz, 1977). The shortest intermolecular S···S contact involves two centrosymmetrically related thione S atoms [S···S 3.569 (2) Å].

Experimental

Substance (9) was prepared from the dithiole (8) (0.45 g) and Lawesson's reagent, (4) (0.46 g), in refluxing toluene overnight. Chromatography of the evaporated reaction mixture on silica eluting with dichloromethane/hexane (1:1) gave the product (0.32 g, 58%), ^{1}H NMR ($CDCl_3$) 7.54 (*s*, 5–H), 7.43 (*d*, *J* = 8.8 Hz, Ar-H_2), 6.98 (*d*, *J* = 8.8 Hz, Ar-H_2), 3.85 (*s*, CH_3), ^{13}C NMR 55.4 (CH_3), 114.6, 124.0, 126.2, 127.8, 128.2, 136.1, 159.9, 214.7 (C=S), *m*/*z* (FAB, NOBA matrix) 297 (M + 1)$^+$, found C 48.5, H 2.6%; $C_{12}H_8OS_4$ requires C 48.6, H 2.7%.

Crystal data

$C_{12}H_8OS_4$
$M_r = 296.42$
Monoclinic
$P2_1/a$
$a = 7.495\ (1)$ Å
$b = 12.180\ (1)$ Å
$c = 13.750\ (1)$ Å
$\beta = 104.38\ (1)°$
$V = 1215.9\ (2)$ Å^3
$Z = 4$
$D_x = 1.619$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 250 reflections
$\theta = 2.3$–$25.0°$
$\mu = 0.758$ mm^{-1}
$T = 150\ (2)$ K
Plate
0.42 × 0.27 × 0.10 mm
Yellow

Data collection

Enraf–Nonius FAST system diffractometer
Method: see Danopoulos, Wilkinson, Hussain-Bates & Hursthouse (1991)
Absorption correction: refined from ΔF (*DIFABS*; Walker & Stuart, 1983)
$T_{\min} = 0.80$, $T_{\max} = 1.00$

4990 measured reflections
1826 independent reflections
1522 observed reflections $[I > 2\sigma(I)]$
$R_{\rm int} = 0.0754$
$\theta_{\max} = 25.03°$
$h = -6 \rightarrow 8$
$k = -13 \rightarrow 13$
$l = -16 \rightarrow 15$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.0551$
$wR(F^2) = 0.1312$
$S = 1.011$
1826 reflections
186 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.0885P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = 0.054$
$\Delta\rho_{\max} = 0.927$ e Å^{-3}
$\Delta\rho_{\min} = -0.616$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from Cromer & Mann (1968) for C, O, S atoms and Stewart, Davidson & Simpson (1965) for H atoms

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

$$U_{\rm eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
S1	0.09374 (12)	0.26719 (8)	0.72981 (7)	0.0244 (3)
S2	−0.10318 (13)	0.38504 (9)	0.54524 (7)	0.0386 (3)
S3	−0.11270 (11)	0.14127 (9)	0.55835 (7)	0.0315 (3)
S4	−0.02150 (12)	−0.06915 (8)	0.68906 (7)	0.0313 (3)
O1	0.5550 (3)	0.2029 (2)	1.2154 (2)	0.0269 (6)
C1	−0.0464 (5)	0.2706 (3)	0.6073 (3)	0.0289 (9)
C2	−0.0098 (4)	0.0687 (3)	0.6659 (3)	0.0270 (9)
C3	0.1075 (5)	−0.0493 (3)	0.8093 (3)	0.0264 (9)
C4	0.1575 (4)	0.0571 (3)	0.8333 (3)	0.0218 (8)
C5	0.0882 (4)	0.1252 (3)	0.7472 (3)	0.0247 (9)
C6	0.2632 (4)	0.0933 (3)	0.9331 (2)	0.0204 (8)
C7	0.2560 (4)	0.0340 (3)	1.0193 (3)	0.0224 (8)
C8	0.3515 (4)	0.0668 (3)	1.1139 (3)	0.0220 (8)
C9	0.4588 (4)	0.1619 (3)	1.1258 (2)	0.0217 (8)
C10	0.4727 (4)	0.2200 (3)	1.0409 (3)	0.0209 (8)
C11	0.3752 (4)	0.1862 (3)	0.9467 (3)	0.0210 (8)
C12	0.5406 (6)	0.1459 (4)	1.3042 (3)	0.0362 (10)

Data collection: *SADONL* (Pflugrath & Messerschmidt, 1989). Cell refinement: *SADONL*. Data reduction: *SADONL*. Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *ZORTEP* (Zsolnai & Pritzkow, 1996). Software used to prepare material for publication: *SHELXL*93.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: HA1162). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Allen, F. H., Kennard, O., Watson, D. G., Brammer, L., Orpen, A. G. & Taylor, R. (1987). *J. Chem. Soc. Perkin Trans. 2*, pp. S1–19.

Cromer, D. T. & Mann, J. B. (1968). *Acta Cryst.* A**24**, 321–324.

Danopoulos, A. A., Wilkinson, G., Hussain-Bates, B. & Hursthouse, M. B. (1991). *J. Chem. Soc. Dalton Trans.* pp. 1855–1860.

Engler, E. M., Patel, V. V., Andersen, J. N., Schumaker, R. R. & Fukushima, A. A. (1978). *J. Am. Chem. Soc.* **100**, 3769–3776.

Hiemstra, H. & Kiers, C. T. (1979). *Acta Cryst.* B**35**, 1140–1143.

Ozturk, T. (1996). *Tetrahedron Lett.* **37**, 2821–2824.

Ozturk, T., Rice, C. R. & Wallis, J. D. (1995). *J. Mater. Chem.* pp. 1553–1556.

Pflugrath, J. W. & Messerschmidt, A. (1989). *MADNES.* Version 11 September 1989. Delft Instruments, Delft, The Netherlands.

Rosenfield, R. E., Parthasarathy, R. & Dunitz, J. D. (1977). *J. Am. Chem. Soc.* **99**, 4860–4862.

Santalo, H., Veciana, J., Rovira, C., Molins, E., Miravitlles, C. & Claret, J. (1991). *Synth. Met.* **42**, 2205–2209.

Sheldrick, G. M. (1985). *SHELXS86. Program for the Solution of Crystal Structures.* University of Göttingen, Germany.

Sheldrick, G. M. (1993). *SHELXL93. Program for Crystal Structure Refinement.* University of Göttingen, Germany.

Stewart, R. F., Davidson, E. R. & Simpson, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.

Walker, N. & Stuart, D. (1983). *Acta Cryst.* A**39**, 158–166.

Williams, J. M., Beno, M. A., Wang, H. H., Leung, P. C. W., Emge, T. J., Geiser, U. & Carlson, K. D. (1985). *Acc. Chem. Res.* **18**, 261–267.

Zsolnai, L. & Pritzkow, H. (1996). *ZORTEP. An Interactive ORTEP Program.* University of Heidelberg, Germany.

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L-Histidyl-L-alanine Dihydrate

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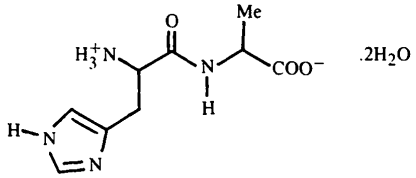
Abstract

The title dipeptide, $C_9H_{14}N_4O_3.2H_2O$, crystallizes as a zwitterion. The side chain of the histidine residue is uncharged. The peptide C═O group does not accept any conventional hydrogen bonds, only C—H···O interactions.

Comment

The crystal structure of the dipeptide L-His-L-Ala, (I), was determined in order to study the possible occurrence of weak hydrogen-bonding effects.



(I)

As expected, dipeptide (I) crystallized from aqueous solution as a zwitterion with the imidazole moiety of the histidine residue uncharged (Fig. 1). Two water molecules are co-crystallized per dipeptide. The conformation of the peptide backbone is conventional. The histidine conformation is characterized by the torsion angles C2—C1—C5—C6 −177.3 (2) and C1—C5—C6—C7 98.9 (3)°, *i.e.* the Cβ—Cγ bond (C5—C6) is oriented *trans* with respect to the Cα—CO bond (C1—C2) and the imidazole plane is roughly perpendicular to Cα—Cβ—Cγ (C1—C5—C6); this is one of the most frequently observed histidine conformations (Steiner, 1996*a*). Bond lengths and angles have normal values.

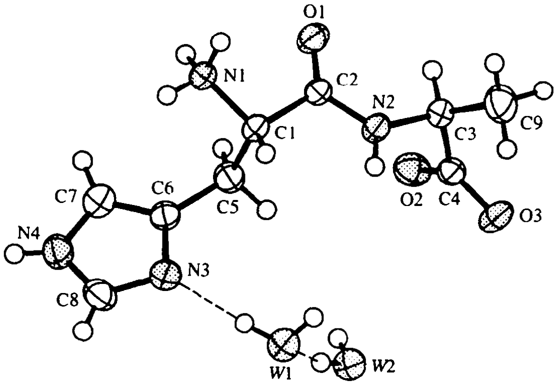


Fig. 1. The molecular structure and atom labelling of the title compound. Displacement ellipsoids are drawn at the 50% probability level. O and N atoms are shaded, and *W*1 and *W*2 represent O*W*1 and O*W*2, respectively.

The system of conventional N—H···O, O—H···O and O—H···N hydrogen bonds is shown in Fig. 2; for numerical data, see Table 3. The NH_3^+ and COO^- groups of neighbouring peptide molecules are connected by an infinite chain of hydrogen bonds joining the N1 atom to O3 atoms above and below in the *a*-axis direction. The co-crystallized water molecules form an infinite chain in the *a*-axis direction; ···H—O*W*2—H···O*W*1···H—O*W*2′—H···O*W*1′.

The hydrogen-bond coordination of the peptide C═O group, which is known to be a strong acceptor group (Jeffrey & Saenger, 1991), is of interest. The shortest