40. Electrical Properties of the Organic Metallic Compound bis(Tetrathiotetracene)-Triiodide, $(TTT)_2$-I_3

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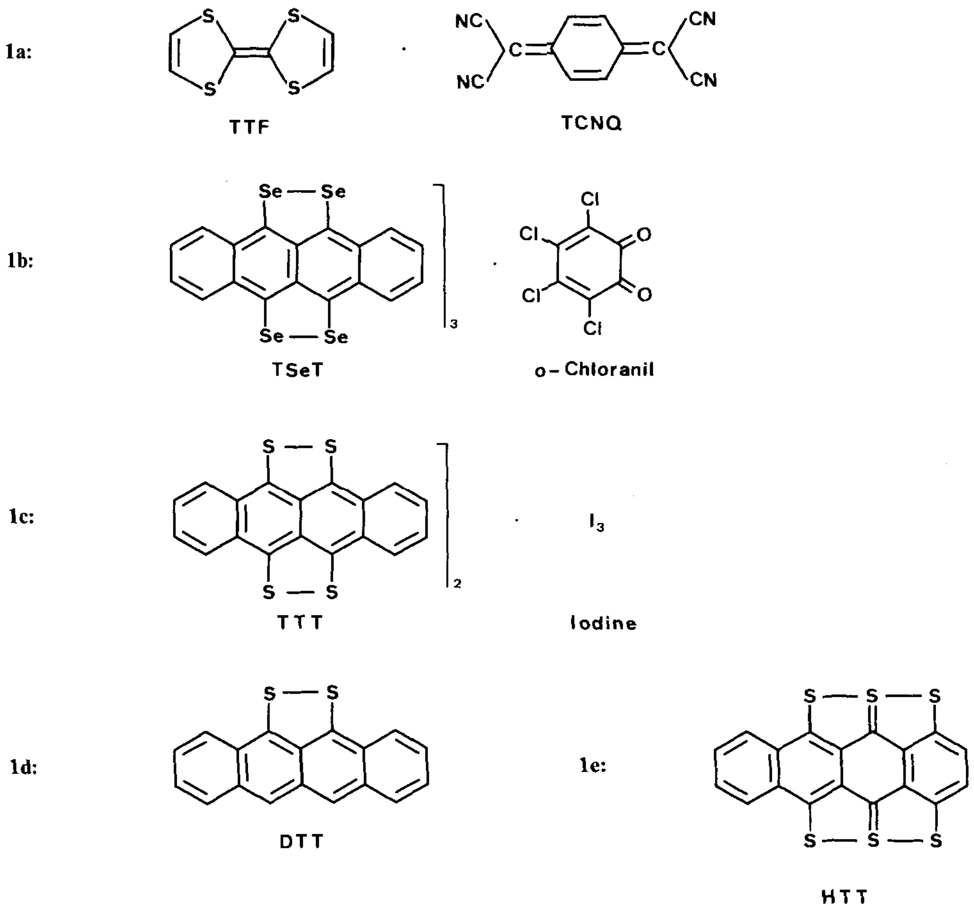
Summary

The maximum of the d.c. conductivity of single crystals of the title compound ($(TTT)_2$-I_3), grown by cosublimation, is shown to be at about 35 K. The ratio of the *b*-axis (needle axis) conductivity at the temperature of its maximum ($T_m \cong 35$ K) and its value at T = 300 K (normalized conductivity $\sigma_b''(T_m)/\sigma_b''(300)$) is strongly sample dependent. Values for $\sigma_b''(T_m)/\sigma_b''(300)$ as high as 8 have been obtained. From 300 K to about 120 K the conductivity σ_b'' is proportional to $T^{-1.3}$. In the temperature interval $40\,K \leq T \leq 120\,K$ we found: $\sigma_b'' \propto T^{-1}$. On the low temperature side of the maximum ($6\,K \leq T \leq 20\,K$) the conductivity is proportional to T^{α}, with α ranging from 2 to 2,5. It is shown that impurities, misfit of the stoichiometry and/or physical sample quality (crystal perfection) drastically shift the minimum of the resistivity to higher temperatures *(Fig. 5)*, thereby altering also the temperature dependence of the resistivity on both sides of the minimum. Our crystallographic data differ from the results published by *Isett et al.* and *Buravov et al. (Table 1)* with regard to the iodine spacings. We argue that the polarisability of the I_3^{-1} ions in their chain direction contributes significantly to the high conductivity ($\sigma_b'' = 1000$ to $10000\ \Omega^{-1}\ cm^{-1}$) along the crystallographic *b*-axis (needle axis).

Introduction. - The discovery of the high conductivity of the charge-transfer salt TTF-TCNQ (*Scheme 1,* **1a**), containing TTF as a donor and TCNQ as the acceptor molecule, has led to intensive investigations of the physical properties of this quasi metallic compound [1-3]. Also, a great number of systems with electronic properties similar to metals have been produced subsequently within the TTF-TCNQ class [4-6]. In this family of compounds the cations and anions build up separate chains. Although the electronic interaction between the chains is ultimately necessary to explain the details of the phase transitions from the metallic to a semiconducting state at low temperatures (38, 49 and 54 K for TTF-TCNQ) it is, nevertheless, the electron gas along the chains formed by the TCNQ molecules which dominates the electronic properties at higher temperatures (say above 80 K) of these salts.

Scheme 1



Scheme 1. *Structure of organic metallic compounds*

1a TTF-TCNQ: Tetrathiafulvalen-tetracyano quinodimethane

1b $(TSeT)_3$-(o-chloranil): Complex formed upon oxidation of 5,6,11,12-tetraselenotetracene with *o*-chloranil [7]

1c $(TTT)_2$-I_3: Complex formed upon oxidation of 5,6,11,12-tetrathiotetracene with iodine [8-12]

1d DTT: dithiotetracene

1e HTT: hexathiotetracene.

In [7] we showed a way to achieve a highly conducting organic metallic CT(charge-transfer)-salt by reacting an appropriate semiconducting heteroaromatic compound with an organic acceptor other than TCNQ, namely by oxidizing 5,6,11,12-tetraselenotetracene (TSeT) with o-chloranil (=tetrachloro-*o*-benzoquinone), thus forming the complex $(TSeT)_3$-(o-chloranil) (*Scheme 1*, **1b**). During the subsequent work to explore this new class of metallic compounds based on chalcogenated aromatic hydrocarbons in more detail, it soon became apparent that the synthesis of analogue donor structures indicates many new challenges for the organic chemist. Also, in order to find the metallic phases of such compounds, new techniques of crystallisation had to be developed. One of the new compounds, $(TTT)_2$-I_3 [8] (*Scheme 1,* **1c**), has been reported recently in the literature by others [9-11]. (For the research done on the TTT-TCNQ or TTT-$(TCNQ)_2$ CT-salts see *e.g.* *Buravov et al.* and *Delhaes et al.* [12] [13]). In view of some discrepancies with respect to the electrical conductivity of this new CT-system of the results of [9] [11] compared with our earlier findings [8], we consider it worth-while communicating our results in more detail, and put forward some general properties on the electrical behaviour of $(TTT)_2$-I_3, which seem to be equally representative of the other metals derived from the chalcogenated aromatic structures [14].

Experimental Part. - The preparation of the tetrathiotetracene was performed according to the procedure of *Marschalk* [15], modified by *Perez-Albuerne* [16]. Purification of the raw material was carried out by first oxidizing it with H_2O_2 in formic acid, and then reducing it with $TiCl_3$. This step eliminated most of a hexathiotetracene (*Scheme 1,* **1e**) HTT; structure not fully established) present as a by-product. Sixfold recrystallisation in 1,2,4-trichlorobenzene under a nitrogen atmosphere eliminated most of the 5,6-dithiotetracene (*Scheme 1d,* DTT) also present in the raw material. Further purification was performed by repeated gradient sublimation in a high vacuum of approx. 10^{-5} Torr. This procedure, applied 16 times, completely eliminated the forezones, comprising DTT (dithiotetracene) and sulfur, and reduced the backzones to a small amount of *ca.* 10 ppm by weight. Taking only the TTT from the centre of the main zones of the last 4 sublimation steps, we were left with enough material to proceed with the growth of single crystals according to the novel principle which we described in some detail in [8]. We would like to point out here that this very effective method of growing $(TTT)_2$-I_3 single crystals by introducing TTT vapour and I_2 vapour by means of two separate gas flows into a reaction chamber is applicable to the growth of single crystals of most of the CT-salt preferentially derivable from neutral constituents. This is especially so because of the great variety of easily adjustable parameters, such as pressure and flowrate of the carrier gas, sublimation rate of the constituent compounds *etc.* The iodine used was 'Suprapur', (*Merck,* Darmstadt, West Germany). It is interesting to note that the same procedure was found some time later by *Isett* [10].

In *Figure 1* we show some photographs of $(TTT)_2$-I_3 crystals. The crystals have a brilliant golden lustre and can be grown within times ranging from a fraction of an hour to a few days.

The crystals were mounted on 4 suspended gold wires of 10 or 20 microns diameter [17]; the contacts made were of the wrapping type on the thinner crystals (0,5 to 3μ broad), and of the wrapping type, or on a single surface on broader crystals (3-50 μ thick and 3-200 μ broad), by applying Pt-paste 308 *(Degussa).* The d.c. conductivity measurements were carried out by feeding a current of 1 μ A and measuring the d.c. potential with a *Keithly* 610 C instrument. The sample holder was designed to accommodate 18 crystals and was lowered slowly into a liquid nitrogen bath, or into a liquid helium bath, respectively [18]. In order to avoid breakage of the crystals, the lowering rate of the temperature was about 10 K/h. It was noticed during the measurements that crystals of the zone C, (*Fig. 5,* see also the related text) are mechanically the most stables ones. This supports the conclusions drawn in the context of *Figure 5.*

Results and discussion. - In *Scheme 2* we illustrate the crystal structure of $(TTT)_2$-I_3 viewed down the *b*-axis. The structure has also been determined by *Isett et al.* [11], and *Buravov et al.* [12]. We compare the results in the *Table 1.*

The orthorhombic crystal structure consists of segregated donor- and acceptor-stacks. Its space group is Cmca. All the interplanar TTT spacings in the stacks are identical (3,32 Å). Parallel to the TTT stacks are 4 columns of iodine per unit cell projection area. At room temperature the iodine chains are uncorrelated with each

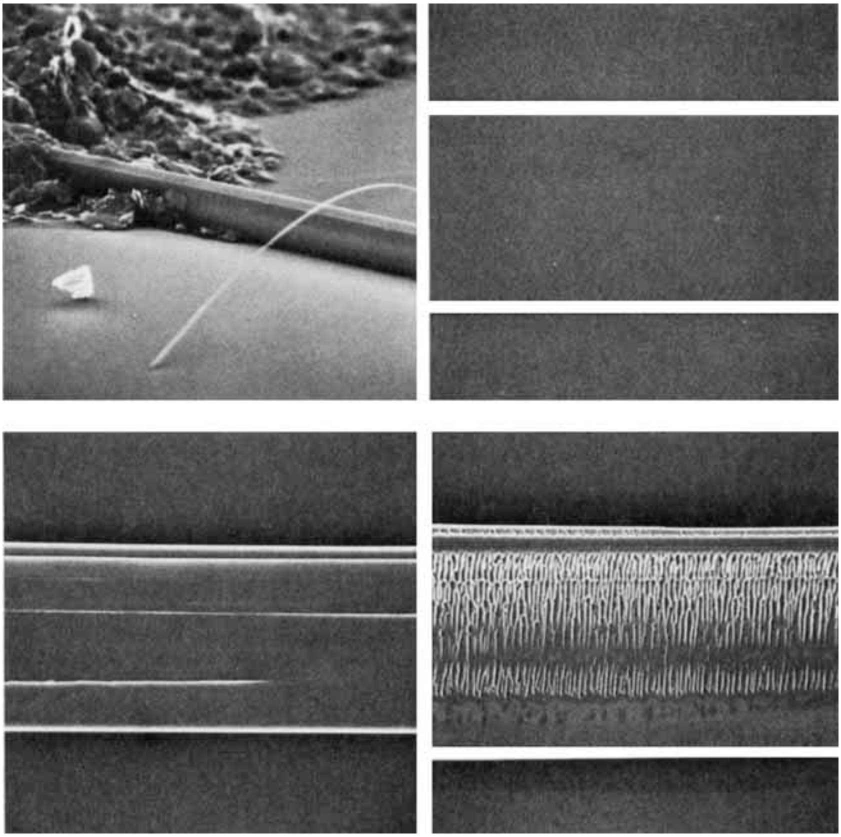


Fig. 1. *Electron microscope photographs of* $(TTT)_2$-I_3 *single crystals.*
Top left: (2100 ×) showing also a very thin fibre.
Top right: (500 ×) demonstrates smooth surface.
Bottom left: (500 ×) shows cracks in the (*a*, *b*)-plane.
Bottom right: (500 ×) shows defects as induced *e.g.* by strong iodine misfit.

other in the *b* direction. We find for the iodine spacing a sequence of 2.93, 2.93 and 3.75 Å, suggesting essentially the presence of the triiodide anion form as put forward by *Isett* [10] [11]. The presence of uncorrelated I_3-chains has also been mentioned recently [20] [21] for some other complexes. The iodine lattice is incommensurate with the TTT sublattice. The difference between the *b*-axis and *b'*-axis implies that the complex could be of the form $(TTT)_2(I_3)_{1.026}$. As can be inferred from *Table 1*, there are some respectable differences in the *b'*-axis data. If, again, we put tentatively the iodine content as being proportional to its *b'*-axis period, the above-mentioned differences show up in different iodine contents (*e.g. Isett* [11] reports $(TTT)_2(I_3)_{1.04}$). These differences may be real, resulting from the different crystallisation procedures used by the groups cited. For short, we shall denote the complex under discussion as being $(TTT)_2$-I_3, as we have no means as yet of measuring directly

Scheme 2. *Crystal structure of* $(TTT)_2$-I_3 *viewed down the* b-*axis* (orthorhombic, space group Cmca)

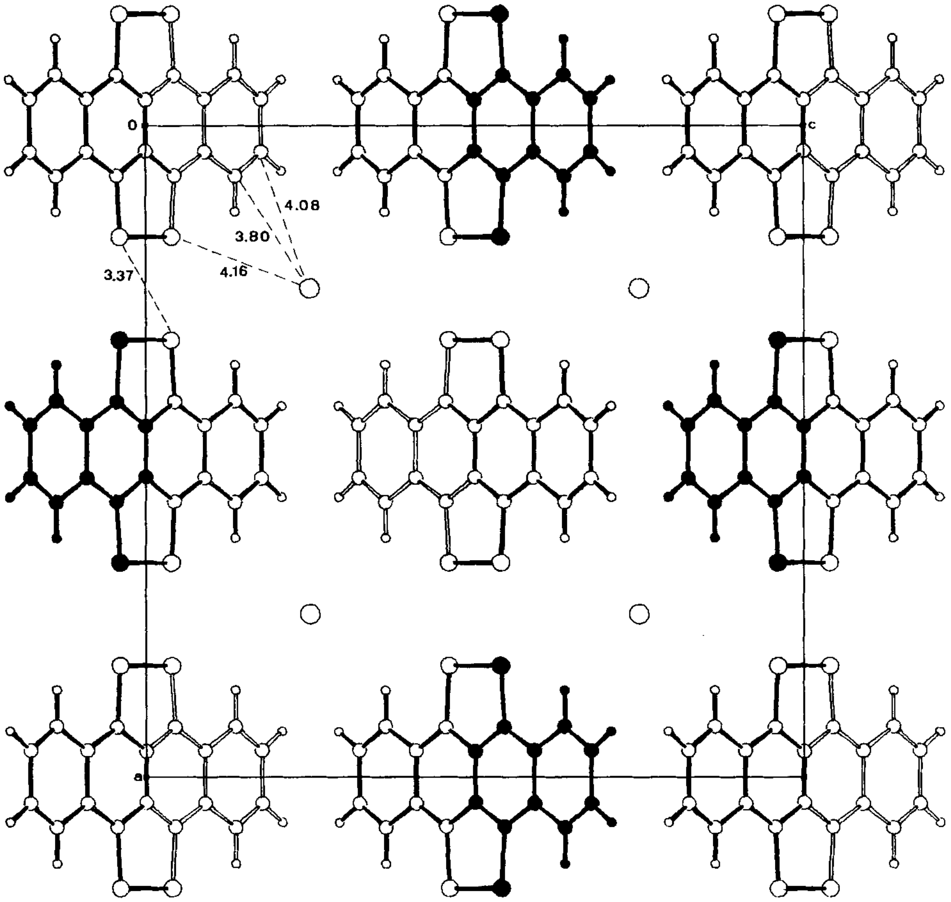


Table 1. *Summary of structural data of* $(TTT)_2$-I_3

	Buravov et al. [12]	*Isett et al.* [11]	*Ciba-Geigy (G. Rihs)* [19]
c-axis (Å)	18.353	18.319	18.377
a-axis	18.464	18.394	18.484
b-axis	4.962	4.962	4.945
Iodine *b'*-axis	2 × 4.962 = 9.924	2 × 4.77 = 9.54	2 × 4.82 = 9.64

the iodine content of one single crystal to the required accuracy of better than 3%. The S-S distance along the chains of TTT is 3.67 Å. The shortest intermolecular distance of S-S (3.37 Å) is found, however, in the direction indicated in *Scheme 2*. As a comparison, the sum of the *Van der Waals* radii of S-S is 3.7 Å. We come back to this finding later.

The room temperature d.c. conductivity along the *b*-axis (σ''_b(300)) of the complex measured by 2-probe and/or by the 4 probe configuration [17]) varies from 1,000 to 10,000 Ω^{-1} cm^{-1}. The reason for this relatively wide spread of the values is not established at present. With correction for the contact resistance, which is about 2 ohms at room temperature compared to about 20-150 ohms of the crystals, both electrode configurations yield the same results. The anisotropy σ''_b (300)/σ_a (300) resp. σ''_b (300)/σ_c (300) varies from about 100 to 1000.

We can make a rough estimate of the free mean path Λ of the charge carriers, using the formula derived by *Heeger et al.* [22].

$$\Lambda = v_F\tau = \sigma\pi\hbar/2Ne^2b \tag{1}$$

Assuming that, due to presence of some kind of triiodide anions, a charge transfer of about 0.5 electron per TTT molecule is to be expected, we find, with $N = 1{,}2 \times 10^{21}$ cm^{-3}, $\sigma = (10^3 - 10^4)$ Ω^{-1} cm^{-1}, and the *b*-axis spacing $b = 4.9$ Å, Λ is of the order of 2 to 20 lattice constants.

The above formula was derived for the 1-dimensional limit of a tight binding band. The value thus obtained for the mean free path (Λ) justifies the application of the band theory. There is, however, some uncertainty as to the degree of dimensionality of this compound. Firstly, we mention that the reflectivity, as measured with a *Beckmann* DK 2 on a compacted powder sample, shows 5% reflection throughout the VIS, and a steep rise at 1.1 μ to 29% reflection. This behaviour is characteristic of a 1-dimensional conductor [23].

Secondly, from *Scheme 2* we infer that there are effectively two channels for the electronic motion along the stacks of TTT molecules. The first channel is given by the overlap of the sulfur hybridized (s,p) orbitals (to some extent also their d-orbitals may participate) of adjacent molecules of the same stack. The second channel is opened up in the *a, b*-plane, this time by the overlap of the (s,p) orbitals of the sulfur atoms (or again, to some extent d-orbitals will be mixed in) of two neighbouring molecules belonging to two different stacks. This latter overlap has a nonvanishing projection on to the *b*-axis and thus contributes to the *b*-axis conductivity. The projection on the *a*-axis, however, does not seem to be very effective, as is shown by the conductivity ratio σ''_b/σ''_a given above. We might thus argue that the second channel is also much less effective for the conductivity along the *b*-axis than the first channel. However, the *b*-axis projection of the conductivity of the second channel might be strongly influenced by the electronic and ionic *b*-axis polarizability [22] of the neighbouring iodine chains.

Figure 2 shows the temperature dependence of the d.c. conductivity of 3 single crystals of the $(TTT)_2$-I_3 complex. The observed data can be fitted within the experimental accuracy of 5% by:

$$\sigma''_b \propto T^{-1.3} \quad \text{for} \quad 120\,K \lesssim T \lesssim 300\,K \tag{2}$$

and

$$\sigma''_b \propto T^{-1} \quad \text{for} \quad 40\,K \lesssim T \lesssim 120\,K \tag{3}$$

No attempt has been made to describe the σ-behaviour near the transition point of 35 ± 3 K.

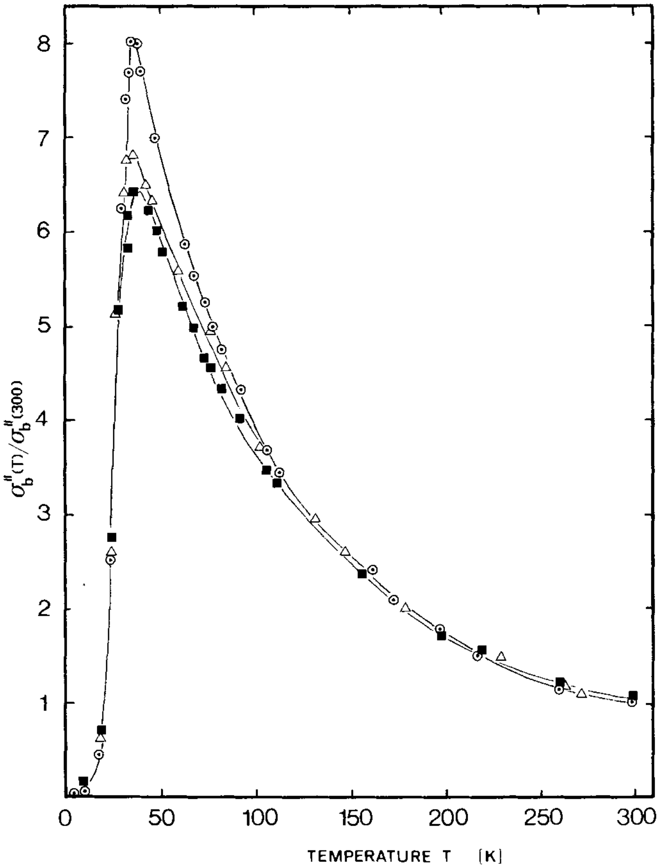


Fig. 2. *Normalized d.c. conductivity of* $(TTT)_2$*-*I_3 *single crystals showing intrinsic behaviour*

Figure 3 shows results of crystals having a much lower $\sigma''_{b,\max}(T)/\sigma''_b(300)$, and also exhibiting quite a different temperature dependence than crystals of *Figure 2.* We come back to this point below when discussing *Figure 5.*

The detailed behaviour of the d.c. conductivity for temperatures below the transition temperature is redrawn in *Figure 4*. The results can be described by:

$$\sigma''_b \propto T^a \qquad a = 2\text{–}2{,}5 \qquad 6\,\mathrm{K} \leq T \leq 20\,\mathrm{K} \tag{4}$$

At first glance one is tempted to describe these data as a consequence of a temperature dependent gap $E(T)$. A normalization procedure which may be used is to then set the gap to zero at the transition temperature [24]. The gap derived by this procedure should then converge monotonically towards a constant value for $T \rightarrow 0$. If we calculate $E(T)$ from:

$$\sigma''_b \propto T^a \cdot e^{-E(T)/T} \tag{5}$$

for reasonable values of $0 < (a) \leqslant 2$, we find that $E(T)$ peaks at about 20 K. Hence, present data do not justify this procedure.

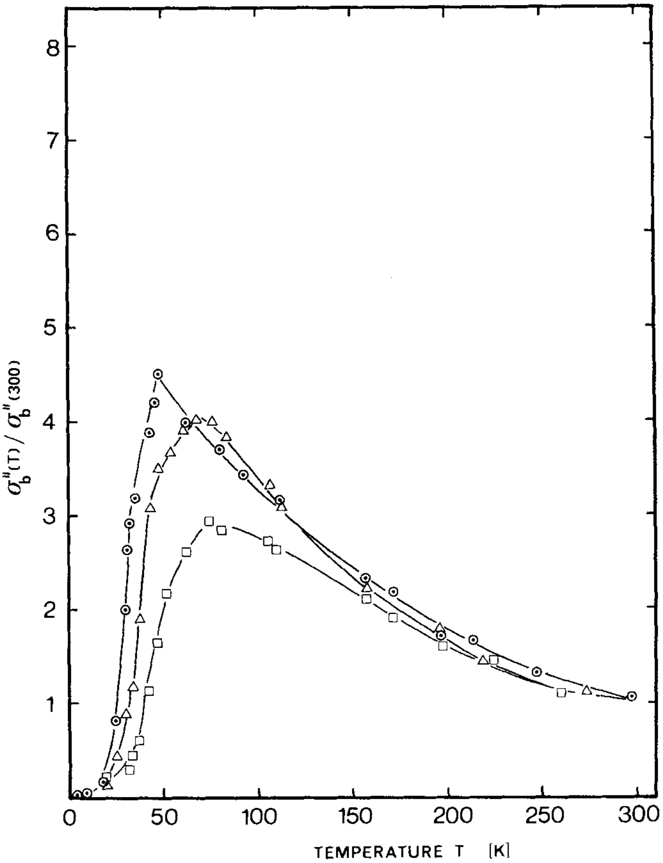


Fig. 3. *Normalized d.c. conductivity of* $(TTT)_2$-I_3 *single crystals, showing extrinsic behaviour*

We have also measured the temperature dependence of the d.c. conductivity in the *a* and *b* directions. These measurements still suffer from mechanical and thermal stresses due to the contacts, leading to tiny breaks along the *a, b*-plane, as *e.g.* shown in *Figure 1*, bottom left. We can, however, conclude from the present data that the behaviour in this direction is much less metallic, and probably more of the hopping type.

Figure 5 illustrates the d.c. conductivity behaviour of single crystals of $(TTT)_2$-I_3, as dependent on sample quality. To some extent, the following remarks are also applicable to other organic metals derived from the chalcogenated aromatic hydrocarbons, *e.g.* $(TSeT)_3$-(o-chloranil) [17] [18].

We denote with A the region of crystals of low quality. Such crystals generally results from an inadequate crystallization procedure, or sometimes from a strong misfit in the stoichiometric ratio, which, in addition, induces so many microdefects as to spoil the intrinsic properties. The starting materials necessary to obtain crystals which gave values in this region can be of quite low purity. Region B, of course, is a transition region. Here, the impurities introduced by the starting

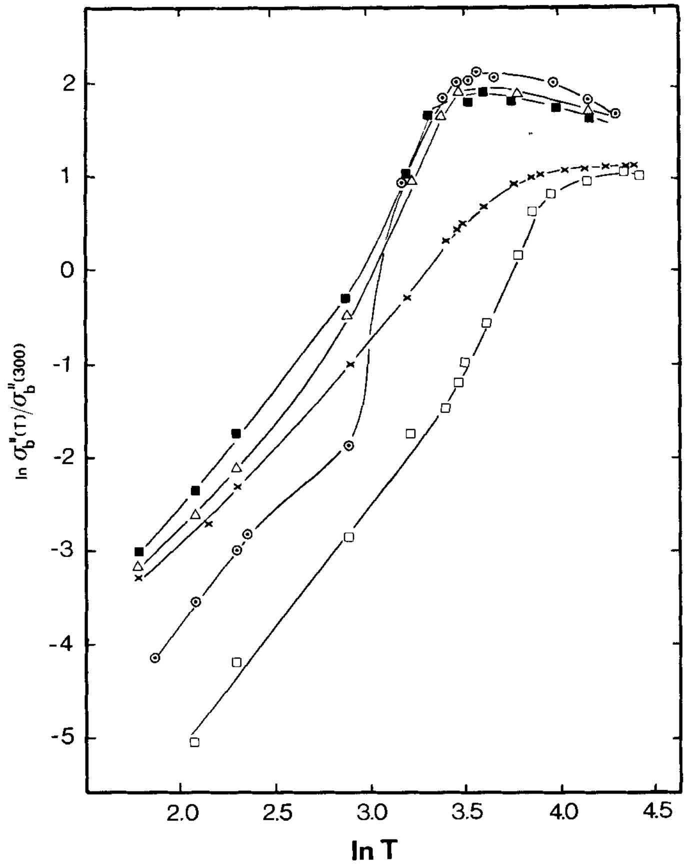


Fig. 4. *Normalized d.c. conductivity of* $(TTT)_2$-I_3 *single crystals at temperatures near and below the temperature of the conductivity maximum*

materials or by the crystal growth procedure, itself, begin to influence the temperature behaviour. The lower part of region C, finally, is only reached with high purity compounds, prepared *e.g.* as described above, and with perfect-looking crystals. *Figure 2* makes it clear that the maximum of the conductivity can be quite sharp, and *Figure 5* demonstrates the difficulties involved in finding the temperature of the intrinsic conductivity maximum of this material. *Shchegolev et al.* [25] reported a transition temperature of about 33 K as measured by microwaves, and we are tempted to conclude from this that we have indeed achieved the intrinsic values by d.c. measurements. Yet, it seems highly improbable to us that their crystals had exactly the same stoichiometry as ours. In fact, we have analysed the X-ray spectra of 3 crystals giving the same result as tabulated in *Table 1*; however, the crystals of *Figures 2* and *3* could not be analysed. Work to define each measured crystals by X-ray, and to try to set up a strict correlation between the electrical behaviour and the iodine spacing, is under way. In addition, *Shchegolev* [25] mentioned a microwave ratio of $\sigma_{\max}/\sigma$ (300) of the order of 1000, and a d.c. behaviour which falls into region B. Therefore, we are inclined to put forward the assumption that

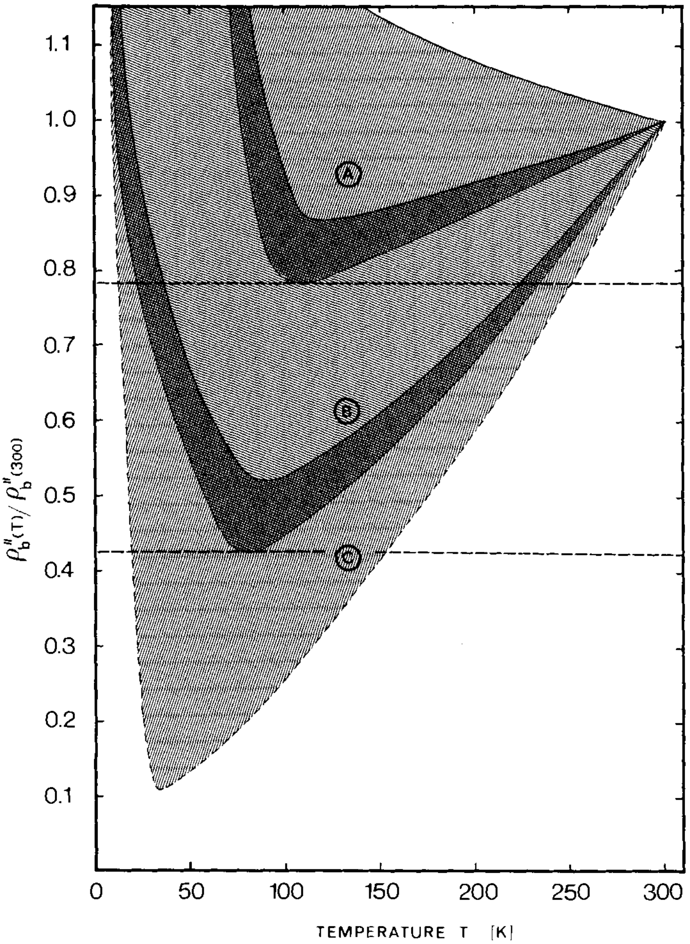


Fig. 5. *Typical convergence to intrinsic properties* (A to C) *of the normalized d.c. resistivity of* $(TTT)_2$-I_3 *single crystals*

the impurity-induced microcracks dominate the d.c. conductivity of regions B and C.

In conclusion, we believe that $(TTT)_2$-I_3 is a metallic compound physically as complicated as, *e.g.* TTF-TCNQ, despite its simpler anion chain. We feel positive that much further investigation in analogy with the work on KCP ($K_2Pt(CN)_4$-$Br_{0.3} \cdot 3H_2O$, see *e.g.* [26] [27]) and TTF-TCNQ will be carried out by the, now numerous, research groups in this field.

Our conductivity results are explicable in terms of one-dimensional scattering mechanisms [28]. On the other hand, they are also indicative of, *e.g.*, a charge density wave current assuming strong interchain repulsion for the charge carriers, a model which has recently been elaborated [29]. However, it seems too early to decide whether a single particle or a collective particle model is dominant in this compound, that is, until much more information from, *e.g.* magnetic, optical, X-ray and neutron-scattering experiments becomes available.

We are grateful to Mrs. *G. Rihs* for the X-ray analysis contribution. We thank Miss *Chr. Brücher* for the electronmicroscope photographs. We also thank *K. Hauenstein* for the help in the synthesis and wish to express our appreciation to *J. Pfeiffer* for his experimental assistance.

Note added in proof. A recent publication by *G. Mihaly et al.* [30] infers that, with crystals grown from solution, sample dependent variations of the temperature behaviour of the conductivity do also occur.

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