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Synthesis, Structure and Physical Properties of a Two-Dimensional Organic Metal, Di[bis(ethylenedithiolo)tetrathiofulvalene] triiodide, (BEDT-TTF)⁺₂ I⁻₃

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Synthesis, Structure and Physical Properties of a Two-Dimensional Organic Metal, Di[bis(ethylene-dithiolo)tetrathiofulvalene] triiodide, (BEDT-TTF) $^+_2$ I $^-_3$

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Electrical oxidation of bis(ethylenedithiolo)tetrathiofulvalene (BEDT-TTF) **1** in a nitrogen saturated tetrahydrofurane solution containing $(n\text{-C}_4\text{H}_{10})_4\text{N}^+\text{I}_3^-$ as electrolyte results in the deposition of crystal plates of $(\text{BEDT-TTF})_2^+\text{I}_3^-$, $(\text{C}_{10}\text{H}_8\text{S}_8)_2\text{I}_3$. These two dimensional crystals are triclinic, space group $\text{P}\bar{1}$, $a = 9.211(2)$, $b = 10.850(4)$, $c = 17.488(5)$ Å, $\alpha = 96.95(2)$, $\beta = 97.97(2)$, $\gamma = 90.75(2)^\circ$, $V = 1717$ Å 3 , $M_r = 1150.01$, $Z = 2$, $D_x = 2.22$ g cm $^{-3}$, $R_w = 0.037$ for 2462 observed reflections. Sheets of alternating cations and anions occur in the compound. The most prominent intermolecular S—S contacts (~ 3.5 Å) are found between the stacks of BEDT-TTF. The stacking of the molecules and the interstack contacts give the compound a two-dimensional character which influences the physical properties.

The room temperature conductivities in the ab plane range typically between 60 and 250 (Ω cm) $^{-1}$. The conductivity anisotropy in this plane is small with a ratio of $\sigma_a/\sigma_b \leq 2$, while in the direction perpendicular to the ab -plane at least a 1000 times smaller value is found. The temperature dependent conductivity and thermopower measurements show that in the temperature range between 135 and 300 K the crystals

behave like a two dimensional metal, while below 135 K a metal-insolator transition occurs. The thermopower values indicate that the high temperature conductivity is dominated by holes. An estimate of the Fermi energy ϵ_F gives a value of $\epsilon_F \approx 0.3$ eV.

1. INTRODUCTION

The aim of the present investigation was twofold:

(i) to find new radical solids with polyiodide counterions which might support the electronic conduction of these materials,

(ii) to synthesize new and more isotropic organic metals. The building blocks of such solids should be connected by strong intermolecular contacts and exchanges in *more than one* direction. The polarizable polyiodides might help in these interionic contacts.

An interesting variety of crystallized cation radical salts can be obtained if iodides are used as counter anions.^{1,2} Instead of the singly charged I^- ions different polyiodide ions I_n^- ($n = 3, 4, 5 \dots$) can be stabilized in the crystals. This leads—besides the more structural implications in “linear” systems of this type³—to rather unusual formal oxidation numbers for the “average” radical cation. Consequently different degrees of band fillings result if the radical ions interact to give metallic systems. One of the most interesting and recently widely investigated donors is bis(ethylenedithiolo)-tetrathiofulvalene (BEDT-TTF) **1**. Its electrochemical oxidation in the presence of counterions like ClO_4^- , BF_4^- e.g. results in compounds of varying compositions and structures and therefore varying physical properties,^{4–8} including superconductivity in the ReO_4^- salt.⁵ A polyiodide has so far not been reported. Since the degree of band filling is essential for the physical properties of a metal we electrochemically synthesized a polyiodide of **1** to investigate its properties mainly in relation to the other radical solids of this donor.

Radical salts of BEDT-TTF have another advantage. They are reported to be electrically less anisotropic than other organic metals suggesting the notion of a two-dimensional (2d) metal.⁴ In order to prove the 2d intermolecular contacts the structures of a perchlorate and a perrhenate salt have recently been published,^{5,7} as well as studies of their diffuse X-ray scattering⁸ hinting at a structural phase transition below 200 K. Since the voluminous polyiodide counterions could either enhance existing 2d contacts or even provide new pathways for additional 3d exchanges we prepared the title compound in the hope to reduce the anisotropy of the conductivity. Here we report the structure and physical properties of a new organic metal, the

electrical conductivity of which is almost isotropic in the highly conducting plane of the crystal.

2. EXPERIMENTAL

2.1. Preparation of 1

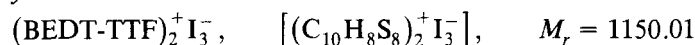
1 was prepared according to Hartke *et al.*⁹ and Mizumo *et al.*¹⁰ by reduction of carbon disulfide with potassium in dimethylformamide and subsequent reaction with 1,2-dibromoethane. The intermediate thione C₅H₄S₅ (yellow plates from ethanol, m.p. = 121–122 °C) was coupled with triethylphosphite in inert atmosphere at 120 ° and recrystallized twice from chlorobenzene to give bright red needles with m.p. 258–260 ° (dec.).

Tetra-*n*-butylammonium triiodide was prepared following a procedure of Buckles *et al.*¹¹ by mixing 0.02 moles tetrabutylammonium iodide with 0.05 moles of iodine in 500 ml of CCl₄ and recrystallizing the black precipitate in methanol to give black needles (m.p. 67 °).

2.2. Electrochemical syntheses

Crystals of (BEDT-TTF)₂⁺I₃⁻ were prepared using standard electrochemical techniques in a 100 ml electrochemical cell of 3 compartments. Glass filters were used to separate the compartments from each other. 0.1 g BEDT-TTF and 0.5 g Bu₄NI₃ (Bu₄N⁺ = tetrakis(*n*-butyl)ammonium ion) were dissolved in 100 ml tetrahydrofuran (THF; Merck Uvasol, dried over basic aluminium oxide) and saturated with dry nitrogen. The crystals were grown using a constant current of 15 μA resulting in a potential of about 1.25 V, at room temperature and under exclusion of light. The crystals grow as plates of 3–10 mm diameter on the anode and have the following composition.

Analysis:



Calc.: C = 20.88%, H = 1.41%, S = 44.60%, I = 33.10%

Found: C = 20.98%, H = 1.57%, S = 45.46%, I = 33.49%

The crystals were collected on a glass filter, washed with THF and dried. Thin crystals are brown, while thicker crystals are black with a metallic luster.

TABLE 1
Atom coordinates ($\times 10^4$) and temperature factors ($\text{\AA}^2 \times 10^3$)

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i>
I(1)	0	5000	5000	40(1) ^a
I(2)	3064(1)	5716(1)	4940(1)	56(1) ^a
I(3)	5000	0	5000	38(1) ^a
I(4)	8086(1)	−688(1)	5118(1)	55(1) ^a
S(1)	8861(6)	−574(5)	1127(3)	36(2) ^a
S(2)	7011(6)	1460(5)	663(3)	39(2) ^a
S(3)	7228(6)	2890(5)	2204(3)	39(2) ^a
S(4)	9420(6)	440(5)	2807(3)	39(2) ^a
S(5)	8310(6)	−1913(5)	−680(3)	35(2) ^a
S(6)	6451(6)	143(5)	−1100(3)	37(2) ^a
S(7)	8104(6)	−3237(5)	−2256(3)	39(2) ^a
S(8)	5965(6)	−722(5)	−2794(3)	34(2) ^a
C(1)	7800(32)	47(27)	376(18)	32(12) ^a
C(2)	8601(14)	622(11)	1867(7)	25(5) ^a
C(3)	7750(20)	1556(17)	1646(11)	35(8) ^a
C(4)	8280(20)	2769(18)	3170(11)	34(8) ^a
C(5)	8299(20)	1458(18)	3393(11)	33(8) ^a
C(6)	7548(20)	−481(17)	−379(11)	31(8) ^a
C(7)	7628(19)	−1942(17)	−1673(10)	29(7) ^a
C(8)	6779(20)	−970(18)	−1873(11)	32(7) ^a
C(9)	7464(19)	−2850(16)	−3241(10)	27(7) ^a
C(10)	5932(15)	−2313(11)	−3313(7)	32(5) ^a
S(9)	4154(5)	3234(5)	9335(3)	39(2) ^a
S(10)	5506(5)	5454(4)	8878(3)	38(2) ^a
S(11)	3569(6)	1886(4)	7763(3)	42(2) ^a
S(12)	5157(6)	4550(4)	7196(3)	45(2) ^a
C(11)	4944(18)	4740(15)	9635(9)	23(6) ^a
C(12)	4307(18)	3250(16)	8346(10)	24(7) ^a
C(13)	4893(14)	4235(12)	8142(7)	30(5) ^a
C(14)	4223(14)	2062(12)	6858(7)	28(5) ^a
C(15)	3976(15)	3353(13)	6593(7)	38(6) ^a
S(13)	8830(5)	3352(4)	9328(3)	38(2) ^a
S(14)	10776(5)	5267(4)	8900(3)	37(2) ^a
S(15)	8199(4)	1965(3)	7764(2)	37(1) ^a
S(16)	10354(4)	4326(3)	7211(2)	40(2) ^a
C(16)	9927(18)	4718(15)	9639(9)	30(6) ^a
C(17)	9116(16)	3259(14)	8345(8)	22(6) ^a
C(18)	9965(17)	4112(15)	8151(9)	26(6) ^a
C(19)	8330(19)	2343(16)	6776(10)	35(7) ^a
C(20)	9881(14)	2774(11)	6691(8)	35(6) ^a

^aEquivalent isotropic *U* defined as one third of the trace of the orthogonalised U_{ij} tensor.

FIGURE 1 BEDT-TTF molecule (A) with bond distances (Å) and angles (°). Thermal ellipsoids at the 50% probability level.

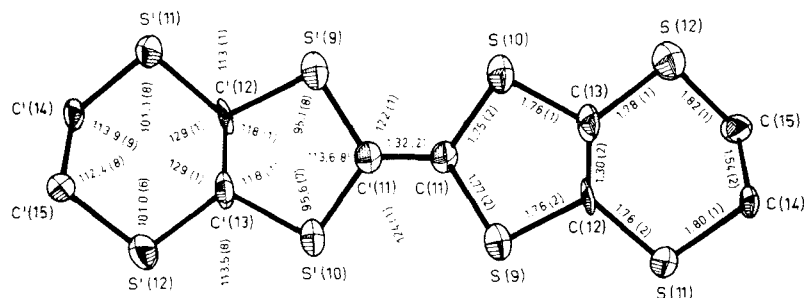


FIGURE 2 Molecule (B), analogous to Figure 1.

Figure 4 shows a stereoview of the structure. The organic cations form stacks parallel to the *a*-axis. Two crystallographically different stacks occur. Stack I is composed of the BEDT-TTF species with its center of mass at a general position, .76, $-.02, 0$ (molecule A), and its counterpart generated by the inversion center $0.5, 0, 0$. The interplanar distances along this stack (defining the molecular plane as the least-squares plane through the eight S atoms) are $3.92(5)$ and $3.81(5)$ Å. The two corresponding overlap patterns are shown in Figures 5 and 6, the shortest S—S contacts are indicated.

Stack II consists of the two molecules with centers of mass at special positions, $0.5, 0.5, 0$ (molecule B) and $0, 0.5, 0$ (molecule C) alternating along the stack. As there is a dihedral angle of $11.0(5)^\circ$ between the two molecular planes, an interplanar distance cannot be specified. Figure 7 shows the overlap pattern (by symmetry identical along the stack) with the shortest S—S contacts.

As indicated in Figure 4 much shorter S—S contacts occur *between* the stacks, the shortest one being $3.493(8)$ Å, and many others are shorter than the v.d.Waals distance of about 3.7 Å. These link the

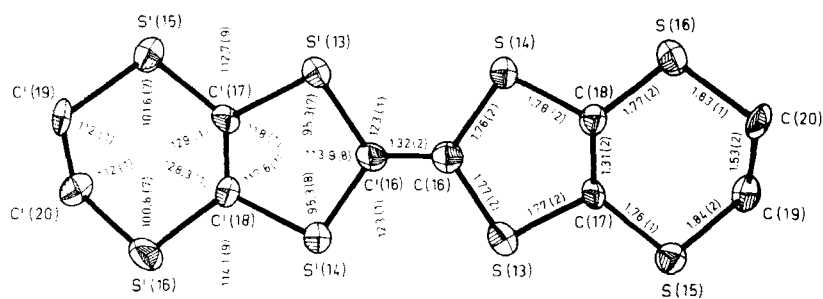


FIGURE 3 Molecule (C), analogous to Figure 1.

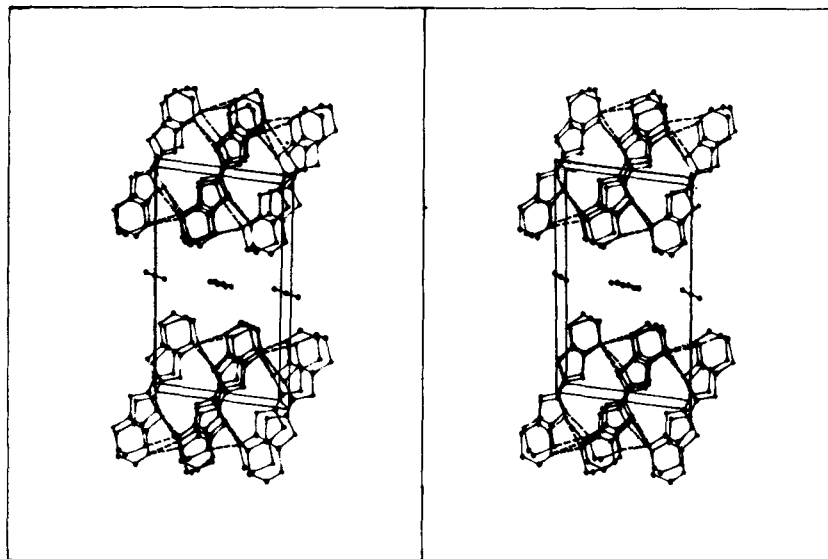


FIGURE 4 Stereoview of the structure seen along *a*. Intermolecular S—S contacts < 3.70 Å are drawn as broken lines.

stacks to sheets parallel to the *ab*-plane and give the compound a two-dimensional character. This situation, however, is different from that found in the ReO_4^- and ClO_4^- salts,^{5,7} where the molecular planes in adjacent stacks are parallel, and where the stacks are

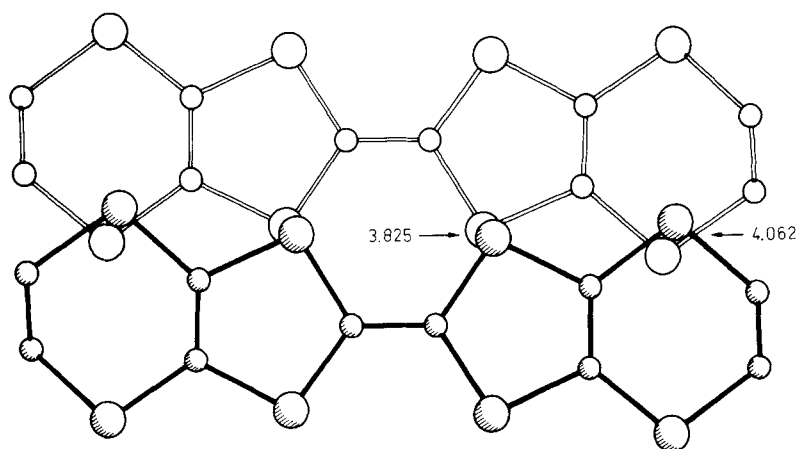


FIGURE 5 Overlap pattern of two molecules (A) in stack (I) with the larger interplanar distance (3.92(5) Å). The shortest S—S contacts (esd \approx 0.007 Å) are indicated.

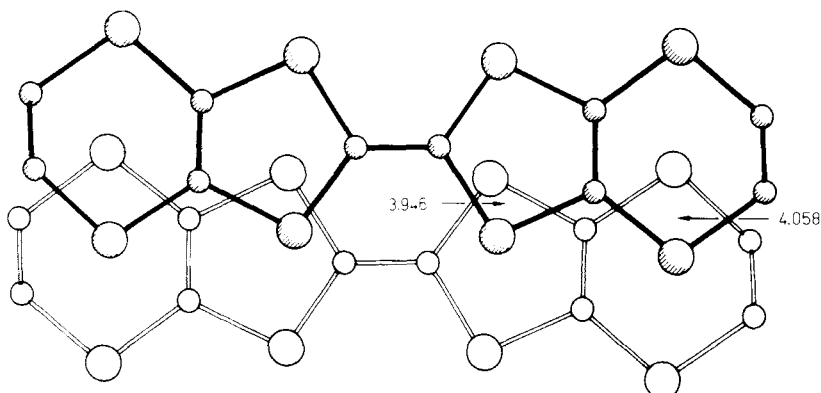


FIGURE 6 Overlap pattern of two molecules (A) in stack (I) with the shorter interplanar distance (3.81(5) Å) analogous to Figure 5.

crystallographically identical. In the triiodide salt adjacent stacks are crystallographically different, and there are large dihedral angles between their molecular planes, $59.4(5)^\circ$ and $70.4(5)^\circ$. This is made clear in Figure 8, a projection of the unit cell perpendicular to the molecular planes of stack I. Sections of this figure are shown in Figures 9 and 10, which contain pairs of adjacent molecules A and B, and A and C, respectively. The values of the interstack S—S contacts are indicated.

This type of two-dimensionality is new in the field of organic metals. It may be speculated that even a three-dimensional conducting organic system could be obtained. This would require that adjacent stacks are displaced by about half a molecular donor unit in a

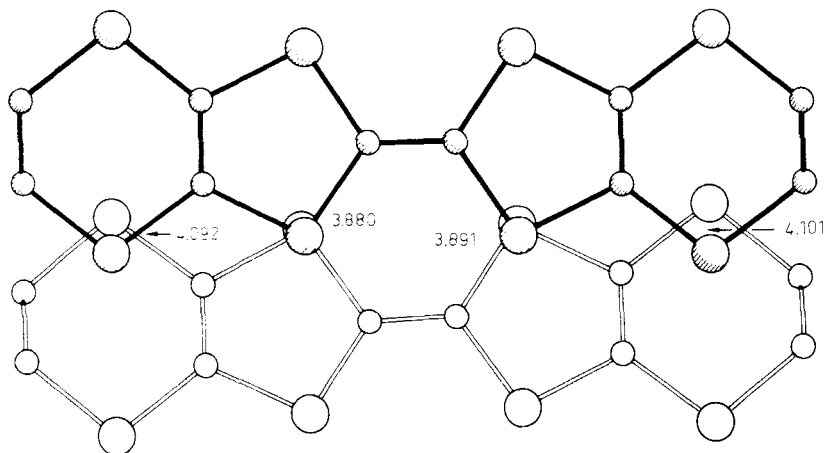


FIGURE 7 Overlap of molecules (B) and (C) in stack (II), viewed perpendicularly to molecule (C); analogous to Figure 5.

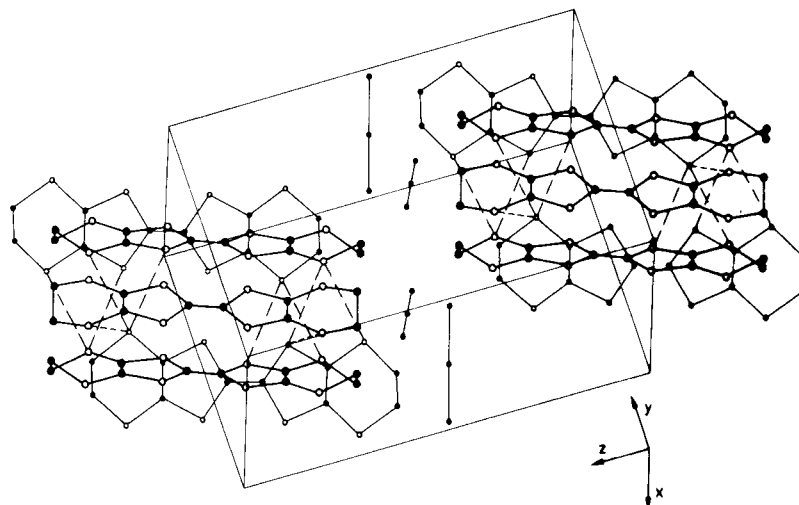


FIGURE 8 Projection of the unit cell perpendicular to the molecular planes in stack I.

direction perpendicular to the sheets, with the anions filling holes or channels in this matrix.

The sheets of BEDT-TTF are interleaved by sheets of triiodide anions. A section of a sheet is shown in Figure 11. The I_3^- anions form zig-zag chains with short interionic contacts along the chains, 3.897(2) and 3.904(2) Å, well below the v.d. Waals distance of 4.2 Å. The direction perpendicular to the sheets (*c*-axis) is the direction normal to the plate like crystals.

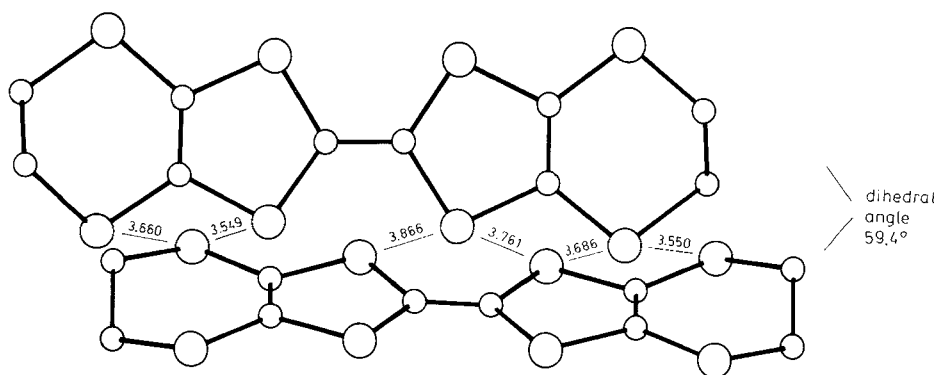


FIGURE 9 A pair of molecules A and B in adjacent stacks I and II, viewed perpendicularly to molecule A. The interstack S—S contacts (esd \approx 0.007 Å) are indicated.

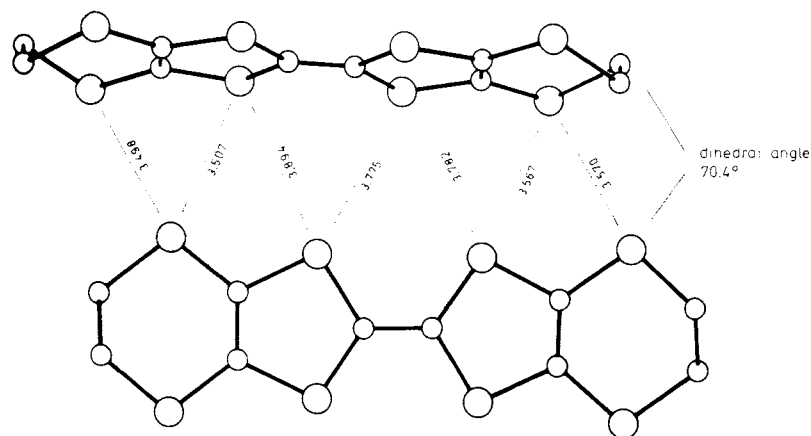
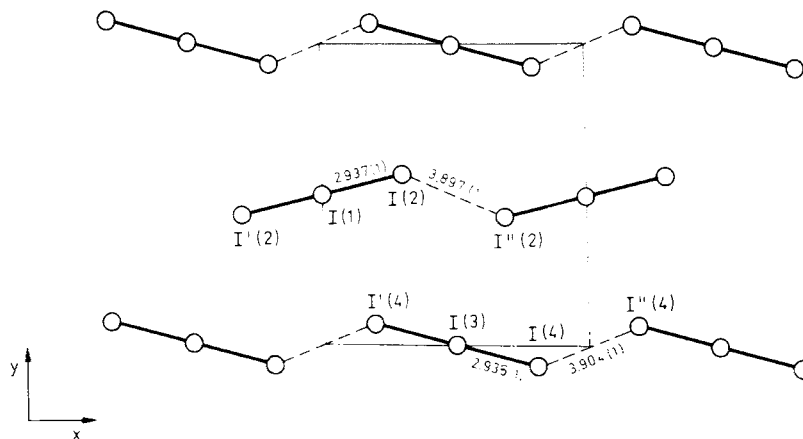


FIGURE 10 A pair of molecules A and C, analogous to Figure 9.

3. PHYSICAL PROPERTIES

The conductivity of $(\text{BEDT-TTF})_2^+ \text{I}_3^-$ crystals was measured by the standard four probe method with dc and lock-in-technique of 4 Hz. The contacts were made with silver or gold paint and had a resistance of a few ohms. Both dc- and lock-in methods gave identical results. The used apparatus was described recently.^{14,15}

Crystal stripes along different directions in the *ab*-plane were used for the conductivity and thermopower measurements. In addition measurements of the conductivity anisotropy in the *ab*-plane were

FIGURE 11 The I_3^- sheet viewed along *c*.

made with the Montgomery method,¹⁶ using nearly quadratic crystal plates. The typical observed room temperature conductivities in the *ab*-plane range between 60 and 250 (Ω cm)⁻¹. The conductivity perpendicular to the *ab*-plane, i.e. along the direction where cation and anion sheets alternate, is at least 1000 times smaller. The observed room temperature conductivity anisotropy in the *ab*-plane is small and the ratio $\sigma_a/\sigma_b \leq 2$ demonstrates the two dimensional character of the crystals. This small conductivity anisotropy is very similar⁴ to that found in (BEDT-TTF)₂⁺ClO₄⁻(1,1,2-trichloroethane)_{0.5} $\frac{2}{3}$ while in the (BEDT-TTF)₄⁺(ReO₄)₂⁻ $\frac{3}{2}$ crystals a ratio of $\sigma_a/\sigma_b \approx 20$ was observed.⁵ Nevertheless in the (BEDT-TTF)₂⁺I₃⁻ crystals the two dimensionality arises less by a side by side arrangement of the BEDT-TTF molecules as in the case^{4,6} of $\frac{2}{3}$ than from the two crystallographically inequivalent stacks with the inclined molecules as described in the structural section.

Figure 12 shows the temperature dependence of the conductivity normalized to the room temperature value ($\sigma(T)/\sigma(300)$) of a typical crystal stripe. By lowering the temperature from room temperature an increase in the conductivity is observed, indicating a metallic regime. At 135 K a phase transition occurs. Below this temperature the conductivity decreases with decreasing temperature showing a semi-conducting behaviour.

The metallic conduction in the high temperature region could be confirmed by temperature dependent thermopower measurements. The device for the thermopower measurement was similar to that described by Chaikin and Kwak.¹⁷ Figure 12 shows in addition to the conductivity data the temperature dependence of the thermopower *S*. In the temperature range between 135 and 300 K a linear temperature dependent thermopower *S* is found. This behavior is characteristic for a degenerate electron gas and metallic conduction. The positive sign of *S* implies that the conductivity is dominated by holes. Such a behavior can be expected by simply assuming that the formal charge on a BEDT-TTF molecule of $\frac{1}{2}$ results in a $\frac{3}{4}$ filled band. Assuming further that no conduction occurs along the anions would lead to conduction by holes in the $\frac{3}{4}$ filled band.

From the slope of the linear temperature dependent part of the thermopower *S* an estimate of the Fermi-energy ϵ_F can be obtained. Taking the model of a free electron gas in a two dimensional case and assuming an energy independent collision time ($T(\epsilon) = \text{const}$) results in a diffusion thermoelectric power¹⁸

$$S = \frac{\pi^2 k_B^2 \cdot T}{3e \cdot \epsilon_F}$$

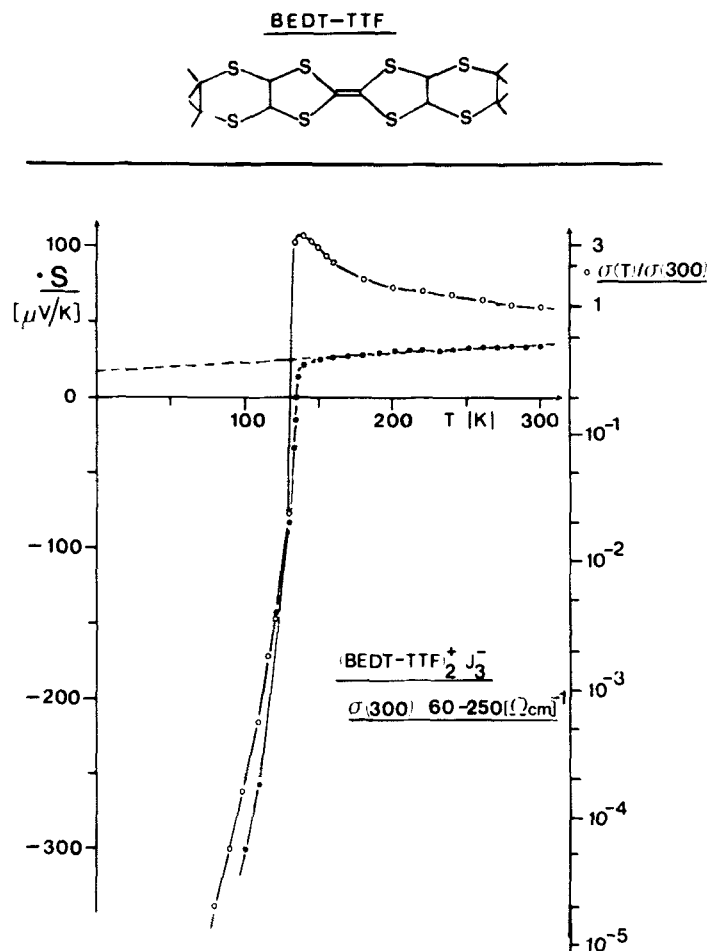


FIGURE 12 Temperature dependence of normalized conductivity $[\sigma(T)/\sigma(300)]$ (\circ , right scale) and of thermopower S ($*$, left scale) in the ab -plane of $(\text{BEDT-TTF})_2\text{I}_3$.

where k_B is the Boltzmann constant, T the temperature and e the negative or positive charge of the electron or holes. By using the data of Figure 12 a Fermi energy $\epsilon_F \approx 0.3$ eV for the holes is obtained. This value gives an order of magnitude which should not be much affected by the weak anisotropy in the ab -plane.

The large nonlinear thermopower S below 135 K indicates that a metal insulator transition has taken place and the conduction in the semiconducting range is dominated by electrons.

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