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Publication details, including instructions for authors and subscription information:

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**To cite this Article** Otsuka, Akihiro, Saito, Gunzi, Ohfuchi, Kazuyo and Konno, Michiko (1992) 'C<sub>1</sub>TET-TTF and its Related Compounds as Single Component Molecular Conductors', *Phosphorus, Sulfur, and Silicon and the Related Elements*, 67: 1, 333 – 338

**To link to this Article:** DOI: 10.1080/10426509208045855

**URL:** <http://dx.doi.org/10.1080/10426509208045855>

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# C<sub>1</sub>TET-TTF AND ITS RELATED COMPOUNDS AS SINGLE COMPONENT MOLECULAR CONDUCTORS

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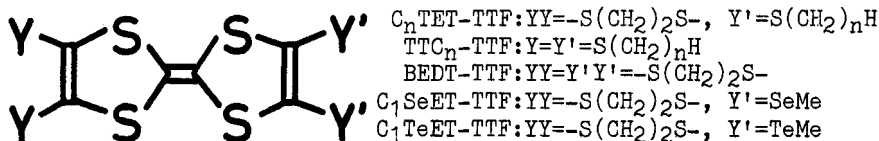
**Abstract** Bis(methylthio)ethylenedithio-TTF (C<sub>1</sub>TET-TTF) single crystals showed the room temperature resistivity of  $5.4 \times 10^5 \Omega \text{cm}$ . X-Ray crystal determination indicates that boat shaped molecules of C<sub>1</sub>TET-TTF construct two-dimensional network of the intermolecular S··S atomic contacts. C<sub>10</sub>TET-TTF showed the value of  $1.0 \times 10^6 \Omega \text{cm}$  in compaction though only two alkyl chains are attached to its  $\pi$ -electron moiety.

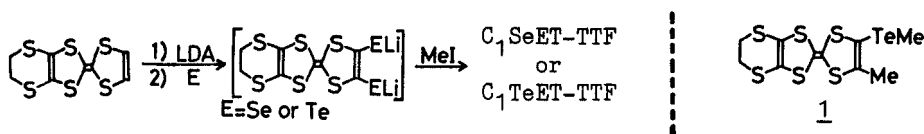
## INTRODUCTION

Organic neutral molecules can construct conductive assemblies by themselves. Although no metallic material has been obtained from such single component molecular assemblies, fairly good electrical conductivities have been recently reported on some neutral solids of the molecules made of carbon, hydrogen, nitrogen, and chalcogen atoms.<sup>1</sup> We have been interested in the chalcogen substituted TTF derivatives not only as the electron donors in charge transfer complexes but also as single component conductors.

## RESULTS AND DISCUSSION

C<sub>n</sub>TET-TTF (n=1, 2, 4, 7, 10, 13, 16, 18)<sup>2</sup> was synthesized by the coupling reaction between corresponding ketones and was separated from its symmetrical analogues by silica gel column chromatography. The syntheses of C<sub>1</sub>SeET-TTF and C<sub>1</sub>TeET-TTF are in progress (Scheme 1), and (1) has been detected (m/e=452)<sup>3</sup> in which only one Te atom is inserted. The resistivities were measured by a two-probe or a quasi-



SCHEME 1 Synthetic route to  $C_1\text{SeET-TTF}$  or  $C_1\text{TeET-TTF}$ .

four-probe dc-method with silver or gold paste as electrical contacts. The influence of oxygen was not observed, and the measurements were performed under ambient pressure of nitrogen gas. The X-ray diffraction data of  $C_1\text{TET-TTF}$  single crystals were collected at room temperature by use of an automated four-circle diffractometer. Crystal structure was solved by a direct method and was refined by a full-matrix least-squares program (monoclinic,  $P2_1/c$ ,  $a=7.7821(9)$ ,  $b=31.303(6)$ ,  $c=13.021(1)$  Å,  $\beta=98.10(1)^\circ$ ,  $V=3140.4(7)$  Å<sup>3</sup>,  $Z=8$ ,  $R=4.9\%$ ).

#### Electrical Resistivities of $C_n\text{TET-TTF}$

Table I shows the dc-electrical resistivities of  $C_n\text{TET-TTF}$  together with that of BEDT-TTF at room temperature.

For  $n \geq 2$ , the resistivities of  $C_n\text{TET-TTF}$  tend to decrease as  $n$  increases, then seem to converge into a value of  $10^6 \sim 10^7$  Ωcm in compaction pellets. Especially in the case of  $C_{10}\text{TET-TTF}$ , its value of  $1.0 \times 10^6$  Ωcm in compaction is comparable to that of single crystal of  $\text{TTC}_{10}\text{-TTF}^4$  ( $3.7 \times 10^5$  Ωcm). Such an  $n$  dependence of resistivity, in which the resistivity decreases as  $n$  increases, has been already observed on  $\text{TYC}_n\text{-TXF}$  series ( $Y=\text{S, Se or Te for } X=\text{S}; Y=\text{S or Se for } X=\text{Se}$ ) and has been understood as "molecular fastener effect"<sup>5</sup>.

$C_n\text{TET-TTF}$  has only two normal alkyl chains, and the  $\pi$ -electronic segment is placed at the other end of the molecule. This forms a striking contrast to  $\text{TTC}_n\text{-TTF}$  in which the  $C_6S_8$  segment is placed at

TABLE I The room temperature resistivities of  $C_n\text{TET-TTF}$  and BEDT-TTF.

$n$	$\rho_{\text{rt}}/\Omega\text{cm}$	$n$	$\rho_{\text{rt}}/\Omega\text{cm}$
1	$5.34 \times 10^5$ ( $E_a=0.26$ eV, //a)	13	$*2.26 \times 10^7$
	$*1.17 \times 10^8$	16	$*1.83 \times 10^7$
2	$6.44 \times 10^9$ ( $E_a=0.45$ eV)	18	$*1.85 \times 10^7$
	$*4.81 \times 10^9$	BEDT-TTF	$2.60 \times 10^9$ ( $E_a=0.44$ eV, //a)
10	$*1.01 \times 10^6$		$*1.31 \times 10^9$

\*: Compaction pellet.

the center of the molecule with four alkyl chains surrounding it. Considering both the total number and the location of the alkyl chains in a molecule, it may be easy to imagine that the "fastening" of the C<sub>6</sub>S<sub>8</sub> segments by the alkyl chains would be less effective in C<sub>n</sub>TET-TTF than in TTC<sub>n</sub>-TTF. However, both compounds exhibit the almost equal value of the resistivity (*vide supra*).

Since the single crystals of C<sub>10</sub>TET-TTF have not been obtained, we have conjectured its rough molecular packing by means of powder X-ray diffraction. A series of diffraction peaks which corresponds to a repeating unit of 38 Å was observed. Considering that TTC<sub>10</sub>-TTF<sup>6</sup> has a distance of  $d_{010}=32.77$  Å between the ac planes, it is likely that C<sub>10</sub>TET-TTF also crystallizes to form a sheetlike structure in which the asymmetric molecules of C<sub>10</sub>TET-TTF are arranged in a head to head manner (Figure 1a).

If it is the case that C<sub>n</sub>TET-TTF ( $n \geq 10$ ) is packed such as Figure 1a, its low resistivity should be ascribed to the substantial packing arrangement of the C<sub>6</sub>S<sub>8</sub> segment of this compound in the crystal. This means that sufficient molecular aligning effect would be achieved by only two alkyl chains attached at one side of the  $\pi$ -system so as to make a conduction path in the crystal. Besides the two alkyl chains of C<sub>n</sub>TET-TTF, the ethylenedithio substituent which is not contained in TTC<sub>n</sub>-TTF, should be noticed. Since the flatness of the C<sub>6</sub>S<sub>8</sub> part in C<sub>n</sub>TET-TTF ( $n \geq 10$ ) is considered to be poor on the analogy of C<sub>1</sub>TET-TTF (*vide infra*) and C<sub>7</sub>TET-TTF·TCNQ<sup>2, 7</sup>, the interactions in the side-by-side direction of the molecule may play an important role in the electrical conduction compared with TTC<sub>n</sub>-TTF.

Single crystals, which have been obtained for C<sub>n</sub>TET-TTF ( $n=1, 2$ ) and BEDT-TTF, show the resistivities smaller by a factor of almost two than those of their compaction specimens respectively. The remarkable fact is that C<sub>1</sub>TET-TTF single crystals show the smallest resistivity among these compounds. The value of  $\rho_{rt}=5.4 \times 10^5$  Ωcm is nearly equal to that of TTC<sub>10</sub>-TTF<sup>4</sup> ( $3.7 \times 10^5$  Ωcm) which is the smallest one among the single component organic semiconductors made from C, H, and S only. This implies that C<sub>6</sub>S<sub>8</sub> segment with ethylene group may have a latent ability to produce a conductor by itself, without the assists by long alkyl chains. BEDT-TTF single crystals also showed the relatively small value of  $2.6 \times 10^7$  Ωcm.

### Molecular and Crystal Structures of $C_{10}$ TET-TTF

Crystallographically independent two molecules (I and II) exist in the crystal (Figure 1b). The  $C_6S_8$  segment of the both molecules takes a boat-form. The conformational features of the methylthio groups are reminiscent of those of  $TTC_1$ -TTF (phase 1<sup>8</sup>, 2<sup>9</sup>), and the features of the ethylenedithio groups are quite similar to those of BEDT-TTF<sup>10</sup>. This may be quite natural, considering that  $C_{10}$ TET-TTF is a hybrid molecule between  $TTC_1$ -TTF and BEDT-TTF.

As for the electronic states of a molecule, the extended-Hückel MO calculations on  $TTC_n$ -TTF ( $n=1, 2$ , and 9) indicated that the molecular-orbital energies hardly depend on whether the  $C_6S_8$  segment is bent or flat.<sup>11</sup> Accordingly, it is suggested that the packing manner of  $C_{10}$ TET-TTF (and other  $n$ ) molecule would dominate its solid

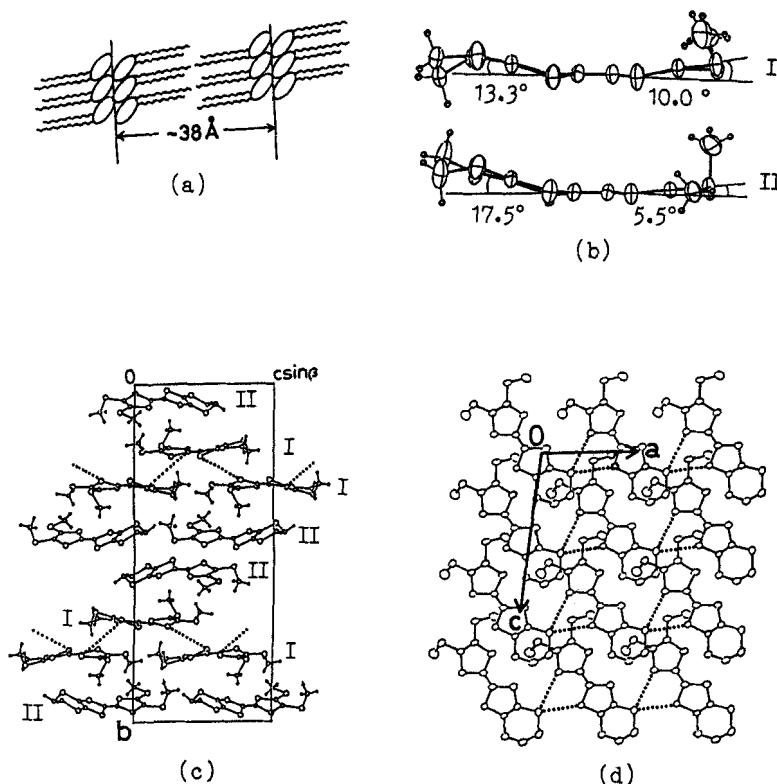


FIGURE 1 (a) A schematic representation of the packing of  $C_{10}$ TET-TTF; (b) Molecular side views of  $C_{10}$ TET-TTF; (c) Crystal structure of  $C_{10}$ TET-TTF projected along the  $a$  axis; (d) The side-by-side arrangements of the molecule I in the  $ac$  plane.

state properties.

Figure 1c shows the crystal structure of C<sub>1</sub>TET-TTF projected along the a axis. Eight molecules are contained in the asymmetric unit, and they are piled up along the b axis which is the longest crystallographic one. The resistivity measurements were performed in the direction parallel to the most elongated axis of the crystals (*//a*).

Relatively close intermolecular S··S distances, which are shorter than the upper limit of the sum of the van der Waals radii (3.7 Å), are found only among the molecules I. The molecules I form the two-dimensional S··S networks parallel to the ac plane.

The molecules are arranged side-by-side regularly along the a axis (Figure 1d). Four short S··S distances (3.49~3.62 Å) for a molecule I are observed in that direction, which consist of one outer S and two inner S atoms of that molecule. In the direction along the c axis, two close S··S atomic contacts (3.60 Å) for a molecule I are observed which are made of two inner S atoms (Figure 1c).

The molecule II, which is isolated in the crystal judging from atomic contacts, could not directly contribute to the electrical conduction. The molecules II are sandwiched between those sheets made of molecules I.

It is important to notice that the inner S atoms, which are included in TTF skeleton and are expected to have the largest atomic population of HOMO, greatly participate in the formation of the S··S network. The inner S atoms contribute to the formation of four S··S atomic contacts out of six for a molecule I.

What is common to C<sub>1</sub>TET-TTF and TTC<sub>10</sub>-TTF (both show the same order of resistivity, 10<sup>5</sup> Ωcm) seems to be the strong interactions among the conjugated systems. The close S··S network through inner S atoms looks to play an important role in C<sub>1</sub>TET-TTF. The close face to face stacking (3.49 Å) of the C<sub>6</sub>S<sub>8</sub> plane with short S··S contact (3.57 Å) of inner S atoms within a column<sup>6</sup> looks to contribute to the conduction in TTC<sub>10</sub>-TTF.

BEDT-TTF<sup>10</sup> molecules are dimerized in a face to face fashion with 3.69 Å distance between inner S atoms. The dimers are arranged side-by-side regularly to form chains along the a axis. In the eight S··S contacts (3.48~3.69 Å) for a molecule, only three include the inner S

atoms. Such differences in the nature of S··S network from that of C<sub>1</sub>TET-TTF would result in the larger resistivity and activation energy than those of C<sub>1</sub>TET-TTF. Nevertheless, BEDT-TTF showed the resistivity smaller by a factor of three than that of TTC<sub>1</sub>-TTF (phase 1)<sup>4</sup>, and this is presumably due to the side-by-side regular arrangement of BEDT-TTF molecule.

### CONCLUSION

The characteristic feature of the C<sub>1</sub>TET-TTF crystal is the close intermolecular S··S atomic contacts to which the inner S atoms greatly contribute. The poor flatness of the C<sub>1</sub>TET-TTF molecules would have increased a relative importance of the side-by-side interactions.

The resistivity of C<sub>n</sub>TET-TTF was as low as that of TTC<sub>n</sub>-TTF despite the reduction of the number of alkyl chains.

The sulfur atoms of methylthio groups do not participate in the S··S network in the C<sub>1</sub>TET-TTF crystal, however, in TTeC<sub>1</sub>-TTF<sup>5b</sup>, 12 single crystals, the characteristic tellurium atomic contacts play an important role in its high conductivity. Therefore, C<sub>1</sub>SeET-TTF or C<sub>1</sub>TeET-TTF is a candidate expected to exhibit a novel physical and structural properties by means of both ethylenedithio and methyl chalcogeno groups. The synthesis is under way as mentioned above.

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