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3,4-[2,2-Bis(methoxyethoxymethoxymethyl)propylenedithio]-3′,4′-(ethylenedithio)tetrathiafulvalene: a spiro-substituted BEDT–TTF analogue

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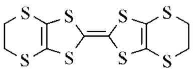
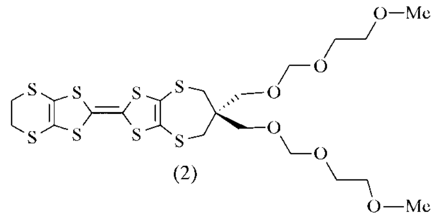
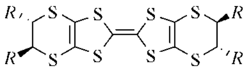
The crystal structure of the title compound [systematic name: 2-(1,3-dithiolo[4,5-*b*][1,4]dithiin-2-ylidene)-6,6-bis(methoxyethoxymethoxymethyl)-1,3-dithiolo[4,5-*b*][1,4]dithiepine], $C_{21}H_{30}O_6S_8$, a spiro-substituted BEDT–TTF analogue [BEDT–TTF is bis(ethylenedithio)tetrathiafulvalene], has a strongly bent heterocyclic framework. The seven-membered ring adopts a pseudo-chair conformation with notably widened ring bond angles, especially at the methylene C atoms [119.49 (11) and 117.60 (11)°]. The axial side chain adopts an extended conformation, but the equatorial side chain curls back on itself and the O atom nearest the ring system is involved in three short contacts to H atoms (2.45–2.53 Å). The molecules pack in centrosymmetrically related pairs, which are isolated from each other by columns of the polyether side chains. This study emphasizes the ease of distortion of the neutral bis(propylenedithio)tetrathiafulvalene ring structure, and how the need to accommodate side chains can easily override the tendency of these donor systems to form stacks in the crystalline state.

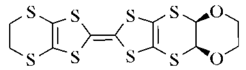
Comment

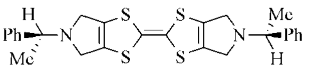
The radical cation salts of BEDT–TTF, (1), have shown a wide variety of electrical behaviour (Rovira, 2004), examples being bifunctional materials where conductivity is combined with magnetic properties. Particular highlights are the superconductor (BEDT–TTF)$_2$Cu(NCS)$_2$ (Williams *et al.*, 1991), the paramagnetic superconductor (BEDT–TTF)$_4$·H$_2$O·Fe(C$_2$O$_4$)$_3$·C$_6$H$_5$CN (Kurmoo *et al.*, 1995) and the ferromagnetic conductor (BEDT–TTF)$_3$[CrMn(oxalate)$_3$] (Coronado *et al.*, 2000). A range of substituted BEDT–TTF derivatives has become available (Wallis & Griffiths, 2005), including some with expanded outer rings (Ozturk *et al.*, 2001). We report here the crystal structure of the title donor, (2), which contains one propylenedithio ring with two methoxyethoxymethoxymethyl substituents on the central Csp^3 atom. We were interested to see whether the substituents would inhibit the usual packing modes of such donors, in which they pack in one- or two-dimensional stacks. Donors (3) (Karrer *et al.*, 1987; Matsumiya *et al.*, 1993), (5) (Yamada *et al.*, 1997) and (6) (Yang *et al.*, 2008) retain the traditional packing modes, despite the increasing bulk of the substituents, while the racemic tetraethyl donor, (4), does not (Kini *et al.*, 1999).

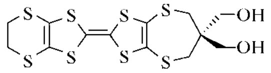

(1)


(2)


(3) R=Me
(4) R=Et


(5)


(6)


(7)

The molecular structure of compound (2), measured at 120 K, is shown in Fig. 1. Selected bond distances, angles and torsion angles are given in Table 1, and details of the hydrogen bonding are given in Table 2.

The most notable feature is the very pronounced bend in the structure of the organosulfur core. Thus, although the four central S atoms (S3, S4, S5 and S6) are almost coplanar [to within 0.0132 (2) Å], the outer four S atoms are displaced by *ca* 1 Å to the same side of that plane (Table 3). Formation of the seven-membered ring has led to expansion of the ring bond angles, most notably at the two methylene atoms, C9 and C11 [119.49 (11) and 117.60 (11)°, respectively], as well as at the two sp^2 atoms, C7 and C8 [126.75 (12) and 126.63 (12)°, respectively]. The angles at atoms S7 and S8 are 103.63 (7) and 102.91 (7)°, respectively. The widest angle at the quarternary centre, C10, is also in the ring system [112.07 (13)°]. The bond lengths from S to the methylene C atoms [1.8166 (16)–1.8182 (16) Å] are considerably longer than those to the Csp^2 atoms [1.7485 (15)–1.7511 (16) Å] (see Table 1).

The dihydrodithiepine ring adopts a pseudo-chair structure, with the two side chains taking up axial and equatorial positions. The equatorial side chain makes smaller angles [105.49 (12) and 106.23 (12)°] with the adjacent ring C—C bonds than the axial side chain [110.75 (13) and 111.79 (13)°]. The first C—O bonds along each chain lie *anti* to a ring C—C bond [C9—C10—C12—O1 = 178.90 (12) and C11—C10—C17—O4 = −170.24 (13)°]. These two substituents adopt quite different conformations (Table 1) and twist for the most part in the opposite sense to each other. The most notable differences are in the conformations about the (ring-C)—C—O—C bond, with only the axial side chain adopting a fully extended conformation [177.13 (18) *cf.* −134.64 (14)°], and in the

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conformations about the (—C)—O—C—(CH_2OMe) bond [134.65 (15) *cf.* 146.78 (14)°] and the only O—C—C—O bond [−75.23 (19) *cf.* −65.53 (19)°], which, in contrast with the rest of the chain, twist in the same sense. The result is that the axial side chain is much more extended, while the equatorial side chain curls back on itself. The first O atom along the equatorial side chain, O4, is involved in three close intramolecular contacts to H atoms (Table 2), from the ring system (H9*B*, 2.53 Å), from the axial side chain (H12*A*, 2.45 Å) and from within the side chain (H19*A*, 2.50 Å). The corresponding contacts to atom O1 of the axial side chain are *ca* 0.15 Å longer. The acetal linkages involving the third and fourth bonds along each chain have similar *gauche* conformations about both C—O bonds. The ethylene bridge at the other end of the donor molecule is disordered between two envelope conformations in which one Csp^3 atom is displaced strongly to the same side of the plane of the other four atoms of the dithiine ring [C1 by −0.826 (4) Å and C2*A* by −0.70 (1) Å], with the other Csp^3 atom lying close to this plane [C2 displayed by −0.068 (5) Å and C1*A* by 0.078 (8) Å].

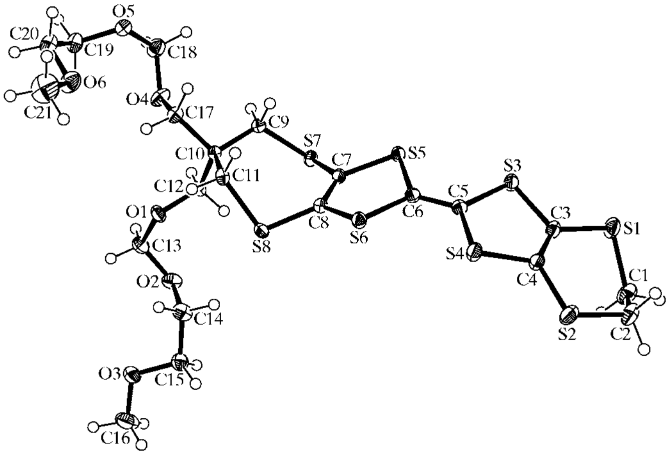

Figure 1
A view of the molecular structure of compound (2), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probabilty level and H atoms are shown as small spheres of arbitrary radii.

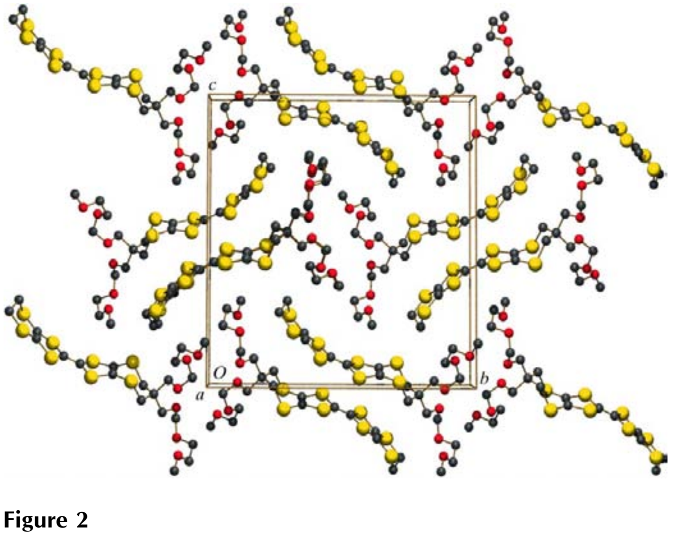

Figure 2
The crystal packing of compound (2), viewed along the *a* axis.

Only a few structures of this donor system and the closely related TTF fused to two dihydro-1,4-dithiepine rings have been measured, and these carry either two fluoro groups (Dautel & Fourmigue, 2000, 2001), two H atoms (Porter *et al.*, 1987), two hydroxymethyl groups (Liu *et al.*, 2004) or a spiro-dioxolane ring (Marshallsay *et al.*, 1993) as substituents in place of polyether side chains. All adopt the pseudo-chair conformation in the seven-membered ring, apart from the bis(hydroxymethyl) derivative, (7), for which O—H···O hydrogen bonding plays an important role in the determination of the crystal structure. Only two of these structures, the unsubstituted bis(dithiepinyl)–TTF and the analogue of (2) bearing a spiro-dioxolane group on the seven-membered ring, show a similar bending of the donor skeleton to that observed in (2). In all these structures, there is no evidence for conformational disorder in the seven-membered ring, which is in contrast with the six-membered rings in BEDT–TTF and its radical cation salts, and indeed in the structure of (2). Comparison of the two rings of the TTF unit in (2) show that there is little difference in their geometries on fusion to a six- or seven-membered ring; the bonds from S atoms to the seven-membered ring junction are just slightly shorter [1.7587 (16) and 1.7643 (15) Å] than those to the six-membered ring junction [1.7699 (17) and 1.7724 (16) Å] (see Table 1).

In the crystal structure of (2), the molecules are packed in centrosymmetrically related pairs, with the best planes containing the four central S atoms lying *ca* 3.28 Å apart (Fig. 2). However, these pairs do not stack face-to-face with others, but are isolated from one another. These pairs of molecules lie more or less on edge in the *bc* plane, with the side chains extending initially in this plane but penetrating into the *a* and −*a* directions as the side chains twist, with one side chain much more extended than the other. The side chains cluster together and form columns of polyether groups stacking in the *a* direction, at the corners and at the centre of the unit cell, and they are separated by the pairs of organosulfur units. Within these clusters there is a short H···O contact (H18*A*···O3^{ii} = 2.59 Å; see Table 2 for details). In contrast, the closest related donor is the bis(hydroxymethyl) donor, (7), which forms stacks in the solid state (Liu *et al.*, 2004). However, its 2:1 salt with triodide contains orthogonal sets of dimers of the donor. Hydrogen bonding of the hydroxyl groups plays an important role in these particular structures.

Experimental

Preparative details have been reported previously (Ozturk *et al.*, 2001). Crystals of (2) were obtained by recrystallization from ethanol. Analysis found: C 39.7, H 4.7%; $C_{21}H_{30}O_6S_8$ requires: C 39.6, H 4.8%. ^{1}H NMR (270 MHz, $CDCl_3$): δ 4.70 (4H, *s*, 2 × OCH_2O), 3.71 (4H, *br s*, 6,6-CH_2O), 3.64 (4H, *m*) and 3.57 (4H, *m*) (2 × OCH_2CH_2O), 3.39 (6H, *s*, 2 × CH_3), 3.28 (5′- and 6′-H_2), 2.75 (4H, *s*, 5- and 7-H_2); ^{13}C NMR (270 MHz, $CDCl_3$): δ 129.6 (*br*, 3a- and 8a-C), 114.6 and 114.1 (2′-, 3a′- and 7a′-C), 109.8 (2-C), 95.7 (OCH_2O), 71.7 and 69.4

(2 × OCH_2CH_2O), 69.4 (*br*, 6,6-CH_2O), 66.9 (2 × CH_3OCH_2), 59.0 (2 × OCH_3), 44.2 (5- and 7-C), 37.0 (6-C), 30.1 (5′- and 6′-C); IR (KBr, ν_{max}, cm^{-1}): 1300, 1244, 1197, 1172, 1137, 1098, 1040, 1012, 892, 864, 847, 837, 770, 722; *m*/*z* (EI): 634 (M^+, 100), 606 ($[M - CH_2CH_2]^+$, 18).

Crystal data

$C_{21}H_{30}O_6S_8$
$M_r = 634.93$
Monoclinic, $P2_1/n$
$a = 6.8227$ (10) Å
$b = 19.7775$ (4) Å
$c = 20.3661$ (4) Å
$\beta = 94.9050$ (10)°
$V = 2738.1$ (4) Å^3
$Z = 4$
Mo $K\alpha$ radiation
$\mu = 0.69$ mm^{-1}
$T = 120$ (2) K
0.24 × 0.10 × 0.07 mm

Data collection

Bruker–Nonius KappaCCD diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2001)
$T_{min} = 0.85$, $T_{max} = 0.95$
45147 measured reflections
6272 independent reflections
5278 reflections with $I > 2\sigma(I)$
$R_{int} = 0.044$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.029$
$wR(F^2) = 0.063$
$S = 1.04$
6272 reflections
439 parameters
H-atom parameters constrained
$\Delta\rho_{max} = 0.33$ e Å^{-3}
$\Delta\rho_{min} = -0.25$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

S1—C3	1.7541 (17)	S4—C4	1.7699 (17)
S1—C1*A*	1.785 (5)	S5—C6	1.7617 (16)
S1—C1	1.831 (3)	S5—C7	1.7643 (15)
S2—C4	1.7496 (17)	S6—C8	1.7587 (16)
S2—C2*A*	1.803 (8)	S6—C6	1.7606 (16)
S2—C2	1.806 (4)	S7—C7	1.7511 (16)
S3—C5	1.7581 (16)	S7—C9	1.8182 (15)
S3—C3	1.7724 (16)	S8—C8	1.7485 (16)
S4—C5	1.7593 (16)	S8—C11	1.8166 (16)
C7—S7—C9	103.63 (7)	C10—C9—S7	119.49 (11)
C8—S8—C11	102.91 (7)	C12—C10—C9	110.75 (13)
C8—C7—S7	126.75 (12)	C12—C10—C11	111.79 (13)
C8—C7—S5	116.78 (12)	C9—C10—C11	112.07 (13)
S7—C7—S5	116.47 (9)	C12—C10—C17	110.22 (13)
C7—C8—S8	126.63 (12)	C9—C10—C17	106.23 (12)
C7—C8—S6	117.32 (12)	C11—C10—C17	105.49 (12)
S8—C8—S6	116.02 (9)	C10—C11—S8	117.60 (11)
C9—C10—C12—O1	178.90 (12)	C11—C10—C17—O4	−170.24 (13)
C13—O1—C12—C10	177.18 (13)	C18—O4—C17—C10	−134.64 (14)
C12—O1—C13—O2	64.71 (18)	C17—O4—C18—O5	−57.5 (2)
C14—O2—C13—O1	62.64 (18)	C19—O5—C18—O4	−64.15 (19)
C13—O2—C14—C15	134.65 (15)	C18—O5—C19—C20	146.78 (14)
O2—C14—C15—O3	−75.19 (18)	O5—C19—C20—O6	−65.38 (19)
C16—O3—C15—C14	178.92 (15)	C21—O6—C20—C19	−177.42 (17)

Table 2
Hydrogen-bond and short-contact geometry (Å, °).

$D—H\cdots A$	$D—H$	$H\cdots A$	$D\cdots A$	$D—H\cdots A$
C2—H2*A*···O5^{i}	0.99	2.26	3.181 (4)	154
C9—H9*B*···O4	0.99	2.53	2.951 (2)	106
C12—H12*A*···O4	0.99	2.45	2.812 (2)	101
C12—H12*B*···S7	0.99	2.87	3.2839 (17)	106
C18—H18*B*···O3^{ii}	0.99	2.59	3.528 (2)	158
C19—H19*A*···O4	0.99	2.50	2.904 (2)	104

Symmetry codes: (i) $-x + 2, -y, -z + 1$; (ii) $-x + 2, -y + 1, -z + 1$.

Table 3
Displacements (Å) of the outer S atoms from the mean plane of the inner TTF S atoms (S3, S4, S5 and S6).

S1	−0.9035 (8)	S7	−1.2026 (7)
S2	−1.0328 (8)	S8	−1.0717 (8)

A 0.664 (7):0.336 (7) disorder between two positions for the C1/C1*A* and C2/C2*A* atoms in the dihydrodithiine ring was refined without applying any constraints. All H atoms were placed in calculated positions and treated as riding atoms, with C—H = 0.98–0.99 Å and $U_{iso}(H) = 1.5$ or $1.2U_{eq}(C)$.

Data collection: *COLLECT* (Hooft, 1998); cell refinement: *DENZO* (Otwinowski & Minor, 1997) and *COLLECT*; data reduction: *DENZO* and *COLLECT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3* (Farrugia, 1997) and *PLATON* (Spek, 2003); software used to prepare material for publication: *SHELXL97*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SU3017). Services for accessing these data are described at the back of the journal.

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