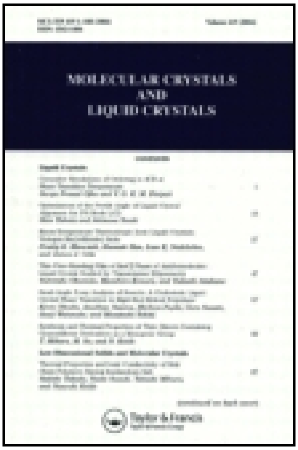

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# The Crystal Structure of Tetratellurotetracene (TTeT) and Polymorphism of Tetraselenotetracene (TSeT)

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# THE CRYSTAL STRUCTURE OF TETRATELLUROTETRACENE (TTeT) AND POLYMORPHISM OF TETRASELENOTETRACENE (TSeT)

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The crystal structure of TTeT has been determined; salient features include a linear chain structure and very short intermolecular Te-Te contacts. A previously unreported polymorph of TSeT was found to be isomorphous to TTeT. These data, taken with the reported data for TTT, indicate a series of three crystals each with a lattice constant which is approximately twice the van der Waals radius of the chalcogen.

## INTRODUCTION

The observation of a lattice constant of 4.023Å in the initial⁽¹⁾ structural study of tetrathiafulvalene (TTF) indicating a uniform chain structure was important in early work on TTF-TCNQ since it suggested a means to avert the conventional⁽²⁾ mixed stack structure if the TTF chains persisted after charge transfer. While such a lattice constant

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is not reported(3) for the tetramethyl derivative of TTF nor for the selenium analog(4) of this compound, a constant of 3.968Å is observed(5) in tetrathiotetracene (TTT), another prototype organosulfur donor for quasi-one-dimensional metals. Crystallographic studies of neutral organochalcogen donors are of continuing interest with respect to binding forces(3) in these solids and the use of molecular geometry to infer degree of charge transfer in molecular complexes derived from these donors.(6)

The availability of the tellurium analogs of the organoselenium donors which give the presently known low temperature organic metals and superconductors has been anticipated.(7) Pursuant to our interest(8) in peri-dichalcogenide derivatives of the aromatic hydrocarbons, we have synthesized and characterized tetratellurotetracene (TTeT,1).(9) We note that the 2:1 chloride of tetraselenotetracene (TSeT) has been reported to remain metallic below 30°K and to reach conductivities in excess of $10^5(\text{ohm-cm})^{-1}$ under high pressure.(10)

The lattice constants of solution grown single crystals of TTeT derived from photographic data are given in Table 1, and a complete structural determination(11) was undertaken in an alternate setting of the unit cell, with $\underline{a}$ = 11.746(4), $\underline{b}$ = 4.364(2), $\underline{c}$ = 15.831(5)Å; β = 90.57(5)°, space group $P2_1/n$. Full-matrix least-squares refinement of positional and anisotropic thermal parameters for Te and C atoms, using 1283 observed reflections for which $F > 3.92\sigma(F)$ and $\theta_{MoK\alpha} < 26.5°$, led to $R = 0.030$ and $R_w = 0.037$. The molecule occupies a crystallographic center of symmetry (see Figure 1); important intramolecular distances are: Te-Te, 2.673(1) and Te-C, 2.112(4)Å (average). These distances compare favorably with those observed, *e.g.*, in diphenylditelluride(12): Te-Te, 2.712(2); Te-C, 2.115(16) (average). Figure 1 shows a portion of the two symmetry-related stacks along the $\underline{b}$ axis. Within a stack, the packing is dominated by Te-Te contacts at *ca.* 4.3Å, or approximately twice the van der Waals radius. However, there are extremely short interstack Te-Te contacts of 3.701(1)Å, which also bridge between individual molecules in a stack (see Figure 1).(13)

The observation of the very short Te-Te contacts in TTeT is particularly significant in that, analogous to TSeT(14), short chalcogen contacts may now be anticipated in ion-radical solids derived from TTeT. It is also of interest to anticipate the structural features involving Te in the hexamethylene derivative of tetratellurofulvalene and its ion-radical solids mentioned(15) at this Conference.

Table 1

## CRYSTAL DATA FOR TETRACHALCOGENOTETRACENES

| | SULFUR* | SELENIUM$_{(V)}$† | SELENIUM$_{(S)}$‡ | TELLURIUM‡ |
|---|---|---|---|---|
| a | 9.890 | 17.184 | 15.70 | 15.83 |
| b | 18.226 | 15.719 | 4.093 | 4.366 |
| c | 3.968 | 5.598 | 11.47 | 11.75 |
| $\alpha$ | 87.63° | 90° | 90° | 90° |
| $\beta$ | 79.73° | 90° | 92.9° | 90.3°(5) |
| $\gamma$ | 96.48° | 90° | 90° | 90° |
| V | 699.52Å$^3$ | 1512Å$^3$ | 736.7Å$^3$ | 812.1Å$^3$ |
| Z | 2 | 4 | 2 | 2 |
| $D_c$ | 1.65 | 2.37 | 2.43 | 3.01 |
| $D_o$ | 1.63 | — | 2.43 | 3.01 |
| Space Group | PI or P$\bar{\text{I}}$ | $P2_12_12_1$ | $P2_1/n$ | $P2_1/n$ |

* Reference 5
† Reference 14
‡ Present Work.

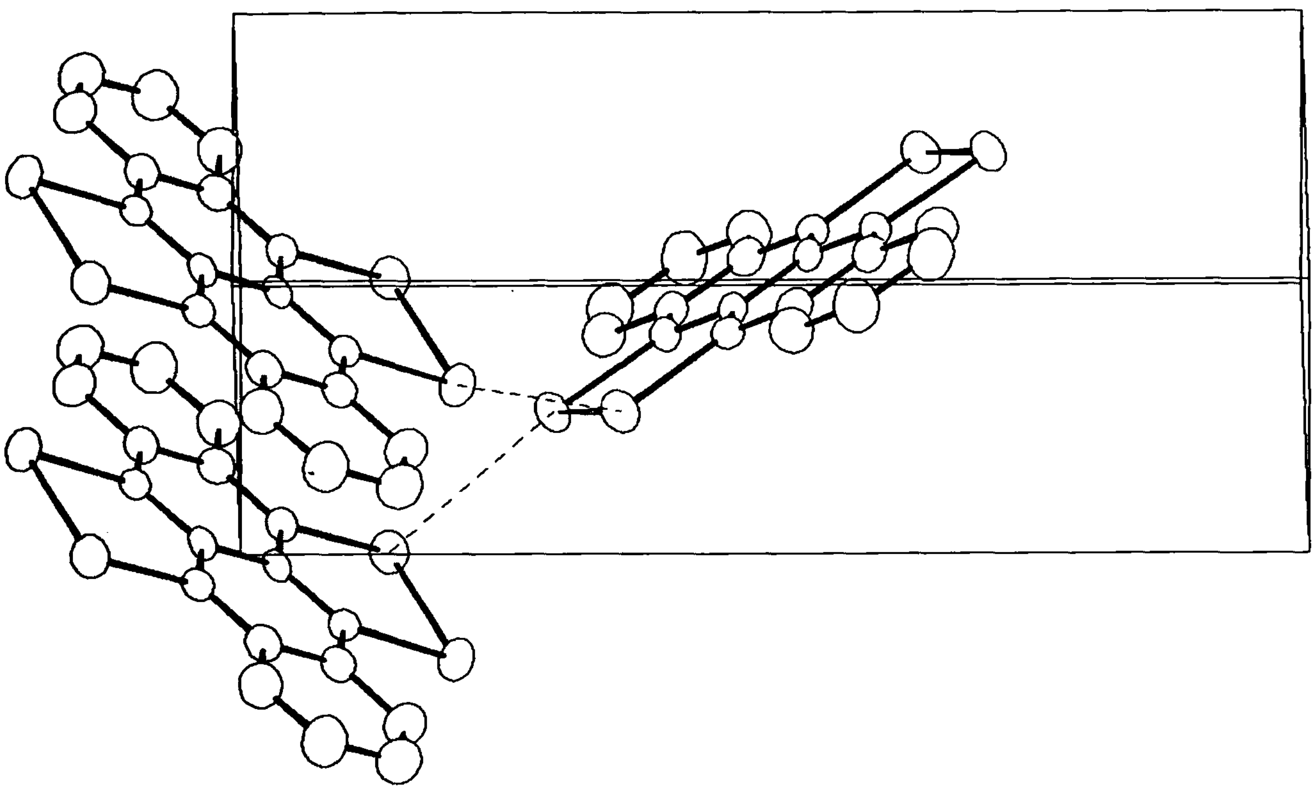

FIGURE 1 Partial packing diagram of $C_{18}H_8Te_4$ (TTeT), showing individual molecules stacked along the b direction as well as important 3.701Å Te-Te interstack contacts (dashed lines). (In this view the b axis has been rotated by 20° toward the reader.)

When compared to the lattice constants for TTT and TTeT in Table 1, the absence of a constant of *ca.* 4.0Å in the reported(14) structure of TSeT, performed on crystals grown by sublimation, was striking. Given the availability of high purity TSeT(16), we anticipated and isolated from solution a new phase of TSeT. The lattice constants of the new polymorph of TSeT, derived from single crystal photographs, are given in Table 1 and reveal a phase isomorphous to TTeT with a *b*-constant of 4.09Å. Interestingly, neither differential scanning calorimetry nor diffuse reflectance spectroscopy reveals experimentally significant differences in the TSeT polymorphs.(16) In subsequent experimentation, we have found that samples of TSeT isolated by sublimation and by solution crystallization are mixtures of the two phases in Table 1.

With reference to Table 1, the solution grown crystals of the tetrachalcogenotetracenes each exhibit a lattice constant which is approximately twice the van der Waals radius of the respective chalcogen. To our present knowledge, this is the first example of this situation in structural organochalcogen chemistry.

The occurrence of polymorphism in the tetrachalcogenotetracenes appears somewhat more widespread than shown in Table 1. We were recently informed(17) of the existence of an orthorhombic form of TTT, and we are also exploring possible indications of the phenomenon in TTeT.

The interaction of TTeT with a range of acceptor materials to give new conducting solids will be subsequently reported.

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