

Intramolecular and intermolecular geometry of thiophenes with oxygen-containing substituents

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Abstract

The intramolecular and intermolecular geometries of six thiophenes carrying oxygen-containing substituents have been determined. Crystals of 2-methoxythiophene and 3-methoxythiophene were grown *in situ* on a diffractometer from liquid samples. The 2-methoxy group introduces significant distortions to the thiophene nucleus and each molecule participates in four S···O contacts leading to an infinite bilayer. The extended structure of 3-methoxythiophene comprises zigzag chains of molecules linked by S···O contacts. Molecules of 2-acetyl-3-methoxythiophene are arranged in pairs about inversion centres, with ring centroids 3.835 Å apart. 5-Cyano-3-hydroxythiophene adopts the hydroxythiophene tautomeric form which allows conjugation between the S atom and the nitrile group: O—H···N hydrogen bonding leads to chains which are cross-linked by S···O contacts to give infinite two-dimensional layers. 5-(Methylthio)thiophen-3(2*H*)-one exists exclusively as the thiophen-3(2*H*)-one form in the solid state, allowing maximum conjugative interaction of both the ring heteroatom and the substituent with the carbonyl group: each molecule is linked to two of its neighbours through pairwise C—H···O interactions, forming ribbons. Spiro[cyclohexane-1,2'-2',3'-dihydrothiophen]-3'-one crystallizes with four independent molecules in the asymmetric unit with only minor differences between these: the five- and six-membered rings in each molecule are approximately orthogonal and C—H···O hydrogen bonding generates chains. The last two structures differ from the others in that they lack a fully aromatic thiophene system.

1. Introduction

There is considerable current interest in the properties of electron-rich thiophenes with oxygen-containing substituents, for example as structural elements of photographic colour couplers (Clark *et al.*, 1995) or as oligomers in electro-optical and electronic devices (Miller & Yu, 1995, and references therein). However, very little basic structural information is known for

compounds of this type. In this paper we aim to rectify these deficiencies with a comprehensive crystallographic study of a range of six oxygenated thiophenes (1)–(6). The structural types we have studied include the parent 2-methoxythiophene (1) and the 3-methoxythiophenes (2) and (3); both (1) and (2) are liquids at room temperature. 3-Hydroxythiophenes can exist in solution as mixtures of keto [thiophen-3(2*H*)-one] and enol (3-hydroxythiophene) tautomers (Hunter & McNab, 1995). In the solid state the 5-cyano derivative (4) is entirely in the enol form, whereas the 5-methylthio compound (5) is entirely in the keto form; the spiro-derivative (6) provides a model thiophen-3(2*H*)-one lacking polar substituents. As far as possible we have obtained data for derivatives with the minimum number of other substituents so that our results can fulfil the role of reference compounds in their class. The available structural data for the thiophene system in general has been reviewed by Gronowitz & Hörnfeldt (1991).

2. Experimental

2.1. Synthesis

Compounds (1) and (2) are commercially available. 2-Acetyl-3-methoxythiophene (3) was made by Friedel–Crafts acylation of 3-methoxythiophene (Sommerville, 1995) and was recrystallized from *n*-hexane. The 5-cyano compound (4) was obtained by flash vacuum pyrolysis (FVP) of 5-(1-cyano-1-methylthio)methylene-2,2-dimethyl-1,3-dioxane-4,6-dione (Morrow, 1994) and recrystallized from acetone. The thiophenones (5) and (6) were also made by FVP of appropriate Meldrum's acid derivatives (Hunter & McNab, 1995) and their crystals were obtained from *n*-hexane/ethyl acetate and *n*-hexane, respectively.

2.2. Crystal preparation

2-Methoxythiophene (1) was purchased from Aldrich Chemical Co. Ltd, purified by Kugelrohr distillation and the clear liquid distillate placed in a thin-walled Pyrex capillary tube of outer diameter < 0.5 mm which was

then flame-sealed. This tube was fixed into a thermally insulating Tufnol pip which was then mounted in an arcless Stoë goniometer head. The goniometer head was transferred to a Stoë Stadi-4 four-circle diffractometer equipped with an Oxford Cryosystems Cryostream open-flow nitrogen cryostat (Cosier & Glazer, 1986). The sample exhibited marked supercooling, only solidifying when cooled to below 200 K and being subjected to rapid thermal cycling. The melting range was then established as 210–215 K. The compound did not crystallize readily and a range of techniques were investigated. Melting almost all the solid material present followed by cooling at a rate of 60 K h⁻¹ afforded an apparently homogeneous region but, under polarized light, this was shown to consist of several crystals. Moreover, several of the attempts visibly resulted in competition between overlapping growth fronts. Adjusting the position of the Cryostream nozzle did not succeed in producing a unique growth front. Finally, a cooling regime consisting of somewhat more rapid cooling (120 K h⁻¹) from 214.5 to 210 K produced an apparently uniform region under polarized light: this region was remelted and recooled to produce a single stable growth front which could be manipulated to produce a single crystal. Following the successful indexing of a list of reflections found from a combination of photographic and random search procedures, a preliminary dataset was collected at 207 K and a fuller dataset at 100 K. The collection of the first set is a precaution against loss of the crystal through phase changes or other phenomena encountered upon cooling.

3-Methoxythiophene (2) was purchased from Aldrich Chemical Co. Ltd and purified and encapsulated as for (1). Although the presence of supercooling in the sample required cooling to 187 K before solidification occurred, crystal growth proved more facile than for (1). The solid sample appeared to melt in the range 260–267 K and melting almost the entire sample followed by cooling to 260 K at 15 K h⁻¹ gave a controllable solid-liquid interface. Unfortunately the resulting crystal was not single in polarized light, so the sample temperature was raised to 264 K and cooled at a considerably higher

rate of 120 K h⁻¹, whereupon a single crystal was obtained. After indexing as for (1) a preliminary dataset was collected at 256 K and a fuller dataset at 100 K, for reasons described above.

Prior to data collection, crystals of (3) and (4) were mounted on glass fibres and those of (5) and (6) in Lindemann glass capillary tubes.

2.3. Data collection and processing

Crystal data and the details of the structure determinations are given in Table 7.† All datasets were collected on a Stoë Stadi-4 four-circle diffractometer, employing an Oxford Cryosystems open-flow cryostat (Cosier & Glazer, 1986) for all except (3). Lattice parameters were obtained from 2θ values derived from measurements at ±ω in order to minimize errors arising from crystal mis-centring: this was particularly important for (1) and (2) where the crystals were not visible within the capillary tube in which they had been grown. Significant decay in the intensity standards was observed for (2) and (3) and linear isotropic corrections were found to be satisfactory. Corrections for absorption were applied only to (2), being found unnecessary for the other compounds.

2.4. Structure solution and refinement

All the structures were solved using direct methods (Sheldrick, 1990), which gave the positions of all non-H atoms, and refined on F^2 using *SHELXL97* (Sheldrick, 1997). In compounds (1)–(4) all H atoms were refined freely with isotropic displacement parameters. In (5) and (6) they were introduced at geometrically calculated positions and thereafter allowed to ride on their parent C atoms with $U_{\text{iso}}(\text{H}) = xU_{\text{eq}}(\text{C})$, where $x = 1.5$ for the methyl H atoms in (5) and 1.2 for all others. Figures were produced using *SHELXTL* (Sheldrick, 1994).

3. Results and discussion

3.1. 2-Methoxythiophene (1)

The structure of 2-methoxythiophene (1) has been previously reported as a solvate of a rhodium complex (Jones & Chin, 1992), but otherwise the only reported structure of this type is of a highly substituted derivative and the data are of poor quality (Heine *et al.*, 1987). Our data show that (1) is close to being planar (Fig. 1, Table 1), with an r.m.s. deviation of only 0.0013 Å for the five-ring atoms, and that the methyl group of the methoxy substituent lies *Z* to the 2,3-bond, with O2 and C2M lying 0.016(2) Å above and 0.043(2) Å below the ring plane, respectively. The *Z* conformation has the effect of increasing the size of the angle C3–C2–O2 [to

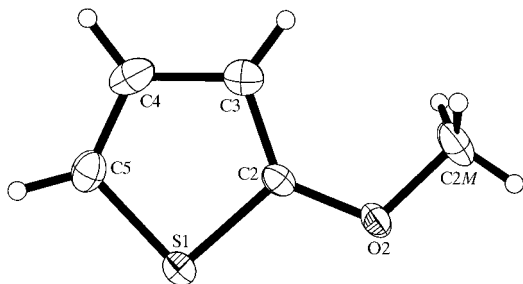


Fig. 1. A view perpendicular to the least-squares mean plane through (1). Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown with an arbitrary radius.

† Supplementary data for this paper are available from the IUCr electronic archives (Reference: HA0185). Services for accessing these data are described at the back of the journal.

Table 1. *Experimental details*

For all compounds, the atomic scattering factors were taken from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4). Computer programs: data collection and cell refinement: *DIF4* [Stoe & Cie, 1992a, for (1)–(4); Stoe & Cie, 1988a, for (5) and (6)]; data reduction: *REDU4* [Stoe & Cie, 1992b, for (1)–(4); Stoe & Cie, 1988b, for (5) and (6)]; structure solution: *SHELXS86–97* (Sheldrick, 1990); structure refinement: *SHELXL97* (Sheldrick, 1997) for (1)–(3). Software used to prepare material for publication: *SHELXL97* (Sheldrick, 1997).

	(1)	(2)	(3)	(4)	(5)	(6)
Crystal data						
Chemical formula	C ₅ H ₆ OS	C ₅ H ₆ OS	C ₇ H ₈ O ₂ S	C ₅ H ₃ NOS	C ₅ H ₆ OS ₂	C ₉ H ₁₂ OS
Chemical formula weight	114.16	114.16	156.19	125.14	146.22	168.25
Cell setting	Monoclinic	Orthorhombic	Triclinic	Monoclinic	Orthorhombic	Monoclinic
Space group	<i>P</i> 2 ₁ / <i>a</i>	<i>P</i> 2 ₁ 2 ₁ 2 ₁	<i>P</i> 1	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> n2 ₁ / <i>a</i>	<i>P</i> 2 ₁ / <i>c</i>
<i>a</i> (Å)	6.848 (3)	6.641 (4)	7.5941 (9)	7.516 (2)	19.513 (6)	10.826 (2)
<i>b</i> (Å)	7.540 (4)	7.109 (4)	7.8219 (10)	8.332 (2)	8.083 (2)	17.065 (2)
<i>c</i> (Å)	11.111 (5)	11.594 (5)	7.9811 (9)	9.059 (2)	4.046 (2)	19.190 (3)
α (°)	90	90	63.112 (5)	90	90	90
β (°)	106.010 (5)	90	64.660 (5)	100.19 (3)	90	91.011 (12)
γ (°)	90	90	89.636 (5)	90	90	90
<i>V</i> (Å ³)	551.5 (5)	547.4 (5)	371.70 (8)	558.3 (2)	638.2 (4)	3544.7 (10)
<i>Z</i>	4	4	2	4	4	16
<i>D</i> _x (Mg m ⁻³)	1.375	1.385	1.396	1.489	1.52	1.261
Radiation type	Mo <i>K</i> α	Mo <i>K</i> α	Mo <i>K</i> α	Mo <i>K</i> α	Mo <i>K</i> α	Mo <i>K</i> α
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073
No. of reflections for cell parameters	36	15	52	33	50	45
θ range (°)	15–19	14–16	11–13	14–16	12.5–16.0	12.5–15.0
μ (mm ⁻¹)	0.454	0.457	0.367	0.461	0.726	0.305
Temperature (K)	100 (2)	100 (2)	293 (2)	293 (2)	223.0 (2)	223.0 (2)
Crystal form	Cylinder	Cylinder	Block	Tapered column	Lath	Block
Crystal size (mm)	0.50 × 0.32 × 0.32	0.8 × 0.5 × 0.5	0.50 × 0.50 × 0.50	0.86 × 0.47 × 0.35	1.30 × 0.40 × 0.20	0.54 × 0.54 × 0.46
Crystal colour	Colourless	Colourless	Colourless	Brown	Colourless	Pale yellow/green
Data collection						
Diffraction method	Stoe Stadi-4 four-circle	Stoe Stadi-4 four-circle	Stoe Stadi-4 four-circle	Stoe Stadi-4 four-circle	Stoe Stadi-4 four-circle	Stoe Stadi-4 four-circle
Data collection method	$\omega/2\theta$ scans	$\omega/2\theta$ scans	$\omega/2\theta$ scans	$\omega/2\theta$ scans	$\omega/2\theta$ scans	$\omega/2\theta$ scans
Absorption correction	None	ψ scans	None	None	None	None
<i>T</i> _{min}	—	0.624	—	—	—	—
<i>T</i> _{max}	—	0.693	—	—	—	—
No. of measured reflections	1972	1714	1276	1742	825	4638
No. of independent reflections	1609	1560	1253	984	463	4638
No. of observed reflections	1414	1377	1035	910	448	2978
Criterion for observed reflections	<i>I</i> > 2 σ (<i>I</i>)	<i>I</i> > 2 σ (<i>I</i>)	<i>I</i> > 2 σ (<i>I</i>)	<i>I</i> > 2 σ (<i>I</i>)	<i>I</i> > 2(<i>I</i>)	<i>I</i> > 2 σ (<i>I</i>)
<i>R</i> _{int}	0.0648	0.0893	0.0374	0.0198	0.0487	0.0000
θ _{max} (°)	30.05	30.03	24.79	25.00	22.63	22.50
Range of <i>h</i> , <i>k</i> , <i>l</i>	−9 → <i>h</i> → 9 −9 → <i>k</i> → 10 0 → <i>l</i> → 15	−9 → <i>h</i> → 9 0 → <i>k</i> → 9 0 → <i>l</i> → 16	−8 → <i>h</i> → 8 −7 → <i>k</i> → 9 0 → <i>l</i> → 9	−8 → <i>h</i> → 8 −9 → <i>k</i> → 9 0 → <i>l</i> → 10	−3 → <i>h</i> → 21 −8 → <i>k</i> → 0 −4 → <i>l</i> → 4	−11 → <i>h</i> → 11 0 → <i>k</i> → 18 0 → <i>l</i> → 20
No. of standard reflections	3	3	3	3	3	3
Frequency of standard reflections	Every 60 min	Every 60 min	Every 60 min	Every 60 min	Every 60 min	Every 60 min
Intensity decay (%)	0	0	0	0	0	3

Table 1 (cont.)

	(1)	(2)	(3)	(4)	(5)	(6)
Refinement						
Refinement on $R[F^2 > 2\sigma(F^2)]$	F^2 0.0433	F^2 0.0487	F^2 0.0321	F^2 0.0243	F^2 0.0424	F^2 0.0374
$wR(F^2)$	0.1230	0.1425	0.0878	0.0651	0.0901	0.0935
S	1.15	1.07	1.06	1.09	1.21	1.14
No. of reflections used in refinement	1609	1560	1253	981	463	4638
No. of parameters used	88	89	124	86	73	398
H-atom treatment	All H-atom parameters refined	All H-atom parameters refined	All H-atom parameters refined	All H-atom parameters refined	Riding model	Riding model
Weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.066P)^2 + 0.264P]$ where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.089P)^2 + 0.490P]$ where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.054P)^2 + 0.050P]$ where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.040P)^2 + 0.148P]$ where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.068P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.054P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max}$	0.004	0.001	0.001	-0.013	0.001	0.003
$\Delta\rho_{\max}$ ($e \text{ \AA}^{-3}$)	0.57	0.34	0.25	0.19	0.46	0.26
$\Delta\rho_{\min}$ ($e \text{ \AA}^{-3}$)	-0.44	-0.46	-0.17	-0.26	-0.33	-0.22
Extinction method	None	<i>SHELXL</i>	<i>SHELXL</i>	<i>SHELXL</i>	None	<i>SHELXL</i>
Extinction coefficient	-	0.004 (11)	0.026 (15)	0.002 (4)	-	0.00018 (14)

130.79 (16)°, as has been noted for aromatic methoxy derivatives (Krygowski *et al.*, 1994). The 2-methoxy group induces significant distortion of the thiophene nucleus by increasing the length of the 2,3-bond [to 1.398 (2) Å] and reducing that of the 4,5-bond [to

1.353 (3) Å]. These trends are also apparent when the 2-methoxythiophene is present in a solvate (Jones & Chin, 1992), although the present data are of better quality.

Molecules of (1) are linked by intermolecular S...O contacts $S1 \cdots O2^i$ 3.386 (2) and $S1 \cdots O2^{iii}$ 3.402 (2) Å [symmetry codes: (i) $-x, 1 - y, -z$; (iii) $\frac{1}{2} + x, \frac{1}{2} - y, z$] such that each molecule participates in a total of four such contacts (shown as dashed lines in Fig. 2), two with a molecule related by inversion and one to each of two molecules related by glide plane operations. The angles subtended at S1 and O2 by their pairs of intermolecular O...S...O and S...O...S contacts are 80.47 (3) and 128.22 (4)°, respectively, and their environment can be described as distorted tetrahedral. This pattern of contacts results in a bilayer of 2-methoxythiophene molecules infinite within the *ab* plane: the S and O atoms from each individual layer face each other across the central plane of the bilayer, while its upper and lower surfaces are exclusively hydrocarbon.

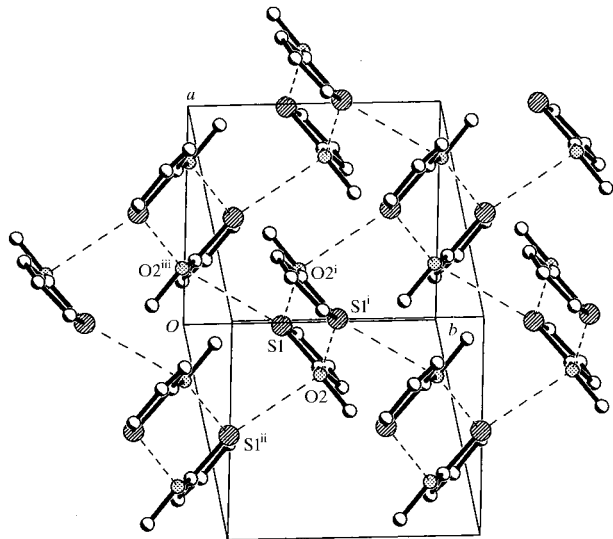


Fig. 2. A packing diagram for (1) showing intermolecular S...O contacts $S1 \cdots O2^i$ 3.386 (2) and $S1 \cdots O2^{iii}$ 3.402 (2) Å as dashed lines. Each molecule participates in a total of four such contacts, leading to a bilayer of 2-methoxythiophene molecules infinite within the *ab* plane. Symmetry codes: (i) $-x, 1 - y, -z$; (ii) $x - \frac{1}{2}, \frac{1}{2} - y, z$; (iii) $\frac{1}{2} + x, \frac{1}{2} - y, z$.

3.2. 3-Methoxythiophenes (2) and (3)

Although a number of structures have been reported containing the 3-alkoxythiophene unit, all are contained within polythiophene frameworks (*e.g.* Marsella *et al.*, 1995; Miller & Yu, 1995; Paulus *et al.*, 1988, 1989). We find that the ring systems of both (2) and (3) are planar, having r.m.s. deviations for the ring atoms of only 0.002 and 0.003 Å, respectively: as in (1), the atoms of the methoxy substituent in (2) (Fig. 3, Table 2) are displaced

Table 2. Selected geometric parameters (\AA , $^\circ$) for (1)

S1—C5	1.715 (2)	C3—C4	1.440 (3)
S1—C2	1.7232 (17)	C4—C5	1.353 (3)
C2—O2	1.350 (2)	O2—C2M	1.433 (2)
C2—C3	1.398 (2)		
C5—S1—C2	91.35 (9)	C2—C3—C4	109.11 (16)
O2—C2—C3	130.79 (16)	C5—C4—C3	114.43 (17)
O2—C2—S1	116.20 (12)	C4—C5—S1	112.10 (15)
C3—C2—S1	113.01 (13)	C2—O2—C2M	114.42 (15)

Table 3. Selected geometric parameters (\AA , $^\circ$) for (2)

S1—C5	1.706 (3)	C3—C4	1.424 (4)
S1—C2	1.710 (3)	C4—C5	1.380 (4)
C2—C3	1.372 (4)	O3—C3M	1.425 (4)
C3—O3	1.361 (3)		
C5—S1—C2	92.76 (16)	C2—C3—C4	113.0 (2)
C3—C2—S1	111.0 (2)	C5—C4—C3	111.9 (2)
O3—C3—C2	127.2 (3)	C4—C5—S1	111.4 (2)
O3—C3—C4	119.8 (2)	C3—O3—C3M	114.8 (2)

from the ring plane in opposite directions, by 0.010 (4) \AA for O3 and by 0.050 (6) \AA for C3M. The pattern of deviations [0.007 (3), 0.170 (4) \AA in the same direction] is different for the 2-acetyl product (3) where non-bonded interactions between the two substituents are possible (Fig. 4, Table 3). The methoxy substituent is *Z* to the 2,3-bond in (2) and *Z* to the 3,4-bond in (3); comparison with the literature data suggests that the former conformation is preferred in the absence of a 2-substituent as in (7), but not in (8) where a 2-substi-

tuent is present (Paulus *et al.*, 1988, 1989). The largest exocyclic ring angle at the methoxy group of (2) and (3) is again *Z* to the methyl group of the substituent, but the effect is not as great as for a 2-methoxy substituent. Similarly, the distortions of the thiophene geometry caused by a 3-methoxy group are minimal and much less than those caused by a 2-methoxy group; within experimental error the rings of (2) and (7) have C_{2v} symmetry. The presence of a 2-substituent capable of conjugative interaction with the thiophene system in (3) and (8) has the effect of significantly lengthening the S1—C2 bond and shortening the S1—C5 bond consis-

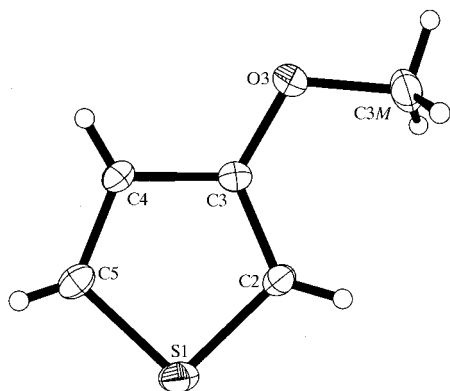


Fig. 3. A view perpendicular to the least-squares mean plane through (2). Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown with an arbitrary radius.

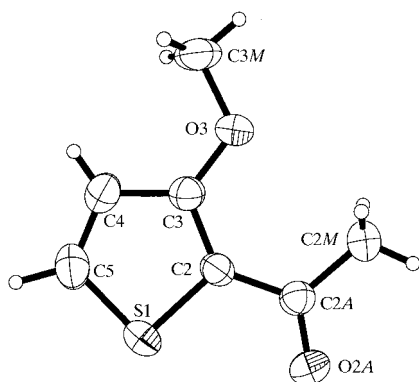


Fig. 4. A view perpendicular to the least-squares mean plane through (3). Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown with an arbitrary radius.

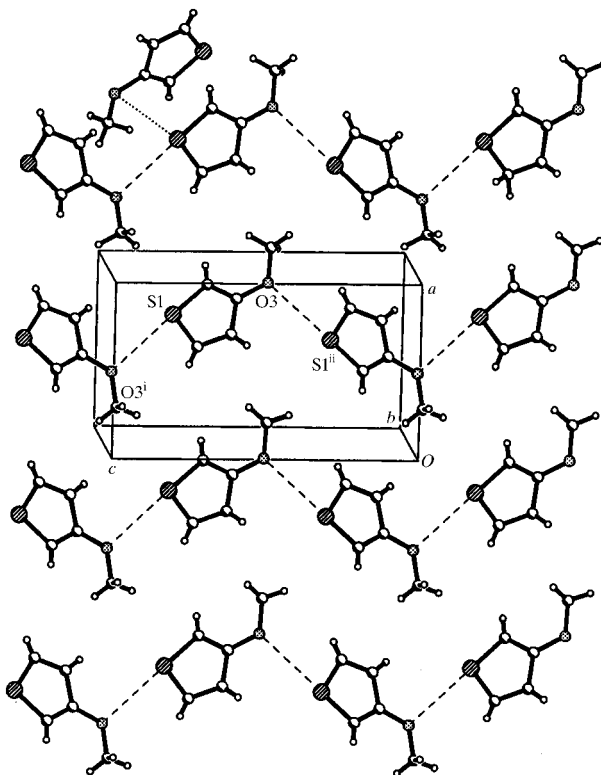


Fig. 5. The extended structure of (2) showing zigzag chains of molecules linked by S...O contacts of 3.200 (3) \AA (dashed lines). S...O contacts of 3.526 (3) \AA between molecules in neighbouring levels, one of which is shown as a dotted line at the upper left, are considerably weaker. Symmetry codes: (i) $\frac{1}{2} - x, -y, \frac{1}{2} + z$; (ii) $\frac{1}{2} - x, -y, -\frac{1}{2} + z$.

tent with the resonance form (3a) [e.g. (3), S1—C2 1.7327 (17), S1—C5 1.699 (2) Å]. In addition, the methoxy group of (3) is able to interact with the 2-acetyl group [as shown in resonance form (3b)] leading to an increase in the length of the C2—C3 bond compared with the 2-unsubstituted analogue (2) [C2—C3: (2) 1.372 (4) Å, (3) 1.392 (3) Å] and a corresponding decrease in the length of the C3—O3 bond [(2) 1.361 (3) Å; (3) 1.347 (2) Å].

The structure of (3) is also of interest since data for the corresponding 3-hydroxythiophene (9) have been published (Danielsen, 1969), and so the effect of a methoxy group *vis-à-vis* a hydroxy group can be ascertained. In fact, the only significant differences occur in the region of the methoxy (hydroxy) group; the C3—O3 bond is marginally longer in (3) [1.347 (2) Å] than in (9) [1.317 (8) Å] and the hydroxy substituent does not cause the distortion of exocyclic angles observed in the methoxy series.

The relocation of the methoxy substituent from the 2-position in (1) to the 3-position in (2) has a marked effect on the geometry of the interactions between molecules: in (2) the main contacts are still of the S···O type, but their geometry is remarkably different, resulting in a motif which consists primarily of zigzag chains of molecules linked by S···O contacts of

Table 4. Selected geometric parameters (Å, °) for (3)

S1—C5	1.699 (2)	C2A—C2M	1.492 (3)
S1—C2	1.7237 (17)	C3—O3	1.347 (2)
C2—C3	1.392 (3)	C3—C4	1.419 (3)
C2—C2A	1.454 (3)	O3—C3M	1.428 (2)
C2A—O2A	1.222 (2)	C4—C5	1.347 (3)
C5—S1—C2	91.63 (10)	O3—C3—C2	121.19 (17)
C3—C2—C2A	131.62 (17)	O3—C3—C4	126.43 (17)
C3—C2—S1	110.52 (14)	C2—C3—C4	112.39 (17)
C2A—C2—S1	117.86 (14)	C3—O3—C3M	117.10 (17)
O2A—C2A—C2	120.20 (17)	C5—C4—C3	112.05 (19)
O2A—C2A—C2M	120.89 (18)	C4—C5—S1	113.42 (17)
C2—C2A—C2M	118.91 (17)		

3.200 (3) Å, shown as dashed lines in Fig. 5. Successive molecules in each chain are related by the operation of the 2_1 screw axis parallel to the *c* axis. The three angles subtended at O3 {C3—O3—C3M 114.8 (2), C3—O3—S1ⁱⁱ 110.14 (17), C3M—O3—S1ⁱⁱⁱ 125.07 (18)} [symmetry code: (ii) $\frac{1}{2} - x, -y, -\frac{1}{2} + z$] sum to 350.0 (3)°, indicating that the environment at O3 deviates significantly from planarity. S···O contacts between molecules in neighbouring levels related by the 2_1 screw axis parallel to *b*, one of which is shown as a dotted line at the upper left of Fig. 5, are considerably weaker [3.526 (3) Å].

There are no short S···O contacts in the crystal lattice of (3), an observation which can be attributed to the presence of the acetyl group in the 2-position: its methyl group effectively blocks the approach of any S atom. Molecules of (3) occur in pairs about inversion centres: in Fig. 6 one member of each pair is shown with solid bonds, the other with hollow bonds. The molecules are parallel to each other, the ring centroids lie 3.835 Å apart and the perpendicular separation of the ring planes is 3.535 Å. One H atom from the methyl group of the acetyl function lies 2.86 Å from the centroid of the opposite ring's π -system and the C—H···centroid angle is 136°.

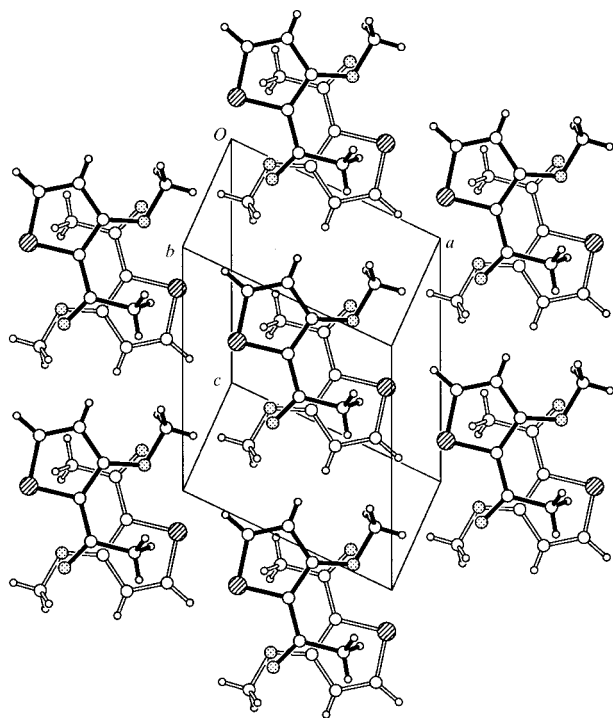


Fig. 6. A packing diagram showing molecules of (3) arranged in pairs about inversion centres: one member of each pair has solid bonds, the other hollow bonds. The molecules are parallel to each other, with ring centroids 3.835 Å apart; the perpendicular separation of the ring planes is 3.535 Å.

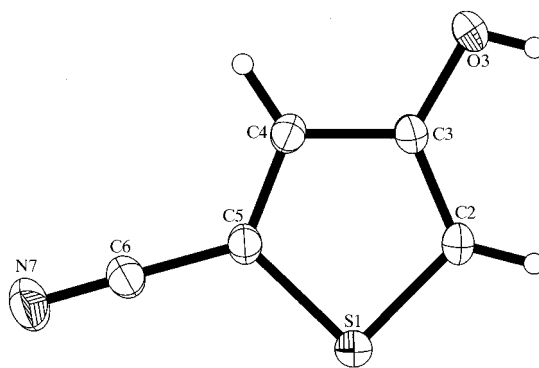


Fig. 7. A view perpendicular to the least-squares mean plane through (4). Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown with an arbitrary radius.

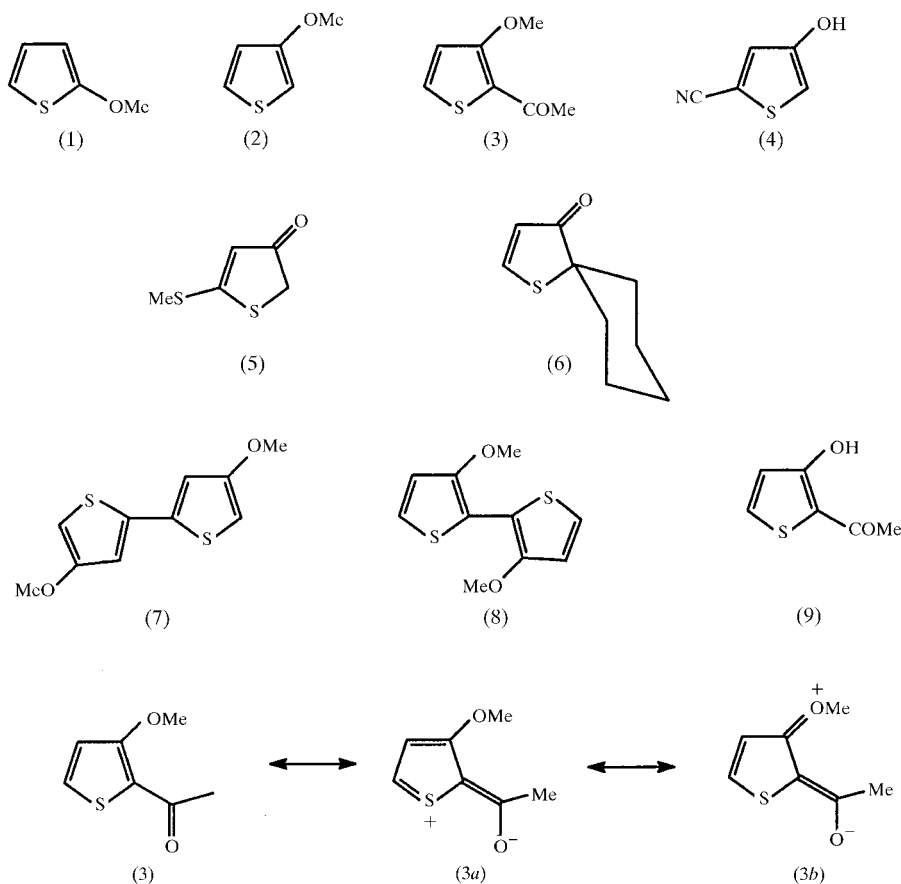
3.3. 5-Cyano-3-hydroxythiophene (4)

Compound (9) is the only 3-hydroxythiophene structure to have been previously reported (Danielsen, 1969). The 5-cyano compound (4) (Fig. 7, Table 4) presumably adopts this tautomeric form [rather than the corresponding thiophen-3(2*H*)-one (4*k*)] to allow conjugation from the S atom to the nitrile group [*cf.* (1)] and this again results in a significant difference between the two C—S bond lengths [S1—C2 1.7062 (14), S1—C5 1.7217 (13) Å]. Otherwise, the data for (4) are very similar to those of the 3-methoxythiophene (2). In particular, the geometry around C3 (length of C—O bond and magnitudes of the exocyclic bond angles) bears more relation to (2) than to the other 3-hydroxythiophene (9) previously discussed. The molecule of (4) again possesses a largely planar heavy-atom skeleton with an r.m.s. deviation of 0.002 Å for the atoms of the ring plane: O3 lies only 0.001 (2) Å from this plane but the deviations of C6 [0.016 (3) Å] and N7 [0.16 (3) Å] are greater.

Table 5. Selected geometric parameters (Å, °) for (4)

S1—C2	1.7062 (14)	C3—C4	1.409 (2)
S1—C5	1.7217 (13)	C4—C5	1.366 (2)
C2—C3	1.368 (2)	C5—C6	1.421 (2)
C3—O3	1.359 (2)	C6—N7	1.147 (2)
C2—S1—C5	91.15 (7)	C5—C4—C3	111.47 (12)
C3—C2—S1	111.82 (10)	C4—C5—C6	127.11 (13)
O3—C3—C2	126.62 (12)	C4—C5—S1	112.37 (11)
O3—C3—C4	120.19 (12)	C6—C5—S1	120.51 (10)
C2—C3—C4	113.18 (12)	N7—C6—C5	179.5 (2)

b axis: these interactions are shown as dashed lines in Fig. 8. The N7···H3ⁱ distance is 2.05 (3) Å, the N7···H3ⁱ—O3ⁱ angle is 171 (3)° and the angle subtended at N7 is 158.5(7)° [symmetry code: (i) $x, -1 + y, z$]. The resulting one-dimensional chains are cross-linked by much weaker S···O contacts {S1···O3^{iv} 3.1957 (14) Å [symmetry code: (iv) $-\frac{1}{2} + x, \frac{5}{2} - y, -\frac{1}{2} + z$]



The principal intermolecular contact in (4) is a hydrogen bond between the N atom of the cyano substituent in one molecule and the OH group of the molecule related to it by a unit-cell translation along the

shown as dotted lines} to give the infinite two-dimensional layer shown. This layer has an r.m.s. deviation of only 0.152 Å for all atoms and 0.123 Å for the non-H atoms.

3.4. Thiophen-3(2*H*)-ones (5) and (6)

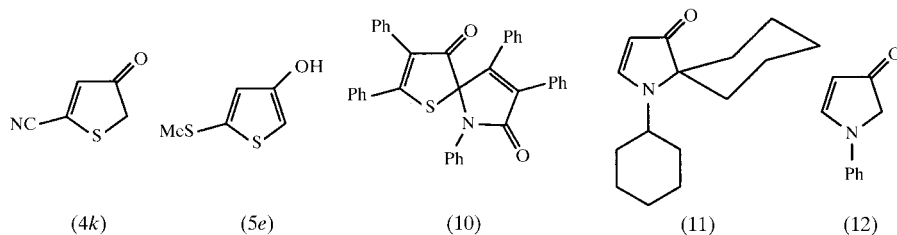
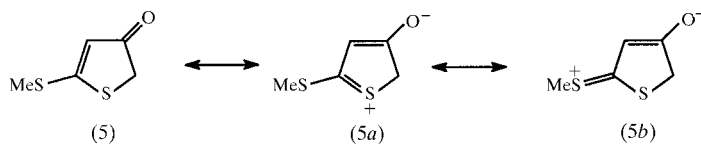
These two structures are fundamentally different from the previous four, since a fully aromatic thiophene system is not present. Instead, the systems derive stability through the 'push-pull' alkene system linking the electron-donating heteroatom with the electron-withdrawing carbonyl group. There are just two examples of such unfused thiophen-3(2*H*)-one structures in the literature (Lenz *et al.*, 1984; Yasuoka *et al.*, 1985) and both are complex polysubstituted examples [*e.g.* (10)]. We have previously reported data on the related pyrrolone structures (11) (Hickson *et al.*, 1986) and (12) (Blake *et al.*, 1988). The five-membered ring systems of both (5) (Fig. 9, Table 5) and (6) (Fig. 10, Table 6) are planar [r.m.s. deviations are 0.008 and average 0.02 Å, respectively] and the methylthio substituent of (5) shows only minor deviations from this plane [0.039 (7) Å for S5 and 0.181 (11) Å for C5A]. The *spiro* derivative (6) crystallizes with four independent molecules in the asymmetric unit (identified by suffix *A, B, C* or *D*) but there are only very minor differences between these. As can be seen from Table 6, the similarities extend even to very trivial conformational differences among the four cyclohexyl rings (the signs of the torsion angles are arbitrary and should be ignored for the purposes of comparison). The least-squares mean plane through each six-membered ring is approximately orthogonal to that through its attached five-membered ring. The 5-methylthio derivative (5) is capable of tautomerism to the 3-hydroxythiophene (5*e*), but it occurs exclusively as the thiophen-3(2*H*)-one form in the solid state. This allows maximum conjugative interaction of both the ring heteroatom and the substituent with the carbonyl group

Table 6. Selected geometric parameters (Å, °) for (5)

S1—C5	1.757 (5)	C3—C4	1.434 (6)
S1—C2	1.809 (4)	C4—C5	1.340 (6)
C2—C3	1.510 (7)	C5—S5	1.724 (5)
C3—O3	1.229 (6)	S5—C5A	1.803 (5)
C5—S1—C2	91.0 (2)	C5—C4—C3	113.5 (4)
C3—C2—S1	107.7 (3)	C4—C5—S5	130.3 (4)
O3—C3—C4	126.5 (4)	C4—C5—S1	115.6 (4)
O3—C3—C2	121.3 (4)	S5—C5—S1	114.1 (2)
C4—C3—C2	112.2 (3)	C5—S5—C5A	101.9 (2)

of (5) [C5—S5 1.724 (5) Å] is significantly shorter than the corresponding value for the endocyclic parameter [S1—C5 1.757 (5) Å], which suggests that delocalization *via* the 'W'-shaped path as in the resonance form (5*b*) is more efficient than *via* the 'sickle'-shaped path of (5*a*).

The 5-methylthio substituent of (5) adopts a configuration which is *Z* to the 4,5-bond, and the corresponding exocyclic angle (C4—C5—S5) is significantly obtuse [130.3 (4)°] owing to non-bonded interactions in a quantitatively similar fashion to that described above for a 2-methoxy group. The exocyclic angles at the carbonyl group of (5) or (6) decrease in the order C4—C3—O3 > C2—C3—O3, independent of the presence of the substituents at C2 in (6) [*e.g.* (5), C4—C3—O3 126.5 (4)°, C2—C3—O3 121.3 (4)°]. A similar trend is present in the polysubstituted derivative (10). Indeed, apart from an abnormally short C=O bond length in (10), there are few substantial differences in thiophenone geometry in (5), (6) or (10), which suggests that this structural unit is able to maintain its integrity in a wide variety of situations. Perhaps more surprisingly, all



[(II)]. In agreement with this interpretation, the bond lengths S1—C5 in (5) and (6) [mean values 1.757 (5) and 1.717 (3) Å, respectively] are both much shorter than those of S1—C2 in (5) and (6) [1.809 (4) and 1.838 (2) Å (average), respectively]. The exocyclic C—S bond length

the C—C and C—O bond lengths of the pyrrolones (11) and (12) are also closely similar to those of the thiophenones.

Unlike compounds (1), (2) and (4) the structure of (5) displays no contacts of type S...O: each molecule is

Table 7. Selected geometric parameters (\AA , $^\circ$) for (6)

S1A—C5A	1.718 (3)	S1C—C5C	1.722 (3)
S1A—C2A	1.840 (2)	S1C—C2C	1.839 (2)
C2A—C3A	1.520 (4)	C2C—C3C	1.521 (3)
C2A—C10A	1.522 (3)	C2C—C10C	1.522 (3)
C2A—C6A	1.538 (3)	C2C—C6C	1.527 (3)
C3A—O3A	1.221 (3)	C3C—O3C	1.218 (3)
C3A—C4A	1.437 (4)	C3C—C4C	1.439 (4)
C4A—C5A	1.334 (4)	C4C—C5C	1.326 (4)
C6A—C7A	1.513 (4)	C6C—C7C	1.519 (4)
C7A—C8A	1.507 (4)	C7C—C8C	1.516 (4)
C8A—C9A	1.511 (4)	C8C—C9C	1.506 (4)
C9A—C10A	1.514 (3)	C9C—C10C	1.519 (3)
S1B—C5B	1.718 (3)	S1D—C5D	1.711 (3)
S1B—C2B	1.840 (2)	S1D—C2D	1.831 (3)
C2B—C10B	1.525 (3)	C2D—C3D	1.522 (4)
C2B—C3B	1.528 (4)	C2D—C10D	1.519 (3)
C2B—C6B	1.528 (4)	C2D—C6D	1.528 (4)
C3B—O3B	1.221 (3)	C3D—O3D	1.212 (3)
C3B—C4B	1.428 (4)	C3D—C4D	1.443 (4)
C4B—C5B	1.330 (4)	C4D—C5D	1.328 (4)
C6B—C7B	1.511 (4)	C6D—C7D	1.516 (4)
C7B—C8B	1.512 (4)	C7D—C8D	1.509 (4)
C8B—C9B	1.507 (4)	C8D—C9D	1.509 (4)
C9B—C10B	1.512 (3)	C9D—C10D	1.515 (3)
C5A—S1A—C2A	91.93 (13)	C5C—S1C—C2C	92.11 (13)
C3A—C2A—C10A	110.3 (2)	C3C—C2C—C10C	111.06 (19)
C3A—C2A—C6A	110.6 (2)	C3C—C2C—C6C	109.1 (2)
C10A—C2A—C6A	110.1 (2)	C10C—C2C—C6C	110.4 (2)
C3A—C2A—S1A	105.09 (17)	C3C—C2C—S1C	105.23 (17)
C10A—C2A—S1A	111.00 (16)	C10C—C2C—S1C	111.09 (17)
C6A—C2A—S1A	109.59 (17)	C6C—C2C—S1C	109.87 (17)
O3A—C3A—C4A	125.8 (3)	O3C—C3C—C4C	126.2 (2)
O3A—C3A—C2A	121.0 (2)	O3C—C3C—C2C	121.4 (2)
C4A—C3A—C2A	113.2 (2)	C4C—C3C—C2C	112.4 (2)
C5A—C4A—C3A	112.8 (3)	C5C—C4C—C3C	113.9 (3)
C4A—C5A—S1A	116.8 (2)	C4C—C5C—S1C	116.1 (2)
C7A—C6A—C2A	112.2 (2)	C7C—C6C—C2C	112.8 (2)
C8A—C7A—C6A	112.6 (2)	C6C—C7C—C8C	111.0 (2)
C7A—C8A—C9A	111.0 (2)	C7C—C8C—C9C	111.3 (2)
C8A—C9A—C10A	111.4 (2)	C8C—C9C—C10C	111.2 (2)
C9A—C10A—C2A	113.2 (2)	C9C—C10C—C2C	112.66 (19)
C5B—S1B—C2B	91.96 (13)	C5D—S1D—C2D	92.25 (13)
C10B—C2B—C3B	110.3 (2)	C3D—C2D—C10D	110.88 (19)
C10B—C2B—C6B	110.4 (2)	C3D—C2D—C6D	109.0 (2)
C3B—C2B—C6B	111.2 (2)	C10D—C2D—C6D	110.2 (2)
C10B—C2B—S1B	110.40 (16)	C3D—C2D—S1D	105.40 (18)
C3B—C2B—S1B	104.70 (17)	C10D—C2D—S1D	111.34 (17)
C6B—C2B—S1B	109.71 (18)	C6D—C2D—S1D	109.88 (17)
O3B—C3B—C4B	126.2 (3)	O3D—C3D—C4D	125.7 (3)
O3B—C3B—C2B	120.4 (2)	O3D—C3D—C2D	122.0 (2)
C4B—C3B—C2B	113.3 (2)	C4D—C3D—C2D	112.2 (2)
C5B—C4B—C3B	113.0 (3)	C5D—C4D—C3D	113.4 (3)
C4B—C5B—S1B	116.9 (2)	C4D—C5D—S1D	116.5 (2)
C7B—C6B—C2B	112.6 (2)	C7D—C6D—C2D	112.7 (2)
C6B—C7B—C8B	112.0 (2)	C6D—C7D—C8D	111.2 (2)
C9B—C8B—C7B	110.7 (2)	C7D—C8D—C9D	110.5 (3)
C8B—C9B—C10B	111.8 (2)	C8D—C9D—C10D	111.3 (2)
C9B—C10B—C2B	112.8 (2)	C9D—C10D—C2D	112.9 (2)
C5A—S1A—C2A—C10A	122.6 (2)	C5C—S1C—C2C—C10C	-124.8 (2)
C5A—S1A—C2A—C6A	-115.5 (2)	C5C—S1C—C2C—C6C	112.8 (2)
C10A—C2A—C3A—O3A	56.9 (3)	C10C—C2C—C3C—O3C	-55.5 (3)
C6A—C2A—C3A—O3A	-65.2 (3)	C6C—C2C—C3C—O3C	66.4 (3)
C10A—C2A—C3A—C4A	-123.8 (3)	C10C—C2C—C3C—C4C	125.3 (3)
C6A—C2A—C3A—C4A	114.1 (3)	C6C—C2C—C3C—C4C	-112.9 (3)

Table 7 (cont.)

C3A—C2A—C6A—C7A	173.9 (2)	C3C—C2C—C6C—C7C	-174.9 (2)
C10A—C2A—C6A—C7A	51.8 (3)	C10C—C2C—C6C—C7C	-52.6 (3)
S1A—C2A—C6A—C7A	-70.6 (2)	S1C—C2C—C6C—C7C	70.3 (3)
C2A—C6A—C7A—C8A	-54.1 (3)	C2C—C6C—C7C—C8C	54.6 (3)
C6A—C7A—C8A—C9A	55.0 (3)	C6C—C7C—C8C—C9C	-55.9 (3)
C7A—C8A—C9A—C10A	-54.8 (3)	C7C—C8C—C9C—C10C	56.1 (3)
C8A—C9A—C10A—C2A	54.9 (3)	C8C—C9C—C10C—C2C	-55.0 (3)
C3A—C2A—C10A—C9A	-175.1 (2)	C3C—C2C—C10C—C9C	173.7 (2)
C6A—C2A—C10A—C9A	-52.7 (3)	C6C—C2C—C10C—C9C	52.6 (3)
S1A—C2A—C10A—C9A	68.9 (2)	S1C—C2C—C10C—C9C	-69.6 (2)
C5B—S1B—C2B—C10B	-121.8 (2)	C5D—S1D—C2D—C10D	123.9 (2)
C5B—S1B—C2B—C6B	116.3 (2)	C5D—S1D—C2D—C6D	-113.8 (2)
C10B—C2B—C3B—O3B	-58.6 (3)	C10D—C2D—C3D—O3D	54.3 (4)
C6B—C2B—C3B—O3B	64.3 (3)	C6D—C2D—C3D—O3D	-67.1 (3)
C10B—C2B—C3B—C4B	122.6 (3)	C10D—C2D—C3D—C4D	-124.7 (3)
C6B—C2B—C3B—C4B	-114.6 (3)	C6D—C2D—C3D—C4D	113.9 (3)
C10B—C2B—C6B—C7B	-51.9 (3)	C3D—C2D—C6D—C7D	174.0 (2)
C3B—C2B—C6B—C7B	-174.6 (2)	C10D—C2D—C6D—C7D	52.1 (3)
S1B—C2B—C6B—C7B	70.0 (3)	S1D—C2D—C6D—C7D	-70.9 (3)
C2B—C6B—C7B—C8B	54.4 (3)	C2D—C6D—C7D—C8D	-55.2 (4)
C6B—C7B—C8B—C9B	-55.5 (3)	C6D—C7D—C8D—C9D	56.6 (4)
C7B—C8B—C9B—C10B	55.5 (3)	C7D—C8D—C9D—C10D	-56.7 (3)
C8B—C9B—C10B—C2B	-54.9 (3)	C8D—C9D—C10D—C2D	55.4 (3)
C3B—C2B—C10B—C9B	175.4 (2)	C3D—C2D—C10D—C9D	-173.0 (2)
C6B—C2B—C10B—C9B	52.1 (3)	C6D—C2D—C10D—C9D	-52.1 (3)
S1B—C2B—C10B—C9B	-69.4 (2)	S1D—C2D—C10D—C9D	70.0 (3)
<i>D</i> —H··· <i>A</i>	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> —H··· <i>A</i>
C5B—H5B···O3A ⁱ	2.39	3.263 (4)	155
C5A—H5A···O3B ⁱⁱ	2.49	3.376 (4)	158
C5D—H5D···O3C ⁱ	2.40	3.248 (4)	151
C5C—H5C···O3D ⁱⁱ	2.54	3.380 (4)	150

Symmetry codes: (i) $-x, \frac{1}{2} + y, \frac{3}{2} - z$; (ii) $1 - x, y - \frac{1}{2}, \frac{3}{2} - z$.

linked to two of its neighbours (Fig. 11), with each linkage comprising pairwise C—H···O interactions of 2.55 and 2.46 Å {C2ⁱ—H2Aⁱ···O3 and C4ⁱⁱ—H4ⁱⁱ···O3, respectively [symmetry codes: (i) $-x - 1, y - \frac{1}{2}, -z - 1$; (ii) $-x + 1, y + \frac{1}{2}, -z - 1$]. The angle subtended at O3 by its two O···H contacts is 112°, and those at H2A and H4 are 141 and 168°, respectively: the three angles at O3 sum to 357°. The resulting extended structure is a ribbon of molecules running in the direction of the crystal-

lographic *b* axis, with alternate molecules related by the 2₁ screw axis. The fringes of each ribbon consist of S atoms and methyl groups, neither of which participate in any short inter-ribbon contacts.

The structure of (6) also contains extensive C—H···O hydrogen bonding, but the motif is quite different. As noted above, the asymmetric unit comprises four independent molecules (*A*–*D*): molecules of types *A* and *B* alternate within chains which run parallel to the *a* axis,

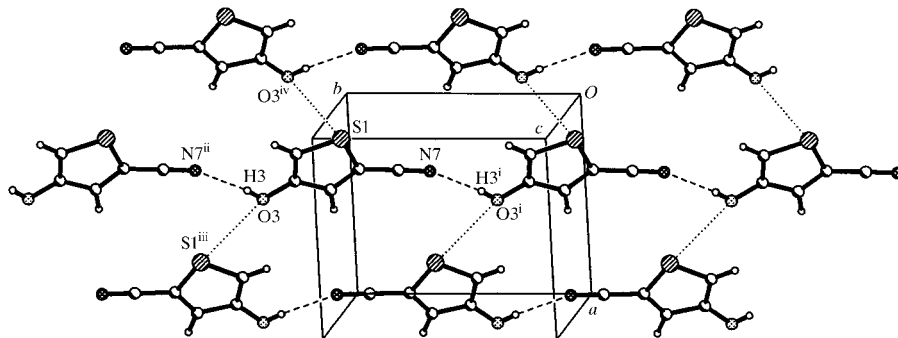


Fig. 8. A packing diagram of (4) showing molecules linked into chains by O—H···N hydrogen bonding (dashed lines). These chains are cross-linked by S···O contacts of 3.1957 (14) Å (dotted lines) to give infinite two-dimensional layers. Symmetry codes: (i) $x, -1 + y, z$; (ii) $x, 1 + y, z$; (iii) $x + \frac{1}{2}, \frac{5}{2} - y, z + \frac{1}{2}$; (iv) $-\frac{1}{2} + x, \frac{5}{2} - y, -\frac{1}{2} + z$.

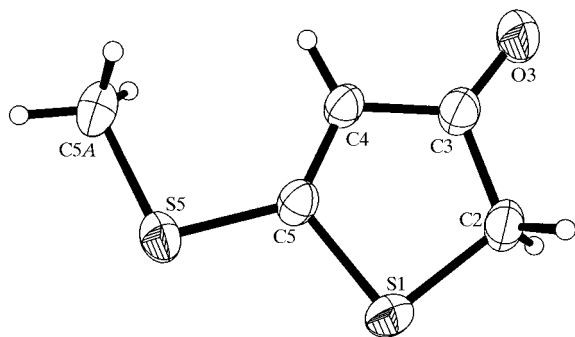


Fig. 9. A view perpendicular to the least-squares mean plane through (5). Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown with an arbitrary radius.

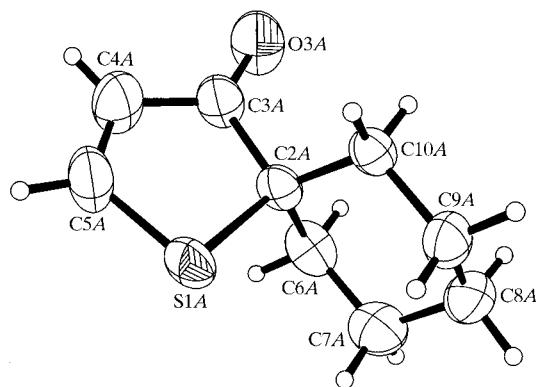


Fig. 10. A view of the structure of (6). Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown with an arbitrary radius.

while those of types *C* and *D* form parallel chains which are almost completely out of phase (Fig. 12), with the vector between successive occurrences of the same type of molecule within any chain corresponding to a translation of one unit cell along the *a* axis. An approximate, non-crystallographic 2_1 screw axis relates adjacent molecules in any chain. The hydrogen-bonding parameters within the $\cdots ABABAB \cdots$ and $\cdots CDCDCD \cdots$ chains are generally similar (Table 6), with $O \cdots H$ distances of 2.39–2.53 Å, $C=O \cdots H$ angles of 125–128° and $C-H \cdots O$ angles in the range 150–158°.

4. Conclusions

We have examined the structures of six thiophene derivatives having oxygen-containing substituents. In the first four of these the thiophene aromatic system is intact. Intra- and intermolecular geometries have been described and rationalized in terms of the tautomeric forms identified. The intermolecular contacts observed comprise $S \cdots O$ and $C-H \cdots \pi$ contacts and $O-H \cdots N$ and $C-H \cdots O$ hydrogen bonding.

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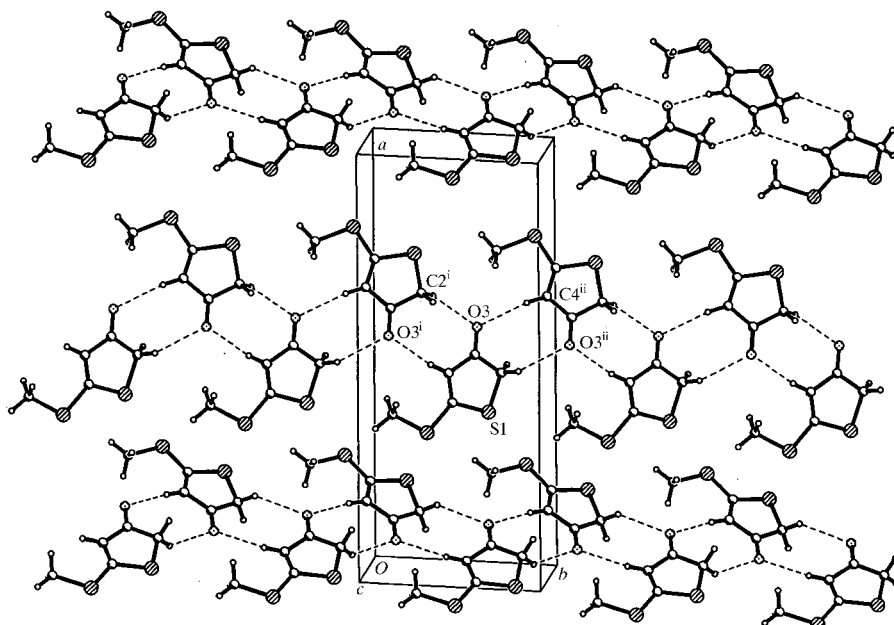


Fig. 11. A packing diagram for (5) showing each molecule linked to two of its neighbours through pairwise $C-H \cdots O$ interactions, forming a ribbon of molecules running parallel to *b*. Symmetry codes: (i) $-x + 1, y - \frac{1}{2}, -z - 1$; (ii) $-x + 1, y + \frac{1}{2}, -z - 1$.

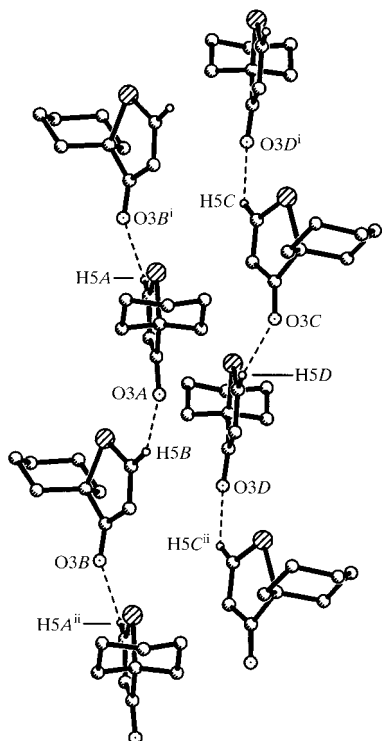


Fig. 12. A packing diagram showing the C—H...O hydrogen bonding in (6): molecules of types *A* and *B* alternate within one chain [...*ABABAB*...], those of types *C* and *D* within the other [...*CDCDCD*...]. Both chains are directed parallel to the *a* axis. Symmetry codes: (i) $1 - x, -\frac{1}{2} + y, \frac{3}{2} - z$; (ii) $-x, \frac{1}{2} + y, \frac{3}{2} - z$.

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