

Crystal structure of the organic superconductor (BEDT-TTF)₂I₃

V. F. Kaminskii, T. G. Prokhorova, R. P. Shibaeva, and É. B. Yagubskii
Institute of Chemical Physics, Academy of Sciences of the USSR

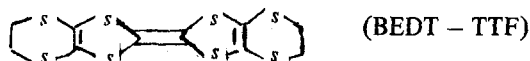
(Submitted 31 October 1983)

Pis'ma Zh. Eksp. Teor. Fiz. **39**, No. 1, 15-18 (10 January 1983)

An x-ray diffraction analysis of (BEDT-TTF)₂I₃ crystals is performed. The packing of the BEDT-TTF cation radicals indicates the existence of a two-dimensional conducting system in these crystals.

PACS numbers: 61.65. + d, 74.70.Rv

(BEDT-TTF)₂I₃ crystals, whose superconducting properties are described in the preceding paper in this issue,¹ were obtained by electrochemical oxidation of bis(ethylene dithiolo) tetrathiofulvalene (BEDT-TTF)



in a solution of benzonitrile on the platinum anode in the constant-current regime with $I = 4 \mu\text{A}$. Tetrabutylammonia triiodide was used as the electrolyte. The crystals grew on the electrode in the form of plates and needles. It was found that the plates have two crystalline modifications with different physical properties, one of which undergoes a sharp metal-insulator transition at a temperature near 140 K, while the other does not exhibit any signs of a dielectric instability and at $T < 2 \text{ K}$ goes over into the superconducting state.¹ The identity of the superconducting crystal plates and needles was proved by x-ray diffraction analysis, while the crystals (plates) exhibiting the metal-insulator transition have completely different lattice parameters. In this paper, we present the results of an x-ray diffraction analysis of the superconducting crystals.

The basic crystallographic data are: the crystals (C₁₀H₈S₈)₂I₃ are triclinic, with space group $p\bar{1}$, $a = 6.609(1)$, $b = 9.083(1)$, $c = 15.267(2)\text{\AA}$, $\alpha = 85.63(2)$, $\beta = 95.62(2)$, $\gamma = 70.22(2)^\circ$, $V = 852.2 \text{\AA}^3$, $Z = 1$. Experimental data, which include 2007 independent reflections with $I \geq 3\sigma(I)$, were obtained in a Sinteks- $p\bar{1}$ diffractometer (MoK α radiation, graphite monochromator, $\theta/2\theta$ scanning, $2\theta_{\text{max}} = 50^\circ$, crystal sizes $0.8 \times 0.1 \times 0.05 \text{ mm}$, correction introduced for absorption). The structure was determined by the heavy-atom method and refined by the method of least squares in the anisotropic approximation to $R = 0.031$. All the basic calculations were performed on a Nova-3 computer with the SHELXTL complex of programs in the Nikolet-R3 system.

We first point out some characteristics of the intramolecular structure of BEDT-TTF in this compound. First of all, the BEDT-TTF molecule is not completely flat. In addition to the fact that the end methylene groups CH₂ extend beyond the central plane of the entire molecule, only the central fragment consisting of two C atoms and four S atoms is actually planar. The displacements of the remaining atoms out of the

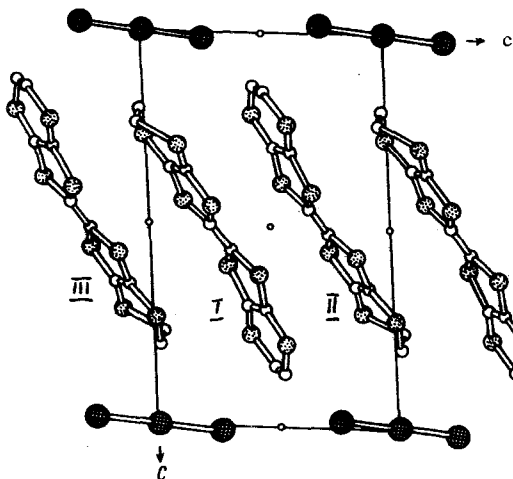


FIG. 1. Projection of the crystal structure along the a axis. Molecules I, II, and III are related to each other by symmetry operations: I (xyx) , II $(\bar{x}, 1-y, 1-z)$, III $(1-x, \bar{y}, 1-z)$.

plane of this central fragment vary from -0.18 to 0.54 Å. Second, there is some positional disordering of one of the ethylene groups, which is indicated by the large thermal parameters of the corresponding carbon atoms. Similar characteristics of the molecular structure of BEDT-TTF were observed previously in the structures $(\text{BEDT-TTF})_4(\text{ReO}_4)_2^2$, α $(\text{BEDT-TTF})_2\text{PF}_6^3$ and $(\text{BEDT-TTF})_2(\text{ClO}_4)(\text{C}_2\text{H}_3\text{Cl}_3)_{0.5}^4$.

Figure 1 shows the projection of the crystal structure of $(\text{BEDT-TTF})_2\text{I}_3$ along the direction a . The BEDT-TTF cations-radicals are packed in the crystal plane to plane, which is typical for all quasi-one-dimensional organic metals.⁵ However, in this case, the cation-radical stacks are not arranged along the shortest period of the crystal, a . Figure 2 demonstrates the characteristic overlapping of neighboring cation-radicals in a stack. It should be noted that all $\text{S} \dots \text{S}$ distances in the stacks, which are much larger than the interstack distances $\text{S} \dots \text{S}$, are not less than the sum of the van der

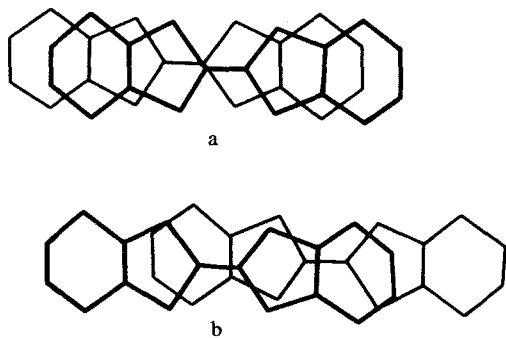


FIG. 2. Overlapping of neighboring BEDT-TTF in a stack: a) for I and II; b) for I and III.

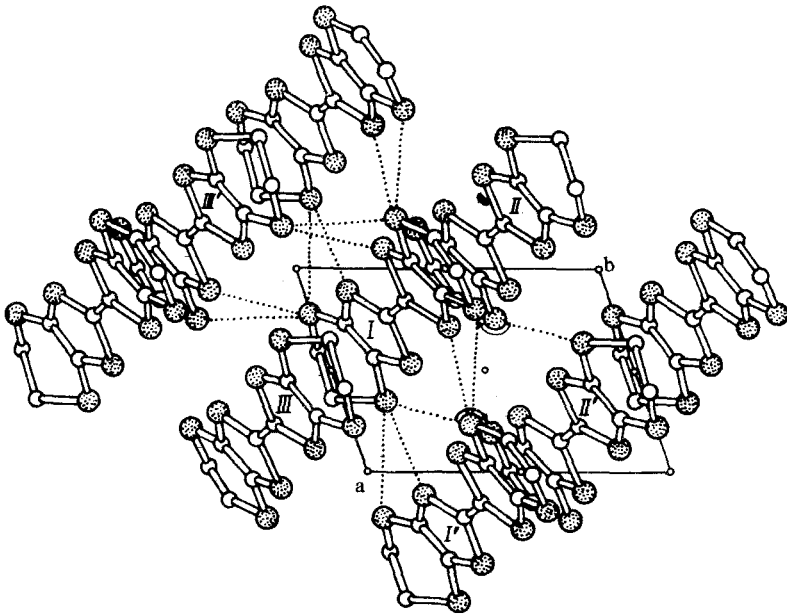


FIG. 3. Projection of the layer of BEDT-TTF cation radicals along the c axis. See Fig. 1 for the symmetry operations for I, II, and III; for the others: I' ($1 + x, y, z$), II' ($1 - x, 1 - y, 1 - z$), III' ($\bar{x}, \bar{y}, 1 - z$).

Waal's radii 3.70 Å. This gives rise to the minimum Coulomb repulsion for cation radicals.

The mutual positioning of the cation-radical stacks in the crystal is such that layers are formed parallel to the ab plane, and the linear anions I_3 with an inversion center are located in the channels between these layers. The projection of the BEDT-TTF cation-radical layer along the direction c is shown in Fig. 3. As is evident from this figure, there is an appreciable coupling between the stacks, which is manifested by the specific orientation of BEDT-TTF molecules (sulfur molecules from the neighboring stacks are oriented toward each other) and by the presence of a number of slightly shortened S...S contacts. All contacts of this type for a single independent molecule I are marked in the figure by the dashed line and their sizes vary from 3.568 to 3.688 Å.

Thus $(\text{BEDT-TTF})_2I_3$ crystals, according to their structure and physical properties, are a two-dimensional organic metal. An increase in the dimensionality of the conducting system, as proposed in Ref. 6, is apparently the decisive factor for stabilization of the metallic state. The slight shortening of the intermolecular contacts S...S is, on the one hand, the reason for the unexpected low conductivity of $(\text{BEDT-TTF})_2I_3$ crystals at room temperature ($\sigma \sim 30 \Omega^{-1} \text{cm}^{-1}$); on the other, it may be assumed that with decreasing temperatures, a large degree of freedom exists in these crystals, allowing for a considerable synchronous decrease in intermolecular distances, and the strong drop in the resistance is apparently related precisely to the good compressibility of the crystals.

We are grateful to V. K. Bel'skiĭ and V. I. Zavodnik for the experimental data obtained on the diffractometer and to G. M. Mikhaĭlova for help in writing the paper.

¹É. B. Yagubskii, I. F. Shchegolev, V. N. Laukhin, P. A. Kononovich, M. V. Kartsovnik, A. V. Zvarykina, and L. I. Buravov, *Pis'ma Zh. Eksp. Teor. Fiz.* **39**, 12 (1983) [*JETP Lett.* **39**].

²S. S. Parkin, E. M. Engler, R. R. Schumaker, R. Lagier, V. Y. Lee, J. C. Scott, and R. L. Greene, *Phys. Rev. Lett.* **50**, 270 (1983).

³H. Kobayashi, R. Kato, T. Mori, A. Kobayashi, Y. Sasaki, G. Saito, and H. Inokuchi, *Chemistry Lett.* (in press).

⁴G. Saito, T. Enoki, K. Toriumi, and H. Inokuchi, *Solid State Comm.* **42**, 557 (1982).

⁵R. P. Shibaeva, in: *Extended Linear Chain Compounds*, Ed. J. S. Miller, Plenum Press, New York, 1982, p. 437-467.

⁶V. N. Laukhin and I. F. Shchegolev, *Izv. Akad. Nauk Latv. SSR, Ser. Fiz.* **6**, 78 (1981).

Translated by N. E. Alferieff

Edited by S. J. Amoretty