organic compounds

5-(4,5-Ethylenedithio-1,3-dithiol-2-ylidene)-1,3,4,6-tetrathiapentalen-2-one (EDTO–TTP) and 5-[4,5-(ethene-1,2-diyldithio)-1,3-dithiol-2-ylidene]-1,3,4,6-tetrathiapentalen-2-one (VDTO–TTP)

Hong-Feng Chen,[a] Qi Fang,[a]* Wen-Tao Yu,[a] Andrei S. Batsanov[b] and Judith A. K. Howard[b]

[a]State Key Laboratory of Crystal Materials, Shandong University, Jinan 250100, Shandong Province, People's Republic of China, and [b]Department of Chemistry, University of Durham, South Road, Durham DH1 3LE, England
Correspondence e-mail: fangqi@sdu.edu.cn

The title sulfur-rich organic molecular crystals, namely EDTO–TTP ($C_9H_4OS_8$) and VDTO–TTP ($C_9H_2OS_8$), are characterized by conjugated C—S bonds and S···S intermolecular short contacts. The planar EDTO–TTP molecules are parallel packed and exhibit strong intermolecular interactions, including side-by-side transverse S···S contacts, face-to-face longitudinal π–π interactions and C—H···O hydrogen bonding. On cooling the EDTO–TTP crystal from 220 to 120 K, the cell dimensions and the intermolecular distances (such as S···S contacts and especially π–π spacings) become shorter, while the intramolecular bonds become longer. The curved VDTO–TTP molecules are packed in such a way as to make the crystal fully depolarized. The intermolecular interactions of the VDTO–TTP crystal are relatively weak, because of the weak π–π interactions and the lack of hydrogen bonding.

Comment

Chalcogen-rich electronic donors play a central role in the field of molecular conductors. Except for several alkali metal salts of C_{60}, all the reported organic charge-transfer superconductors belong to the chalcogen-rich type. In fact, chalcogen-rich donors have more important applications, for example, as single component molecular conductors (Ashizawa et al., 2004) or as organic field-effect transistors in the field of semiconductors. Some tetrathiafulvalene (TTF) derivatives were recently reported to have a very high field-effect mobility, which can well match the mobility of the silicon-based inorganic field-effect transistors (Mass-Torrent et al., 2004). It is well known that the basic structural necessity for molecular conductors and semiconductors is the existence of strong intermolecular interactions in the crystals.

For a long time, TTF and its derivative bis(ethylene-dithio)tetrathiafulvalene (BEDT–TTF) have been regarded as the most dominant electronic donors (Williams et al., 1992). In recent years, a new multi-sulfur moiety, 1,3,4,6-tetrathiapentalene (TTP), has received intense attention, and various TTP-based novel electronic donors have been synthesized. Several 2,5-bis(1,3-dithian-2-ylidene)-1,3,4,6-tetrathiapentalene (BDA–TTP)-based charge-transfer salts, among other TTP derivatives, have been reported to exhibit superconductivity (Misaki et al., 1993; Yamada et al., 1999, 2001). Our strategy in exploring new molecular conductors is to combine the structural factors of TTF and TTP. With this idea in mind, we synthesized the title compounds (namely EDTO–TTP and VDTO–TTP) and determined their X-ray structures. The synthesis of EDTO–TTP was once briefly mentioned by Mori et al. (1998), but no details of the synthesis or the crystal structure have been reported. We report here the structure at 220 K, (I), and 120 K, (II). VDTO–TTP, (III), is a new compound.
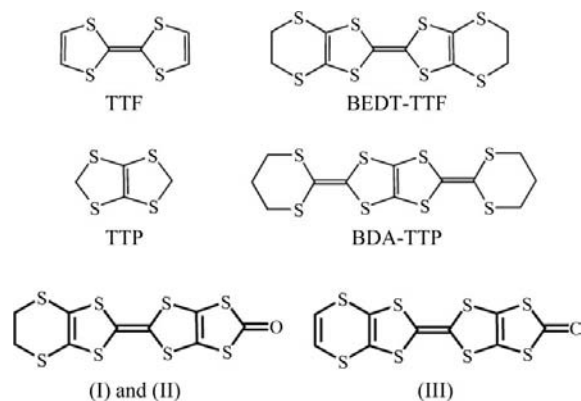
In (I) and (II), the EDTO–TTP molecule adopts a planar conformation. Except for the terminal –CH$_2$—CH$_2$– ethylene group, all the other atoms are perfectly coplanar, and the least-squares plane based on these atoms is defined as the molecular plane hereafter (see Fig. 1). In (III), the curved
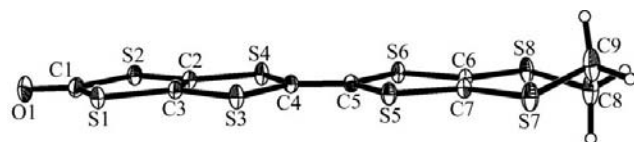

Figure 1
The molecular structure of (I). Displacement ellipsoids are drawn at the 30% probability level.
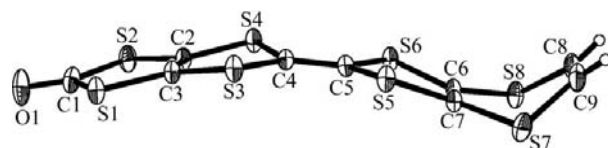

Figure 2
The molecular structure of (III). Displacement ellipsoids are drawn at the 30% probability level.
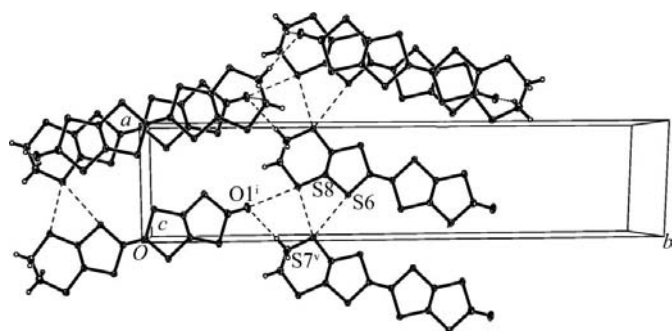
Figure 3
A view, along the c axis, of the crystal structure of (I), showing the transverse side-by-side S···S and S···O short intermolecular contacts (dashed lines). The longitudinal face-to-face eclipsed π–π overlap is also displayed. [Symmetry codes: (i) $-x + \frac{1}{2}, y - \frac{1}{2}, -z + \frac{3}{2}$; (v) $x - 1, y, z$.]

VDTO–TTP molecule looks like a wingless jet, the –CH=CH– vinylene group being the empennage (see Fig. 2). Atoms O1, C1, C2, C3, S1, S2, S3 and S4 (plane 1), atoms C6, C7, S5, S6, S7 and S8 (plane 2), and the empennage atoms (C8, C9, S7, S8, H8 and H9; plane 3) form three separate planes, the dihedral angles being 26.6 (1) (between planes 1 and 2) and 53.3 (1)° (between planes 2 and 3).

As shown in Tables 1 and 3, the bond characteristics of (I) and (II) are the same. Any non-H bond of (II) is slightly longer than its corresponding bond in (I), *i.e.* the EDTO–TTP molecule appears larger at low temperature. Thus, when discussing general bond characteristics below, structure (II) is not discussed unless (I) and (II) are being compared. For the three structures, all the C—S bond lengths, except for two C—S single bonds in (I), lie between the values for single C—S and double C=S bonds, showing the π-conjugated nature of these molecules. The S7—C9 and S8—C8 bonds in (I), involving the ethylene group, are single bonds with an average length of 1.796 (3) Å. The average of the S7—C9 and S8—C8 bond lengths [1.764 (2) Å; Table 5] in (III), however, is obviously shorter than its counterpart in (I) because of the influence of the vinylene group. The three C=C bonds in the TTF moiety and the C=O bond are double bonds. Owing to the influence of the neighbouring C=O bond, the C1—S1 and C1—S2 bonds are the longest π-conjugated C—S bonds, while C2—S2 and C3—S1 are the shortest. The single C8—C9 bond [1.475 (4) Å] in the terminal ethylene group in (I) and the

double C8=C9 bond [1.309 (3) Å] in the vinylene group in (III) have been confirmed.

The planar EDTO–TTP molecules pack as parallel layers. As shown in Fig. 3, all the molecular planes can be indexed as ($\bar{1}05$); they lie parallel to the b axis and roughly perpendicular to the c axis [87.04 (1)°]. In a molecular layer, the sum of the molecular dipole moments is along the +b direction. In a neighbouring molecular layer, however, the sum of the dipole moments is along the opposite, −b, direction, causing the polarization of the crystal to vanish. There are several transverse short intermolecular S···S and S···O contacts between neighbouring molecules. In (I), for example, the S6···S7($x − 1$, y, z), S8···S7($x − 1$, y, z) and S8···O1($-x + \frac{1}{2}, y − \frac{1}{2}, -z + \frac{3}{2}$) distances are 3.470 (1), 3.396 (1) and 3.225 (2) Å, respectively. At low temperature in (II), these contacts have shortened to 3.443 (1), 3.377 (1) and 3.216 (2) Å, respectively. Along the c-axis direction, molecules are face-to-face overlapped, forming eclipsed molecular columns or stacks (see Fig. 4). The alternate spacings of the neighbouring molecular planes in the one-dimensional stacks are 3.540 (3) and 3.601 (3) Å in (I), and 3.507 (3) and 3.561 (3) Å in (II), showing the much enhanced π–π longitudinal intermolecular interactions at low temperature. The average thermal expansion coefficients are $\alpha_a = 2.9 \times 10^{-5}$ K^{-1}, $\alpha_b = -0.90 \times 10^{-5}$ K^{-1} and $\alpha_c = 10.0 \times 10^{-5}$ K^{-1}. The high anisotropy of the thermal expansion and the large α_c value indicate that the π-stack direction is more condensable and has more potential to strengthen π–π interactions. Moreover, there are four C—H···O hydrogen bonds: the two stronger bonds, C8—H81···O1($-x + 1, -y + 1, -z + 2$) and C9—H92···O1($-x + 1, -y + 1, -z + 1$), are longitudinal and the other two are transverse (see Fig. 4 and Table 2). Again, the hydrogen bonds in (II) (Table 4) are stronger than those in (I). It is thus revealed that, when cooling the EDTO–TTP crystal, the cell dimensions and the intermolecular distances become shorter, while the intramolecular bonds become longer.

The packing of the curved molecule of (III) shows some differences from the packing of the planar EDTO–TTP molecule. If a pencil-like molecule is put into a 'pencil box', the dipolar molecule has two ways of packing: head-to-tail [the case of the longitudinal face-to-face neighbourhood of (I)] or head-to-head [the transverse side-by-side neighbourhood of (I)]. The curve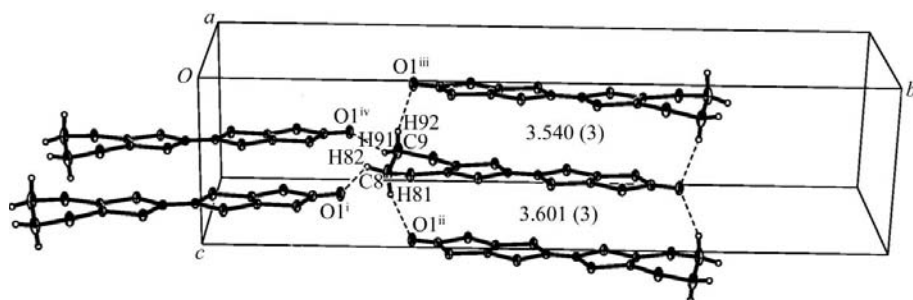d 'pencil' of molecule (III), however, has four ways of arranging: head-right, head-left, curve-up and curve-down. As shown in Fig. 5, among the four neighbours of a molecule of (III), none of its neighbours adopts the same arrangement as the central molecule: in other words, (III) is fully depolarized. Although (I) is also centrosymmetric, it is not fully depolarized. There are also strong transverse S···S and S···O intermolecular short contacts in (III), characterized by the lengths of 3.431 (1) Å for S6···S7($-x + \frac{1}{2}$, $y − \frac{1}{2}$, z), 3.400 (1) Å for S8···S7($-x + \frac{1}{2}$, $y − \frac{1}{2}$, z), and 3.052 (2) Å for O1···

Figure 4
A view, along the a axis, of the crystal structure of (I). Dashed lines denote intermolecular hydrogen bonds. [Symmetry codes: (i) $-x + \frac{1}{2}, y − \frac{1}{2}, -z + \frac{3}{2}$; (ii) $-x + 1, -y + 1, -z + 2$; (iii) $-x + 1, -y + 1, -z + 1$; (iv) $-x + \frac{3}{2}, y − \frac{1}{2}, -z + \frac{3}{2}$.]
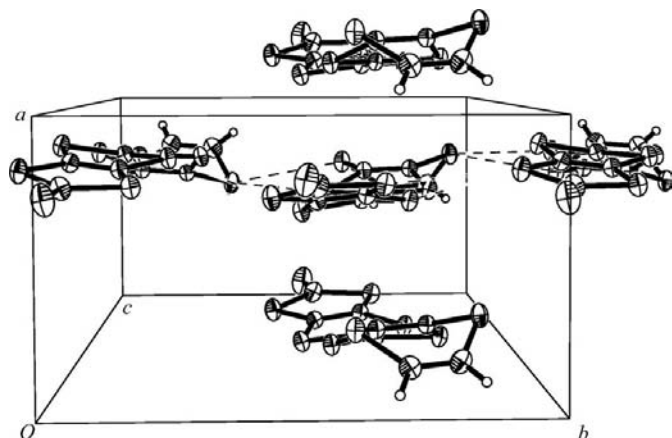
organic compounds

Figure 5
The neighbourhood of a molecule of (III), showing that no neighbours take the same orientation. Thus (III) is fully depolarized.
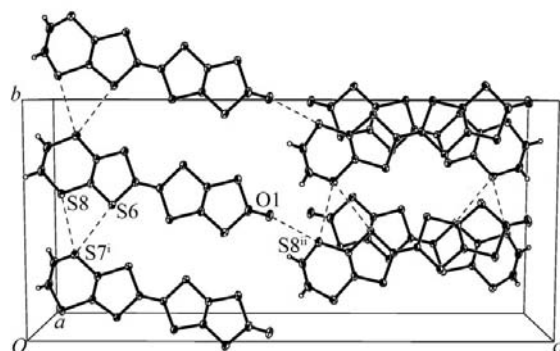

Figure 6
The packing of (III). Dashed lines denote intermolecular S···S and S···O short contacts. [Symmetry codes: (i) $-x + \frac{1}{2}, y - \frac{1}{2}, z$; (ii) $-x + \frac{1}{2}, -y + 1, z + \frac{1}{2}$.]

$S8(-x + \frac{1}{2}, -y + 1, z + \frac{1}{2})$ (Fig. 6). However, the π–π interactions in (III) are relatively weak, since the overlap of the two face-to-face molecules is staggered rather than eclipsed and the planarity of the molecule is poor. The greatest difference is that there are no hydrogen bonds in (III). Thus, the intermolecular interactions of (III) should be weaker than those of (I).

Above all, the EDTO–TTP crystal structure exhibits strong intermolecular interactions, including transverse S···S interactions, longitudinal π–π interactions and hydrogen bonding. We believe that these strong intermolecular interactions may endow it with some applications in the semi-conductor field.

Experimental

For the synthesis of VDTO–TTP, 2,3-bis(2-cyanoethylsulfanyl)-6,7-vinylenedithiotetrathiafulvalene (Xue *et al.*, 2004) (0.35 g, 0.76 mmol) was dissolved in acetone (30 ml) and excess CsOH·H$_2$O (0.78 g, 4.6 mmol) was added in the presence of N$_2$ at room temperature. Stirring was continued for 4 h at room temperature. Zinc chloride (0.42 g, 3.5 mmol) was added to the orange reaction mixture, followed by Bu$_4$NBr (0.68 g, 2.1 mmol) under N$_2$. After 2 h, the

reaction mixture was dried *in vacuo*. The residue was suspended in tetrahydrofuran (30 ml) and then an excess of triphosgene (0.55 g, 1.9 mmol) at 195 K was added under the protection of N$_2$. The solution was stirred overnight. An orange precipitate was obtained and dried *in vacuo*. The precipitate was dissolved in carbon disulfide, washed with water and dried with anhydrous magnesium sulfate. Compound (III) was isolated by silica-gel column chromatography using carbon disulfide as eluant. Orange prism-shaped crystals were formed on slow evaporation of the carbon disulfide solvent at room temperature. IR (v, cm^{-1}): 3030 (*w*, CH), 2920 (*w*, CH), 1676 (*vs*, C=O), 1616 (*m*), 1489 (*m*), 965 (*m*), 900 (*m*), 875 (*m*), 794 (*m*), 750 (*m*), 692 (*s*), 682 (*s*), 671 (*m*), 407 (*s*). EDTO–TTP was synthesized by a similar procedure. IR (v, cm^{-1}): 2970 (*w*, CH$_2$), 2922 (*w*, CH$_2$), 1664 (*vs*, C=O), 1624 (*vs*), 1609 (*vs*), 1414 (*m*), 969 (*m*), 881 (*s*), 857 (*m*), 766 (*s*), 757 (*s*), 409 (*vs*). Note that the carbonyl vibration of EDTO–TTP has a 12 cm^{-1} redshift relative to that of VDTO–TTP.

Compound (I)

Crystal data

C$_9$H$_4$OS$_8$	$V = 1315.25$ (13) Å^3
$M_r = 384.60$	$Z = 4$
Monoclinic, $P2_1/n$	Mo $K\alpha$ radiation
$a = 6.4948$ (4) Å	$\mu = 1.34$ mm^{-1}
$b = 28.7194$ (16) Å	$T = 220$ K
$c = 7.1503$ (4) Å	$0.23 \times 0.19 \times 0.02$ mm
$\beta = 99.548$ (1)°	

Data collection

Siemens SMART 1K CCD area-detector diffractometer	11099 measured reflections
	2682 independent reflections
Absorption correction: multi-scan (*SADABS*; Bruker, 2005)	2107 reflections with $I > 2\sigma(I)$
$T_{min} = 0.749$, $T_{max} = 0.974$	$R_{int} = 0.032$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.029$	179 parameters
$wR(F^2) = 0.064$	All H-atom parameters refined
$S = 1.09$	$\Delta\rho_{max} = 0.54$ e Å^{-3}
2682 reflections	$\Delta\rho_{min} = -0.32$ e Å^{-3}

Table 1
Selected bond lengths (Å) for (I).

S1—C3	1.728 (2)	S6—C6	1.759 (2)
S1—C1	1.780 (3)	S7—C7	1.748 (2)
S2—C2	1.728 (2)	S7—C9	1.793 (3)
S2—C1	1.768 (3)	S8—C6	1.751 (2)
S3—C3	1.744 (2)	S8—C8	1.799 (3)
S3—C4	1.765 (2)	O1—C1	1.211 (3)
S4—C2	1.742 (2)	C2—C3	1.344 (3)
S4—C4	1.768 (2)	C4—C5	1.346 (3)
S5—C5	1.756 (2)	C6—C7	1.344 (3)
S5—C7	1.757 (2)	C8—C9	1.475 (4)
S6—C5	1.756 (2)		

Table 2
Hydrogen-bond geometry (Å, °) for (I).

D—H···A	D—H	H···A	D···A	D—H···A
C8—H82···O1^i	0.99 (3)	2.64 (3)	3.266 (3)	121 (2)
C8—H81···O1^{ii}	1.10 (4)	2.40 (4)	3.456 (5)	161 (3)
C9—H92···O1^{iii}	1.07 (4)	2.35 (4)	3.378 (4)	160 (3)
C9—H91···O1^{iv}	0.94 (3)	2.54 (4)	3.407 (3)	153 (3)

Symmetry codes: (i) $-x + \frac{1}{2}, y - \frac{1}{2}, -z + \frac{3}{2}$; (ii) $-x + 1, -y + 1, -z + 2$; (iii) $-x + 1, -y + 1, -z + 1$; (iv) $-x + \frac{3}{2}, y - \frac{1}{2}, -z + \frac{3}{2}$.

Compound (II)

Crystal data

$C_9H_4OS_8$
$M_r = 384.60$
Monoclinic, $P2_1/n$
$a = 6.4762 (4)$ Å
$b = 28.7451 (16)$ Å
$c = 7.0792 (4)$ Å
$\beta = 99.322 (1)°$

$V = 1300.45 (13)$ Å^3
$Z = 4$
Mo $K\alpha$ radiation
$\mu = 1.35$ mm^{-1}
$T = 120$ K
$0.23 \times 0.19 \times 0.02$ mm

Data collection

Siemens SMART 1K CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2005)
$T_{min} = 0.746$, $T_{max} = 0.974$

12766 measured reflections
3072 independent reflections
2537 reflections with $I > 2\sigma(I)$
$R_{int} = 0.032$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.029$
$wR(F^2) = 0.061$
$S = 1.10$
3072 reflections

179 parameters
All H-atom parameters refined
$\Delta\rho_{max} = 0.44$ e Å^{-3}
$\Delta\rho_{min} = -0.34$ e Å^{-3}

Table 3
Selected bond lengths (Å) for (II).

S1—C3	1.735 (2)	S6—C6	1.765 (2)
S1—C1	1.780 (2)	S7—C7	1.752 (2)
S2—C2	1.731 (2)	S7—C9	1.807 (2)
S2—C1	1.775 (2)	S8—C6	1.753 (2)
S3—C3	1.745 (2)	S8—C8	1.810 (2)
S3—C4	1.768 (2)	O1—C1	1.215 (2)
S4—C2	1.742 (2)	C2—C3	1.350 (3)
S4—C4	1.772 (2)	C4—C5	1.347 (3)
S5—C5	1.758 (2)	C6—C7	1.346 (3)
S5—C7	1.763 (2)	C8—C9	1.503 (3)
S6—C5	1.761 (2)		

Table 4
Hydrogen-bond geometry (Å, °) for (II).

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
C8—H82$\cdots$O1^i	1.02 (3)	2.55 (3)	3.247 (3)	126 (2)
C8—H81$\cdots$O1^{ii}	1.05 (3)	2.39 (3)	3.382 (3)	158 (3)
C9—H92$\cdots$O1^{iii}	0.99 (3)	2.37 (3)	3.342 (3)	167 (2)
C9—H91$\cdots$O1^{iv}	0.97 (3)	2.48 (3)	3.390 (3)	156 (2)

Symmetry codes: (i) $-x + \frac{1}{2}, y - \frac{1}{2}, -z + \frac{3}{2}$; (ii) $-x + 1, -y + 1, -z + 2$; (iii) $-x + 1, -y + 1, -z + 1$; (iv) $-x + \frac{3}{2}, y - \frac{1}{2}, -z + \frac{3}{2}$.

Compound (III)

Crystal data

$C_9H_2OS_8$
$M_r = 382.59$
Orthorhombic, $Pbca$
$a = 7.3308 (1)$ Å
$b = 12.7832 (3)$ Å
$c = 28.0416 (6)$ Å

$V = 2627.81 (9)$ Å^3
$Z = 8$
Mo $K\alpha$ radiation
$\mu = 1.34$ mm^{-1}
$T = 296$ K
$0.26 \times 0.14 \times 0.10$ mm

Data collection

Bruker APEXII CCD area-detector diffractometer
Absorption correction: multi-scan (*APEX2*; Bruker, 2005)
$T_{min} = 0.723$, $T_{max} = 0.881$

13259 measured reflections
3037 independent reflections
2499 reflections with $I > 2\sigma(I)$
$R_{int} = 0.028$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.027$
$wR(F^2) = 0.070$
$S = 1.10$
3037 reflections

171 parameters
All H-atom parameters refined
$\Delta\rho_{max} = 0.35$ e Å^{-3}
$\Delta\rho_{min} = -0.20$ e Å^{-3}

Table 5
Selected bond lengths (Å) for (III).

S6—C6	1.7583 (18)	S3—C4	1.7617 (18)
S6—C5	1.7575 (18)	S1—C3	1.7337 (18)
S5—C5	1.7549 (19)	S1—C1	1.781 (2)
S5—C7	1.7567 (17)	S7—C7	1.7430 (18)
S2—C2	1.7269 (19)	S7—C9	1.765 (2)
S2—C1	1.777 (2)	S8—C6	1.7515 (18)
S4—C2	1.7455 (18)	S8—C8	1.763 (2)
S4—C4	1.7603 (18)	C9—C8	1.309 (3)
S3—C3	1.7450 (18)		

All H atoms were located in a difference Fourier map and refined in the isotropic approximation [C—H = 0.94 (3)–1.10 (4), 0.97 (3)–1.05 (3) and 0.84 (2)/0.95 (2) Å for (I), (II) and (III), respectively].

For (I) and (II), data collection: *SMART* (Bruker, 1998); cell refinement: *SAINT* (Bruker, 2007); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 2008); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*. For (III), data collection: *APEX2* (Bruker, 2005); cell refinement: *APEX2*; data reduction: *APEX2*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL*; software used to prepare material for publication: *WinGX* (Farrugia, 1999).

References

Ashizawa, M., Kimura, S., Mori, T., Misaki, Y. & Tanaka, K. (2004). *Synth. Met.* **141**, 307–313.
Bruker (1998). *SMART*. Bruker AXS Inc., Madison, Wisconsin, USA.
Bruker (2005). *APEX2* and *SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA.
Bruker (2007). *SAINT*. Bruker AXS Inc., Madison, Wisconsin, USA.
Farrugia, L. J. (1999). *J. Appl. Cryst.* **32**, 837–838.
Mass-Torrent, M., Durkut, M., Hadley, P., Ribas, X. & Rovira, C. (2004). *J. Am. Chem. Soc.* **126**, 984–985.
Misaki, Y., Matsui, T., Kawakami, K., Nishikawa, H., Yamabe, T. & Shiro, M. (1993). *Chem. Lett.* pp. 1337–1340.
Mori, T., Ashizawa, M., Aragaki, M., Murata, K., Misaki, Y. & Tanaka, K. (1998). *Chem. Lett.* pp. 253–254.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Williams, J. M., Ferraro, J. R., Thorn, R. J., Carlson, K. D., Geiser, U., Wang, H. H., Kini, A. M. & Whangbo, M.-H. (1992). In *Organic Superconductors (including Fullerenes)*. New Jersey: Prentice Hall.
Xue, G., Yu, W.-T. & Fang, Q. (2004). *Z. Kristallogr. New Cryst. Struct.* **219**, 171–172.
Yamada, J.-I., Watanabe, M., Akutsu, H., Nakatsuji, S., Nishikawa, H., Ikemoto, I. & Kikuchi, K. (2001). *J. Am. Chem. Soc.* **123**, 4174–4180.
Yamada, J.-I., Watanabe, M., Anzai, H., Nishikawa, H., Ikemoto, I. & Kikuchi, K. (1999). *Angew. Chem. Int. Ed.* **38**, 810–813.