

Table 1. Selected geometric parameters (\AA , $^\circ$)

| | | | |
|----------|-----------|----------|-----------|
| C1—C4 | 1.531 (1) | C5—N1 | 1.136 (1) |
| C4—C5 | 1.475 (1) | C6—N2 | 1.133 (1) |
| C4—C6 | 1.476 (1) | | |
| C5—C4—C6 | 108.9 (8) | N1—C5—C4 | 177.2 (1) |
| C5—C4—C1 | 112.3 (8) | N2—C6—C4 | 179.5 (1) |
| C6—C4—C1 | 112.0 (7) | | |

Reflection intensities were evaluated by profile fitting of a 96-step peak scan using a 2θ shell procedure (Diamond, 1969) and then corrected for Lorentz–polarization effects. Standard uncertainties, $\sigma(I)$, were estimated from counting statistics. H atoms have been treated isotropically [U_{iso} varies from 0.035 (3) to 0.061 (4) \AA^2]. C—H bond lengths range from 0.95 (1) for C4—H4 to 1.01 (2) \AA for C3—H3. All calculations were performed on a μ -VAX 3400 and on an AXP DecStation 3000/400.

Data collection: *P3/V* (Siemens, 1989). Cell refinement: *P3/V*. Data reduction: *XDISK* (Siemens, 1990). Program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997b). Program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997a). Molecular graphics: *XPW* (Siemens, 1996). Software used to prepare material for publication: *PARST95* (Nardelli, 1995) and *SHELXL97*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: NA1363). Services for accessing these data are described at the back of the journal.

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2'-(1,3-Dithiolan-2-ylidene)-4'-(1,3-dithiol-2-ylidene)spiro[1,3-dithiole-2,5'-(4*H*-5',6'-dihydro-1',3'-dithiapentalene)], the Self-Condensation Product of an Extended Tetrathiafulvalene Derivative

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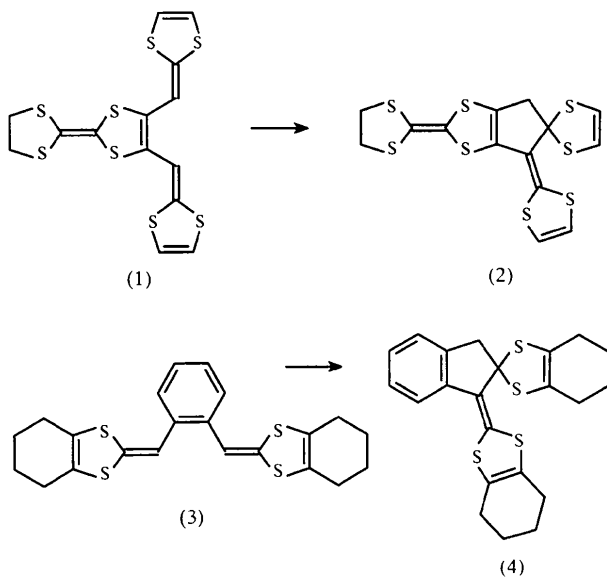
Abstract

Silica-gel treatment of the extended tetrathiafulvalene derivative 2,3-bis(1,4-dithiafulven-6-yl)-6,7-dihydro-tetrathiafulvalene, bearing two 1,4-dithiafulven-6-yl groups in vicinal positions, afforded the title compound, C₁₄H₁₀S₈, as a cyclization product. While one dithiafulvenyl group is still conjugated with the tetrathiafulvalene moiety, the other one gives rise to a strongly folded 1,3-dithiole group linked to the molecule through a spiro-C atom. Two short non-bonding intramolecular 1,5-S···S contacts are also identified in the title compound.

Comment

Extended tetrathiafulvalene derivatives such as (1) (see scheme below) have proved to be interesting candidates as precursors for the synthesis of novel organic conducting materials (Sallé *et al.*, 1996). We recently reported that the electrocrystallization of (1) in the presence of *n*-Bu₄NClO₄ affords a 1:1 salt with ClO₄[−] (Sallé *et al.*, 1993). This salt exhibits a novel mode of overlap, which allows the outer dithiafulvenyl groups of (1) to interleave in a direction perpendicular to the stacking axis.

However, other attempts to electrocrystallize this donor proved very disappointing. One possible explanation lies in the difficult purification of (1), since attempted chromatography (on silica gel) leads to its irreversible degradation. Attempts to substitute deactivated alumina for silica gel proved unsuccessful. An intramolecular transformation has already been identified in similar systems bearing two dithiafulvalenyl groups, such as (3), from which an acid-catalyzed process was shown to generate the novel spiro heterocycle (4), whose structure has been reported (Benahmed-Gasmi *et al.*, 1993; Frère *et al.*, 1994). During our purification trials of (1), we isolated a similar cyclized compound, (2), crystallized from CS₂, whose structure is described here.



Important bond distances in the conjugated part of (2) are given in Table 1. The C—S bond lengths of the conjugated part of the molecule compare favourably with those observed, for example, in the neutral tetrathiafulvalene (1.72–1.76 Å; Cooper *et al.*, 1971), while the C—S bonds involving Csp³ atoms (C5, C6 and C8) are notably longer. Except for the outer ethylenic bridge (C5=C6), the dihydrotetrathiafulvalene moiety is almost planar, with a folding angle between the S3/C4/S4 and C3/S1/C1/C2/S2 mean planes of 2.2 (5)°, while atoms C5 and C6 are displaced from the S3/C4/S4 mean plane by 0.165 (9) and 0.819 (9) Å, respectively. The dithiafulvalene ring (built on S5 and S6) is nearly coplanar [1.7 (2)°] with the dithiole ring (built on S1 and S2) of the tetrathiafulvalene moiety, confirming the extended π delocalization. On the other hand, the new C1/C2/C7/C8/C11 ring is slightly distorted [atoms C7 and C8 are displaced above and below the C1/C2/C11 mean plane by 0.19 (1) and 0.09 (1) Å, respectively], and the spiro-linked dithiole ring (built on S7 and S8) is strongly folded [35.1 (2)°] along the S7···S8 axis, away

from the dithiafulvalene ring (built on S5 and S6). Such a large folding angle is frequently observed in 1,3-dithiole rings with a Csp³ atom in the 2-position (Krebs *et al.*, 1993, and references therein). Of particular note are the short non-bonding intramolecular S···S distances observed for S1···S5 and S6···S8, at 3.160 (2) and 3.241 (2) Å, respectively. Albeit larger than in (1), where similar short S···S distances are observed at 3.035 and 3.031 Å, this distance is still much shorter than the sum of the van der Waals radii (3.6 Å) and indicates the occurrence of a strong intramolecular S···S interaction, as discussed recently by Favard *et al.* (1998).

In the solid state, the molecules associate in pairs about inversion centres, with the shortest intermolecular S···S contact within a pair observed at 3.576 (3) Å, a slightly shorter distance than the sum of the van der Waals radii.

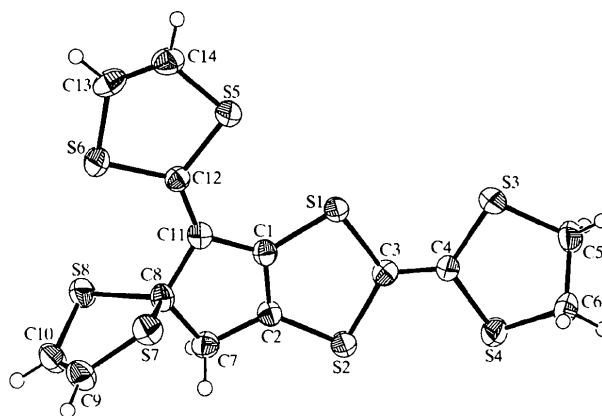


Fig. 1. The molecular structure of (2), showing 50% probability displacement ellipsoids. H atoms are drawn as spheres of arbitrary radii.

Experimental

The title compound was obtained by elution of a solution of (1) in toluene on a silica-gel column following a Soxhlet extraction (dichloromethane) of the crude compound. The preparation of (1) has been described elsewhere (Sallé *et al.*, 1996).

Crystal data

C₁₄H₁₀S₈
M_r = 434.70
 Monoclinic
*P*2₁/*n*
a = 9.1055 (8) Å
b = 13.124 (2) Å
c = 13.796 (3) Å
 β = 92.429 (11)°
V = 1647.1 (4) Å³
Z = 4
D_v = 1.753 Mg m⁻³
D_m not measured

Mo K α radiation
 λ = 0.71073 Å
 Cell parameters from 25 reflections
 θ = 4.8–13.1°
 μ = 1.074 mm⁻¹
T = 293 (2) K
 Parallelepiped
 0.12 × 0.12 × 0.12 mm
 Red

Data collection

| | |
|--|-------------------------------------|
| Enraf–Nonius CAD-4 diffractometer | $R_{\text{int}} = 0.042$ |
| $\omega/2\theta$ scans | $\theta_{\text{max}} = 25.97^\circ$ |
| Absorption correction: none | $h = -1 \rightarrow 11$ |
| 4100 measured reflections | $k = -1 \rightarrow 16$ |
| 3163 independent reflections | $l = -16 \rightarrow 16$ |
| 1754 reflections with $I > 2\sigma(I)$ | 3 standard reflections |
| | frequency: 60 min |
| | intensity decay: none |

Refinement

| | |
|---|---|
| Refinement on F^2 | $(\Delta/\sigma)_{\text{max}} < 0.001$ |
| $R(F) = 0.040$ | $\Delta\rho_{\text{max}} = 0.480 \text{ e } \text{Å}^{-3}$ |
| $wR(F^2) = 0.086$ | $\Delta\rho_{\text{min}} = -0.365 \text{ e } \text{Å}^{-3}$ |
| $S = 1.116$ | Extinction correction: none |
| 3163 reflections | Scattering factors from |
| 199 parameters | International Tables for |
| H atoms constrained | Crystallography (Vol. C) |
| $w = 1/[\sigma^2(F_o^2) + (0.0448P)^2 + 0.5754P]$ | |
| where $P = (F_o^2 + 2F_c^2)/3$ | |

Table 1. Selected bond lengths (Å)

| | | | |
|--------|-----------|--------|-----------|
| S1—C1 | 1.755 (4) | S6—C13 | 1.737 (5) |
| S1—C3 | 1.776 (5) | S6—C12 | 1.756 (5) |
| S2—C2 | 1.726 (5) | S7—C9 | 1.740 (5) |
| S2—C3 | 1.767 (4) | S7—C8 | 1.854 (4) |
| S3—C4 | 1.757 (4) | S8—C10 | 1.744 (5) |
| S3—C5 | 1.818 (5) | S8—C8 | 1.839 (4) |
| S4—C4 | 1.760 (4) | C1—C2 | 1.347 (6) |
| S4—C6 | 1.810 (5) | C1—C11 | 1.439 (6) |
| S5—C14 | 1.730 (5) | C3—C4 | 1.326 (6) |
| S5—C12 | 1.761 (4) | | |

Data collection: CAD-4-PC (Enraf–Nonius, 1994). Cell refinement: CAD-4-PC. Data reduction: XCAD4 (Harms, 1993). Program(s) used to solve structure: SHELXS86 (Sheldrick, 1990). Program(s) used to refine structure: SHELXL93 (Sheldrick, 1993). Molecular graphics: ORTEPII (Johnson, 1976). Software used to prepare material for publication: SHELXL93.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG1493). Services for accessing these data are described at the back of the journal.

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Dibromo[(Z)-2-bromo-2-(hydroxymethyl)-vinyl](n-butyl)tellurium(IV)

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Abstract

In the title compound, [TeBr₂(C₄H₉)(C₃H₄BrO)] or C₇H₁₃Br₃OTe, the primary geometry about the Te^{IV} atom is a pseudo-trigonal-bipyramidal arrangement with axial bromines and one equatorial position vacant. If an intermolecular secondary Te···O bond of 3.041 (5) Å, *trans* to the Te—C(vinyl) bond, is taken into consideration, the structure may be regarded as pseudo-octahedral. Distances and angles are: Te—Br 2.7295 (10) and 2.6115 (10), Te—C 2.092 (6) and 2.134 (7) Å, Br—Te—Br 176.59 (3), Br—Te—C 88.87 (19), 89.0 (3), 89.65 (19) and 88.2 (3), and C—Te—C 99.7 (3)°. The lattice is formed by hydrogen-bonded centrosymmetric dimers [O···Br = 3.399 (6) Å], which, in turn, are linked by the intermolecular secondary Te···O bond.

Comment

Vinyl tellurides are intermediates in the synthesis of vinyl lithium compounds, which are, in turn, important intermediates in organic synthesis, either as precursors of the widely used vinyl cuprate compounds or as nucleophiles leading to chain-elongation products by