Monoclinic
$P2_1/c$
$a = 7.873$ (3) Å
$b = 5.771$ (2) Å
$c = 8.813$ (2) Å
$\beta = 107.07$ (2)°
$V = 382.8$ Å^3
$Z = 2$
$D_x = 1.44$ Mg m^{-3}

Cell parameters from 25 reflections
$\theta = 7$–10°
$\mu = 0.58$ mm^{-1}
$T = 173$ K
Tablets
0.4 × 0.4 × 0.4 mm
Colourless
Crystal source: sublimation

Data collection

Enraf–Nonius CAD-4 diffractometer
θ–2θ scans
Absorption correction: none
1279 measured reflections
1214 independent reflections
972 observed reflections [$F^2 > 2\sigma(F^2)$]

$R_{\rm int} = 0.02$
$\theta_{\rm max} = 30°$
$h = 0 \rightarrow 11$
$k = 0 \rightarrow 8$
$l = -12 \rightarrow 12$
2 standard reflections
frequency: 60 min
intensity variation: −0.5%

Refinement

Refinement on F
$R = 0.056$
$wR = 0.072$
$S = 2.8$
972 reflections
58 parameters
All H-atom parameters refined

$w = 1/\sigma^2(F)$
$(\Delta/\sigma)_{\rm max} = 0.03$
$\Delta\rho_{\rm max} = 0.42$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.65$ e Å^{-3}
Atomic scattering factors from Enraf–Nonius *MolEN* programs (Fair, 1990)

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

Transformation by the space group symmetry operator (x, $1 - y$, $-\frac{1}{2} + z$), makes these coordinates equivalent to those of Pelletier & Brisse (1994). H atoms were refined isotropically; for non-H atoms $U_{\rm eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j$.

	x	y	z	$U_{\rm iso}/U_{\rm eq}$
S†	0.24966 (7)	0.16898 (9)	−0.37718 (6)	0.040 (1)
C1†	0.0751 (2)	−0.0230 (3)	−0.4317 (2)	0.034 (1)
C2	0.1006 (2)	−0.2180 (3)	−0.3282 (2)	0.058 (1)
C3	0.2676 (3)	−0.1898 (4)	−0.2062 (2)	0.049 (1)
C4	0.3581 (3)	0.0051 (4)	−0.2190 (2)	0.048 (1)
H2	0.009 (3)	−0.340 (4)	−0.320 (3)	0.062 (8)
H3	0.305 (4)	−0.291 (5)	−0.131 (3)	0.094 (10)
H4	0.472 (3)	0.073 (5)	−0.148 (3)	0.060 (7)

† Site occupancy: S = 0.91, C1 = 1.28, to simulate 15% presence of cisoid structure.

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

S—C1	1.720 (2)	S—C4	1.694 (2)
C1—C1$^{\rm i}$	1.444 (3)	C1—C2	1.425 (3)
C2—C3	1.443 (2)	C2—H2	1.03 (2)
C3—C4	1.354 (3)	C3—H3	0.87 (3)
C4—H4	1.01 (2)		
C1—S—C4	92.20 (9)	S—C1—C1$^{\rm i}$	120.4 (1)
S—C1—C2	112.3 (1)	C1$^{\rm i}$—C1—C2	127.3 (2)
C1—C2—C3	108.3 (2)	C1—C2—H2	128 (1)
C3—C2—H2	122 (1)	C2—C3—C4	114.8 (2)
C2—C3—H3	122 (2)	C4—C3—H3	124 (2)
S—C4—C3	112.4 (1)	S—C4—H4	116 (2)
C3—C4—H4	132 (2)		

Symmetry code: (i) $-x, -y, -1 - z$.

In contrast to the other reported structure determinations (Visser *et al.*, 1968; Pelletier & Brisse, 1994), we found no crystal decay at all during data collection.

The rings are slightly disordered, with an 0.85 occupancy as shown in Fig. 1 and 0.15 occupancy for the molecule rotated by 180° about C1—C1′. The S and C2 sites were given the corresponding averaged scattering factors. The function minimized was $\Sigma w(|F_o| - |F_c|)^2$.

We thank EOARD for a grant to SRG.

Lists of structure factors and anisotropic displacement parameters have been deposited with the IUCr (Reference: HA1074). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Bithiophene at 133 K

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Abstract

The crystal structure of bithiophene (2,2′-dithienyl), $C_8H_6S_2$, has been reinvestigated in order to obtain more accurate values for the bond distances and angles. At 133 K, the centrosymmetric molecule of bithiophene is planar and the S atoms are *trans* to each other. The two S—C bond distances are nearly equal [1.698 (4) and 1.713 (3) Å], while the two S—C—C angles are identical [112.5 (2) and 112.1 (3)°]. However, the two C—C—C angles differ significantly. The central C—C bond length is 1.448 (4) Å; the two angles involving the central bond are markedly different [121.2 (2) and 126.4 (3)°].

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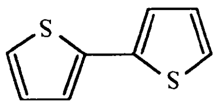
Comment

We are analyzing a series of substituted bithiophene molecules (Pelletier, Brisse, Cloutier & Leclerc, 1995) to discover the effect of the position and number of substituents on the geometry of the thiophene rings. In order to quantify these effects, good values for the bond distances and angles in bithiophene are required. The structure of bithiophene was first reported by Visser, Heeres, Wolters & Vos (1968). The authors noted that the crystals decompose rapidly, even though the X-ray intensities were collected (Weissenberg) at 133 K and only the *h*0*l* (71) reflections and *h*4*l* (97) reflections were used in the anisotropic refinement. The final *R* value was 0.08 and the e.s.d.'s on the bond distances and angles were of the order of 0.02–0.03 Å and 1–2°, respectively. Thus we have undertaken a re-examination of the crystal structure of bithiophene (I) in order to obtain a more accurate description of the molecular geometry.



(I)

A view of the molecule and that atomic numbering are show in Fig. 1.

The bond distances and angles calculated with the final refined coordinates are given in Table 2 where they are compared to the corresponding values obtained by Visser *et al.* (1968). The two C—S distances are not significantly different and are close to the average of 1.712 Å (Allen, Kennard, Watson, Brammer, Orpen & Taylor, 1987). The two S—C—C angles are identical. The thiophene ring, however, does not possess an approximate mirror symmetry because the two C—C distances are significantly different ($\Delta = 0.075$ Å), as are the two C—C—C angles ($\Delta = 6.9°$). Furthermore, the S—C2—C2′ and C3—C2—C2′ angles are also very different ($\Delta = 5.2°$). In the first approximation, all the ring atoms are coplanar ($\chi^2 = 18$) and thus the bithiophene molecule is also planar. However, when the S atom is excluded from the least-squares plane calculation the remaining four C atoms form a better plane ($\chi^2 = 2.1$). The deviations from the mean plane are of about 1 e.s.d. At the same time, it is clear that the S atom is out of the plane; its deviation from the best plane is 0.021 (1) Å. As a result of a crystallographic inversion centre at the midpoint of the C2—C2′ bond, the two S atoms are *trans* to each other. The equivalent isotropic displacement parameters (Table 1) are not unacceptably large considering the 'history' of the crystal under X-ray exposure. The packing of the molecules, shown by the stereopair in Fig. 2, is of the herringbone type with molecules alternately tilted along the diagonal of the *ac* face of the unit cell.

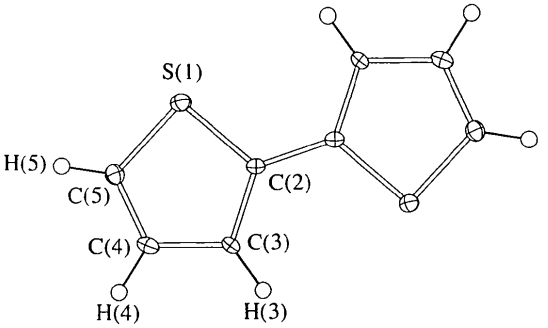


Fig. 1. *ORTEP* (Johnson, 1965) view of a bithiophene molecule and atomic numbering. Displacement ellipsoids are plotted at the 50% probability level.

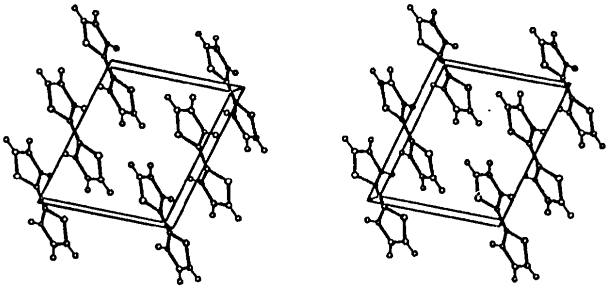


Fig. 2. Packing of the molecules. The *a* and *b* axes of the unit cell are in the plane of the figure with *a* horizontal.

The unit-cell dimensions reported in this paper differ significantly from the values given by Chaloner, Gunatunga & Hitchcock (1994) at 173 K, so that a reinvestigation was deemed necessary. In order to establish why the unit-cell dimensions are so different we measured them, using crystals grown from toluene solutions, at various temperatures down to 123 K. These values are listed in Table 3 and are shown graphically in Fig. 3. The variation of the *a* and *b* dimensions with temperature is relatively smooth. The values reported by Chaloner *et al.* (1994) (173 K; black squares in Fig. 3) and ours (223 K; black diamonds) follow the general trend. However, the variation of the *c* dimension is more erratic as the temperature is lowered, especially below 183 K. It should be noted that for temperatures below 153 K the crystals often, but not always, break up or splinter into smaller pieces. When this happens, the centring of the reflections is more difficult and the e.s.d.'s become fairly large (0.01–0.02 Å).

Except for our *b* dimension, our values and those of Visser *et al.* (1968) are clearly 'off' and deviate in the same way from the quantities plotted in Fig. 3 (at 133 K our values are indicated by white stars in black circles, those of Visser *et al.*, by black circles).

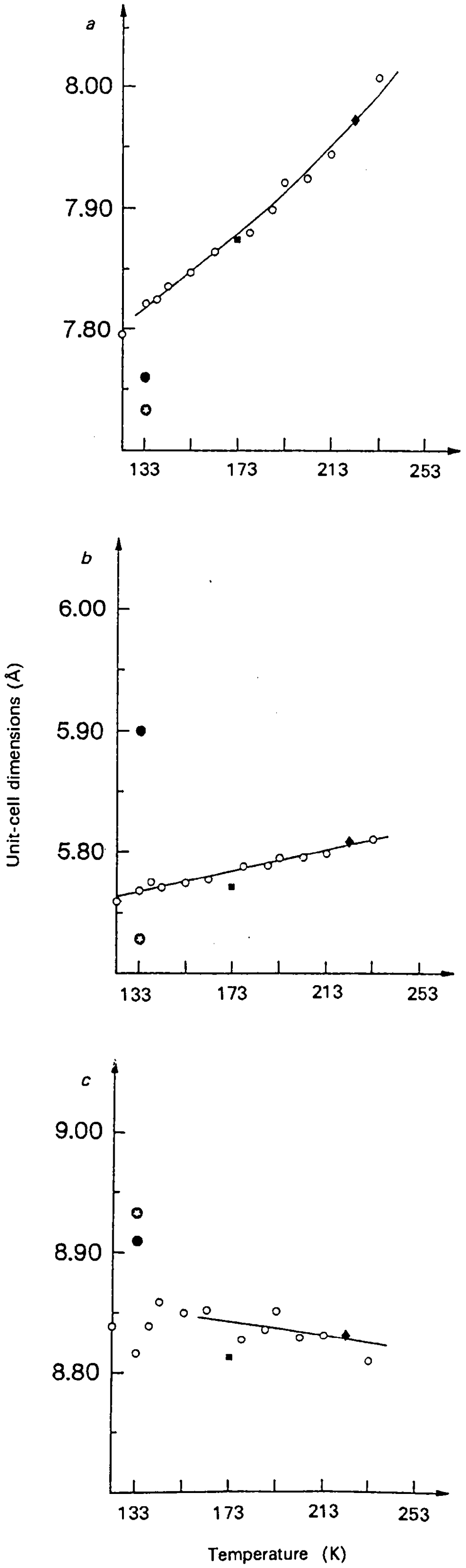


Fig. 3. Variation of the a, b and c unit-cell dimensions with temperature.

The 'unusual' b value of Visser *et al.* (1968) might result from the fact that, as stated by the authors, only film data for $h0l$ and $h4l$ were retained. It is worth stressing that our crystal did not decompose under X-ray exposure as is attested to by the stability of the reference reflections (largest fluctuation 2.6%).

All these observations seem to point to the existence of two phases: one stable fully ordered phase and another one (more common) less stable and partially disordered. In order to see whether a phase transition could be revealed, a differential scanning calorimetry experiment on the partially disordered crystals was undertaken. However, no thermal event either upon cooling to 113 K or during reheating to room temperature was detected.

Experimental

Bithiophene (Aldrich) was recrystallized in toluene. Although single crystals could be obtained readily they were difficult to handle because their melting point is so close to room temperature. A crystal was mounted at 273 K in a cold room then quickly transferred to the diffractometer.

Crystal data

$C_8H_6S_2$
$M_r = 166.26$
Monoclinic
$P2_1/c$
$a = 7.734$ (4) Å
$b = 5.729$ (3) Å
$c = 8.933$ (5) Å
$\beta = 106.72$ (4)°
$V = 379.0$ (3) Å^3
$Z = 2$
$D_x = 1.457$ Mg m^{-3}
$D_m = 1.42$ Mg m^{-3}
D_m measured by flotation in $ZnCl_2$ solution

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 25 reflections
$\theta = 9$–12°
$\mu = 0.5$ mm^{-1}
$T = 133$ K
Irregular
0.48 × 0.40 × 0.10 mm
Yellowish

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: none
2387 measured reflections
671 independent reflections
606 observed reflections [$I \geq 1.96\sigma(I)$]

$R_{\rm int} = 3.3$
$\theta_{\rm max} = 25°$
$h = -9 \rightarrow 9$
$k = -6 \rightarrow 6$
$l = -10 \rightarrow 10$
5 standard reflections monitored every 400 reflections intensity variation: <2.6%

Refinement

Refinement on F
$R = 0.046$
$wR = 0.064$
$S = 3.147$
606 reflections
49 parameters
Only H-atom U's refined
$w = 1/\sigma(I)$
$(\Delta/\sigma)_{\rm max} = 0.09$

$\Delta\rho_{\rm max} = 0.49$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.34$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from Cromer & Mann (1968) (S,C) and Stewart, Davidson & Simpson (1965) (H)

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 *SHELX76* (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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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.