Crystal and Molecular Structure of Thieno[2″,3″:4′,5′]thieno[2′,3′-*d*]thieno-[3,2-*b*]thiophene as a Hydrogen-poor Heterocycle

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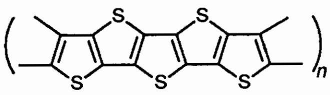
The crystal and molecular structure of the polythiophene **4** and its charge-transfer complex with tetracyanoquinodimethane (TCNQ) have been determined. Crystal data: **4**, $C_{10}H_4S_4$, $M = 252.38$, monoclinic, $P2_1/n$, $a = 11.462(1)$, $b = 4.026(1)$, $c = 10.437(1)$ Å, $\beta = 103.77(1)°$, $V = 467.8(1)$ Å^3, $Z = 2$, $D = 1.792$ g cm^{-3}; **4**·(TCNQ), $C_{22}H_8N_4S_4$, $M = 456.60$, triclinic, $P\bar{1}$, $a = 7.533(1)$, $b = 10.807(1)$, $c = 7.094(2)$ Å, $\alpha = 90.12(2)$, $\beta = 92.13(2)$, $\gamma = 124.55(1)°$, $V = 475.1(2)$ Å^3, $Z = 1$, $D = 1.596$ g cm^{-3}. The molecules in the crystals of **4** are arranged in a zig-zag fashion along the diagonal line through the *a* and *c* axes, with notably short intermolecular S–S distances (3.482 and 3.526 Å). The occurrence of short S–S contacts, which are not observed in the lower homologues of the linearly-condensed polythiophenes **2** and **3**, are discussed in terms of the low S:H ratio on the molecular periphery. A short S–S contact (3.604 Å) was also observed in the crystal of a 1:1 charge–transfer complex of **4** with TCNQ, which forms a mixed stack of donor and acceptor molecules.

Crystalline polythiophene and thiophene oligomers are materials of considerable technological importance. Although a variety of related thiophene compounds have been explored, linearly-condensed polythiophene **1** would be a very promising goal in the field of electroactive materials. Our interest in **1** is in its intermolecular interactions and packing modes in the crystalline state, since it bears essentially no hydrogen atoms in the molecular periphery. Compound **1** itself has not yet been isolated, but we have prepared thieno[2″,3″:4′,5′]thieno[2′,3′-*d*]thieno[3,2-*b*]thiophene (**4**) as a prototype for hydrogen-poor **1**.[1,2] Now we report the crystal and molecular structure of **4** in comparison with those of the lower homologues thieno[3,2-*b*]thiophene[3] (**2**) and thieno[3,2-*b*]thieno[2′,3′-*d*]thiophene[4] (**3**). The results of the present study support the characteristic aggregation properties of the solid **4**, which have already been disclosed on the basis of the polarization energy.[2]



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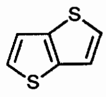

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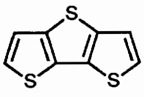

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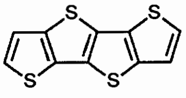

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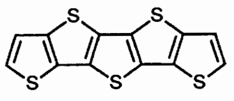

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Experimental

Preparation of Samples.—Compound **4** was prepared according to our earlier procedure.[2] Single crystals of **4** appropriate for the structural analysis were grown by slow crystallization from benzene. Crystals of the 1:1 complex of **4** with TCNQ were prepared by a diffusion method in acetonitrile–benzene (1:1).

X-Ray Crystallography.—A crystal of **4** (0.6 × 0.5 × 0.5 mm^3) was used for the analysis. X-Ray data were collected with graphite-monochromated Mo-Kα (λ = 0.710 69 Å) radiation on a RIGAKU AFC-5 four-circular diffractometer. Unit cell parameters were obtained by least-squares refinement of 25 reflections ($8 < 2\theta < 25°$). Data were collected in the (*hkl*) range (−17, 0, 0) to (17, 6, 16) with three reflections monitored in every 100. A total of 1336 unique data were collected, with 946 of $F > 3.0\sigma$. No absorption correction was applied to the data and the structure was solved under $P2_1/n$ symmetry by direct methods using SAPI 85,[5] and other analytical calculations were performed using a UNICS–III[6] program system on a PANAFACOM A-70 computer system. Hydrogen atoms were located from difference Fourier syntheses and block-diagonal least-square refinement was carried out with anisotropic thermal parameters for all non-hydrogen atoms and isotropic thermal parameters for all hydrogen atoms. Refinement of 73 parameters converged to $R = 0.038$ and $R_w = 0.043$. The results are summarized in Tables 1 and 2.

A crystal of the 1:1 complex of **4** with TCNQ (0.5 × 0.2 × 0.2 mm^3) was used for the analysis. Data were collected as described above in the (*hkl*) range (−10, −14, 0) to (10, 14, 9) with three reflections monitored every 200. A total of 2443 unique data were collected with 1784 of $F > 3.0\sigma$. No absorption correction was applied to the data and the structure was solved under $P\bar{1}$ symmetry by direct methods. Refinement of 153 parameters converged to $R = 0.033$ and $R_w = 0.037$. The results are summarized in Tables 1–5. Tables of thermal parameters and hydrogen atom coordinates have been deposited at the Cambridge Crystallographic Data Centre (CCDC).†

Results and Discussion

Molecular Structure of **4**.—Crystal data are summarized in Table 1. The molecular structure is illustrated, together with the

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† For details, see 'Instructions for Authors', *J. Chem. Soc., Perkin Trans. 2*, 1992, Issue 1.

Table 1 Crystallographic data for polythiophene **4** and the 1:1 complex of **4** with TCNQ

	4	**4**·TCNQ
Formula	$C_{10}H_4S_4$	$C_{22}H_8N_4S_4$
M	252.38	456.60
Crystal system	Monoclinic	Triclinic
Space group	$P2_1/n$	$P\bar{1}$
a/Å	11.462(1)	7.533(1)
b/Å	4.026(1)	10.807(1)
c/Å	10.437(1)	7.094(2)
α/°	90.0	90.12(2)
β/°	103.77(1)	92.13(2)
γ/°	90.0	124.55(1)
Z	2	1
V/Å^3	467.8(1)	475.1(2)
D/g cm^{-3}	1.792	1.596
μ_{calc}/cm^{-1}	9.23	4.974
Scan mode	$\omega/2\theta$	$\omega/2\theta$
2θ range/°	3–55	3–55
No. of reflections measured	1336	2443
No. of reflections used in refinements $F > 3\sigma$	946	1784
No. of parameters refined	73	153
$R(I)$	0.038	0.033
$R_w(I)$	0.043	0.037

Table 2 Bond distances and angles for **4**[a]

Bond distances/Å			
S(1)–C(3)	1.738(2)	C(3)–C(6)	1.414(3)
S(1)–C(4′)	1.736(2)	C(3)–C(7)	1.387(3)
S(2)–C(5)	1.723(3)	C(4)–C(4′)	1.382(3)
S(2)–S(7)	1.717(2)	C(5)–C(6)	1.359(3)
		C(7)–C(4)	1.417(3)
Bond angles/°			
C(4)–S(1)–C(3)	90.4(1)	C(6)–C(3)–C(7)	113.6(2)
C(5)–S(2)–C(7)	90.9(1)	C(3)–C(7)–C(4)	112.3(2)
S(1)–C(4′)–C(4)	112.7(2)	C(3)–C(7)–S(2)	111.0(2)
S(1)–C(4′)–C(7′)	135.1(2)	S(2)–C(7)–C(4)	136.7(2)
C(4)–C(4′)–C(7′)	112.2(2)	S(2)–C(5)–C(6)	113.6(2)
S(1)–C(3)–C(7)	112.4(2)	C(3)–C(6)–C(5)	110.9(2)
S(1)–C(3)–C(6)	134.0(2)		

[a] Estimated standard deviations in the least significant digits are given in parentheses.

Table 3 Selected bond distances and angles for the 1:1 complex of **4** and TCNQ[a]

Bond distances/Å			
S(1)–C(3)	1.733(2)	N(8)–C(15)	1.135(3)
S(1)–C(6)	1.733(2)	N(9)–C(11)	1.139(4)
S(2)–C(4)	1.719(2)	C(10)–C(12)	1.442(3)
S(2)–C(7)	1.723(3)	C(10)–C(14)	1.349(3)
C(3)–C(4)	1.391(3)	C(11)–C(13)	1.429(3)
C(3)–C(5)	1.418(3)	C(12)–C(13)	1.374(3)
C(4)–C(6′)	1.415(3)	C(12)–C(14′)	1.438(3)
C(5)–C(7)	1.352(4)	C(13)–C(15)	1.431(3)
C(6)–C(6′)	1.399(3)		
Bond angles/°			
C(3)–S(1)–C(6)	90.3(1)	C(12)–C(10)–C(14)	121.2(2)
C(4)–S(2)–C(7)	90.7(1)	N(9)–C(11)–C(13)	178.3(3)
S(1)–C(3)–C(4)	112.8(2)	C(10)–C(12)–C(14′)	118.2(2)
C(4)–C(3)–C(5)	113.3(2)	C(11)–C(13)–C(12)	122.7(2)
S(2)–C(4)–C(3)	111.1(2)	C(11)–C(13)–C(15)	114.9(2)
S(1)–C(6)–C(6′)	113.0(2)	C(12)–C(13)–C(15)	122.4(2)
C(4′)–C(6)–C(6′)	111.6(2)	C(10)–C(14)–C(12′)	120.6(2)
S(2)–C(7)–C(5)	114.1(2)	N(8)–C(15)–C(13)	177.3(3)

[a] Estimated standard deviations in the least significant digits are given in parentheses.

Table 4 Positional parameters for **4**[a] (× 10^4)

Atom	x	y	z
S(1)	9 632(0)	1 795(1)	6 754(0)
S(2)	7 119(0)	−2 827(1)	3 726(1)
C(3)	8 307(2)	110(5)	5 813(2)
C(4)	10 371(2)	771(5)	5 537(2)
C(5)	6 407(2)	−1 812(6)	4 953(2)
C(6)	7 131(2)	−244(6)	5 999(2)
C(7)	8 444(2)	−1 176(5)	4 624(2)

[a] Esds given in parentheses.

Table 5 Positional parameters for **4**:TCNQ[a] (× 10^4)

Atom	x	y	z
S(1)	6 994(1)	7 904(0)	4 891(1)
S(2)	12 806(1)	8 572(1)	3 477(1)
C(3)	8 901(3)	7 607(2)	4 171(2)
C(4)	10 967(3)	8 923(2)	4 180(2)
C(5)	8 817(3)	6 315(2)	3 605(3)
C(6)	8 977(3)	9 806(2)	5 222(2)
C(7)	10 800(4)	6 682(2)	3 205(3)
C(8)	−3 730(3)	−5 150(2)	8 333(3)
C(9)	3 153(3)	−2 499(3)	8 106(3)
C(10)	1 926(3)	167(2)	9 559(2)
C(11)	1 685(3)	−2 495(2)	8 423(3)
C(12)	−99(3)	−1 289(2)	9 411(2)
C(13)	−194(3)	−2 539(2)	8 827(3)
C(14)	2 023(3)	1 397(2)	10 125(3)
C(15)	−2 187(3)	−3 986(2)	8 577(3)

[a] Esds given in parentheses.

numbering scheme, in Fig. 1. Bond distances and angles are given in Table 2.

Each five-membered ring in the molecule is planar and the molecule as a whole is essentially planar; sulfur atoms deviate only 0.001 Å from the least-squares plane. The four S–C bond lengths are not the same (Table 2); the two shorter bonds are located at the outer thiophene rings. The peripheral C=C bonds (1.359 Å) are much shorter than those of the inner double bonds (1.387 and 1.382 Å), the former length being rather close to an isolated C=C bond distance, *e.g.*, 1.339 Å observed in ethene. The inner rings are therefore concluded to be highly expanded as compared with the outer two. This trend has also been observed in the central thiophene ring of polythiophene **3**,[4] in which the bond lengths and angles for the central thiophene ring (C=C, 1.380, 1.342 Å; C–S, 1.729 Å; C–S–C, 90.3°) are in good agreement with those for the inner rings of **4**. Besides, the two C–S–C angles of **4** are similar with each other and also with those of **3**.

The lengths of the peripheral C=C bonds in a series of polythiophenes are 1.36, 1.342 and 1.359 Å for **2**,[3] **3**[4] and **4**, respectively. These results are in line with the data derived from the NMR spectra;[2] the vicinal proton–proton coupling constants are almost equal (5.1 Hz) in a series of polythiophenes and show no correlation with the number of condensed thiophene rings.

Crystal Structure of **4**.—The crystal packing of **4** is shown in Fig. 2 as a projection along the *a* axis and in Fig. 3 as a projection on the *ac* plane. The molecules form columnar stacks along the *b* axis with an interplanar distance of 3.576 Å. The interstack molecules are arranged in a zig-zag fashion along the diagonal line through the *a* and *c* axes with two short intermolecular S–S contacts, which leads to side-by-side molecular arrangements with bay-regions of a molecule gearing alternately into sulfur atoms of the adjacent molecules. The shortest intermolecular S–S contact distance is 3.482 Å [S(1′)–S(2′)], which is evidently shorter than twice the van der Waals radii[7] (3.70 Å), and the other short S–S contact is 3.526 Å for contact S(2)–S(2′).

Desiraju and Gavezzotti have explored a systematic analysis of the crystal structures of polynuclear aromatic hydrocarbons and have defined four basic packing types based on the shortest crystallographic axis (SA);[8] *i.e.*, herringbone packing (SA > 5.4 Å), sandwich-herringbone packing, γ-type (4.6 > SA > 4.0 Å) and β-type (SA < 4.0 Å). These packing patterns are associated with the C:H stoichiometric ratios of the aromatic hydrocarbons. Thus, linearly-condensed polynuclear aromatic hydrocarbons such as chrysene and naphthacene are more likely to use C–H interactions and to select herringbone packing, in which the mean plane of one molecule is steeply inclined to that of its nearest neighbours. In spite of its geometrical similarity with hydrocarbon acenes, polythiophene **4** does not pack in a herringbone motif; the shortest axis of the crystal of **4** is 4.029 Å and the interplanar angle is 54.7°. These results are obviously attributable to the small number of hydrogen atoms in the molecular periphery.

Along a series of hydrocarbon acenes there is no significant change in SA, as shown in Table 6. All of these hydrocarbons adopt the herringbone packing. However, for a series of polythiophenes, there is a significantly large difference of SA between the crystal of **4** and those of **2** and **3**; the shortest axis (4.029 Å) in **4** is much shorter than those of **2** or **3** (Table 4) and corresponds rather to SA in the β-motif.

Table 6 The crystallographic shortest axis (SA) of a series of polythiophenes and related polynuclear aromatic compounds

Compound	SA/Å	Ref.
2	6.127	3
3	6.005	4
4	4.029	*a*
Naphthalene	5.97	9
Phenanthrene	6.16	10
Chrysene	5.78	11
Picene	6.15	12

[a] This study.

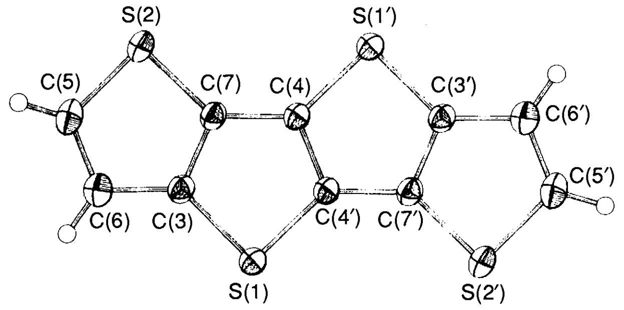

Fig. 1 ORTEP drawing of **4** with the atomic numbering

These results indicate that the C:S ratio in the molecular periphery is an important factor in engineering the short axis structure for planar sulfur heterocycles.[13] Thus, the C:S ratio in a series of polythiophenes increases in the order **4** > **3** > **2**. It is likely that there is a threshold C:S ratio which leads to short directional molecular contacts. In the extreme case of **1**, therefore, molecules are assumed to align side-by-side in a zipper-like arrangement. The intermolecular orbital interaction has been suggested by the polarization energies for **4**, but not for **2** and **3**.[2] The crystal structure of **4** has been revealed to be consistent with an investigation of the polarization energies.

The short molecular contacts together with the orbital interactions can serve in organizing the molecular aggregation into two-dimensional motifs. In this context, we measured the DC electrical resistivity, ρ, of a compacted disk of **4** by a two-probe method, to test the effect of π-orbital interaction on the electronic transport properties. The result, $\rho = 1.7 \times 10^{12}\ \Omega$ cm at room temperature in dry air, is no greater than those for much more highly-condensed polycyclic aromatic hydrocarbons, *e.g.*, $\rho = 3.7 \times 10^{12}\ \Omega$ cm for violanthrene A[14] which is composed of nine benzene rings, whereas the value is not very small for those of single-component organic solids. This leads to the conclusion that the additional intermolecular interaction in solid **4** is fairly efficient for its electronic properties.

Charge-transfer Complex of **4** *with TCNQ.*—We have prepared a charge-transfer complex by employing polythiophene **4** as an electron-donor molecule: the 1:1 crystalline complex with tetracyanoquinodimethane (TCNQ) was obtained from an acetonitrile–benzene (1:1) solution of a *ca.* 1:1 mixture of **4** and TCNQ. The electrical resistivity, $10^6\ \Omega$ cm as measured on compacted pellets by a standard four-probe method, is decreased by the complexation, but by much more than those of organic charge-transfer complexes with high conductivities, *e.g.*, $\sigma = 2.5 \times 10^{-3}\ \Omega$ cm for TTF–TCNQ.[15]

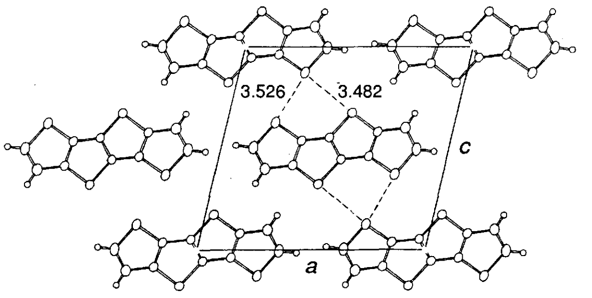

Fig. 3 Crystal structures of **4**; projection on the *ac* plane and short intermolecular sulfur-to-sulfur distances

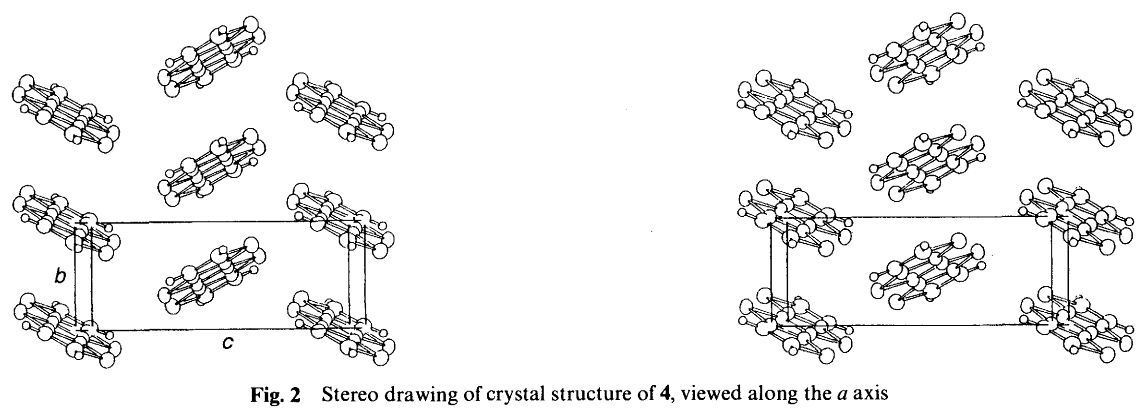

Fig. 2 Stereo drawing of crystal structure of **4**, viewed along the *a* axis

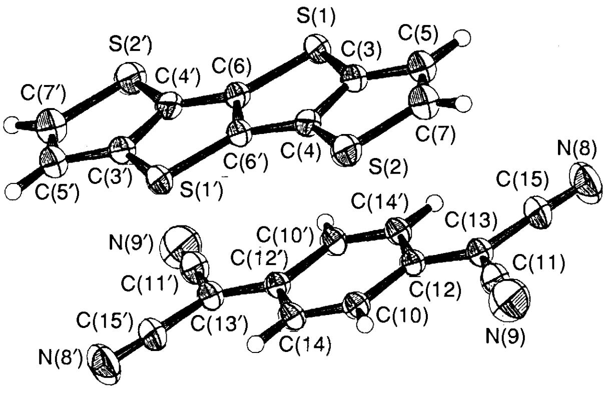

Fig. 4 ORTEP drawing of the charge-transfer complex of **4** with TCNQ, illustrating the atomic numbering

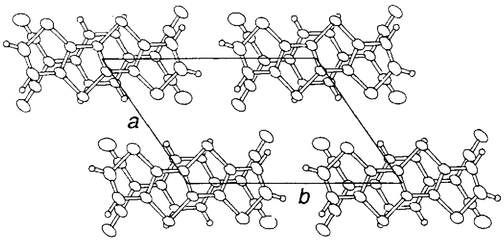

Fig. 5 Crystal structure of the charge-transfer complex of **4** with TCNQ viewed along the *c* axis

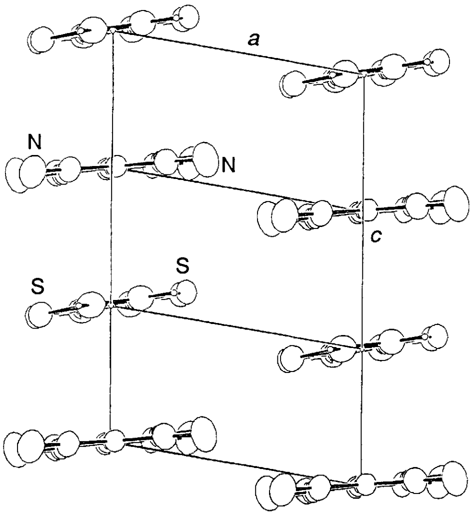

Fig. 6 Crystal structure of the charge-transfer complex of **4** with TCNQ viewed along the *b* axis

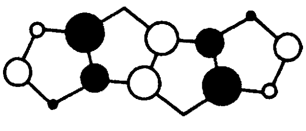

Fig. 7 Highest occupied molecular orbital (HOMO) of **4**

Crystal data are listed in Tables 1, 3 and 5. The ORTEP drawing of the donor and acceptor molecules are given in Fig. 4, together with the atomic numbering. The molecular packing in the unit cell is shown in Fig. 5. The donor and acceptor molecules, both of which are completely planar, form uniform face-to-face mixed stacking along the *c*-axis (Fig. 6). A donor molecule in such a stack is situated close to an acceptor molecule in the adjacent stack with no significantly short intermolecular contacts. The shortest inter-stack contact (3.601 Å) is observed at S(2) ··· S(2′) between two molecules located on a slant with respect to each other. The interplanar distance between the donor and acceptor molecules in a stack is 3.37 Å.

A notable difference in bond length (Table 3) from the neutral to cationic forms for donor **4** is observed for the central C=C bond [1.399(3) Å], which is much longer than that in neutral states [1.382(3) Å]. The other inner C=C bonds are also longer than that of the neutral state. This is simply explained by considering the mode in the HOMO of **4** shown in Fig. 7. Removal of electrons from the HOMO orbital will cause lengthening of the central bond in the resulting oxidized state. The positive charge appears to be localized on the central C=C bond.

As for the acceptor molecule, no significant changes in the molecular structure were observed going from the neutral to the reduced state. We have estimated the degree of charge–transfer on the basis of the bond length ratio procedure of Kistenmacher *et al.*[16] The degree of CT falls by *ca.* 8%, indicating that only a small degree of charge is transferred from the donor to acceptor.

Acknowledgements

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