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A substituted EDOT precursor: diethyl 3,4-dihydroxythiophene-2,5-dicarboxylate

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The title compound, $C_{10}H_{12}O_6S$, has been obtained as dark-yellow chunk-shaped crystals, together with the expected thin white needles. The structures of the two phases are identical. Two independent molecules compose the asymmetric unit: one molecule is totally planar, whereas a methyl group of the second molecule points out of the plane. Each molecule participates in several intra- and intermolecular hydrogen bonds and short contacts. The overall structure can be regarded as parallel sheets of molecules. Within a sheet, molecules are connected to one another in an infinite network *via* numerous short intermolecular contacts. Sheets are connected *via* hydrogen bonds and short contacts, in particular involving the methyl groups.

Comment

Electrically conducting polymers are a widely and intensively researched class of materials in both industry and academia (Skotheim *et al.*, 1998). One particular family of conducting polymers, namely poly(ethylenedioxythiophenes) (PEDOTs), have shown extraordinary promise in a variety of applications because of their low oxidation potentials, high conductivity, oxidation-state stability and thin-film transparency (Groenendaal *et al.*, 2003). Several commercially available products use a PEDOT-based material (Groenendaal *et al.*, 2000). Utilizing the electronic properties of PEDOTs, which are superior to those of other conducting polymer systems, we set out to design and synthesize substituted PEDOT-based polymers.

According to previously reported procedures, PEDOTs can be readily derivatized at the ethylenedioxy bridge (Sankaran & Reynolds, 1997; Lima *et al.*, 1998). During purification of the substituted EDOT precursor diethyl 3,4-dihydroxythiophene-2,5-dicarboxylate, (II), which was prepared from the diethyl thiodiglycolate, (I), in two steps, unexpected dark-yellow chunk-like crystals formed alongside the expected and previously reported white needles. The ^{1}H NMR data for the

two samples were the same and agreed with previously reported data (Sankaran & Reynolds, 1997). The stark contrast in crystal morphology and color, yet similar NMR properties, piqued our interest in determining the crystal structure of the unexpected product.
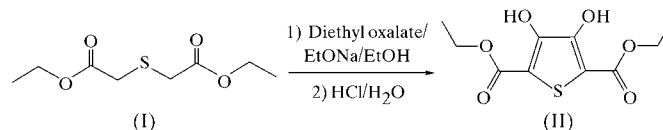
The asymmetric unit of the title compound contains two independent molecules, named hereafter as *A* and *B* (Fig. 1), which lie almost in the same plane, close to (101). The planes of molecules *A* and *B* form an angle of ∼1.52 (4)°. Comparison of intramolecular bond lengths (Table 1) and angles does not show any discrepancies between units *A* and *B*. For each type of bond, distances are very homogeneous, except for one methyl group (see below). The only structural difference between these two units is the conformation of one of the terminal methyl groups. In molecule *A*, the methyl group that involves atom C7 points out of the plane of the molecule [C7 lies 1.128 (3) Å from the molecular plane], whereas molecule *B* is almost planar [the largest deviation is 0.164 (1) Å for atom O15].

The result of this non-planarity in molecule *A* is the existence of one short intermolecular contact, which can be regarded as a potential hydrogen bond between *A* and *B* via atoms C7, H71 and O12(1 − x, 1 − y, 2 − z) (see Table 2). As a result of these short contacts, the C—H bond lengths around atom C7 [mean distance = 1.02 (4) Å] are slightly larger than those of the other methyl groups [mean distance = 0.96 (4) Å]. Atom C17 is also involved in a short intermolecular contact with atoms O5(2 − x, 1 − y, 1 − z) and H173 [C—H =
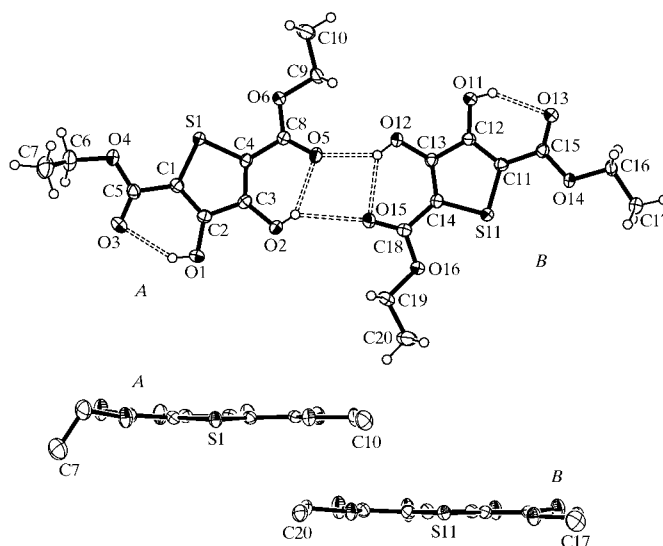

Figure 1
The molecular structure of (II), with 50% probability displacement ellipsoids (top: projection on to the plane of the molecules; bottom: side view of the molecules). Hydrogen bonds are represented by dashed lines.
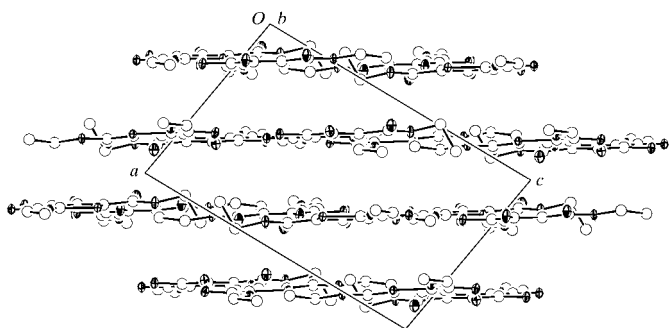
Figure 2
A projection of the structure of (II) along the *b* axis (S and O atoms are represented by shaded ellipsoids).

0.95 (2) Å, H···O = 2.57 (3) Å and C···O = 3.384 (3) Å], but this contact cannot be regarded as a potential hydrogen bond because the C17—H173···O5 angle [144 (2)°] is relatively bent. There is also another short contact, of 3.458 (2) Å, between atoms C17 and S1(1 + *x*, *y*, −1 + *z*). In contrast, the other methyl groups (C10 and C20) are not involved in any intermolecular contacts shorter than the sum of the van der Waals radii.

Contrary to what is observed in (I) (Hada *et al.*, 1993), the hydroxy groups of (II) lie in the plane of the molecules. This planarity leads to a larger number of potential intra- and intermolecular hydrogen bonds between units than are present in (I) (see Table 2); in (II), each hydroxy group is involved in one intra- and one intermolecular contact, whereas in (I), only half of the OH groups generate such contacts. In addition, there are also some short intermolecular contacts between non-H atoms. These numerous short intermolecular contacts involve only nearly coplanar molecules, thus creating a relatively dense network of interactions within and between molecules of (II). Therefore, the overall structure of the title compound can be regarded as sheets of molecules (Fig. 2), which extend parallel to the *b* axis, almost in the (101) plane. However, the sheets are not independent of one another, since there are intersheet contacts (Table 2). These contacts involve not only the out-of-plane methyl group (C7) and one of the hydroxy groups (O12) but also other heteroatoms in the molecule (see Table 2). As a result of these intersheet contacts, the intersheet distance is relatively short (~3.55 Å). The observed hydrogen bonding and other intermolecular interactions are likely to be the main reasons for the low solubility of the compound in lower polarity solvents. The compound was recrystallized in small portions from large amounts of boiling ethyl acetate. The compound is more soluble in higher polarity solvents, such as methanol and, to a lesser extent, ethanol.

The structure of the needle phase has also been determined, but its low quality (due to the very thin morphology and the poor diffracting power of the sample) prevents its presentation in this article. Nevertheless, the needle phase exhibits the same structural arrangement as the block phase, with the same features.

Experimental

Compound (II) was synthesized from (I) and purified in 72% yield using previously reported procedures (Sankaran & Reynolds, 1997; Lima *et al.*, 1998). During purification/recrystallization in ethyl acetate, white needles were obtained, along with a lesser amount of dark-yellow chunk-like crystals. The ^{1}H NMR data were in agreement with reported previously data (Sankaran & Reynolds, 1997) for (II).

Crystal data

$C_{10}H_{12}O_6S$	Mo $K\alpha$ radiation
$M_r = 260.27$	Cell parameters from 7998
Monoclinic, $P2_1/c$	reflections
$a = 8.7337$ (9) Å	$\theta = 2.4–25.9°$
$b = 19.8208$ (14) Å	$\mu = 0.29$ mm^{-1}
$c = 13.6271$ (15) Å	$T = 160$ (2) K
$\beta = 99.059$ (13)°	Block, yellow
$V = 2329.5$ (4) Å^3	$0.48 \times 0.23 \times 0.10$ mm
$Z = 8$	
$D_x = 1.484$ Mg m^{-3}	

Data collection

Stoe IPDS diffractometer	3225 reflections with $I > 2\sigma(I)$
φ scans	$R_{int} = 0.069$
Absorption correction: multi-scan	$\theta_{max} = 26.0°$
(Blessing, 1995)	$h = -10 \rightarrow 10$
$T_{min} = 0.928$, $T_{max} = 0.971$	$k = -24 \rightarrow 24$
20 063 measured reflections	$l = -16 \rightarrow 16$
4535 independent reflections	

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0369P)^2]$
$R[F^2 > 2\sigma(F^2)] = 0.035$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.072$	$(\Delta/\sigma)_{max} = 0.001$
$S = 0.94$	$\Delta\rho_{max} = 0.28$ e Å^{-3}
4535 reflections	$\Delta\rho_{min} = -0.21$ e Å^{-3}
403 parameters	
All H-atom parameters refined	

Table 1
Selected interatomic distances (Å).

S11—C14	1.7275 (19)	S1—C4	1.7196 (19)
S11—C11	1.7277 (18)	S1—C1	1.7217 (18)
O11—C12	1.337 (2)	O1—C2	1.345 (2)
O12—C13	1.337 (2)	O2—C3	1.340 (2)
O13—C15	1.215 (2)	O3—C5	1.216 (2)
O14—C15	1.333 (2)	O4—C5	1.326 (2)
O14—C16	1.455 (2)	O4—C6	1.467 (3)
O15—C18	1.212 (2)	O5—C8	1.214 (2)
O16—C18	1.335 (2)	O6—C8	1.327 (2)
O16—C19	1.455 (2)	O6—C9	1.464 (2)

All H-atom parameters were refined freely [C—H = 0.95 (3)–1.05 (4) Å and O—H = 0.77 (3)–0.83 (3) Å].

Data collection: *IPDS Software* (Stoe & Cie, 1996); cell refinement: *IPDS Software*; data reduction: *IPDS Software*; program(s) used to solve structure: *SIR*97 (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*-3 (Farrugia, 1997) and *CAMERON* (Watkin *et al.*, 1996); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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Table 2
Hydrogen-bonding geometry and intermolecular contacts (Å, °).

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
O1—H1$\cdots$O3	0.82 (3)	2.10 (3)	2.799 (2)	144 (2)
O1—H1$\cdots$O11^{i}	0.82 (3)	2.44 (3)	3.116 (2)	141 (2)
O2—H2$\cdots$O5	0.77 (2)	2.09 (2)	2.7409 (19)	143 (2)
O2—H2$\cdots$O15	0.77 (2)	2.46 (2)	3.101 (2)	141 (2)
O11—H11$\cdots$O13	0.77 (3)	2.09 (3)	2.750 (2)	144 (3)
O11—H11$\cdots$O3^{ii}	0.77 (3)	2.22 (3)	2.723 (2)	123 (2)
O12—H12$\cdots$O5	0.84 (3)	2.04 (3)	2.752 (2)	142 (2)
O12—H12$\cdots$O15	0.84 (3)	2.19 (3)	2.8475 (19)	135 (2)
C7—H71$\cdots$O12^{iii}	1.00 (3)	2.60 (3)	3.563 (3)	162 (2)
C17—H173$\cdots$O5^{iv}	0.95 (2)	2.57 (3)	3.384 (3)	144 (2)

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

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1705). Services for accessing these data are described at the back of the journal.

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