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

$U_{\rm iso}$ for H atoms; $U_{\rm eq} = (1/3)\Sigma_i\Sigma_jU_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j$ for others.

	x	y	z	$U_{\rm iso}/U_{\rm eq}$
S1	0.25109 (12)	0.82728 (15)	0.12408 (10)	0.0294
C2	0.0753 (4)	1.0206 (5)	0.0687 (3)	0.0201
C3	0.0981 (4)	1.2170 (5)	0.1717 (3)	0.0180
C4	0.2649 (5)	1.1860 (6)	0.2945 (4)	0.0277
C5	0.3575 (5)	0.9888 (6)	0.2833 (4)	0.0283
H3	0.0176	1.3453	0.1611	0.032 (3)
H4	0.3068	1.2954	0.3769	0.041 (3)
H5	0.4688	0.9460	0.3561	0.028 (3)

Table 2. *Selected geometric parameters* (Å, °)

	This work	Visser *et al.* (1968)
S1—C2	1.713 (3)	1.70 (2)
C2—C3	1.432 (4)	1.43 (2)
C3—C4	1.444 (5)	1.43 (2)
C4—C5	1.357 (5)	1.37 (3)
C5—S1	1.698 (4)	1.72 (2)
C2—C2′	1.448 (4)	1.49 (2)
S1—C2—C3	112.5 (2)	114 (1)
C2—C3—C4	108.0 (3)	107 (1)
C3—C4—C5	114.9 (3)	116 (2)
C4—C5—S1	112.1 (3)	111 (1)
C5—S1—C2	92.5 (2)	91.6 (8)
S1—C2—C2′	121.2 (2)	121 (1)
C3—C2—C2′	126.4 (3)	125 (1)

Table 3. *Variation of the unit-cell dimensions of bithiophene with temperature*

T (K)	a (Å)	b (Å)	c (Å)	β (°)	V (Å^3)
233	7.977 (6)	5.810 (3)	8.809 (7)	107.32 (6)	390.7
223[a]	7.972 (3)	5.809 (2)	8.830 (2)	107.19 (2)	390.6
213	7.948 (4)	5.799 (3)	8.830 (7)	107.11 (5)	389.0
203	7.926 (4)	5.796 (2)	8.829 (6)	107.02 (5)	387.8
193	7.913 (10)	5.795 (3)	8.851 (8)	107.14 (9)	387.9
188	7.904 (3)	5.789 (2)	8.826 (7)	106.90 (5)	386.4
178	7.878 (6)	5.788 (5)	8.817 (12)	107.02 (9)	384.4
173[b]	7.873 (3)	5.771 (2)	8.813 (2)	107.07 (2)	382.8
173	7.891 (6)	5.785 (5)	8.791 (13)	106.95 (9)	383.8
163	7.865 (2)	5.779 (2)	8.853 (3)	106.89 (2)	385.0
153	7.848 (2)	5.774 (2)	8.850 (4)	106.81 (3)	383.9
143	7.835 (3)	5.769 (2)	8.858 (4)	106.74 (4)	383.4
138	7.823 (8)	5.766 (6)	8.837 (17)	106.71 (12)	381.8
133	7.821 (9)	5.767 (7)	8.816 (21)	106.62 (14)	381.0
133[c]	7.734 (4)	5.729 (3)	8.933 (5)	106.72 (4)	379.0
133[d]	7.76	5.90	8.91	106.6	390.9
123	7.797 (10)	5.758 (5)	8.864 (17)	106.56 (12)	381.5
$\Delta x/x$ (%)	− 2.3	− 0.90	+ 0.62	− 0.71	− 2.4

References: (*a*) this work ($R = 0.062$); (*b*) Chaloner *et al.* (1994); (*c*) this work ($R = 0.046$); (*d*) Visser *et al.* (1968).

Data collection was undertaken at 133 K in order to minimize the degradation of the crystal under X-ray exposure. We examined at least ten crystals of bithiophene on the diffractometer and collected three sets of intensity data. The structure was solved by direct methods using *NRCVAX* (Gabe, Le Page, Charland, Lee & White, 1989). The refinement was completed with *SHELX*76 (Sheldrick, 1976) full-matrix least-squares methods with S and C atoms anisotropic and H atoms isotropic. Three data collections had to be obtained (one at 223 K and two at 133 K) before one was suitable and yielded an R factor of less than 0.06. The data set collected at 223 K was refined and converged to $R = 0.0625$. However, since the structure was partially disordered (we thought that the crystal might be twinned), the refinement was not pursued. As indicated earlier, the crystals were difficult to handle because of their low melting point. Even at 133 K the first data collection could not be completed because of the decomposition of the crystal. It seems that four days of X-ray exposure is all that a crystal can endure.

We thank the Natural Sciences and Engineering Research Council of Canada for financial support and Mr M. Simard for the measurements on the Nonius diffractometer.

Lists of structure factors, anisotropic displacement parameters and least-squares-planes data for the thiophene ring have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71789 (6 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: CD1056]

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Acta Cryst. (1994). C**50**, 1945–1947

2,2′-Bithiophene-5-carbaldehyde

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Abstract

The structure of 2,2′-bithiophene-5-carbaldehyde, $C_9H_6OS_2$, has been determined and shows a predominantly cisoid structure for the bithiophene rings.

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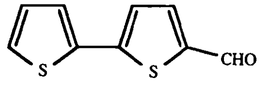
Comment

There is considerable interest in the structure of oligothiophenes and polythiophenes, because of their potential both as conducting polymers and as materials for third-harmonic generation (Roncali, 1992). The structure of 2,2′-bithiophene has recently been redetermined with good accuracy (Chaloner, Gunatunga & Hitchcock, 1994; Pelletier & Brisse, 1994). The structure of 2,2′-bithiophene is predominantly transoid, but there is 15% disorder towards a cisoid structure. Disorder in thiophene structures is relatively common (Korte, Lipka & Mootz, 1985).

The structure of the aldehyde of bithiophene, (1), represents a rare example in which the S atoms have a predominantly cisoid structure about the ring junction, although there is 20% disorder towards the transoid form. The two rings and the aldehyde group are almost coplanar. The disorder has observable effects on the molecular parameters. Because of the relative sizes of the contributing components, the S1 site is shifted only very slightly from the true S1 position, but the C3 site is shifted significantly from the true C3 position. This results in an apparently elongated C3—C4 bond [1.504 (6) Å]. It is important to understand that this apparent elongation is an artefact of the disorder and should not be taken at face value.



(1)

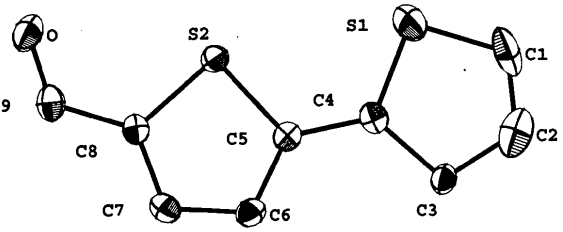


Fig. 1. Molecular structure and numbering scheme for 2,2′-bithiophene-5-carbaldehyde. Displacement ellipsoids are drawn at the 20% probability level.

Experimental

Crystal data

$C_9H_6OS_2$
$M_r = 194.3$
Orthorhombic
Pbca
$a = 7.490$ (2) Å
$b = 21.689$ (3) Å
$c = 11.170$ (6) Å
$V = 1815$ Å^3
$Z = 8$
$D_x = 1.42$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 25 reflections
$\theta = 7–10°$
$\mu = 0.51$ mm^{-1}
$T = 293$ K
Blocks
Cut to 0.15 × 0.15 × 0.1 mm
Pale green
Crystal source: recrystallization from Et_2O/hexane

Data collection

Enraf–Nonius CAD-4 diffractometer
$\theta–2\theta$ scans
Absorption correction: none
2522 measured reflections
2522 independent reflections
1111 observed reflections [$|F^2| > 2\sigma(F^2)$]

$\theta_{max} = 28°$
$h = 0 \rightarrow 9$
$k = 0 \rightarrow 28$
$l = 0 \rightarrow 14$
2 standard reflections
frequency: 60 min
intensity variation: −1.2%

Refinement

Refinement on F
$R = 0.065$
$wR = 0.066$
$S = 1.6$
1111 reflections
109 parameters
H atoms were fixed in calculated positions with $U_{iso} = 1.3U_{eq}$ of the parent atom

$w = 1/\sigma^2(F)$
$(\Delta/\sigma)_{max} = 0.01$
$\Delta\rho_{max} = 0.41$ e Å^{-3}
$\Delta\rho_{min} = -1.0$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *MolEN* (Fair, 1990)

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

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

	x	y	z	U_{eq}
S1†	−0.01915 (31)	0.34416 (9)	0.77758 (22)	0.107 (1)
S2	0.07723 (16)	0.48964 (5)	0.78663 (10)	0.051 (1)
O	0.1032 (5)	0.6261 (2)	0.7193 (3)	0.082 (2)
C1	−0.0190 (9)	0.2738 (3)	0.8327 (7)	0.114 (5)
C2	0.0679 (9)	0.2696 (3)	0.9351 (6)	0.109 (5)
C3‡	0.1412 (5)	0.3242 (2)	0.9792 (3)	0.055 (2)
C4	0.0966 (6)	0.3738 (2)	0.8898 (4)	0.055 (3)
C5	0.1449 (6)	0.4380 (2)	0.8956 (4)	0.044 (2)
C6	0.2437 (7)	0.4670 (2)	0.9815 (4)	0.057 (3)
C7	0.2636 (7)	0.5303 (2)	0.9603 (4)	0.060 (3)
C8	0.1810 (6)	0.5497 (2)	0.8583 (4)	0.048 (2)
C9	0.1743 (7)	0.6115 (2)	0.8116 (4)	0.065 (3)

† Site occupancy: 80% S + 20% C.
‡ Site occupancy: 80% C + 20% S.

Table 2. *Selected geometric parameters* (Å, °)

S1—C1	1.645 (7)	S1—C4	1.654 (5)
S2—C5	1.729 (4)	S2—C8	1.715 (4)
O—C9	1.203 (6)	C1—C2	1.320 (10)
C2—C3	1.395 (7)	C3—C4	1.504 (6)
C4—C5	1.442 (6)	C5—C6	1.365 (6)
C6—C7	1.400 (7)	C7—C8	1.362 (6)
C8—C9	1.440 (6)		
C1—S1—C4	94.4 (3)	C5—S2—C8	91.7 (2)
S1—C1—C2	112.9 (5)	C1—C2—C3	116.2 (6)
C2—C3—C4	106.6 (4)	S1—C4—C3	110.0 (3)
S1—C4—C5	122.7 (4)	C3—C4—C5	127.3 (4)
S2—C5—C4	121.4 (3)	S2—C5—C6	110.8 (3)
C4—C5—C6	127.8 (4)	C5—C6—C7	113.0 (4)
C6—C7—C8	113.3 (4)	S2—C8—C7	111.2 (3)
S2—C8—C9	121.5 (3)	C7—C8—C9	127.3 (4)
O—C9—C8	124.8 (4)		

The ring containing S1 is disordered such that the S atom is 80% at the site labelled S1 and 20% at the site labelled C3. Appropriately averaged scattering factors were used for the two positions.

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1988). Cell refinement: *CAD*-4 *Software*. Data reduction: *MolEN* (Fair, 1990). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985). Program(s) used to refine structure: *MolEN*. Molecular graphics: *ORTEP*II (Johnson, 1976).

We thank the SERC and Synthetic Chemicals Ltd for a PhD CASE Studentship (MRS).

Lists of structure factors, anisotropic displacement parameters and H-atom coordinates have been deposited with the IUCr (Reference: HA1104). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Tris(5-acetyl-3-thienyl)methane–Cyclononanone (1/1) Inclusion Compound

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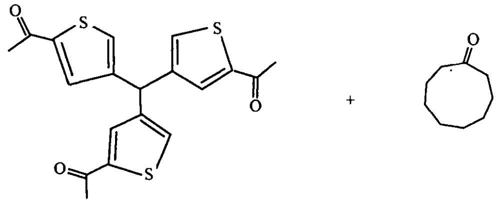
Abstract

Tris(5-acetyl-3-thienyl)methane (TATM) forms an inclusion compound with cyclononanone in a host/guest ratio of 1/1, $C_{19}H_{16}O_3S_3.C_9H_{16}O$. The crystal belongs to the monoclinic system. The cavity formed by the TATM molecule is of a zigzag-channel type, parallel to the *c* axis. The cyclononanone guest molecule occupies two orientationally disordered positions with occupation factors of 25 and 75%. The two cyclononanone molecules each have the $(g^-g^-ggg^-g^-sg^-s)$ conformation.

Comment

The tris(5-acetyl-3-thienyl)methane (TATM) molecule forms host/guest inclusion compounds with a large number of organic molecules (Bin Din & Meth-Cohn, 1977). The crystal structures of a few TATM inclusion compounds have been published recently, with ethyl acetate (Van Rooyen & Roos, 1991*a*), benzene (van Rooyen & Roos, 1991*b*), *n*-hexane (Roos & Dillen, 1992) and ethanol (Dillen & Roos, 1992) as guest molecules. These compounds belong to the triclinic system and have a host/guest ratio of 2/1. The crystal obtained in this work for the cyclononanone inclusion compound (1) is monoclinic $P2_1/c$ and has a host/guest ratio of 1/1. The cyclononanone guest molecule is larger than the other guest molecules whose structures were reported with 2/1 stoichiometry. This leads to a rearrangement of the structural units, which now crystallize with a host/guest ratio of 1/1. Similar changes in stoichiometry are often encountered in inclusion compounds (Atwood, Davies & MacNicol, 1984). There are four TATM host molecules and four cyclononanone guest molecules in the unit cell. The TATM host molecules are ordered, but the cyclononanone guest molecules are disordered over two orientations with 25 and 75% occupancy; they have nearly the same conformation and very similar orientations (Fig. 1).



(1)

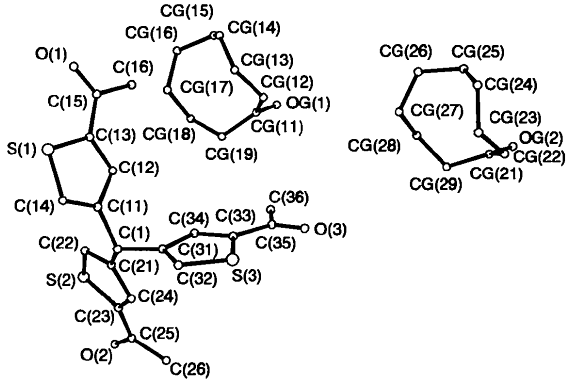


Fig. 1. The molecular structure of the title complex with the atomic numbering scheme. The guest molecule on the right is the major component.

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