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A Unique Molecular Donor Containing Two Tetrathiafulvalene (TTF) Units Fused to 1,4 - Ditellurin: Synthesis, X-Ray Structure and Cyclic Voltammetry

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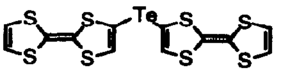
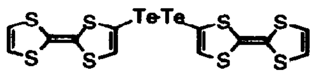
Abstract: A new molecular donor composed of two TTF moieties fused to 1,4-ditellurin (3) has been synthesized and the structure has been characterized by X-ray diffraction. The cyclic voltammetry of both 3 and its methyl analogue 4 display two reversible two-electron oxidation waves.

The synthesis of molecular donors containing covalently bridged TTF moieties (dimeric TTF) is attracting considerable attention of chemists in pursuit of improved organic electrical conductivity and superconductivity. The type and nature of the bridge in such donor systems are perhaps the most decisive factors that influence their electrochemical behavior and solid state properties. For the past few years, quite a few dimeric TTF structures incorporating different linkages have been prepared[1-8]. Among these, only two incidentally obtained dimeric TTFs containing respectively one and two tellurium atoms as a single bridge (1[1a] and 2[1b]) have been reported. Due to the very limited solubility of 2 in common organic solvents, the cyclic voltammetry of only 1 was studied, but it showed interesting oxidation features, possibly related to the bridge tellurium atom[1a]. However, the lack of additional examples of similar tellurium containing compounds, which are considered promising donor systems for producing conductive or superconductive material, has made their solution electrochemistry and their solid state properties somewhat enigmatic. Here we report the one-pot synthesis and X-ray structure of a unique dimeric TTF (3) featured by a fused 1,4-ditellurin ring acting as a rigid double bridge between the two TTF units. The cyclic voltammetries of 3 and its methyl analogue 4[2], which exhibit different features from that of 1, are also reported.



1



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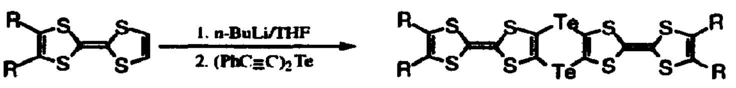
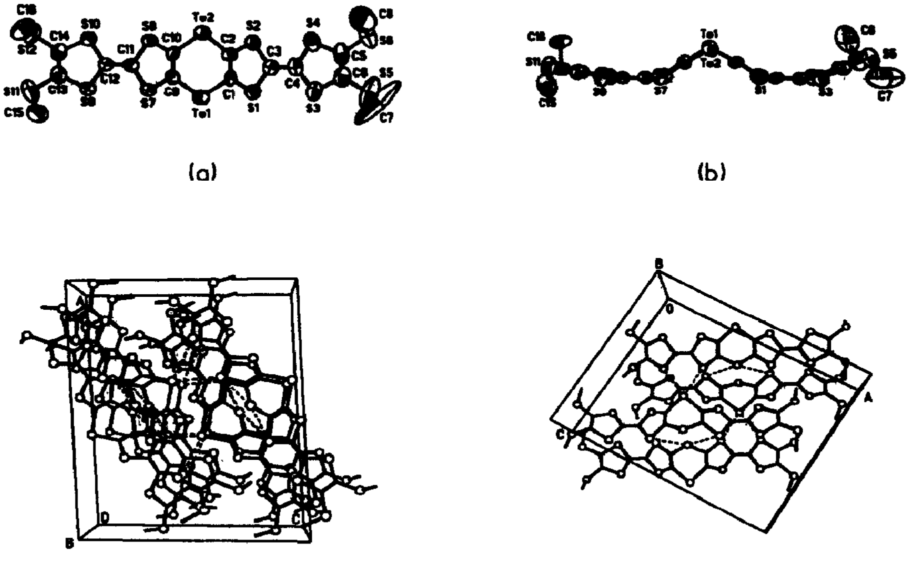


3: R = MeS 4: R = Me

To a solution of 2,3-bis(methylthio)TTF[9] (30 mg, 0.1 mmol) in 5 ml of dry THF, BuLi (0.21 mmol) was syringed in at -40 °C dropwise under argon. The mixture was stirred for 1 h then cooled to -60 °C, followed by the addition of solid bis(phenylacetylenyl) telluride (33 mg, 0.1 mmol) in one portion. The cooling and stirring conditions were maintained 4 h with the original cooling liquor in a Dewar flask and a magnetic stirrer. Afterwards, the cooling bath was removed and the reaction completed by overnight stirring at rt. The solvent was removed by vacuum evaporation and the residual was washed several times with water, dissolved in CS_2 and filtered through silica gel. The filtrate was concentrated and purified by silica gel chromatography with 1:1 mixture of 40-60 °C petroleum ether and CS_2 as eluent, yielding 11 mg (26%) of 3. Crystallization of 3 from CS_2 affords dark yellow plates in good quality[10]. The crystal of 3 was not stable when subjected to heating in air. It changed into an opaque black solid at about 270 °C, and no melting point could be obtained.



(a)

(b)

(c)

(d)

Figure 1. (a) Top view of molecular structure of 3. (b) Edge-on view of 3. (c) and (d) Packing of 3, showing the Te···S contacts less than 3.86 Å.

The X-ray single crystal analysis of 3 shows that the molecules in the crystal exhibit a non planar " sombrero-like" conformation (Fig.1b). It has been shown that attaching methylthio groups onto TTF periphery can lead to distortion of its 1,3-dithiole five-membered ring[11]. In the molecule of 3 the same kind of distortion (folding around the transannular S3···S4 and S9···S10 axes) was found. At the same time, the dithiole rings which are fused to the central six-membered 1,4-ditellurin are also bent about the S1···S2 and

S7···S8 axes. The ditellurin ring has the same conformation as in 4 with very similar C-Te-C angels (in 3, 97.1°, 92.3°; in 4^2, 92.3°, 93.6° respectively). In spite of the fact that no stacks are found in the structure of 3, a 2-D network of short Te···S contacts are observed (Figure 1c, 1d). The packing in this structure is again similar to that in 4, but in the latter S···S interactions appear to dominate. It is the formation of these two-dimensional networks which is believed to be a necessary condition for electrical conductivity in complexes and salts of TTF derivatives, and the existence of such a network in both 3 and 4 holds some promise that their complexes and salts will be conducting as well.

As witnessed by the structures of tetrakis(methylthio) TTF in both neutral and charged states[12], this kind of dithiole distortion in 3 and 4^2 could possibly be suppressed by doping, and molecular stacks with extended Te···S and S···S networks might also be brought about at the same time.

The solution electrochemistry of 3 as well as its methyl analogue 4 have been studied by cyclic voltammetry and the potentials are summarized in Table 1. Both 3 and 4 exhibit a pair of two-electron redox couples and repeated cycling between 0.00 V and 1.20 V established that these two waves are reversible. Further scanning up to +1.60 V does not lead to any other oxidations. This is different from the single tellurium bridged system 1, which displays a third irreversible oxidation wave.

Table 1. Half Wave Potentials of Some Related Donors (V)^a

Compounds	$E^1_{1/2}$	$E^2_{1/2}$	$E^3_{1/2}$	$\Delta E = E^2_{1/2} - E^1_{1/2}$
3^b	0.57	0.84		0.27
2,3-$(MeS)_2$TTT^b	0.50	0.83		0.33
4^c	0.48	0.83		0.35
2,3-Me_2TTF^b	0.36	0.79		0.43
1^d	0.47	0.85	1.0	0.38
TTF^b	0.42,	0.83		0.41

a) Supporting electrolyte: 0.1 M TBA-ClO_4 in PhCN. Working electrode: Pt. Reference : Ag/AgCl. Sweep rate: 100 mV/s. b) 2.5 x 10^{-4}M. c) saturated. d) Data from ref. 1a and corrected to TTF $E_{1/2}$ (0.42, 0.38 V)

The absence of the third and more oxidation stages from 3 and 4 might be accounted for by considering the tellurium double bridge as an "electronic isolator". It divides the molecule into two nearly independent TTF halves and prevents intramolecular coulombic interactions between them. In contrast, π-extended dimeric and oligmeric donor systems usually result in more than two redox stages, though a whole molecular charge delocalization is still in question, as reviewed by Mullen and coworker quite recently[8]. The other possible explanation is that the additional oxidation waves in some of the multiple TTF systems are resulted from intermolecular interactions such as complexion between the charged and uncharged donor moieties. The formation of the ditellurin ring in 3, 4 and cyclizations in other previous examples[4,6] lead to molecular rigidity and restricted geometry, therefore, prevent from intermolecular interactions during the oxidation.

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10. Crystallographic data: An orange plate of 3 (0.38 x 0.31 x 0.11 mm) was used for X-ray structure analysis: $C_{16}H_{12}S_{12}Te_2$, monoclinic, sp.gr. $P2_1/c$, at 298K, a= 19.521(4), b= 8.571(2), c=15.877(4)Å, β= 92.81(2)°, Z=4, V= 2653(1) $Å^3$, F(000)=1616. 4609 reflections were collected on a Syntex $P\bar{1}$ diffractometer [$\lambda(MoK_\alpha)$ =0.71069Å, graphite monochromator, $\omega/2\theta$–scan, $2\theta < 48°$]. 2297 reflections with $F_o > 4\sigma(F_o)$ were observed from 2382 independent reflections. The structure was solved by direct methods and refined by least-squares in full-matrix approximation for non-hydrogen atoms: 271 parameters, R= 4.69%, Rw = 4.76%, GOF = 1.47. The hydrogen atoms were included at geometrically calculated positions and U_{iso}= 0.08$Å^2$. DIFABS was done for absorption correction. SHELX-76 and SHELX-86 programs were used for all calculations and SCHAKAL-92 for drawings. Atomic coordinates, bond lengths and angles and anisotropic parameters have been deposited at the Cambridge Crystallographic Data Center.
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