Synthesis and X-Ray Structure of a Novel Organoditelluride: Di(tetrathiafulvalenyl) Ditelluride [(TTFTe)$_2$]

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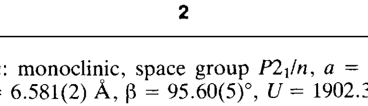
The synthesis, crystal structure and conductivity of TTF (tetrathiafulvalene) disubstituted ditelluride [(TTFTe)$_2$] are described.

Very few examples of molecules which contain two TTF units are known. These examples include TTF moieties linked directly to form a conjugated dimer,[1] or indirectly *via* a fused ring system,[1] bridges[2] of –S[CH$_2$]$_n$S– and $C_6H_4(CH_2S\text{–})_2$ (3 isomers), or a chalcogen atom: Te,[3] Se[4] and S.[4,5]

In the present paper we report the preparation, crystal structure and conductivity of a unique molecule **1** which involves two TTF moieties linked *via* ditelluride. The new compound was obtained by coincidence, following our previously published procedure of attaching Te atoms into the TTF frame.[5] We intended to react *in situ* the tetratelluride of TTF with *ortho*-dichlorobenzene, in order to obtain the multi-fused system **2**. Instead, compound **1** was isolated in 28% yield; presumably the *ortho*-dichlorobenzene plays the role of an electron acceptor in this process. In a typical experiment, Li$_4$TTF (1 mmol) in tetrahydrofuran (THF; 30 ml) was prepared at −78 °C and stirred for 2 h under argon atmosphere.[6] Amorphous Te (520 mg) was then added to the cold mixture. The latter was slowly allowed to warm to room temperature and left under argon overnight, then cooled again to −78 °C, following which *ortho*-dichlorobenzene (2.5 mmol) in THF (5 ml) was introduced. The mixture was warmed to 0 °C, and water and chloroform were added. Filtration yielded (90 mg, 28%) a red-purple crystalline material of **1**. ^{1}H NMR in CS$_2$–CDCl$_3$ showed two singlets at δ 6.25 (4H) and 6.52 (2H); MS(EI) afforded a molecular ion at *m/z* 662 (36%) (based on ^{128}Te). Compound **1** is insoluble in most common organic solvents, but slightly soluble in CS$_2$, from which knife-shaped opaque black crystals were precipitated, by slow cooling and subsequent evaporation. The melting point could not be determined since the compound apparently undergoes a solid state reaction during heating. Owing to its very limited solubility, no electrochemical measurements could be carried out to characterize its redox properties. However, four-probe conductivity measurements could be conducted on small single crystals of **1** (dimensions 0.42 × 0.14 × 0.08 mm, elongated along [001]), by developing a new technique which is based on photolithography methods used for printed circuits, scaled down in this case to microscopic dimensions.[7] The results of these measurements clearly indicate that compound **1** is a semiconductor (5×10^{-5} S cm^{-1}). This property of an *undoped* donor containing Te atoms being a semiconductor has been observed before by a Japanese group.[8] The molecular structure[†] is shown in Fig. 1. The dihedral angle between the essentially planar [maximum deviation = 0.007(4) Å] TTF units is 38.6°, and the torsion angle about the Te(1)–T(2) bond is 80.9(5)°.

1



2

[†] *Crystal data*: monoclinic, space group $P2_1/n$, a = 24.734(5), b = 11.743(3), c = 6.581(2) Å, β = 95.60(5)°, U = 1902.3(1.4) Å^3, D_c = 2.295 g cm^{-3}, M = 661.2, Z = 4, λ(Mo-Kα) = 0.71069 Å. The irregular shape of the crystals obviated the determination of the crystal form. Of a total of 2607 unique reflections 2048 independent ones above the 2σ level were observed. The final residuals based on a weighting scheme $w = 2.0259/[\sigma^2(F) + 0.0006F^2]$ were R = 0.0495, R_w = 0.0511, for 199 parameters, including anisotropic refinement of all the non-hydrogen atoms and fixed positions for the hydrogen atoms based on the geometry about the carbon atom to which they were attached. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

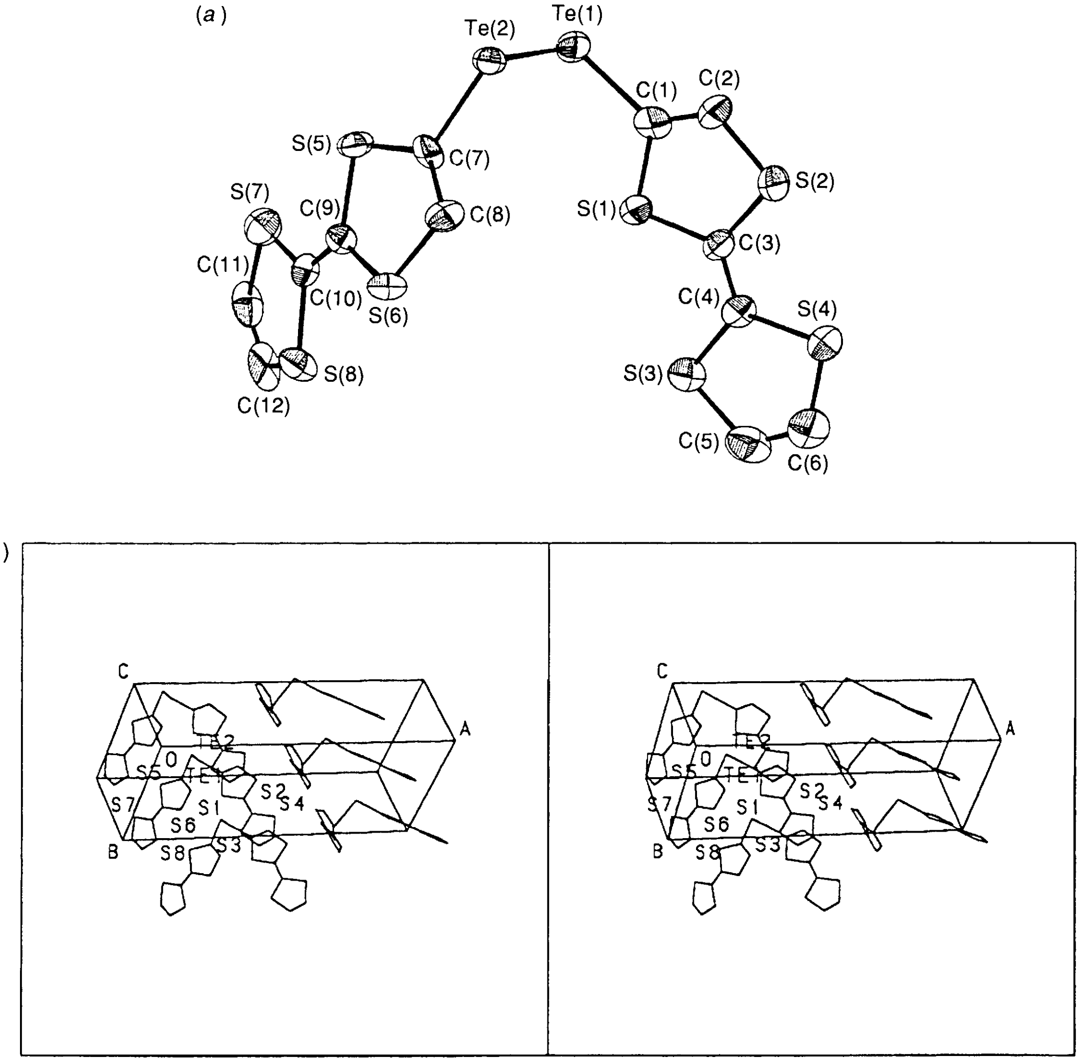


Fig. 1 (*a*) ORTEP plot of the molecule, including atomic numbering. Selected geometric features and those exhibiting statistically different values for chemically equivalent pairs: Te(1)–Te(2) 2.734(1) Å; Te(2)–Te(1)–C(1) 99.9(4)°; Te(1)–Te(2)–C(7) 97.7(4)°; S(1)–C(1)–Te(1) 116.1(8)°, S(5)–C(7)–Te(2) 120.6(6)°; C(2)–C(1)–Te(1) 127(1)°, C(8)–C(7)–Te(2) 120(1)°; C(2)–C(1)–S(1) 116(1)°, C(8)–C(7)–S(5) 120(1)°; C(7)–C(8)–S(6) 115(1)°, C(1)–C(2)–S(2) 119(1)°; Te(1)–Te(2)–C(7)–S(5) −77.9(7)°; Te(2)–Te(1)–C(1)–S(1) 92.5(7)°. (*b*) Stereoview of the crystal structure, showing the stacking along the *c* axis. The molecule with labels for Te and S is that for the published coordinates. Those above and below are related by translations along the *c* crystallographic axis. The neighbouring stack of molecules is related by the glide operation. For the sake of clarity, molecules related by the screw axis and the inversion centre have not been included.

The crystal structure of **1** is formed by stacks due to translation along the *c* crystallographic axis [Fig. 1(*b*)], with a plane-to-plane relationship for neighbouring S(1)–S(4) TTF rings, and an edge-to-edge relationship for the S(5)–S(8) TTF units. The nature of the plane-to-plane registry and *c*-axis length of 6.6 Å preclude any short S···S distances, but there are notable Te···S distances of 4.034(4), 3.530(4) and 3.851(5) Å for Te(1) with S(1), S(3) and S(6), respectively, while the last sulfur is 3.740(4) Å from Te(2). There are also edge-to-edge contacts which are not significant. Other remarkable intermolecular distances include Te(2)···S(4) (related by the screw axis on *b*) 3.739(5) Å; Te(2)···S(6) (related by the inversion centre) 3.487(4) Å; S(4)···S(7) (related by the *n*-glide) 3.635(7) Å. Additional details of the structure, together with band calculations will be discussed in a separate publication.[9]

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