There would appear to be no abnormal bond lengths. The molecules lie in columns parallel to the *a* axis, and adjacent molecules within each column are antiparallel (Fig. 2). The normal to the weighted least-squares molecular plane is 41·20 (1)° offset with respect to the column axis; this plane makes an angle of 3·18 (3)° with the (212) plane. The interplanar spacing for (212) planes is 3·306 Å and because there are substantial deviations from the molecular plane, all molecular distances (excluding those involving hydrogen) below 3·50 Å were calculated; there are 16 of these. The intermolecular linkages are due to van der Waals forces and there are no abnormal intermolecular distances.

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The Structure of 3,3′,4,4′-Tetrakis(ethyltelluro)-2,2′,5,5′-tetrathiafulvalene (TTeC$_2$-TTF)

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Abstract. $C_{14}H_{20}S_4Te_4$, tetra(telluroethyl)-TTF (TTeC$_2$-TTF), $M_r = 826{\cdot}4$, monoclinic, $P2_1/n$, $a = 9{\cdot}242\ (2)$, $b = 9{\cdot}039\ (3)$, $c = 14{\cdot}787\ (6)$ Å, $\beta = 112{\cdot}92\ (2)°$, $V = 1137{\cdot}8\ (6)$ Å^3, $Z = 2$, $D_x = 2{\cdot}41$ g cm^{-3}, λ(Mo $K\alpha$) $= 0{\cdot}71069$ Å, $\mu = 50{\cdot}7$ cm^{-1}, $F(000) = 752$, $T = 293$ K, final $R = 0{\cdot}062$ for 2026 independent observed reflections, $wR = 0{\cdot}065$. The ethyl groups which are directed out of the TTF-moiety plane prevent close approach of the molecules. The shortest Te···Te distance is 3·99 Å which is 0·35 Å longer than that reported for TTeC$_1$-TTF.

Introduction. Te-TTF derivatives are promising molecular π donors for a number of reasons. On the one hand they are expected to stabilize further (compared to the S and Se analogs) the metallic state of radical cation salts derived from them owing to increased intrachain coupling; on the other hand they may increase interchain interactions owing to short intermolecular Te···Te distances analogous to the Se···Se distances found in Se-TTF derivatives (Williams *et al.*, 1985) and the interchain Te···Te distances in elemental tellurium (Cherin & Unger, 1967).

The chemistry of organic tellurium donors has been developing in recent years since the synthesis of

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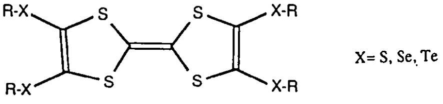
Table 1. *Atomic coordinates* (× 10^4) *and* U_{eq} (Å^2 × 10^4) *for* $TTeC_2$-*TTF*

	x	y	z	U_{eq}
Te(1)	1090 (1)	5849 (1)	1698 (1)	476 (4)
Te(2)	66 (1)	1739 (1)	921 (1)	645 (4)
S(1)	−2733 (3)	6193 (3)	512 (2)	42 (1)*
S(2)	−3520 (3)	3053 (3)	84 (2)	45 (1)*
C(1)	−1161 (1)	4907 (1)	916 (7)	37 (4)*
C(2)	−1536 (1)	3508 (1)	710 (7)	40 (4)*
C(3)	−423 (1)*	485 (1)*	123 (7)	35 (4)*
C(4)	48 (2)*	647 (2)*	295 (1)*	68 (7)*
C(5)	62 (2)*	519 (2)*	359 (1)*	87 (9)*
C(6)	−117 (2)*	12 (2)*	140 (1)*	73 (7)*
C(7)	−113 (2)*	47 (2)*	238 (1)*	90 (9)*
C(3′)	−577 (1)*	515 (1)*	−123 (7)	35 (4)*

* × 10^3 for these figures.

HMTTeF* (Wudl & Aharon-Shalom, 1982). Owing to synthetic difficulties, however, only a relatively few donors of this kind have been prepared (Cowan *et al.*, 1985). The recently reported Te-TTF derivative $TTeC_1$-TTF [(I), R = Me, X = Te], a 'molecular fastener' (Inokuchi *et al.*, 1987), exhibits a Te···Te···Te zigzag structure and is a high-mobility organic one-component semiconductor.



(I)

We have previously reported the synthesis (Aharon-Shalom, Becker, Bernstein, Bittner & Shaik, 1985*a*) of (I) (R = Et, X = Te) and the structure of its complex with TCNQ (Aharon-Shalom, Becker, Bernstein, Bittner & Shaik, 1985*b*). We report here the structure of $TTeC_2$-TTF [(I), R = Et, X = Te] which is the second member of this family of Te-TTF derivatives.

Experimental. Crystals of good quality were obtained by recrystallization from chloroform/petroleum ether (approx. 4:1). Single-crystal melting point is 360·9–362·0 K (Mettler FP-52). X-ray single-crystal data were collected on a Syntex $P\bar{1}$ diffractometer, employing a graphite monochromator. Unit-cell constants were obtained by a least-squares fit of 2θ values for 15 reflections ($28 < 2\theta < 41°$); intensities of 2297 unique reflections, h = 0–±10, k = 0–10, l = 0–14, $\omega/2\theta$ scans ($2\theta < 50°$); three reflections (103, 32$\bar{4}$, 320) monitored every 60 reflections during data collection indicated no crystal deterioration; intensities were corrected for Lorentz and polarization effects, but not for absorption since the data crystal was ground to a nearly spherical shape: 0·15 × 0·12 × 0·10 mm. 2026 reflections considered as observed [$I > 3\sigma(I)$]. The structure was solved by Patterson methods using *SHELX*86 (Sheldrick, 1986) and refined *via* least squares by *SHELX*76 (Sheldrick, 1976). Scattering factors were from *International Tables for X-ray Crystallography* (1974). Minimization with anisotropic thermal parameters of $\sum w(|F_o| - |F_c|)$ with $w = 1$ converged at $R = 0{\cdot}07$. Even though some of the H atoms were located in the difference Fourier map, all H atoms were calculated at convergence for the heavy-atom refinement and neither their positions nor their isotropic thermal parameters were varied in subsequent cycles of refinement. Final $R = 0{\cdot}062$, $wR = 0{\cdot}065$, $w = 0{\cdot}1874/[\sigma^2(F) + 0{\cdot}0016F^2]$, 101 parameters, max. $\Delta/\sigma = 0{\cdot}001$, $\Delta\rho$ variations within $+1{\cdot}5$, $-2{\cdot}5$ e Å^{-3} close to Te. Final positional parameters are listed in Table 1.*

Geometric calculations were carried out by the *GEOM* program (Gilmore, 1979). Illustrations were prepared using *PLUTO*78 (Motherwell, 1978) and *ORTEP* (Johnson, 1965). Molecular geometry is given in Fig. 1; packing diagram is given in Fig. 2; bond lengths and bond angles are listed in Table 2.

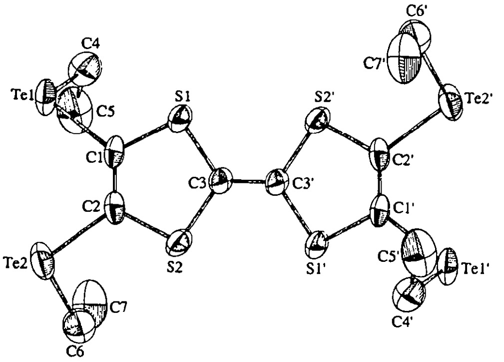


Fig. 1. *ORTEP* drawing of the molecule, showing atomic numbering.

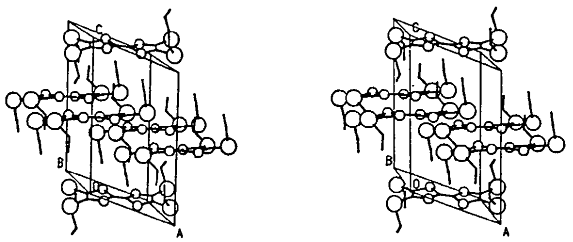


Fig. 2. Stereo plot of the structure, viewed edge-on to the plane of the molecule. Larger circles are Te; smaller ones S. C atoms drawn with zero radius and H atoms omitted for clarity.

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* HMTTeF = hexamethylenetetratellurafulvalene.

* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44886 (12 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Bond lengths* (Å) *and bond angles* (°) *for* *$TTeC_2$-TTF*

Te(1)—C(1)	2·125 (9)	C(4)—Te(1)—C(1)	92·5 (4)
Te(1)—C(4)	2·20 (1)	C(2)—C(1)—Te(1)	128·7 (7)
Te(2)—C(2)	2·12 (1)	C(6)—Te(2)—C(2)	97·7 (5)
Te(2)—C(6)	2·14 (1)	C(1)—C(2)—Te(2)	125·9 (7)
S(1)—C(1)	1·77 (1)	C(3)—S(1)—C(1)	95·5 (5)
S(1)—C(3)	1·758 (9)	S(2)—C(3)—S(1)	113·0 (5)
S(2)—C(2)	1·75 (1)	C(3)—S(2)—C(2)	95·3 (5)
S(2)—C(3)	1·764 (9)	C(3')—C(3)—S(2)	122·6 (7)
C(1)—C(2)	1·32 (2)	S(1)—C(1)—Te(1)	114·9 (5)
C(3)—C(3')	1·35 (1)	C(5)—C(4)—Te(1)	111 (1)
C(4)—C(5)	1·47 (2)	S(2)—C(2)—Te(2)	115·4 (5)
C(6)—C(7)	1·47 (2)	C(7)—C(6)—Te(2)	112 (1)
		C(2)—C(1)—S(1)	116·4 (7)
		C(1)—C(2)—S(2)	118·4 (7)
		S(1)—C(3)—C(3')	124·4 (7)

Discussion. The molecular geometry of $TTeC_2$-TTF is very similar to other molecules of this type, for instance the $TTeC_n$-TTF series (Okada, Yamochi, Shinozaki, Oshima & Saito, 1986). The ditelluro-TTF unit is very nearly planar with a maximum deviation of 0·142 (3) Å for S(1); the next largest deviation is 0·095 (9) Å for C(3). This geometry differs from that exhibited by the sulfur analogs [(I), $X = S$, $R = Me$ (Katayama, Honda, Kumagai, Tanaka, Saito & Inokuchi, 1985)] which are bent so that all methylthio groups and the attached C atoms are displaced significantly from the central ring plane; the tilt angles are about 20° at both ends. The four ethyl groups of the $TTeC_2$-TTF molecule are directed out of the central plane skeleton and pointed away from the long molecular axis, as shown in Fig. 2. This causes steric hindrance which prevents close approach between molecules to form molecular stacks and also probably prevents close Te···Te columnar interactions. The shortest non-H-atom intermolecular distance (3·88 Å) is between the methyl group of one molecule and the methylene group of a molecule related by a *b*-axis translation which is most probably a repulsive interaction. The interplanar distance between tetratelluro-tetrathiafulvalene moieties related by an *a*-axis translation is 4·2 Å. The shortest Te···Te distance is 3·99 Å, longer than those distances found in $TTeC_1$-TTF which are 3·76 and 3·64 Å respectively (the van der Waals Te···Te distance is 4·2 Å).

Tellurium-containing donors tend to crystallize in a packing mode in which Te atoms form zigzag chains similar to that found in the crystalline element (Cherin & Unger, 1967). Two examples are the HMTTeF (Wudl & Aharon-Shalom, 1982) and $TTeC_1$-TTF (Inokuchi *et al.*, 1987). The combination of this packing feature and the short distances mentioned above is probably responsible for the unusual high-mobility semiconducting properties of $TTeC_1$-TTF. The lack of semiconducting properties in HMTTeF is probably due to incipient dimer formation along the stacking direction. Unlike HMTTeF and $TTeC_1$-TTF, $TTeC_2$-TTF does not exhibit the zigzag packing motif owing to the outward orientation of the bulky ethyl groups. This, combined with the lack of close contacts within the stack, can account for its lack of conducting properties.

The ($TTeC_2$-TTF)–TCNQ complex (Aharon-Shalom *et al.*, 1985*b*) is a mixed-stack semiconductor ($\sigma = 10^{-2}\Omega^{-1}\,cm^{-1}$). The ditelluro-TTF unit here is nearly planar (as in the neutral molecule) but the bond lengths are altered in a manner consistent with the behavior of the HOMO orbital of the TTF part of the molecule and is probably due to partial charge transfer. The C—C bonds of the TTF moiety are longer and the C—S bonds are shorter. The differences in the bond lengths are only in the range of 1σ–3σ but are all in the direction which is consistent with partial transfer of charge to the TCNQ molecule in the complex. The distances between donor molecules of the complex are relatively large; the shortest outer chalcogen distance is Te···S (3·99 Å) along the *c* crystallographic axis which is greater than the sum of van der Waals radii of Te (2·10 Å) and S (1·80 Å).

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