X-Ray Investigations of the Low-Temperature Phases of the Organic Metals α- and β-$(BEDT\text{-}TTF)_2I_3$ *

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The structure of single crystals of the organic metals α- and β-$(BEDT\text{-}TTF)_2I_3$* was determined at 100 K, well below the phase transitions indicated by resistivity and thermopower measurements as well as by differential thermal analysis. In the α-phase no unusual change of the room temperature unit cell but a slight variation in the triiodide network and especially a more pronounced dimerization in one of the two donor stacks have been found. The β-phase develops a superstructure with a unit cell volume three times as large as that at room temperature and with pronounced distortions of the I_3^--ions.

Key words: Low-Temperature Structure, Organic Conductors, Superconductors.

Introduction

α- and β-$(BEDT\text{-}TTF)_2I_3$ are two-dimensional organic metals at room temperature [1 – 4]. The α-phase undergoes a first order phase transition to an insulating state at 135 K, indicated by temperature dependent electrical conductivity, thermopower, and thermal conductivity measurements [1, 2, 4] as well as by differential thermal analysis [5]. This phase transition can be suppressed by an isotropic pressure $p > 12$ kbar [6].

The β-phase, on the other hand, shows a metallic behaviour down to low temperatures and becomes superconducting around 1.5 K at ambient pressure [3, 6 – 8]. Nevertheless, thermopower data exhibit a distinct anomaly around 125 K, indicating a phase transition [4]. Further evidence for this phase transition is given by recent annealing experiments [9], showing that the high T_c (8.1 K) superconducting state – which can be stabilized even at atmospheric pressure by a special pressure and temperature cycling procedure [10] – remains stable as long as the annealing temperature does not exceed 125 K.

Therefore we have collected X-ray data of α- and β-$(BEDT\text{-}TTF)_2I_3$ at 100 K in order to obtain the structures of both phases below the phase transitions mentioned above. Our results for the β-phase disagree with a recent report of an incommensurate structural modulation below 200 K [11, 12].

Experimental

The crystals for the X-ray investigations were grown by the usual electrochemical technique [2]. Suitable single crystals of the α- and the β-phase were fixed in glass capillaries and mounted on an Enraf Nonius CAD-4, four-cycle diffractometer. After cooling down to 100 K (in about 5 minutes) the data collection was started (Mo-K_α radiation, graphite monochromator). The unit cell was determined by a least squares refinement of 75 reflections with high theta values. The phase problem

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* BEDT-TTF = Bis(ethylenedithio)tetrathiafulvalene, $C_{10}H_8S_8$. – Partly presented at the "Ninth European Crystallographic Meeting", 1985, Torino, Italy.

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was solved with direct methods and the structures were completed with usual Fourier and difference Fourier techniques. After a full-matrix least squares refinement interatomic distances and angle were calculated. A summary of the programs which have been used is given in [13]. The experimental results are discussed in detail in the following chapter. Due to the poor crystal quality at 100 K, the experimental data of the β-phase will not be deposited.

Results and Discussion

For the α-phase a triclinic unit cell, space group P$\bar{1}$, with $a = 9.068(2)$, $b = 10.721(3)$, $c = 17.403(2)$ Å, $\alpha = 96.56(1)$, $\beta = 97.75(1)$, $\gamma = 91.14(2)°$, $V = 1664.2$ Å^3, $Z = 2$ was observed at 100 K. Besides the usual contraction these values are not principally different from those at room temperature [2], where $a = 9.211(2)$, $b = 10.850(4)$, $c = 17.488(5)$ Å, $\alpha = 96.95(2)$, $\beta = 97.97(2)$, $\gamma = 90.75(2)°$, $V = 1717$ Å^3.

The structure was refined with 7006 observed reflections to $R = 0.050$, $R_w = 0.071$. Atom coordinates are listed in Table 1, bond distances and angles in Table 2*. The numbering scheme of the three independent BEDT TTF moities is shown in Figs. 1 a and 1 b.

Contrary to the β-phase described below, it was not possible to refine the structure of the α-phase in the acentric space group P1. Therefore, the first order phase transition revealed by conductivity, thermopower, thermal conductivity and differential thermal analysis data neither leads to a superstructure nor to a change of the space group symmetry. The most prominent differences between the structures above and below the phase transition lie in the triiodide network and in the degree of dimerization of one of the donor stacks.

Table 1. Final atomic coordinates (× 10^4) of α-(BEDT-TTF)$_2$I$_3$ at 100 K.

Atom	*X*	*Y*	*Z*
I 1	0	5000	5000
I 2		5758 (1)	4936 (1)
I 3	5000	0	5000
I 4	8102 (1)	−756 (1)	5124 (1)
S 1	8918 (2)	−600 (2)	1135 (1)
S 2	7017 (2)	1453 (2)	663 (1)
S 3	7229 (2)	2887 (1)	2208 (1)
S 4	9474 (2)	423 (2)	2822 (1)
S 5	8349 (2)	−1949 (2)	−678 (1)
S 6	6445 (2)	128 (2)	−1098 (1)
S 7	8127 (2)	−3267 (2)	−2265 (1)
S 8	5969 (2)	−717 (1)	−2802 (1)
S 9	4144 (2)	3222 (2)	9335 (1)
S 10	5514 (2)	5468 (2)	8873 (1)
S 11	3549 (2)	1850 (2)	7763 (1)
S 12	5201 (2)	4551 (2)	7181 (1)
S 13	8785 (2)	3340 (2)	9326 (1)
S 14	10817 (2)	5276 (2)	8897 (1)
S 15	8168 (2)	1940 (2)	7755 (1)
S 16	10380 (2)	4342 (1)	7200 (1)
C 1	7839 (7)	36 (6)	381 (4)
C 2	8641 (7)	612 (6)	1873 (4)
C 3	7748 (7)	1562 (6)	1653 (4)
C 4	8260 (8)	2749 (6)	3162 (4)
C 5	8279 (7)	1423 (6)	3379 (4)
C 6	7603 (7)	−528 (6)	−371 (4)
C 7	7652 (8)	−1958 (6)	−1673 (4)
C 8	6776 (7)	−991 (6)	−1870 (4)
C 9	7479 (7)	−2890 (6)	−3239 (4)
C 10	5933 (7)	−2299 (6)	−3305 (4)
C 11	4908 (8)	4733 (6)	9619 (4)
C 12	4268 (7)	3216 (6)	8341 (4)
C 13	4914 (8)	4259 (6)	8116 (4)
C 14	4204 (8)	2038 (6)	6845 (4)
C 15	3998 (7)	3340 (6)	6584 (4)
C 16	9916 (8)	4718 (6)	9628 (4)
C 17	9065 (7)	3257 (6)	8337 (4)
C 18	9966 (7)	4150 (6)	8139 (4)
C 19	8340 (7)	2323 (6)	6774 (4)
C 20	9883 (7)	2777 (6)	6690 (4)

Figure 2 shows a comparison of the triiodide sheet at room and at low temperature: whereas the intraionic bond distances and the interionic contact lengths along the triiodide chains hardly change, the complete triiodide ions are slightly rotated with respect to one another. This results in an increase of the angle formed between the two independent triiodide ions. Along the two chains of triiodide ions the angles at the terminal atoms of the anions decrease when going to low temperature.

Regarding the physical properties, the changes in the stack of the donor species A (S(1) to S(8), C(1) to C(10) occupying a general crystallographic position, compare [2]) seem to be more important (Fig. 3). Taking the distances between the C atoms of the central C=C bonds of adjacent molecules of a stack as a measure of the degree of dimerization, a remarkable change is noted: These distances *increase* within one pair of donors and decrease within the

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* Lists of anisotropic temperature factors, H coordinates, observed and calculated structure factors, and some more details of the structure analysis have been deposited with the Fachinformationszentrum Energie, Physik, Mathematik, D-7514 Eggenstein-Leopoldshafen 2, FRG. Copies may be obtained quoting the deposition number CSD 52142, the authors, and the journal reference.

Table 2. Bond distances (Å) and angles in α-(BEDT-TTF)$_2$I$_3$ at 100 K.

I 1 −I 2	2.931(1)	S 9 −C11	1.740(7)
I 3 −I 4	2.930(1)	S 9 −C12	1.749(7)
		S 10 −C11	1.737(7)
S 1 −C1	1.741(7)	S 10 −C13	1.762(7)
S 1 −C2	1.767(7)	S 11 −C12	1.741(7)
S 2 −C1	1.755(7)	S 11 −C14	1.810(7)
S 2 −C3	1.750(7)	S 12 −C13	1.744(7)
S 3 −C3	1.735(7)	S 12 −C15	1.813(7)
S 3 −C4	1.816(7)	C11 −C11*	1.37 (1)
S 4 −C2	1.757(7)	C12 −C13	1.372(9)
S 4 −C5	1.832(7)	C14 −C15	1.524(9)
S 5 −C6	1.737(7)		
S 5 −C7	1.761(7)	S 13 −C16	1.769(7)
S 6 −C6	1.754(7)	S 13 −C17	1.766(7)
S 6 −C8	1.757(7)	S 14 −C16	1.755(7)
S 7 −C7	1.741(7)	S 14 −C18	1.766(7)
S 7 −C9	1.811(7)	S 15 −C17	1.757(7)
S 8 −C8	1.748(7)	S 15 −C19	1.828(7)
S 8 −C10	1.816(7)	S 16 −C18	1.760(7)
C1 −C6	1.366(9)	S 16 −C20	1.825(7)
C2 −C3	1.371(9)		
C4 −C5	1.51(1)	C16 −C16*	1.354(9)
C7 −C8	1.365(9)	C17 −C18	1.350(9)
C9 −C10	1.546(9)	C19 −C20	1.503(9)
C2 −S 1 −C1	95.7(3)	C2 −C3 −S 2	116.3(5)
C3 −S 2 −C1	96.2(3)	S 3 −C3 −S 2	113.9(4)
C4 −S 3 −C3	102.0(3)	C5 −C4 −S 3	113.7(5)
C5 −S 4 −C2	99.1(3)	C4 −C5 −S 4	112.1(5)
C7 −S 5 −C6	95.7(3)	C1 −C6 −S 6	121.2(5)
C8 −S 6 −C6	95.7(3)	C1 −C6 −S 5	123.8(5)
C9 −S 7 −C7	102.8(3)	S 6 −C6 −S 5	114.9(4)
C10−S 8 −C8	99.9(3)	C8 −C7 −S 7	129.1(5)
C6 −C1 −S 2	121.8(5)	C8 −C7 −S 5	116.9(5)
C6 −C1 −S 1	123.3(5)	S 7 −C7 −S 5	113.9(4)
S 2 −C1 −S 1	114.9(4)	C7 −C8 −S 8	127.7(5)
C3 −C2 −S 4	127.1(5)	C7 −C8 −S 6	116.4(5)
C3 −C2 −S 1	116.9(5)	S 8 −C8 −S 6	115.9(4)
S 4 −C2 −S 1	116.0(4)	C10 −C9 −S 7	113.0(5)
C2 −C3 −S 3	129.8(5)	C9 −C10−S 8	113.0(5)
C12−S 9 −C11	96.0(3)	C11*−C11−S 10	122.8(5)
C13−S 10−C11	96.4(3)	C11*−C11−S 9	122.2(5)
C14−S 11−C12	101.7(3)	S 10 −C11−S 9	114.9(4)
C15−S 12−C13	101.1(3)	C13 −C12−S 11	128.5(5)
		C13 −C12−S 9	117.2(5)
		S 11 −C12−S 9	114.3(4)
		C12 −C13−S 12	128.7(5)
		C12 −C13−S 10	115.5(5)
		S 12 −C13−S 10	115.9(4)
		C15 −C14−S 11	114.5(5)
		C14 −C15−S 12	113.6(5)
C17−S 13−C16	94.8(3)	C16*−C16−S 14	123.0(5)
C18−S 14−C16	95.2(3)	C16*−C16−S 13	122.0(5)
C19−S 15−C17	101.5(3)	S 14 −C16−S 13	115.1(4)
C20−S 16−C18	100.8(3)	C18 −C17−S 15	129.2(5)
		C18 −C17−S 13	117.4(5)
		S 15 −C17−S 13	113.3(4)
		C17 −C18−S 16	127.4(5)
		C17 −C18−S 14	117.3(5)
		S 16 −C18−S 14	115.3(4)
		C20 −C19−S 15	113.2(5)
		C19 −C20−S 16	113.4(5)

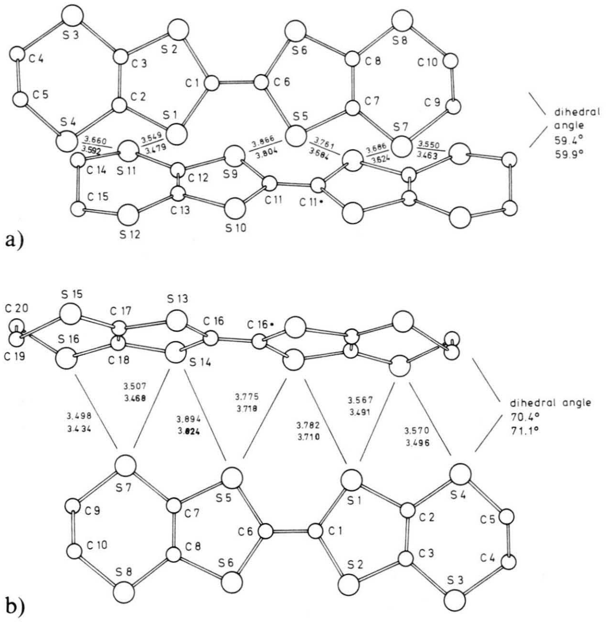

Fig. 1. a) A pair of molecules A and B in adjacent stacks I and II (compare [2]). The shortest S ... S contacts are indicated. Upper numbers refer to room temperature, lower numbers to the structure at 100 K. Estimated standard deviations are of the order of 0.007 Å for room temperature and 0.002 Å at 100 K. b) A pair of molecules A and C analogous to a).

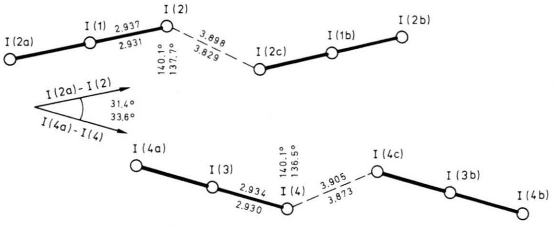

Fig. 2. Comparison of the triiodide chains at high and low temperatures. The projection is along *c*. The central iodine atoms lie on inversion centers and adjacent anions of a chain are related by a unit translation *a*. The contacts between the chains are well above the van der Waals distance. The numbers are arranged analogous to Figure 1. Estimated standard deviations are 0.001 Å and 0.1 °.

adjacent one below the phase transition. Even if the increase is within the limits of significance, the pronounced decrease of 0.14 Å is not. The insignificant increase of 0.01 Å has to be judged against the usual thermal contraction of the intermolecular separations which can be estimated from Fig. 1 and which are in the range of 0.03 to 0.06 Å. This change in the degree of dimerization may be con-

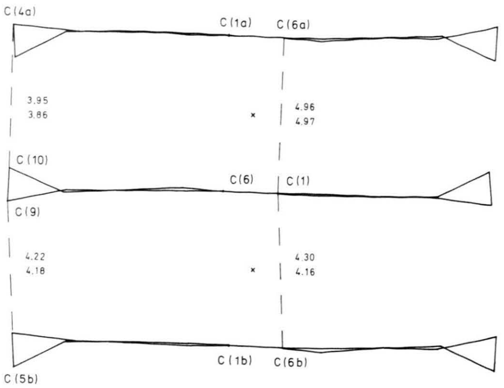

Fig. 3. Selected intrastack separations in the stack of donor species A [S(1) to S(8), C(1) to C(10)]. The crosses stand for crystallographic inversion centers. The numbers are arranged analogous to Fig. 1. Symmetry codes are a) $1-x, -y, -z$; b) $2-x, -y, -z$. Estimated standard deviations are 0.01 to 0.02 Å.

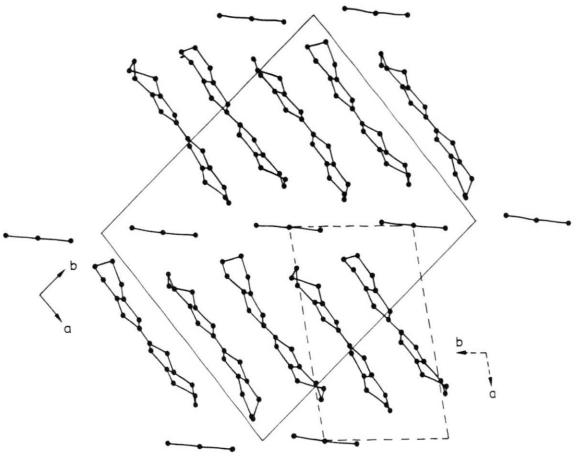

Fig. 4. β-(BEDT-TTF)$_2$I$_3$: Comparison of the low temperature supercell (solid lines) and the room temperature cell (broken lines) in a projection to the *c*-axis. The atom position of the low temperature structure are plotted.

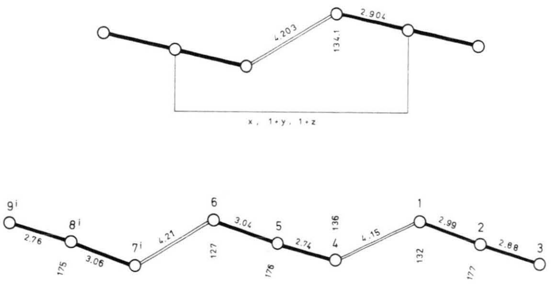

Fig. 5. Comparison of the geometry of the triiodide chains in β-(BEDT-TTF)$_2$I$_3$. Top: room temperature phase, plotted from published data in [15]. Bottom: low temperature phase.

nected with the phase transition observed in the transport properties and supported by anomalies in the thermal contraction of the crystals [14].

Compared with these effects, other differences between the structures at high and low temperature are rather marginal (Figure 1). Especially there are no pronounced changes in the orientation of the methylene groups. An analogous dimerization in the second stack of donors [molecules B and C, S(9) to C(20)] is impossible for reasons of symmetry, as the midpoints of the donors lie on crystallographic inversion centers.

In the investigated crystal of the β-phase we found an acentric superstructure at 100 K with a unit cell volume about three times as large as at room temperature: $a = 18.269(7)$, $b = 21.04(1)$, $c = 6.543(2)$ Å, $\alpha = 93.56(3)$, $\beta = 94.84(3)$, $\gamma = 99.86(3)$°, $V = 2461$ Å^3, space group P1, $Z = 3$. (Room temperature data [15] $a = 15.243(2)$, $b = 9.070(2)$, $c = 6.597(1)$ Å, $\alpha = 109.73(2)$, $\beta = 95.56(2)$, $\gamma = 94.33(2)$°, $V = 848.9$ Å^3, $Z = 1$.)

Figure 4 shows the relation of the chosen unit cell at 100 K to that at room temperature.

Due to the poor crystal quality at 100 K which might be a consequence of the phase transition, the data are relatively inaccurate. Consequently, the structure could not be refined to convergence ($R = 0.133$), and the positions of especially the light atoms are not reliable enough to allow a discussion of interatomic distances. But the basic structural features, especially the iodine positions are surely correct. It must be pointed out that the structure could not be solved in the centric space group P$\bar{1}$. The main differences between the low temperature and the room temperature structures lie in a pronounced distortion of the triiodide chain (Fig. 5), and possibly in different orientations of the methylene groups of the donor molecules.

This superstructure observed here is different from the incommensurate modulated structure observed at 125 K and below [11, 12, 16], which has been interpreted as a displacive modulation, treating the BEDT-TTF-donors and the centrosymmetric I$_3^-$-anions as rigid bodies in a centric super-space group. Leung et al. [16] report that this modulation

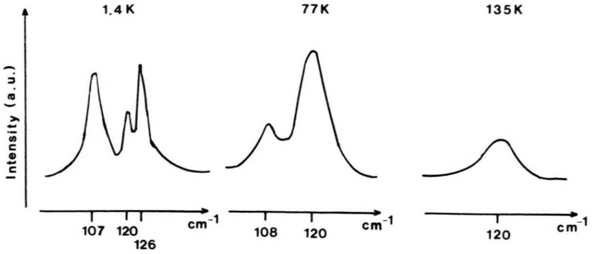

Fig. 6. Part of the Raman spectra of β-(BEDT-TTF)$_2$I$_3$ at 1.4 K, 77 K and 135 K (see text).

develops at around 200 K, at which temperature the physical properties of our crystals do not show any indication of a structural change. This difference in observation – superstructure in our case and incommensurate modulation in the earlier work [16] – cannot be explained at this moment.

On the other hand, if the superstructure at 100 K described here is right, in a high resolution Raman spectrum of the β-phase one should observe below 125 K three or at least two lines belonging to the symmetric breathing mode of the I_3^--anions due to their different I–I distances (see Fig. 5), while at higher temperature only one Raman line can be expected. Figure 6 shows the resonance Raman spectra of a β-(BEDT-TTF)$_2$I$_3$-crystal at 1.4 K, 77 K and 135 K. While in the whole temperature range above 125 K only one Raman line at 120 cm^{-1} – corresponding to the symmetric breathing mode of the linear and symmetric I_3^--anions – can be observed, at 77 K two broad (108 and 120 cm^{-1}) and at 1.4 K three Raman lines (107, 120 and 126 cm^{-1}) are observed in accordance with the expectations. Details of the Raman investigations will be published separately.

Nevertheless it is β-(BEDT-TTF)$_2$I$_3$ either in the superstructure described here or in the modulated structure [12] which becomes superconducting at 1–1.5 K [3, 6–8]. On the other hand, it is assumed that the recently observed narrow and complete superconducting transition at 8.1 K and ambient pressure [10] in the same crystals belongs to the room temperature structure or, more precisely, to a structure in which the I_3^--anions are linear and symmetric as in the room temperature structure. This structure is stabilized down to low temperatures by pressurisation of the crystals up to 1.5 kbar at room temperature and a release of the pressure below 125 K [9, 10].

This assumption is supported by the observation of superconductivity at ambient pressure at about 4.5 K in β-(BEDT-TTF)$_2$IAuI [17] and at 2.5 K in β-(BEDT-TTF)$_2$BrIBr [18]. Both β-phases have room temperature structure isomorphous with β-(BEDT-TTF)$_2$I$_3$, but without a phase transition at around 120 K [17, 18]. Since the unit cell parameters of β-(BEDT-TTF)$_2$IAuI and β-(BEDT-TTF)$_2$BrIBr are somewhat smaller and correspond to those of β-(BEDT-TTF)$_2$I$_3$ under a pressure of about 3 or 5 kbar, respectively, it can be understood that their transition temperatures are lower and reflect the transition temperatures of β-(BEDT-TTF)$_2$I$_3$ under a pressure of 3 or 5 kbar, respectively [19].

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