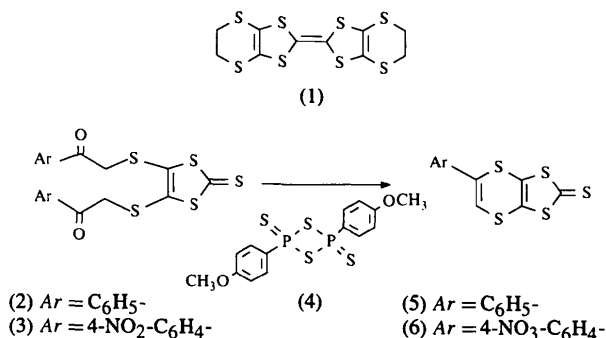


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6-(4-Methoxyphenyl)thieno[2,3-*d*][1,3]-dithiole-2-thione at 150 K

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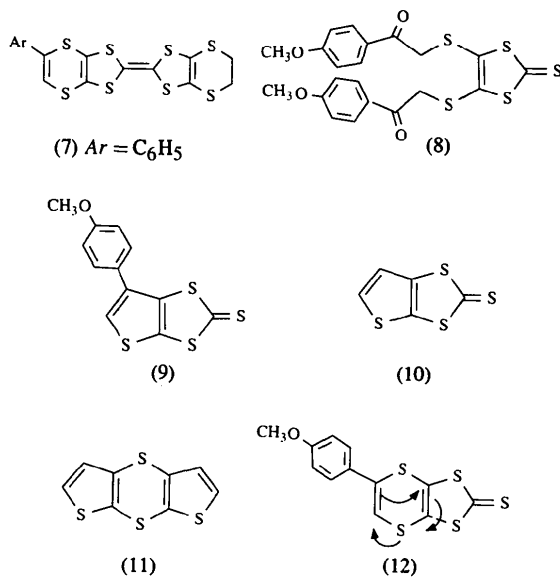
(Received 25 March 1996; accepted 23 April 1996)

Abstract

The structure determination at 150 K of 6-(4-methoxyphenyl)thieno[2,3-*d*][1,3]dithiole-2-thione, C₁₂H₈OS₄, 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.



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

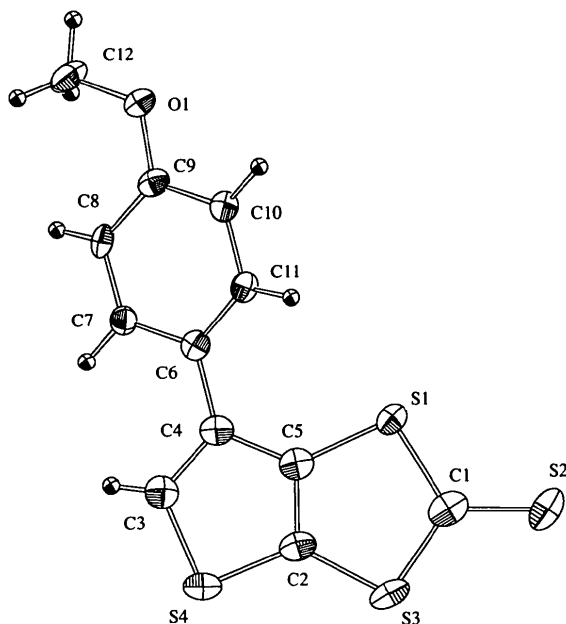


Fig. 1. Molecular structure of (9) (Zsolnai & Pritzkow, 1996) with displacement ellipsoids at the 50% probability level.

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%), ^1H NMR (CDCl_3) 7.54 (s, 5-H), 7.43 (d, J = 8.8 Hz, Ar-H₂), 6.98 (d, J = 8.8 Hz, Ar-H₂), 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%; $\text{C}_{12}\text{H}_8\text{OS}_4$ requires C 48.6, H 2.7%.

Crystal data

$\text{C}_{12}\text{H}_8\text{OS}_4$
 M_r = 296.42

Mo $K\alpha$ radiation
 λ = 0.71069 Å

Monoclinic

$P2_1/a$
 a = 7.495 (1) Å
 b = 12.180 (1) Å
 c = 13.750 (1) Å
 β = 104.38 (1)°
 V = 1215.9 (2) Å³
 Z = 4
 D_x = 1.619 Mg m⁻³
 D_m not measured

Cell parameters from 250 reflections

θ = 2.3–25.0°
 μ = 0.758 mm⁻¹
 T = 150 (2) K
Plate
0.42 × 0.27 × 0.10 mm
Yellow

Data collection

Enraf–Nonius FAST system 4990 measured reflections
diffractometer 1826 independent reflections
Method: see Danopoulos, 1522 observed reflections
Wilkinson, Hussain-Bates [I > 2σ(I)]
& Hursthouse (1991) R_{int} = 0.0754
Absorption correction: θ_{max} = 25.03°
refined from ΔF h = -6 → 8
(DIFABS; Walker & k = -13 → 13
Stuart, 1983) l = -16 → 15
 T_{min} = 0.80, T_{max} = 1.00

Refinement

Refinement on F^2 (Δ/σ)_{max} = 0.054
 $R[F^2 > 2\sigma(F^2)]$ = 0.0551 $\Delta\rho_{\text{max}}$ = 0.927 e Å⁻³
 $wR(F^2)$ = 0.1312 $\Delta\rho_{\text{min}}$ = -0.616 e Å⁻³
 S = 1.011 Extinction correction: none
1826 reflections Atomic scattering factors
186 parameters from Cromer & Mann
All H-atom parameters (1968) for C, O, S atoms
refined and Stewart, Davidson
 $w = 1/[\sigma^2(F_o^2) + (0.0885P)^2]$ & Simpson (1965) for H
where $P = (F_o^2 + 2F_c^2)/3$ atoms

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²)

$$U_{\text{eq}} = (1/3)\sum_i\sum_j U_{ij}a_i^*a_j^*a_i.a_j.$$

	<i>x</i>	<i>y</i>	<i>z</i>	U_{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: *SHELXS86* (Sheldrick, 1985).
Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993).
Molecular graphics: *ZORTEP* (Zsolnai & Pritzkow, 1996).
Software used to prepare material for publication: *SHELXL93*.

We thank the EPSRC X-ray Crystallography Service (Professor M. B. Hursthouse and Mr D. Hibbs) for a dataset, and the University of Kent for financial support.

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.

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L-Histidyl-L-alanine Dihydrate

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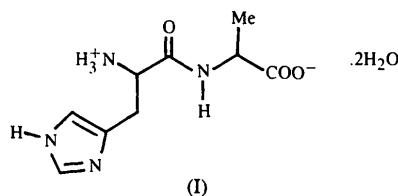
(Received 18 April 1996; accepted 22 May 1996)

Abstract

The title dipeptide, C₉H₁₄N₄O₃·2H₂O, 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.



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 $98.9(3)^\circ$, i.e. the C β —C γ bond (C5—C6) is oriented *trans* with respect to the C α —CO bond (C1—C2) and the imidazole plane is roughly perpendicular to C α —C β —C γ (C1—C5—C6); this is one of the most frequently observed histidine conformations (Steiner, 1996a). Bond lengths and angles have normal values.

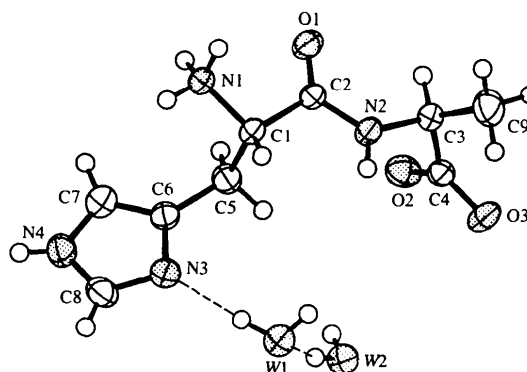


Fig. 1. The molecular structure and atom labelling of the title compound. Displacement ellipsoids are drawn at the 50% probability level. O and N atoms are shaded, and W1 and W2 represent OW1 and OW2, respectively.

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 NH₃⁺ 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—OW2—H···OW1···H—OW2'—H···OW1'.

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