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Redetermination of 2,2′-Bithiophene

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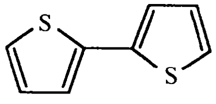
Abstract

The structure of 2,2′-bithiophene, $C_8H_6S_2$, has been redetermined at low temperature (173 K) with a good degree of accuracy. The molecules are planar and although the transoid form predominates, there is some disorder.

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). Although the structures of other bithienyls have been established and a number of oligothiophenes have also been studied (*e.g.* Jayasuriya, Kagan, Huang & Teo, 1988; Visser, Heeres, Wolters & Vos, 1968), a good quality structure of bithiophene, (I), itself had not been reported. An early determination (Visser *et al.*, 1968) was of low accuracy; the crystals, obtained by recrystallization from toluene, decomposed during data collection. In our study the crystals obtained in this way were invariably pale green in colour, as was the commercial material. Colourless crystals were obtained by sublimation, but the colour reappeared on exposure to light. The colourless crystals were used for the structure determination and there was no crystal decomposition during data collection. We assume that some coloured decomposition product is formed photochemically and that this catalyses crystal decay.



(I)

The structure that we found is broadly similar to that previously reported. Since the completion of this work, we have become aware of another low-temperature high-quality determination of the structure of bithiophene (Pelletier & Brisse, 1994). We believe that the same polymorph was obtained in both studies. Different methods of preparation (crystallization and sublimation) have produced crystals which appear slightly different in cell dimensions (by up to 1.5%); furthermore, in the study reported here, there is a detectable degree of disorder. In most of the molecules the S atoms are transoid about the ring junction, but there is 15% disorder towards a cisoid structure. Disorder in thiophene structures is relatively common (Korte, Lipka & Mootz, 1985). This should have observable effects on the molecular parameters. As a result of the disorder, the extent of which was determined by refining site occupancies, the S and C2 sites are at averaged positions with 14.5 electrons at S and 7.5 electrons at C2. The S site will only be shifted very slightly from the true S position, because of the relative sizes of the contributing components, but the C2 site will be significantly shifted away from the true C2 position. Thus the apparent bond length C1═C2 will be abnormally long. This effect is clearly visible in our structure and can also be seen, albeit less clearly, in the structure reported by Pelletier & Brisse (1994).

This structure is important as a benchmark for the effect of substituents, but it is imperative to understand that the long C1═C2 double bond is an artefact of the disorder and is not to be taken at face value. For instance, a comparison can be made with a non-disordered molecule in the structure of 3′-methyl-2,2′:5′,2″-terthiophene (Chaloner, Gunatunga & Hitchcock, 1993) in which this effect is absent. The structure of polythiophenes is conventionally represented as entirely transoid. If a structure with only two unsubstituted thiophene rings is disordered, this must have implications for the accuracy of conventional wisdom in this area.

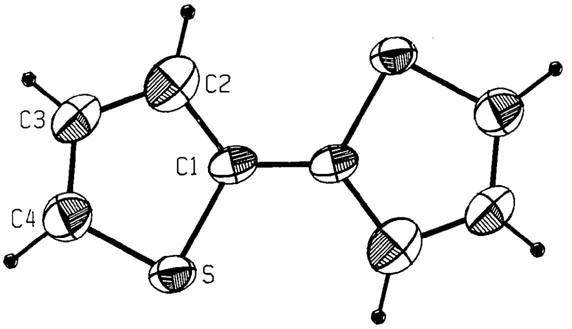


Fig. 1. Displacement ellipsoid plot of a molecule of 2,2′-bithioplene showing the atom-labelling scheme. Displacement ellipsoids are shown at 50% probability.

Experimental

Crystal data

$C_8H_6S_2$	Mo $K\alpha$ radiation
M_r = 166.3	λ = 0.71069 Å

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

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

Data collection

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

$R_{\text{int}} = 0.02$
$\theta_{\text{max}} = 30^\circ$
$h = 0 \rightarrow 11$
$k = 0 \rightarrow 8$
$l = -12 \rightarrow 12$
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

$w = 1/\sigma^2(F)$
$(\Delta/\sigma)_{\text{max}} = 0.03$
$\Delta\rho_{\text{max}} = 0.42$ e Å^{-3}
$\Delta\rho_{\text{min}} = -0.65$ 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 $U_{\text{eq}} = (1/3)\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j$.

	x	y	z	$U_{\text{iso}}/U_{\text{eq}}$
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$^{\text{i}}$	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$^{\text{i}}$	120.4 (1)
S—C1—C2	112.3 (1)	C1$^{\text{i}}$—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 $\sum w(|F_o| - |F_c|)^2$.

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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.

References

Chaloner, P. A., Gunatunga, S. R. & Hitchcock, P. B. (1993). Unpublished data.

Fair, C. K. (1990). *MolEN. An Interactive Intelligent System for Crystal Structure Analysis*. Enraf-Nonius, Delft, The Netherlands.

Jayasuriya, J., Kagan, J., Huang, D. & Teo, B. K. (1988). *Heterocycles*, **27**, 1391–1394.

Korte, L., Lipka, A. & Mootz, D. (1985). *Z. Anorg. Allg. Chem.* **524**, 157–167.

Pelletier, M. & Brisse, F. (1994). *Acta Cryst.* **C50**, 1942–1945.

Roncali J. (1992). *Chem. Rev.* **92**, 711–738.

Visser, G. J., Heeres, C. J., Wolters, J. & Vos, A. (1968). *Acta Cryst.* **B24**, 467–473.

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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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