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3′,4″-Didecyl-2,2′:5′,2″:5″,2‴-quaterthiophene

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Abstract

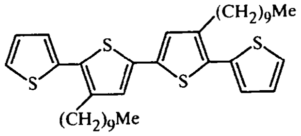
The title compound, $C_{36}H_{50}S_4$, lies about an inversion centre and the four thiophene rings are nearly coplanar. The outer rings are tilted by 3.6 (5)° from the inner rings. Each decyl chain is in the *trans* conformation and all C atoms are nearly coplanar. The dihedral angle between the aliphatic plane defined by atoms C41–C47 and the thiophene ring plane is 8.6 (1)°. There is slight disorder of the last three atoms of each decyl chain and all those of the outer thiophene rings, with occupancy factors of 65:35.

Comment

Recent progress in the synthesis of conjugated poly(3-alkylthiophenes) (P3AT) with flexible alkyl side chains of various lengths has stimulated interest because they are easily processed and maintain electrical and optical properties comparable to those of the unsubstituted polythiophenes (Genies *et al.*, 1990). It is assumed that the π-conjugated coplanar conformation of the backbone chain is retained after long-chain substitutions at suitable positions (Roux *et al.*, 1993).

In order to elucidate the structure–property relationship of novel conducting materials, oligothiophenes have been considered as model compounds for the parent polymer (Liao *et al.*, 1994). However, because of the difficulty of crystallization, X-ray data for oligothiophenes, especially those with long alkyl substituents, are scarce.

In a previous paper, the effects of alkyloxy substituents on the conformation of bithiophene were reported (Pelletier *et al.*, 1995). In order to elucidate the long-side-chain effect on P3AT, we have synthesized and structurally characterized the dialkyl-substituted title quaterthiophene, (I), a model for poly(3-decylthiophene) (P3DT).



(I)

An *ORTEP*II (Johson, 1976) drawing of the molecular structure of (I) with the atomic labelling is shown in Fig. 1. It is of interest that the molecule has a centre of symmetry at the midpoint of C2—C2($\frac{1}{2}-x$, $\frac{1}{2}-y$, $-z$). The two inner thiophene rings are coplanar within 0.12°. The outer thiophene rings and the last three atoms of each side chain are disordered in the proportion 65.0 (4):35.0 (4). The S atoms in adjacent thiophene rings adopt the *anti* conformation in the major conformer, thus minimizing steric crowding. However, in the minor conformer, the S atoms are *syn* between the outer and the inner thiophenes. This result lends support to previous proposals that although the *anti* comformer dominates, the *syn* conformer exists in a small amount, thus generating structural defects in the backbone chain (Salaneck *et al.*, 1988). The molecular plane of each of the outer rings is only slightly tilted from that of the inner rings, with the dihedral angles between their mean planes being 3.6 (5)° in the major conformer and 5.0 (7)° in the minor conformer. Similar observations were noted for alkyl-substituted pentathiophene and hexathiophene (Liao *et al.*, 1994). The aliphatic chain (C41–C50) is in a zigzag conformation and nearly planar. The aliphatic plane defined by atoms C41–C47 is inclined with respect to the plane of the adjacent thiophene ring by 8.6 (1)°. The average C—C distance in the aromatic rings is 1.411 Å, and that in the decyl chains is 1.520 Å. It is observed that the C6—S7 bond [1.758 (7) Å] is longer than the other C—S bonds in the molecule. This feature has been noted previously, for example, in terthiophene and dimethylterthiophene

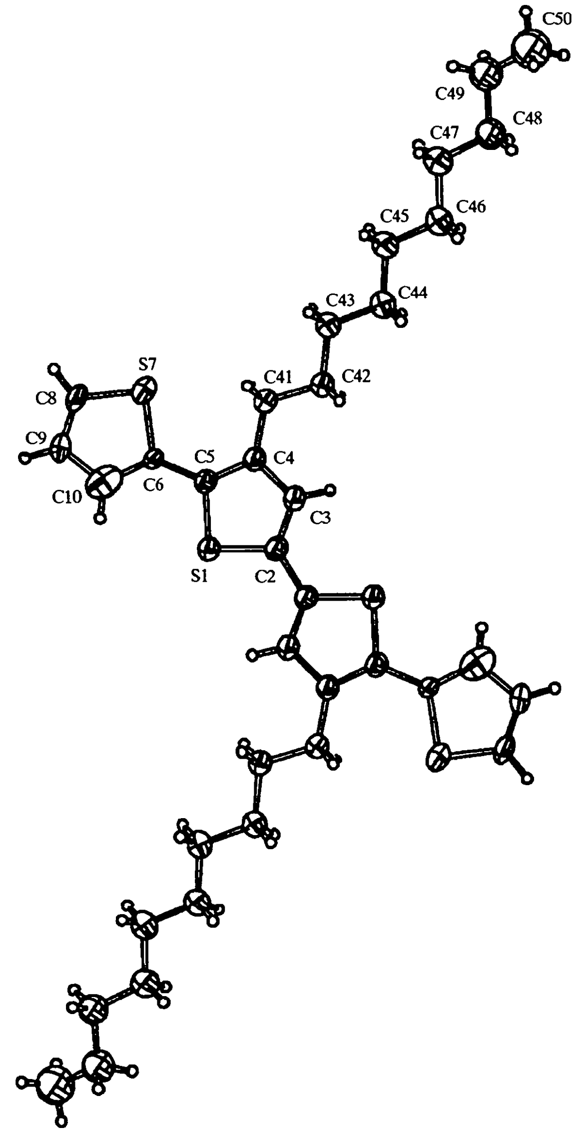


Fig. 1. *ORTEP*II (Johnson, 1976) drawing of the title molecule. Ellipsoids correspond to 40% probability.

(Georges, 1997). The average C—C—C angle in the decyl chains is 114.8°. The C—C—C angles involving the thiophene rings range from 110.1 to 132.9°, with an average value of 119.6°.

The molecular planes are aligned almost perpendicular to each other in the c-axis direction. Unlike most other oligothiophenes, no π-stack is formed in the crystal. The molecules are held together in the crystal by van der Waals forces only.

Experimental

Details of the synthesis of (I) have been described elsewhere (Donat-Bouillud *et al.*, 1998). The starting material, 4,4′-didecyl-2,2′-bithiophene, was synthesized according to the literature method of Belletête *et al.* (1995). Bromine (13.5 mmol) was added to a solution of this compound (2.7 mmol) in chloroform (15 ml). The resulting mixture was stirred for 3 h and then quenched with 50 ml of a 1 *M* NaOH solution. Pure tetrabromo-2,2′-bithiophene was obtained by flash chromatography using hexane as eluent. This compound (6.62 mmol) and [PdCl$_2${1,1′-bis(diphenylphosphine)ferrocene}] (70 mg) in dry diethyl ether (80 ml) were then refluxed for 72 h under nitrogen with a Grignard reagent (derived from 26.5 mmol of magnesium and 26 mmol of 2-iodothiophene in 50 ml of dry diethyl ether at room temperature), to prepare 4′,3″-dibromo-3′,4″-didecyl-2,2′:5′,2″:5″,2‴-quaterthiophene. This compound was then debrominized by reaction with an excess of BuLi, followed by hydrolysis with distilled water. The crude product, (I), was washed with water and dried with MgSO$_4$. Suitable single crystals were grown by slow evaporation of a petroleum ether solution.

Crystal data

$C_{36}H_{50}S_4$
$M_r = 611.00$
Monoclinic
$C2/c$
$a = 36.149\,(11)$ Å
$b = 5.4710\,(10)$ Å
$c = 18.673\,(7)$ Å
$\beta = 109.47\,(3)°$
$V = 3481.8\,(18)$ Å^3
$Z = 4$
$D_x = 1.166$ Mg m^{-3}
$D_m = 1.16$ Mg m^{-3}
D_m measured by flotation in aqueous ZnCl$_2$

Cu $K\alpha$ radiation
$\lambda = 1.5418$ Å
Cell parameters from 25 reflections
$\theta = 20$–$22°$
$\mu = 2.66$ mm^{-1}
$T = 293\,(2)$ K
Platelet
0.37 × 0.36 × 0.12 mm
Translucent light red

Data collection

Nonius CAD-4 diffractometer
$\omega/2\theta$ scan
Absorption correction: by integration (*ABSORP*; Gabe *et al.*, 1989)
$T_{min} = 0.42$, $T_{max} = 0.74$
12 272 measured reflections
3308 independent reflections

2406 reflections with $I > 2\sigma(I)$
$R_{int} = 0.023$
$\theta_{max} = 69.79°$
$h = -44 \rightarrow 44$
$k = -6 \rightarrow 6$
$l = -22 \rightarrow 22$
5 standard reflections frequency: 60 min intensity variation: 1.1%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.048$
$wR(F^2) = 0.133$
$S = 1.076$
3308 reflections
202 parameters
H atoms constrained
$w = 1/[\sigma^2(F_o^2) + (0.0861P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.018$

$\Delta\rho_{max} = 0.352$ e Å^{-3}
$\Delta\rho_{min} = -0.282$ e Å^{-3}
Extinction correction: *SHELXL*96 (Sheldrick, 1996)
Extinction coefficient: 0.00042 (8)
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

S1—C2	1.723 (2)	S7*a*—C6*a*	1.758 (7)
S1—C5	1.729 (2)	S7*b*—C8*b*	1.705 (13)
C4—C41	1.501 (3)	S7*b*—C6*b*	1.758 (12)
S7*a*—C8*a*	1.703 (7)		

C2—S1—C5	91.9 (1)	C8*a*—S7*a*—C6*a*	91.0 (3)
C3—C2—S1	110.6 (2)	C9*a*—C8*a*—S7*a*	115.0 (4)
C2$^{\rm i}$—C2—S1	120.9 (2)	C10*a*—C6*a*—S7*a*	107.7 (6)
C5—C4—C41	124.7 (2)	C5—C6*a*—S7*a*	120.8 (4)
C3—C4—C41	124.2 (2)	C8*b*—S7*b*—C6*b*	87.2 (7)
C4—C5—S1	111.8 (2)	C9*b*—C8*b*—S7*b*	113.3 (12)
C6*a*—C5—S1	115.5 (3)	C10*b*—C6*b*—S7*b*	113.0 (9)
C6*b*—C5—S1	124.9 (5)	C5—C6*b*—S7*b*	108.8 (7)

C4—C41—C42—C43	−176.6 (2)
C41—C42—C43—C44	178.7 (2)
C42—C43—C44—C45	−176.5 (2)
C43—C44—C45—C46	176.6 (3)
C44—C45—C46—C47	−177.1 (3)
C45—C46—C47—C48*a*	−177.0 (3)
C45—C46—C47—C48*b*	158.0 (6)
C46—C47—C48*a*—C49*a*	−177.6 (4)
C47—C48*a*—C49*a*—C50*a*	147.7 (6)
C46—C47—C48*b*—C49*b*	−171.8 (7)
C47—C48*b*—C49*b*—C50*b*	−128.6 (9)

Symmetry code: (i) $\frac{1}{2} - x, \frac{1}{2} - y, -z$.

The disorder of the thiophene ring and the decyl group were treated separately. First, the major peaks in the ΔF map were found around the outer thiophene ring after the first cycles of refinement. Two models were built for the outer thiophene ring and restraints (same 1,2 and 1,3 distances as in the inner thiophene with s.u.) were employed in the subsequent refinements. A free variable 2 was given to the occupation factor of one of the two models. The subsequent refinements gave the proportion 65.0 (4):35.0 (4) for the two models. For the decyl chain, two reasonable models for the last three C atoms were found from the ΔF map; a free variable was then given to the occupation factor of one of the two models. During the refinement, restraints of the 1,2 and 1,3 distances among atoms C47–C50 were applied. Suprisingly, a very similar proportion, 65:35, was obtained for the two models after refinement. Therefore, a common free variable was given to the two parts of disorder in the next refinement. The proportion was found to be 65:35 with an s.u. of 0.4. In the final refinement, the occupation factors were fixed at 0.65 and 0.35. All non-H atoms were refined anisotropically in the major conformer and isotropically, except for the S atoms, in the minor conformer. The same displacement parameter was applied to the three disordered atoms (C48–C50). H atoms were constrained to the parent site using a riding model and refined isotropically (C—H 0.93–0.98 Å). The isotropic displacement parameters were adjusted to $1.5U_{\rm eq}$ for methyl C atoms or $1.2U_{\rm eq}$ for non-methyl C atoms. A final verification of possible voids was performed using *PLATON* (Spek, 1995).

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989). Cell refinement: *CAD*-4 *Software*. Data reduction: *NRC*-2 and *NRC*-2*A* (Ahmed *et al.*, 1973). Program(s) used to solve structure: *SHELXS*96 (Sheldrick, 1990). Program(s) used to refine structure: *NRCVAX* (Gabe *et al.*, 1989) and *SHELXL*96 (Sheldrick, 1996). Molecular graphics: *ORTEP*II (Johnson, 1976) in *NRCVAX*. Software used to prepare material for publication: *NRCVAX* and *SHELXL*96.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG1393). Services for accessing these data are described at the back of the journal.

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trans-2,3-Diiodo-2-butene-1,4-diol

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Abstract

The crystal structure of *trans*-2,3-diiodo-2-butene-1,4-diol, $C_4H_6I_2O_2$, has been refined in space group $I4_1/a$, using data collected at 150 K. Bond angles around the sp^2-hybridized C atom show significant deviations from 120°.

Comment

The title compound, (I), was prepared by iodine addition to the corresponding acetylene as described by Iserson

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