References

Bernstein, J., Davis, R. E., Shimoni, L. & Chang, N.-L. (1995). *Angew. Chem. Int. Ed. Engl.* **34**, 1555–1573.

Coupar, P. I., Ferguson, G. & Glidewell, C. (1996). *Acta Cryst.* C**52**, 2524–2528.

Coupar, P. I., Ferguson, G. & Glidewell, C. (1997). *Acta Cryst.* C**53**, 1978–1980.

Coupar, P. I., Glidewell, C. & Ferguson, G. (1997). *Acta Cryst.* B**53**, 521–533.

Duchamp, D. J. & Marsh, R. E. (1969). *Acta Cryst.* B**25**, 5–19.

Ermer, O. (1988). *J. Am. Chem. Soc.* **110**, 3747–3754.

Ermer, O. & Eling, A. (1988). *Angew. Chem. Int. Ed. Engl.* **27**, 829–833.

Etter, M. C. (1990). *Acc. Chem. Res.* **23**, 120–126.

Ferguson, G. (1997). *PRPCIF97. A WordPerfect-5.1 Macro to Merge and Polish CIF Format Files from NRCVAX and SHELXL93 Programs.* University of Guelph, Canada.

Ferguson, G., Bell, W., Coupar, P. I. & Glidewell, C. (1997). *Acta Cryst.* B**53**, 534–543.

Ferguson, G., Coupar, P. I. & Glidewell, C. (1997). *Acta Cryst.* B**53**, 513–520.

Gabe, E. J., Le Page, Y., Charland, J.-P., Lee, F. L. & White, P. S. (1989). *J. Appl. Cryst.* **22**, 384–387.

Glidewell, C. & Ferguson, G. (1996). *Acta Cryst.* C**52**, 2528–2530.

Johnson, C. K. (1976). *ORTEPII*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.

Nonius (1997*a*). *Kappa-CCD Control Software.* Nonius BV, Delft, The Netherlands.

Nonius (1997*b*). *Kappa-CCD DENZO Processing Software.* Nonius BV, Delft, The Netherlands.

Sharma, C. V. K. & Zaworotko, M. J. (1996). *Chem. Commun.* pp. 2655–2656.

Sheldrick, G. M. (1997*a*). *SHELXS97. Program for the Solution of Crystal Structures.* University of Göttingen, Germany.

Sheldrick, G. M. (1997*b*). *SHELXL97. Program for the Refinement of Crystal Structures.* University of Göttingen, Germany.

Simard, M., Su, D. & Wuest, J. D. (1991). *J. Am. Chem. Soc.* **113**, 4696–4698.

Spek, A. L. (1998). *PLATON. Molecular Geometry Program.* Version of January 1998. University of Utrecht, The Netherlands.

Wang, X., Simard, M. & Wuest, J. D. (1994). *J. Am. Chem. Soc.* **116**, 12119–12120.

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1,8-Bis(2-thienyl)-1,3,5,7-octatetrayne

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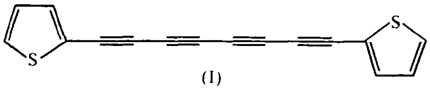
Abstract

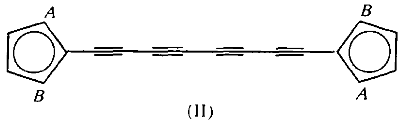
Although the title compound, $C_{16}H_6S_2$, has parallel stacking of the molecules along the *c* axis, and the intermolecular distances between the C atoms of the triple bonds are within the required distance of 4.0 Å, these atoms are not positioned to form a 1,4-addition polymer. The thiophene rings are disordered over two different orientations, with 87:13 relative occupancies. The molecule has $\bar{1}$ symmetry.

Comment

Diacetylenes are known to undergo solid-state 1,4-addition polymerization upon thermal, UV or γ irradiation, to give polydiacetylenes (PDA; Wegner, 1972; Bloor & Chance, 1985). The reaction is a topochemical one, and in a few cases, a single-crystal monomer to single-crystal polymer transformation can be achieved (Wegner, 1972). The quasi-one-dimensional π-conjugation of PDA has attracted attention in the field of third-order non-linear optics. With the aim of preparing a third-order non-linear optical material with enhanced π-conjugation, we prepared 1,8-bis(2-thienyl)-1,3,5,7-octatetrayne, (I) (Sarkar *et al.*, 1998). Like diacetylenes, the tetraynes are also expected to polymerize topochemically. However, crystal packing plays a vital role in determining the reactivity of the monomer. The stacking angle, ϕ, and contact distance, *d*, need to be in a particular range (*ca* 45° and *ca* 5 Å, respectively) for the monomer to undergo 1,4-addition polymerization (Baughman, 1974; Wegner, 1977; Bloor, 1982). The side groups, *R* and *R'*, have a profound influence on the crystal packing, *via* steric and electronic effects. Therefore, it is of the utmost importance to investigate the effect of the side groups on the crystal packing. Here we report the crystal structure of the title compound, (I), which is unreactive towards topochemical polymerization under normal conditions, although at elevated temperatures it reacts in the solid state.



(I)



(II)

The distance between S1 and C5 [1.706 (2) Å] is perhaps different from that of S1—C2 [1.697 (2) Å], but they both still compare well with C—S bond lengths in thiophene (1.712 Å). However, these values for the S—C bond lengths are uncertain because the thiophene ring was found to be disordered over different orientations, as shown in structure (II) above. Approximately 87% of the S atom occupies position *A*, while the remaining 13% occupies position *B*. In turn, the occupancy of the C atom at position *B* is about 87%, while the remaining 13% is at position *A*. As a result, the bond

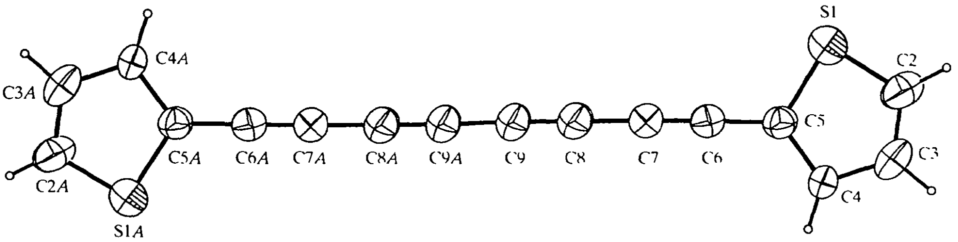


Fig. 1. Molecular structure of (I), showing the atom-labelling system. Displacement ellipsoids are shown at the 50% probability level.

lengths S1—C5 and C4—C5 are compromised. In the cases of 1,4-bis(2-thienyl)-1,3-butadiyne (2DT; Sarkar *et al.*, 1993) and 1-(3-quinolyl)-4-(2-thienyl)-1,3-butadiyne (2TQ; Barrow *et al.*, 1994), the S atom was also found to be disordered between positions 1 and 3 of the thiophene ring. Further, in (I) (Fig. 1), the C3—C4, C4—C5 and C5—C6 bonds have mixed single- and double-bond character. This suggests that the delocalization of π electrons encompasses the acetylenic backbone, as well as the thiophene ring, except for the farthest C—C bond, namely C3—C2 [1.356 (3) Å]. This bond keeps its double-bond character almost intact. The bond length of C5—C6 is relatively short [1.417 (2) Å] for a single bond, but it is typical of a thiophene ring conjugated to an acetylenic unit through its α-carbon.

The crystal packing in the unit cell (Fig. 2) shows that some molecules are stacked in parallel along the *a* axis, and overlap by a translation of 3.927 (1) Å along the *c* axis. Also, the thiophene units within the molecule are parallel, as a result of the $\bar{1}$ symmetry. Along the *a* axis, the distance between adjacent molecules is 10.005 (2) Å, which is too large for the 1,4-addition reaction to take place. The stacking angle of the molecules with respect to the *c* axis, ϕ, is 71°, which is larger than the ideal value of 45° for a 1,4-addition reaction. Moreover, the thiophene ring creates a steric barrier to topochemical polymerization, although at higher temperatures this barrier seems to be overcome.

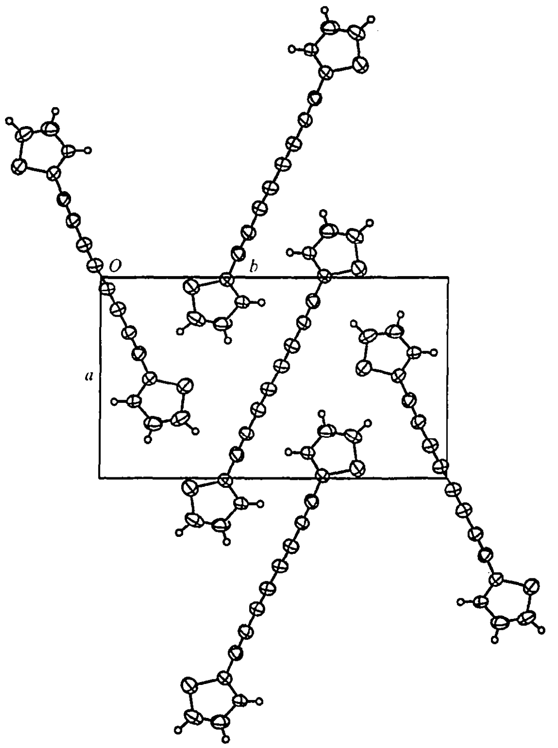


Fig. 2. Packing diagram for (I), viewed down the *c* axis.

Experimental

The synthesis of (I) was carried out by Glasser coupling. Recrystallization was performed from MeOH.

Crystal data

$C_{16}H_6S_2$
$M_r = 262.0$
Monoclinic
$P2_1/n$
$a = 10.005\ (2)$ Å
$b = 16.556\ (2)$ Å
$c = 3.927\ (1)$ Å
$\beta = 99.26\ (1)°$
$V = 642.0\ (2)$ Å^3
$Z = 2$
$D_x = 1.355$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 22 reflections
$\theta = 1.0$–$17.5°$
$\mu = 0.39$ mm^{-1}
$T = 293$ K
Plate
0.35 × 0.30 × 0.01 mm
Yellow

Data collection

MacScience MXC18 diffractometer
$\theta/2\theta$ scans
Absorption correction: refined from ΔF (*DIFABS*; Walker & Stuart, 1983)
$T_{\min} = 0.957$, $T_{\max} = 0.996$
1793 measured reflections
1293 independent reflections

1293 reflections with $F > \sigma(F)$
$R_{\rm int} = 0.028$
$\theta_{\max} = 26.43°$
$h = -12 \rightarrow 12$
$k = 0 \rightarrow 21$
$l = 0 \rightarrow 5$
3 standard reflections every 205 reflections intensity decay: 0.6%

Refinement

Refinement on F
$R = 0.074$
$wR = 0.056$
$S = 1.805$

$w = 1/[\sigma^2(F)]$
$(\Delta/\sigma)_{\max} = 0.083$
$\Delta\rho_{\max} = 0.41$ e Å^{-3}
$\Delta\rho_{\min} = -0.45$ e Å^{-3}

1293 reflections
84 parameters
H-atom parameters not refined

Extinction correction: none
Scattering factors from *International Tables for X-ray Crystallography* (Vol. IV)

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

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U^{ij}a^i a^j \mathbf{a}_i.\mathbf{a}_j.$$

	x	*y*	*z*	U_{eq}
S1†	0.54750 (4)	0.24220 (2)	0.81470 (1)	0.0682 (3)
C2	0.70800 (1)	0.23220 (9)	0.73190 (4)	0.0680 (1)
C3	0.73520 (1)	0.15510 (2)	0.64840 (4)	0.0700 (1)
C4†	0.62370 (1)	0.09620 (7)	0.65330 (3)	0.0839 (8)
C5	0.51110 (1)	0.14230 (7)	0.74560 (3)	0.0519 (7)
C6	0.38400 (1)	0.11030 (7)	0.79260 (4)	0.0564 (8)
C7	0.27890 (1)	0.08220 (8)	0.83780 (4)	0.0600 (9)
C8	0.16000 (1)	0.04850 (8)	0.89910 (4)	0.0625 (9)
C9	0.05800 (1)	0.01790 (8)	0.96390 (4)	0.0636 (9)
S4‡	0.62370 (1)	0.09620 (7)	0.65330 (3)	0.0839 (8)
C1‡	0.54750 (4)	0.24220 (2)	0.81470 (1)	0.0682 (3)

† Site occupancy = 0.874. ‡ Site occupancy = 0.126.

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

S1—C5	1.706 (2)	C7—C6	1.189 (2)
S1—C2	1.697 (2)	C8—C9	1.203 (2)
C4—C5	1.454 (2)	C9—C9^{i}	1.373 (2)
C4—C3	1.484 (2)	C3—C2	1.356 (3)
C5—C6	1.417 (2)	C3—S4	1.484 (2)
C5—S4	1.454 (2)	C2—C1	1.697 (2)
C7—C8	1.370 (2)		
C5—S1—C2	93.4 (1)	C8—C7—C6	178.1 (2)
C5—C4—C3	105.8 (2)	C7—C8—C9	177.7 (2)
S1—C5—C4	113.2 (1)	C8—C9—C9^{i}	179.3 (2)
S1—C5—C6	121.0 (1)	C5—C1—C2	93.4 (1)
S1—C5—S4	113.2 (1)		
C2—S1—C5—C4	−0.1 (1)	C3—C4—C5—S1	−0.5 (1)
C2—S1—C5—C6	177.3 (2)	C3—C4—C5—C6	−177.8 (2)
C5—S1—C2—C3	0.8 (2)	C5—C4—C3—C2	1.1 (2)

Symmetry code: (i) $-x, -y, 2-z$.

The disorder model, with S1 and C4 exchanging their positions in the thiophene ring, was treated by refining the model to include these two atoms having the coordinates of their counterparts, C1 and S4, respectively. After refining, the occupancies of the above atoms were obtained and the extent of disorder was known. The occupancies were then fixed at 0.874 and 0.126 in the final cycles. As suitable ψ-scan data were not available, *DIFABS* (Walker & Stuart, 1983) was used for the absorption correction. The U^{ij} values and their s.u.'s may not be reliable.

Data collection: *CRYSTAN-GM* (Mackay *et al.*, 1994). Cell refinement: *CRYSTAN-GM*. Data reduction: *CRYSTAN-GM*. Program(s) used to solve structure: *SIR* (Altomare *et al.*, 1994). Program(s) used to refine structure: *SIR*. Molecular graphics: *CRYSTAN-GM*. Software used to prepare material for publication: *CRYSTAN-GM*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FR1072). Services for accessing these data are described at the back of the journal.

References

Altomare, A., Cascarano, G., Giacovazzo, C., Guagliardi, A., Burla, M. C., Polidori, G. & Camalli, M. (1994). *J. Appl. Cryst.* **27**, 435.

Barrow, M. J., Milburn, G. H. W., Zeng, Z., Sarkar, A. & Talwar, S. S. (1994). *Acta Cryst.* **C50**, 650–652.

Baughman, R. H. (1974). *J. Polym. Sci.* **12**, 1511–1535.

Bloor, D. (1982). *Developments in Crystalline Polymers*, Vol. 1, edited by D. C. Bassett, p. 151. London: Applied Science Publishers.

Bloor, D. & Chance, R. R. (1985). *Polydiacetylenes*, NATO ASI Series, Series E, Applied Sciences, No. 102. Dordrecht: Martinus Nijhoff.

Mackay, S., Edwards, C. & Gilmore, C. J. (1994). *CRYSTAN-GM Users Manual*. MacScience, Japan.

Sarkar, A., Okada, S., Matsuda, H. & Nakanishi, H. (1998). *Macromolecules*. In the press.

Sarkar, A., Talwar, S. S., Das, K. & Sinha, U. C. (1993). Unpublished results.

Walker, N. & Stuart, D. (1983). *Acta Cryst.* A**39**, 158–166.

Wegner, G. (1972). *Makromol. Chem.* **154**, 35–48.

Wegner, G. (1977). *Chemistry and Physics of One-Dimensional Metals*, edited by H. J. Keller, pp. 297–314. New York: Plenum.

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2-Chloro-3-cyano-6-phenylpyridine

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Abstract

The molecular structure of the title compound (2-chloro-6-phenylpyridine-3-carbonitrile, $C_{12}H_7ClN_2$) is presented. The molecule is nearly planar. Despite strong substituent interactions, the aromaticity of the pyridine fragment is very high.

Comment

2,3,6-Substituted pyridines are very useful compounds for the synthesis of natural products with biological activity, such as vitamins (Perez-Medina *et al.*, 1947). Some of them possess bacteriostatic properties (Lesher & Grvet, 1973). The title compound, (I), crystallizes in the $P2_1/c$ space group. The molecular parameters are in good agreement with those of 2-chloro-3-cyano-4-trifluoromethyl-6-phenylpyridine (Guttsait *et al.*, 1987) and with those of other α-phenylpyridine derivatives [16 precisely measured derivatives taken from the Cambridge Structural Database (Allen *et al.*, 1979, 1991)]. The only significant differences in the latter case

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