

A New Molecular Donor Containing Two Tetrathiafulvalene (TTF) Units Fused to 1,4-Ditellurine: Synthesis, X-Ray Structure, CT Complex and Conductivity

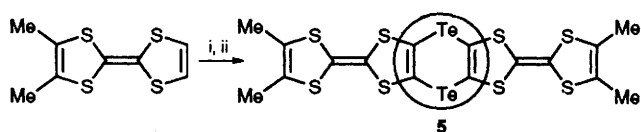
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The one-pot synthesis and X-ray structure of a new and unique donor containing two TTF units fused to a ditellurine ring, and its conducting charge transfer (CT) complex with 2,5-dimethyl-tetracyano-*p*-quinodimethane, are described.

It is quite well established that the introduction of heavy atoms into the molecular components of synthetic metals, particularly donor molecules, increases the intrastack interactions in the solid state and therefore leads to larger conduction bandwidths.¹ Furthermore, heavy atoms also reduce the on-site Coulombic repulsion due to their greater polarizability, and increase interchain interactions which result in extended dimensionality. The latter affords better conductivity in charge transfer (CT) complexes and ion radical salts.¹ The number of tetrathiafulvalene (TTF) derivatives containing tellurium atoms is quite limited compared with sulfur and selenium derivatives, mainly due to the synthetic difficulties encountered with tellurium chemistry. We have reported² that the reaction of $(\text{LiTe})_n\text{TTF}$ intermediates with ethyl iodide affords bis- and tetra-telluro derivatives, **1** and **2**, respectively. In continuing work, Saito and his coworkers³ have developed a synthesis of **2** with a variety of alkyl chain-lengths ($\text{C}_1\text{--C}_{18}$). Quite recently⁴ we have submitted a paper which deals with the synthesis of phenyltelluro analogues of **1** and **2**, by a different method. Attempts to react $(\text{LiTe})_n\text{TTF}$ intermediates with *cis*-1,2-dichloroethylene, or with *o*-dichlorobenzene or 1,1-dichloroethylene, afforded the unexpected products, bistetrathiafulvalenyl telluride **3**⁵ and the corresponding ditelluride **4**,⁶ respectively, instead of the anticipated fused, rigid systems.

Reported herein is the first one-pot synthesis of a donor composed of two TTF moieties linked to each other by two tellurium atoms, which results in a rigid, fused system containing a ditellurine ring (circled) **5** (Scheme 1). The only other reported examples which contain a ditellurine ring are the fused systems of tetratelluranaphthalene⁷ and tetratelluradi-cyclopenta[*b,g*]naphthalene.⁸



Scheme 1 Reagents: i, $\text{Bu}^n\text{Li}/\text{THF}$; ii, $(\text{PhC}\equiv\text{C})_2\text{Te}$

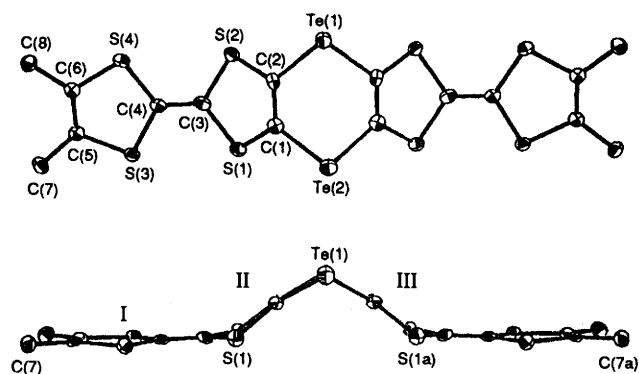


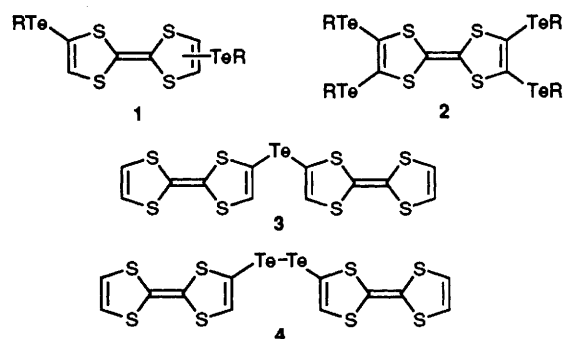
Fig. 1 ORTEP drawings of the molecule **5** at the 50% probability level. Hydrogens have been omitted. (a) View on the molecular plane. (b) View following rotation of (a) 90° about the horizontal axis. The mean deviations from the planes are I -0.048 \AA , II -0.056 \AA . The dihedral angles are I–II 33.1° , II–III 67.8° .

In a typical experiment for the synthesis of **5**, a solution of 2,3-dimethyl TTF⁹ (46.6 mg, 0.2 mmol) in dry THF (10 ml) was cooled to -65°C under argon. *n*-Butyllithium (0.48 mmol) was added dropwise at low temperature, followed by stirring (0.5 h) to afford a yellow transparent solution. Then, a tellurium(II) reagent, bis(phenylacetylenyl) telluride¹⁰ (BPAT, 82 mg, 0.25 mmol), was introduced in one portion and the mixture was stirred for an additional 3 h at -65°C . The temperature was then gradually elevated to -30°C during 4 h, followed by removal of the cooling bath. Overnight stirring at room temperature and suction filtration yielded an orange precipitate which was subjected to washing with THF, H_2O and acetone (each with $3 \times 5 \text{ ml}$). Crystallization of the solid from acetophenone afforded brown-reddish flakes (45.3 mg, 63%), which blacken at about 250°C and gives no melting point below 300°C . Its $^1\text{H NMR}$ (in CS_2) shows one singlet at $\delta 1.72$ (relative to TMS). Slow evaporation of the CS_2 solution afford crystals suitable for X-ray structure analysis.

The molecular and crystal structures of **5**[†] exhibit some unique features. The molecule lies on a mirror plane containing the two Te atoms and the ditellurine moiety is not planar, adopting a boat conformation with an angle of 67.8° around the $\text{Te}\cdots\text{Te}$ axis, which is not unexpected in view of its similarity to 1,4-dioxine. The TTF units are both significantly bent around the intramolecular $\text{S}\cdots\text{S}$ axis [Fig. 1(b)] so that the two (non-planar) TTF moieties form a dihedral angles of 33° with the two mirror-related $\text{Te}\text{--C=C}\text{--Te}$ planes. A similar, but unsymmetric, bending around both $\text{S}\cdots\text{S}$ axes (of 19° and 24°) has been observed in tetrakis(methylthio)-TTF.^{6,13}

The crystal structure is shown in Fig. 2. The *a*-glide leads to a staggered stack [Fig. 2(a)], 'inside' of which there the distance between neighbouring Te atoms is 4.25 \AA , which is just the sum of the van der Waals radius. However, the same Te atom is involved in two symmetrically related $\text{Te}\cdots\text{S}$ contacts of 3.66 \AA [Fig. 2(b)]. This geometric registry of this interaction appears to complement the 'bowed' nature of the molecular conformation, and while we have no evidence to prove that there is a relationship between this interaction and the unusual molecular conformation, the coincidence of the two is suggestive of a connection between them. There is virtually no interaction of stacks related by a translation along the *c* crystal axis, but an interleaving of stacks *via* $\text{S}\cdots\text{S}$ interactions of 3.62 \AA in the slab *y ca. 1/2*, is evident through screw axis related molecule. All other $\text{S}\cdots\text{S}$ distances are greater than 3.70 \AA .

Due to the poor solubility of **5** in most common organic solvents, we were unable to study its electrochemical behav-



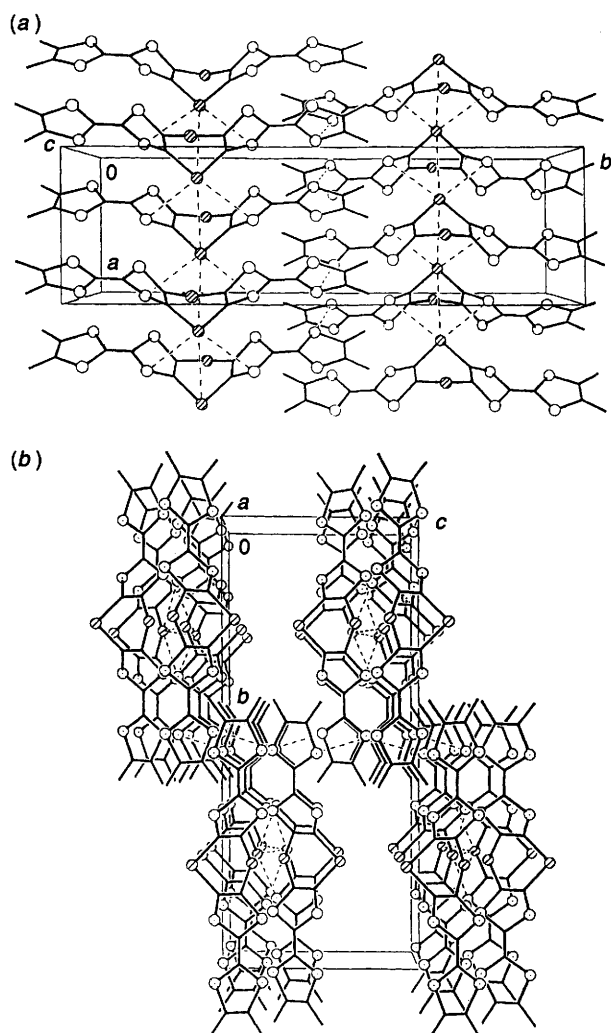


Fig. 2 Two views of the crystal structure of **5**. (a) View on (100). (b) View on (001). In both cases distances equal to and less than the sum of the van der Waals radii (Te = 2.13, S = 1.85 Å) are denoted by dashed lines. Te(2)⋯Te(2) (−0.5 + x, y, 1.5 − z) and Te(2)⋯Te(2) (0.5 + x, y, 1.5 − z) 4.25, Te(2)⋯S(2) (0.5 + x, y, 1.5 − z) and Te(2)⋯S(2) (0.5 + x, 0.5 − y, 1.5 + z) 3.66, S(3)⋯S(4) (−0.5 − x, 1 − y, 0.5 + z) 3.62 Å.

our by cyclic voltammetry. Also, attempts to form CT complexes with various acceptors (tetracyano-*p*-quinodimethane, *p*-dicyanoquinodimine, 2,3-dichloro-5,6-dicyano-benzoquinone and tetracyano-*p*-benzoquinone) were generally unsuccessful. However, in one case, tiny black needles of a complex were obtained by diffusing a CS₂ solution of **5** with acetonitrile solution of 2,5-dimethyltetracyano-*p*-quinodimethane (DMTCNQ). Room temperature electrical conductivity measurement of a pressed pellet of the complex, using the four-probe technique, shows a conductivity of ca. 6 S cm^{−1}.

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Footnote

† Crystal structure for **5**: C₁₆H₁₂S₈Te₂, orthorhombic, space group *Pnma*, at 153 K; *a* = 7.815(3), *b* = 25.990(8), *c* = 11.397(5) Å, *Z* = 4, ρ = 2.05 Mg m^{−3}, μ(Mo-Kα) = 3.24 mm^{−1}, *F*(000) = 1360. 1931 unique reflections with *F*_o > 4σ(*F*) were collected from a total 2138 independent reflections with Syntex P2, diffractometer with LT-1 low temperature device [λ(Mo-Kα) = 0.71069 Å, graphite monochromator, ω/2θ-scan, 2θ < 48°]. The structure was solved by direct methods and refined by full-matrix least-squares procedure using SHELX-86 and SHELX-76¹¹ respectively to *R* = 0.047, *R*_w = 0.0424, GOF = 2.27. SCHAKAL 92¹² was used for drawing all figures.

Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

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