# Crystal Structure and Electrical Conductivity of Tetrathiafulvalene Thiocyanate (TTF)(SCN)$_{0.57}$

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The organic conductor, (TTF) (SCN)$_{0.57}$, is a quasi-one-dimensional non-stoichiometric compound, which crystallizes in a tetragonal system having a P4$_2$/mnm space group. The lattice constants are $a$=11.154 (3) and $c$=3.607 (2) Å. TTF molecules form segregate eclipsed stacks with thiocyanate ions occupying the channels between the stacks. The intermolecular distance between adjacent TTF molecules is 3.607 Å. The room-temperature electrical conductivity is 85—310 (Ω cm)$^{-1}$. A series of *resistance jumps* are observed in the temperature-dependent resistivity curves.

Considerable work has recently been focussed on attempting to understand the unusual physical properties of the quasi-one-dimensional salts of organic radicals. Unlike a crystal of (TTF)(TCNQ) composed of segregated stacks of TTF and TCNQ, crystals of (TTF)(X) (X=I, Br, Cl) contain only TTF columns. The large room-temperature conductivities of (TTF)(X) (200—500 (Ω cm)$^{-1}$), comparable to that of (TTF)-(TCNQ), are attributed to the characteristic columnar structures.[1-4]

In this paper, the crystal structure and the elctrical conductivity of 1,4,5,8-tetrathiafulvalene thiocyanate, (TTF)(SCN)$_{0.57}$, are reported.

## Experimental

Tetrathiafulvalene was synthesized according to the published procedure.[5] After recrystallization twice from a cyclohexane–hexane solution, TTF was converted to tetrafluoroborate (TTF)$_3$(BF$_4$)$_2$. Tetrathiafulvalene thiocyanate crystals having the approximate composition, (TTF)$_{11}$(SCN)$_6$ (or (TTF)(SCN)$_{0.545}$),[6] were easily prepared from (TTF)$_3$(BF$_4$)$_3$ and tetrabutylammonium thiocyanate[7] *via* methathesis in hot acetonitrile.

Oscillation and Weissenberg photographs show the crystals to be tetragonal. The systematic absence of $h0l$ with $h+l=2n+1$ and of $0k0$ with $k=2n+1$ indicate that the space group is P4$_2$/mnm, P4$_2$nm or P$\bar{4}$n2. The unit-cell dimensions, as determined by means of a diffractometer using Mo $K\alpha$ radiation, are $a$=11.154(3) and $c$=3.607(2) Å. The density measured using the flotation method was 1.756±0.015 g cm$^{-3}$ and the corresponding composition of the complex was calculated to be (TTF) (SCN)$_{0.57\pm0.03}$. No additional weak satellite-type reflections[1,2] indicating the existence of two distorted sublattice cations and anions were observed (see note added in proof). The intensity data were collected with a Rigaku automated four-circle diffractometer. Owing to the small size of the specimen, only 120 independent reflections of 461 accessible reflections ($2\theta \leq 55°$) were recorded sufficiently accurately ($|F|>3\sigma$).

## Structure Determination and Discussion

The trial structure was easily deduced from the Patterson syntheses and refined by the block-diagonal least-squares method. In view of the planar structure of TTF, the space group was assumed to be P4$_2$/mnm which was confirmed by the reasonable convergence of the structure at a later stage of refinement. Fourier calculations based on the atomic parameters of TTF showed a columnar distribution of the electron densities at (0,1/2,$z$) ($0 \leq z < 1$) and that the magnitude of the electron density is almost constant along the crystallographic c axis, indicating one-dimensional disorder of the atomic positions of the S, C, and N atoms. Therefore, the scattering factors of the S, C, and N atoms were evaluated by assuming a one-dimensionally random distribution and a common isotropic thermal parameter. The $R$ value was reduced smoothly to 0.045. The final atomic parameters are given in Table 1.

The structure viewed along the c axis is shown in Fig. 1. TTF has D$_{2h}$(mmm) symmetry and is stacked in an eclipsed column. Similar eclipsed stacks have been found in the crystals of TTF–halogen systems. The c axis is perpendicular to the molecular plane. The interplanar distance of 3.607 Å is comparable to those in (TTF)(Br)$_{0.71-0.76}$ (3.57 Å[1]) and (TTF)(I)$_{0.71}$ (3.55 Å[2]) crystals, but is much larger than the interplanar distances of TCNQ in the "ring-external bond type" columns of the high-conductive TCNQ salts (3.17—3.26 Å[8]). Considering the large intermolecular distances, the "metallic" conductivities[1,3,4] are undoubtedly due

TABLE 1. THE FINAL ATOMIC PARAMETERS (×10$^4$)

The standard deviations are in parenthesis. The temperature factors are of the form $\exp[-2\pi^2(h^2U_{11}a^{*2}+k^2U_{22}b^{*2}+l^2U_{33}c^{*2}+2hkU_{12}a^*b^*+2hlU_{13}a^*c^*+2klU_{23}b^*c^*)]$.

| | $x$ | $y$ | $z$ | $U_{11}$ | $U_{22}$ | $U_{33}$ | $U_{12}$ | $U_{13}$ | $U_{23}$ |
|---|---|---|---|---|---|---|---|---|---|
| S | 3054(2) | 4902(3) | 0 | 433(12) | 598(17) | 625(14) | 2(8) | 0 | 0 |
| C(1) | 4580(15) | 4580 | 0 | 347(95) | 347 | 707(112) | 24(20) | 0 | 0 |
| C(2) | 2558(10) | 3423(10) | 0 | 555(65) | 739(75) | 831(89) | −47(22) | 0 | 0 |
| H | 1669(102) | 3452(105) | 0 | 6.9$^{a)}$ | | | | | |
| (SCN)$^{b)}$ | 0 | 5000 | (0—1.0) | 3.5 | | | | | |

a) Isotropic temperature factor (Å$^2$). b) The atomic position of the SCN anion is disordered along the c axis.

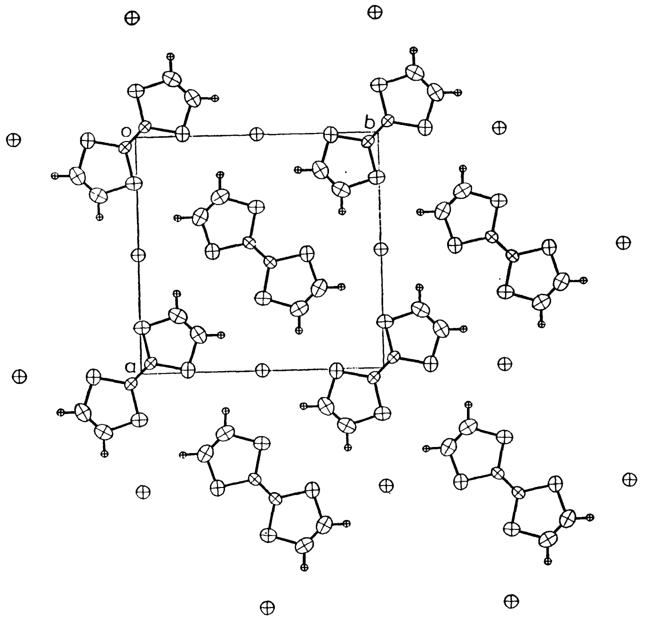


Fig. 1. The (001) projection of the $(TTF)(SCN)_{0.57}$.

to the intermolecular overlap of the atomic orbitals of the sulfur atoms. As observed in the TTF-halogen crystals, the TTF columns form tunnels. Like $(TTF)(SCN)_{0.57}$, $(TTF)(Cl)_{0.92}$ has a tetragonal structure and the tunnels are occupied by the disordered chlorine anions.[2] (see note added in proof). However in $(TTF)(Br)_{0.71-0.76}$ and $(TTF)(I)_{0.71}$, there are separate cation and anion sublattices.[1,2] This incommensurability produces additional "satellite-type" reflections[1,2] due to the periodically-modulated superstructure. As originally pointed out by Johnson and Watson,[2] the general features of the crystal structure of these salts can be summarized as follows:

(1) If the radius of the cation is small enough to enter the tunnel formed by the TTF columns ($r \leqq 1.8$ Å (the Cl ionic radius)), the crystal is tetragonal. Owing to loose packing, the atomic positions of the anions tend to be disordered in the tunnels.

(2) If $r \geqq 1.96$ Å (the Br ionic radius), the anions cannot enter the tunnel without distortion of the "TTF sublattice" so that a modulated superlattice is formed. Due to compact packing, the atoms are regularly arranged.

Consequently, it may be said that the repulsive force between anions and cations plays an important role in the appearance of the modulated superlattices of the TTF-halogen systems.

The tunnel structure of $(TTF)(SCN)_{0.57}$ appears to indicate the non-stoichiometric nature of the crystal. Considering that monoclinic $(TTF)(Br)_x$ can exist over the range of compositions, $0.71 \leqq x \leqq 0.76$, the number of anions stacked in a tunnel does not appear to be necessarily constant. Therefore, the composition obtained by Wudl *et al.*, $(TTF)_{11}(SCN)_6$, may be regarded as approximate. Since the distance between the adjacent atoms (ions) must be larger than the sum of the two van der Waals (ionic) radii, the value of $x$ for the $(TTF)(X)_x$ system must be smaller than $R/2r$, where $R(\approx 3.60$ Å) is the intermolecular distance between neighboring TTF molecules and $r$ is the ionic radius of the anion. The calculated maximum values (with observed values in parenthesis) are 0.83 (0.71), 0.92 (0.71—0.76), 1.0 (0.92), and 0.59 (0.583) (see note added in proof) for the iodide, bromide, chloride and thiocyanate, respectively. In this connection, it may be worthwhile to point out that 1 : 1 bromide ($x=1.0$) is stacked quite differently.[1]

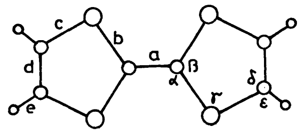
The bond lengths and angles are given in Table 2. Considering the fairly large standard deviations, the values for $(TTF)(SCN)_{0.57}$ appear to be in good agreement with those for other TTF salts.

## Electrical Conductivity

The room-temperature conductivities of $(TTF)(I)_{0.71}$ and $(TTF)(Br)_{0.71-0.76}$ are continuous in the range from 200—500 $(\Omega\,\mathrm{cm})^{-1}$.[1,3,4] For the iodide, a transition occurs between 200 and 230 K, which is similar to that which occurs near 180 K for the bromide. Unlike $(TTF)(Br)_{0.71-0.76}$, $(TTF)(I)_{0.71}$ displays a hysteresis in its conductivity curve upon temperature cycling. Although these systems are considered to undergo metal-insulator transitions at about 200 K, no

TABLE 2. DIMENSIONS OF TTF MOLECULE

| | $(TTF)(SCN)_{0.57}$ 295 K | TTF[a] 295 K | $(TTF)(TCNQ)$[b] 295 K | 45 K | $(TTF)_7(I)_5$[c] 295K | $(TTF)(Cl)_{0.92}$[c] 295 K |
|---|---|---|---|---|---|---|
| $a$(Å) | 1.324(24) | 1.349(3) | 1.372(4) | 1.370(4) | 1.350 | 1.329 |
| $b$ | 1.739(17) | 1.757(2) | 1.745(3) | 1.743(2) | 1.732 | 1.734 |
| $c$ | 1.730(12) | 1.726(2) | 1.739(3) | 1.733(2) | 1.721 | 1.723 |
| $d$ | 1.317(15) | 1.314(3) | 1.326(4) | 1.349(2) | 1.336 | 1.315 |
| $\alpha$(°) | 123.1(1.1) | 122.8(1) | 122.6(2) | 122.4(2) | 122.9 | 123.0 |
| $\beta$ | 113.8(1.6) | 114.5(2) | 114.7(3) | 115.1(1) | 114.3 | 113.9 |
| $\gamma$ | 95.6(0.7) | 94.4(1) | 95.0(1) | 95.0(1) | 95.7 | 95.5 |
| $\delta$ | 117.5(0.9) | 118.3(1) | 117.4(1) | 117.4(2) | 117.2 | 117.4 |
| e | 1.02(12) | | | | | |
| $\varepsilon$ | 106(7) | | | | | |



a) Ref. 9. b) Ref. 10. c) Ref. 2.

direct evidence has been obtained from the temperature dependence of the conductivities.

The conductivity measurements of $(TTF)(SCN)_{0.57}$ were performed along the crystallographic c axis (needle axis of the crystal) using the standard four-probe method with a 25 μm diameter gold wire bonded to the crystal by *duPont* 4817 conductivity paint and/or colloidal graphite (aquadag). The crystals became less conductive after they had been stored for a long time in contact with air. In addition, they are very fragile and are frequently broken by a rapid change in temperature, especially when the temperature change passes through *ca.* 0 °C. Thus, measurements of the temperature-dependent conductivities (300—120 K) were performed for only a few specimens. The room-temperature conductivities for the five samples are 85, 100, 200, and 310 $(\Omega\,cm)^{-1}$, respectively which agree with the value (250 $(\Omega\,cm)^{-1}$) of Wudl. The discrepancies between the conductivities for the various specimens is not as large as those reported for many one-dimensional conductors.[11] Figure 2 shows the d.c. resistivity of $(TTF)(SCN)_{0.57}$ ($R(\Omega\,cm)=1/\sigma$). For most of the specimens, the resistivity does not decrease with temperature. Curve IIa is a typical result and is similar to those for $(TTF)(Br)_{0.71-0.76}$ and $(TTF)(I)_{0.71}$;[3,4] the conductivities decrease slightly with temperature in the high-temperature region ($T>230$ K) and decrease sharply with temperature in the low-temperature region ($T<200$ K). However, for one specimen ($\sigma$(R.T.) = 100 $(\Omega\,cm)^{-1}$), a minimum point, indicative of the possible existence of a metal-insulator transition, is observed in temperature-dependent resistivity curve Ia. This result appears to be consistent with the conductivities reported by wudl who showed that $(TTF)(SCN)_{0.57}$ becomes more conductive over certain low-temperature regions ($\sigma$(R.T.) = 250 $(\Omega\,cm)^{-1}$ and $\sigma$(200 K) = 310 $(\Omega\,cm)^{-1}$).[6] Considering that the disorder and defects in a crystal have great influence on the electrical conductivity and frequently smear out the metal-insulator transition,[12] the difference between the curves can be attributed to a difference in the quality of the samples.

As the temperature was changed, a series of *resistance jumps* were observed. Similar *jumps* observed for $(TTF)(I)_{0.71}$ have been attributed to separate occurrences of the transition in different portions or domains of the crystal. A similar explanation appears to be probable, since a microscopic examination revealed that a $(TTF)(SCN)_{0.57}$ crystal is composed of many *blocks*. At first, it appeared that a *resistance jump* accompanied a *break*

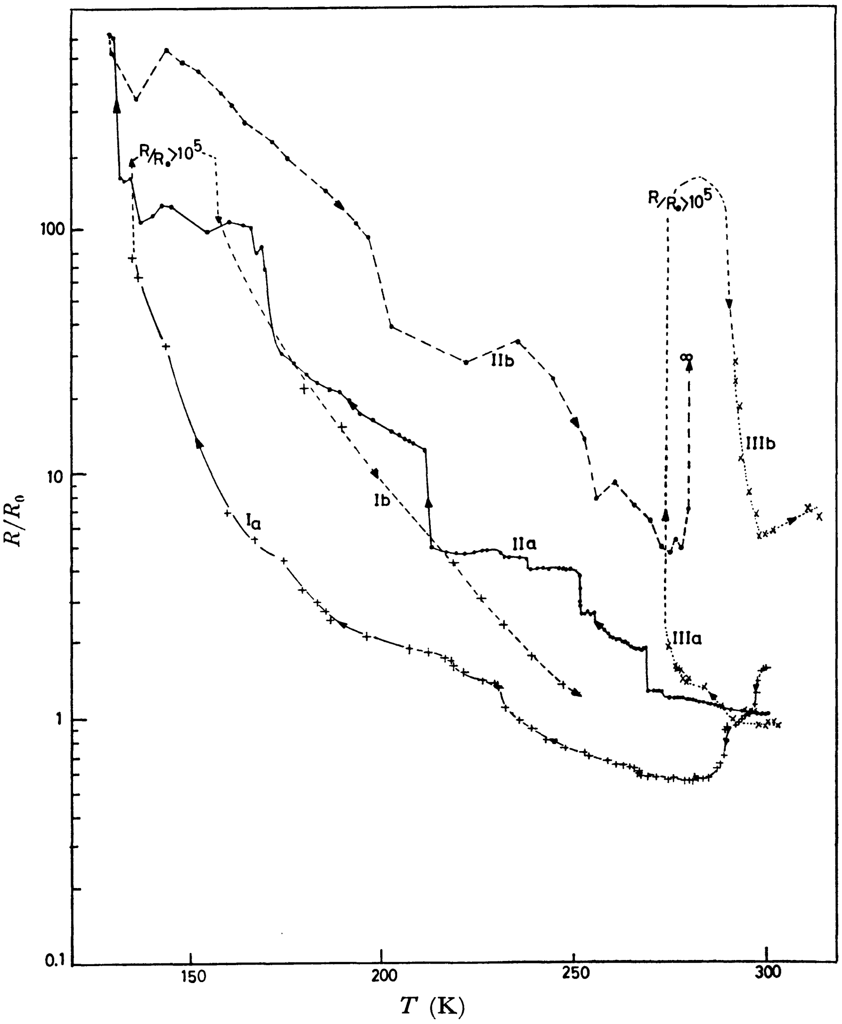


Fig. 2. Temperature dependence of the conductivity along the c axis for three samples. Arrows indicate the direction of temperature change.

Table 3. Comparison of the crystal structure determinations

| | | $(TTF)(SCN)_x$ | System | Space group | $a$ (Å) | $c$ | $D$(g cm$^{-3}$) | |
|---|---|---|---|---|---|---|---|---|
| | | $x$ | | | | | Obsd | Calcd |
| i. | This work | 0.57±0.03 | tetragonal | $P4_2/mnm$ | 11.154 | 3.607 | 1.756±0.015 | — |
| ii. | Wudl *et al.* | 0.545 (=6/11) | tetragonal | P4n2[a)] | 11.205 | 3.633 | — | 1.700 |
| iii. | Somoano *et al.* | 0.583 (=7/12) | tetragonal (or pseudotetragonal) | — | $\sqrt{2}\times 11.11$ | $\begin{cases}3.61^{b)}\\6.15\end{cases}$ | — | 1.76 |

a) This space group[13)] is probably incorrect and the correct one is $P\bar{4}n2$. b) The *C*-centered lattice is used to facilitate comparisons with the $(TTF)_7(I)_5$ structure. 3.61 and 6.15 Å are the lattice constants of the TTF and the SCN sublattices, respectively.

in the *blocks*, because the crystals are very fragile. According to this conjecture, many blocks can be considered to be broken during the cooling process and then the electric conduction paths would become very limited. However, in fact, upon heating to room temperature after cooling to about 130 K, the resistivities again decrease. In addition, the observation of the stepwise decrease in resistivity (curve Ia (for 270—300 K) appears to be inconsistent with the above explanation based on the *breaks* in the *blocks*. Probably, the resistivity jumps are associated with crystal blocks passing through the transition between a high-conductive state and a low-conductive state separately.[2)] The series of transitions appears to indicate that the phase transition is affected by the shape and size of each *block*.

*Note Added in Proof.* After the completion of this paper, investigations of the electronic and structural properties of $(TTF)(SCN)_x$ and $(TTF)(SeCN)_x$ were reported by Wudl *et al.*[13)] and Somoano *et al.*[14)] As shown in Table 3, the crystallographic data given in their papers do not agree with those reported here. It is therefore, appropriate to briefly mention the reason for these discrepancies.

(1) Repeated elemental analysis by Wudl *et al.* results in the formula, $(TTF)_{11}(SCN)_6$ (*i.e.*, $(TTF)(SCN)_{0.545}$), whereas the formula of Somoano *et al.* is $(TTF)_{12}(SCN)_7$ (*i.e.*, $(TTF)(SCN)_{0.583}$), which was determined on the basis of the ratio of the TTF sublattice spacing to the SCN sublattice spacing. Although, in the present work, the samples were prepared according to the method of Wudl, the formula, $(TTF)(SCN)_{0.57\pm0.03}$, obtained on the basis of the measured density (1.756±0.015) agrees rather well with that of Somoano *et al.* The crystal structure of $(TTF)(SCN)_x$ was refined for several $x$-values. For $0.50<x<0.70$, the final structures as well as the temperature factor for SCN, are essentially identical to each other. For $x=0.60$, the lowest $R$-value, 0.045, and the corresponding final atomic parameters listed in Table 1 were obtained.

(2) The lattice constants of the TTF sublattice of Somoano *et al.* agree well with those presented here, whereas the values of Wudl *et al.* appear to differ from the other two, by more than the experimental error.

(3) For the crystals used here, the atomic positions of the S, C, and N atoms are one-dimensionally disordered along the c direction and no indication of the existence of the two sublattices of the TTF and SCN compound were obtained from X-ray diffraction. However, the X-ray examination of Somoano *et al.* revealed the existence of the two spacings, 3.61 Å for TTF and 6.15 Å for SCN, *i.e.*, in their crystals, the translational symmetry of the SCN arrangement is different from that for TTF. Considering that the crystals of Somoano *et al.* were grown by the diffusion method from $(CH_3)_4N(SCN)$ and $(TTF)_3(BF_4)_2$, this disagreement appears to be due to the difference in the sample preparation procedures. Some details of the crystal structure of $(TTF)_{11}(SCN)_6$ were reported by Wudl *et al.* The arrangement of TTF is very similar to that determined here, whereas their conclusion of the regular arrangement of SCN is inconsistent with their c-axis lattice constant, because this constant should be larger than the SCN spacing ($c$/0.545).

In conclusion, the crystals used here appear to be identical with those of Somoano *et al.* except for the orderliness of SCN. The degree of disorder may change according to differences in the procedure of preparation of the crystals. Such disorder has been observed for crystals of *N*-methylphenazinium-TCNQ.[15),16)] It is not clear how the crystals of Wudl *et al.* differ from those of Somoano *et al.* and those used in the present experiments.

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