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CRYSTAL STRUCTURES OF ORGANIC METALS AND SUPERCONDUCTORS OF (BEDT-TTF)-I SYSTEM

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Abstract The first ambient-pressure organic superconductors based on sulfur compounds have been obtained and investigated in (BEDT-TTF)-I system.

The recent years of investigation of low-dimensional organic conductors, an intensively developing field of physics and chemistry of solid state, have been crowned with great achievements. Organic metals have been synthesized on the base of a stable cation-radical of tetramethyltetraselenofulvalene (TMTSeF) of the $(TMTSeF)_2X$ composition (X = PF_6, AsF_6, SbF_6, NO_3, ClO_4). They have been found to have a transition into the superconducting state at 9-10 kbar, one of them, $(TMTSeF)_2$-ClO_4, at ambient pressure and near 1 K.[1-3] In 1982 it was found[4] that the organic metal based on the stable cation-radical of bis(ethylenedithiolo)tetrathiafulvalene of the $(BEDT\text{-}TTF)_4(ReO_4)_2$ composition did not experience dielectric instability at pressures more than 6 kbar and had a transition into the superconducting state at 1.5 K.[4,5] Quite recently new organic superconductors at ambient pressure have been obtained in the (BEDT-TTF)-I system.[6-8] Crystal data and some other characteristics for them are listed in the Table. α- and β-BEDT-TTF salts have been prepared electrochemically in benzonitrile, tetrahydrofurane and methylene chloride when Bu_4NI_3 has been used as an electrolyte. The crystals grow in different morphologies, including plate and needle habits. Among the plates there are two

TABLE Crystal data and some other characteristics for organic metals of (BEDT-TTF) - I system

	α	β	γ	δ	ε
a, Å	10.785	6.609	13.76	10.728	13.974
b, Å	9.172	9.083	14.73	34.14	18.77
c, Å	17.39	15.267	33.61	34.92	17.40
α °	82.08	85.63	90	95.00	67.3
β °	96.92	95.62	90	90	90
γ °	89.13	70.22	90	90	90
V, Å^3	1690.3	852.2	6812	12736	4211
(BEDT-TTF):I	1 : 1.5	1 : 1.5	1 : 2.5	1 : 3	1 : 3.5
Space group	$P\bar{1}$	$P\bar{1}$	Pbnm	C2/c	$P2_1/c$
Z	2	1	4	24	4
d_{calc}, g/cm^3	2.26	2.24	2.06	2.41	2.27
σ_{RT}, ohm^{-1}cm^{-1}	~20-30	~20-30	~20	~10-20	~20
T, K	137(M-I)	1.5(M-SC)	2.5(M-SC)	130(M-I)	2.5(M-SC)

α: $(BEDT\text{-}TTF)_2I_3$; β: $(BEDT\text{-}TTF)_2I_3$; γ: $(BEDT\text{-}TTF)_3(I_3)_{2.5}$;
δ: $(BEDT\text{-}TTF)I_3$; ε: $(BEDT\text{-}TTF)_2I_3(I_8)_{0.5}$

modifications with different physical properties: one of them exhibits a sharp metal-insulator transition near 140 K (Figure 1), the other reveals no signs of

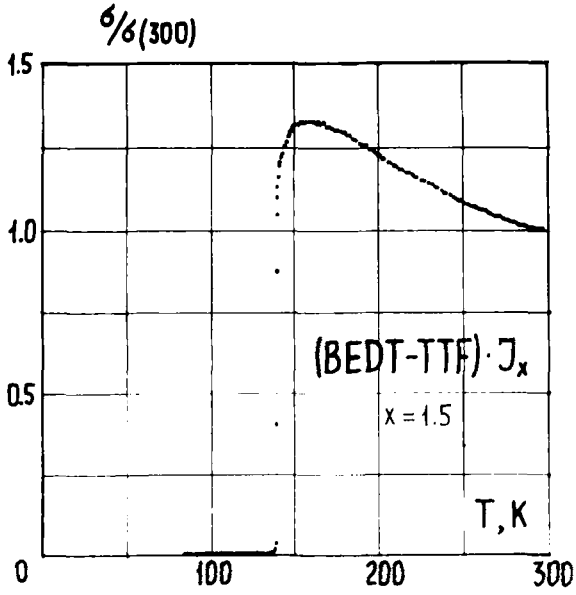

FIGURE 1 ($\underline{\text{BEDT-TTF}})_2\underline{I}_3(\alpha)$ The temperature dependence of a single crystal conductivity.

dielectric instability and becomes a superconductor at ambient pressure and $T < 2$ K.[6,7] X-ray analysis shows the identity of superconducting crystals of plate- and needle habits, while the unit cell of the plates with the metal-insulator transition has quite different parameters. The complete X-ray analysis of both crystals shows them to be of the same chemical composition, i.e. they are polymorphous modifications of the $(BEDT\text{-}TTF)_2I_3$ salt.

Figure 2 shows the bond lengths and angles in the BEDT-TTF cation-radical (β-phase) to be in good agreement with those in the α-$(BEDT\text{-}TTF)_2PF_6$ structure.[9] The following peculiarities of the intramolecular structure of BEDT-TTF should be noted. Firstly, the BEDT-TTF molecule is not quite planar, only its central fragment of two C and four S atoms is planar. Secondly, there is some positional disorder in one of the ethylene groups, which is evidenced by large thermal parameters of corresponding carbon atoms. Similar characteristics of the BEDT-TTF molecular structure have been reported earlier for the $(BEDT\text{-}TTF)_4(ReO_4)_2$,[4,5] α-

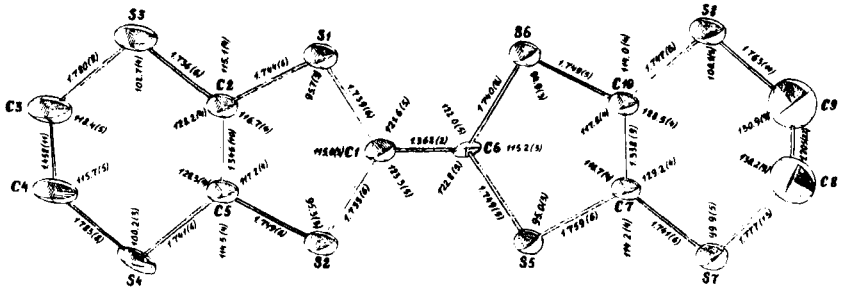

FIGURE 2 $(BEDT\text{-}TTF)_2I_3$ (β). Bond lengths (Å) and angles (°) in the (BEDT-TTF) cation-radical.

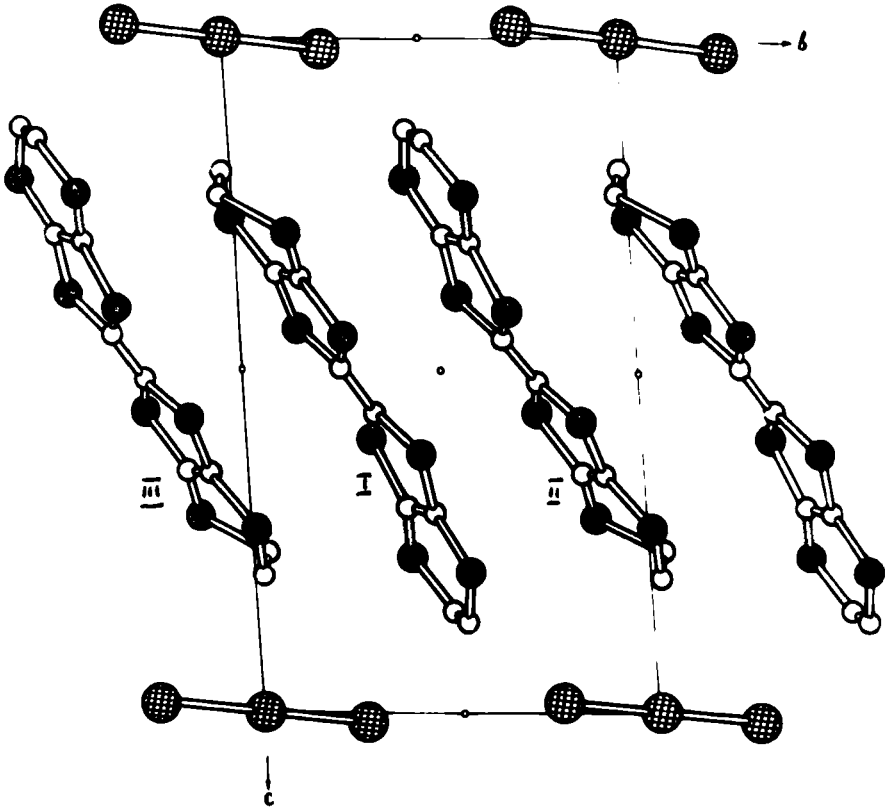

FIGURE 3 $(BEDT\text{-}TTF)_2I_3$ (β). The projection of the structure along a.

$(BEDT\text{-}TTF)_2PF_6$,[9] and $(BEDT\text{-}TTF)_2(ClO_4)(C_2H_3Cl_3)_{0.5}$[10] structures.

The linear I_3^- anions are located on the centers of symmetry and the I-I distance equals to 2.909(1) Å. The shortest interanion I...I distance is 4.204(1) Å, the others are more than 5.193 Å.

The projection of β-structure along a-direction is given in Figure 3. The BEDT-TTF cation radicals are packed face-to-face in the crystal, which is typical for all quasi-onedimansional organic metals.[11] The average BEDT-TTF planes are approximately parallel to (022) plane (the dihedral angle of 7°) and their angles with [100], [010] and [001] directions are 13, 43, and 25°, respectively. The cation-radical stacks do not run along the shortest period a in the crystal. It should be noted that all the intrastack S...S contacts are essentially longer than interstack ones and they are not shorter than the Van der Waals distance (3.70

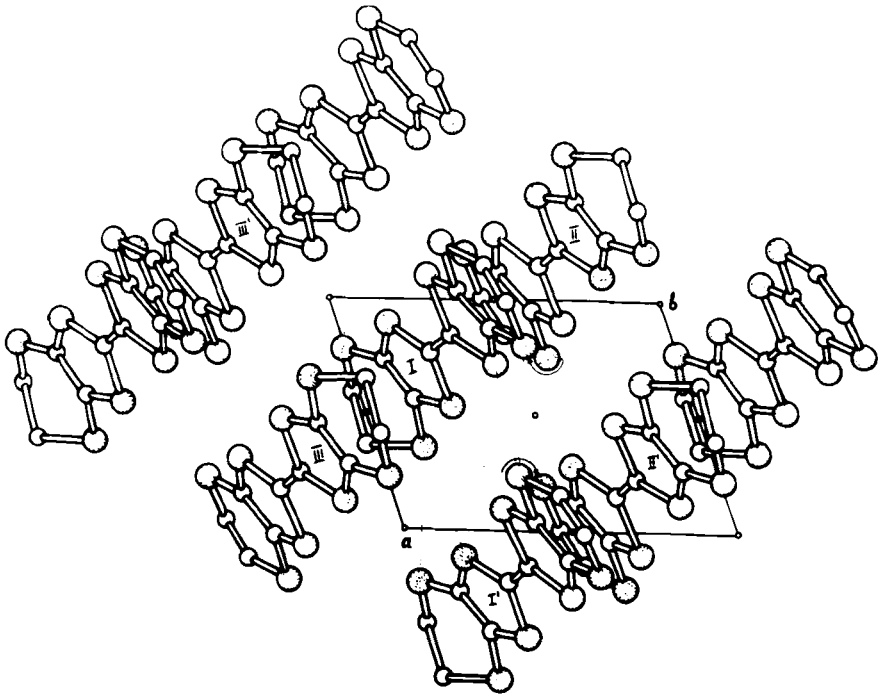

FIGURE 4 $(BEDT\text{-}TTF)_2I_3$ (β). The projection of the cation-radical layer along c.

Å). The average interplanar (BEDT-TTF)-(BEDT-TTF) distances in the stack sre equal to 3.75 Å for I-II and 3.86 Å for I-III (Figure 3). The cation radical stacks in β-crystal form sheets parallel to ab-plane. The centro-symmetric linear anions I_3^- are in the canals between them. The projection of the BEDT-TTF cation-radical layer along c-direction is shown in Figure 4. As seen from the Figure, there is a noticeable interaction between the stacks, which is revealed by the specific side-by-side arrangement of the BEDT-TTF molecules and by a large number of slightly shortened S...S con-

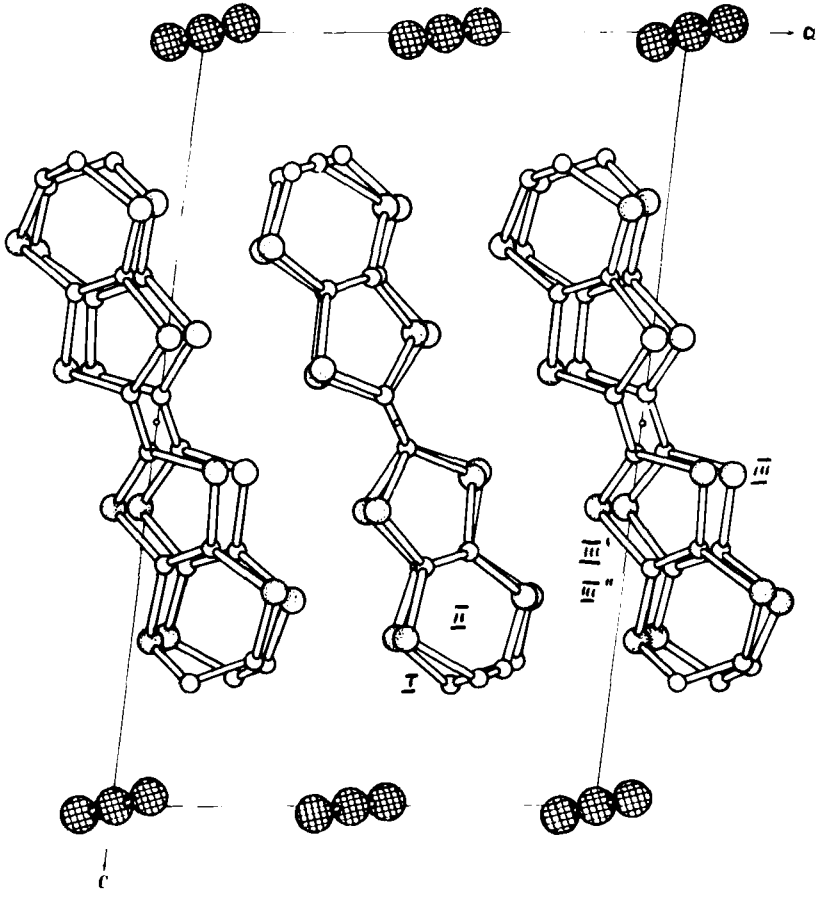

FIGURE 5 $(BEDT\text{-}TTF)_2I_3$ (α). The structure projection along b.

tacts. All such contacts of an independent molecule are shown by dotted lines, their value varying from 3.568 to 3.688 Å.

Thus, $(BEDT\text{-}TTF)_2I_3$ crystals (β) are two-dimensional organic metals in their structure and physical properties.[6] As was supposed,[12] the increase of the dimensionality of the conducting system is probably a decisive factor for the stabilisation of the metallic state.

Now let us consider the structure of α-crystals. As to their morphology, there are two types of habits: alongated plates (along a or b) (Table) and almost square plates with a' and b' sides, where a' = a + b, b' = b - a (a' = 14.263, b' = 14.051, c' = 17.389 Å, α' = 79.49, β' = 90.14, γ' = 99.24°, space group $C\bar{1}$).

The [010]-projection of α-structure is given in Figure 5. The presence of BEDT-TTF cation-radical sheets parallel to ab-plane is characteristic of this structure. There are two types of the BEDT-TTF cation-radicals in the sheets, I and II placed on the symmetry centers and III,III' occupying general positions. The molecular planes I and II are not parallel to each other (dihedral I-II angle is 11°) and make angles of 109.5 and 120.3° with plane III, respectively. There is a large number of slightly shortened S...S contacts which are more numerous and shorter (from 3.468 to 3.669 Å) in α than in β. The centro-symmetric linear I_3^--anions are located in the canals between the layers. The distances between I_3^- in the anion layer of structure α are shorter than those of β and equal to 3.879,

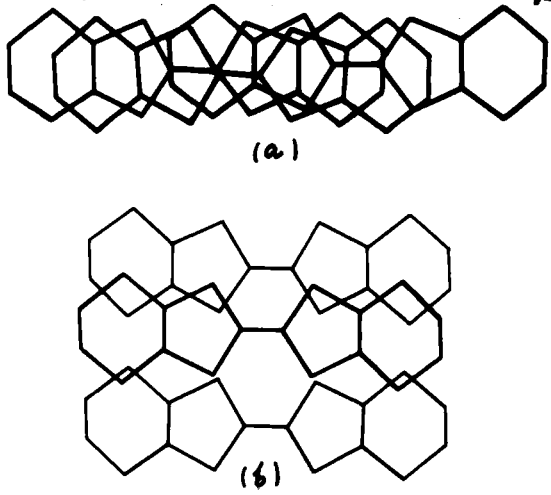

FIGURE 6
The modes of the BEDT-TTF cation-radicals in the stack
a) in β;
b) in α.

3.883, 4.907 and 4.988 Å.

As mentioned above, crystals β and α both are organic metals in their physical properties, crystals β undergoing to the superconducting state at T_c = 1.5 K, while crystals α having the metal-insulator transition at 137 K.[6,7] It should be noted that both crystals have approximately the same and surprisingly low conductivity at room temperature ($\sigma \sim 20\text{-}30$ ohm^{-1}cm^{-1}). The conductivity of (BEDT-TTF)$_2$(ClO_4)($C_2H_3Cl_3$)$_{0.5}$[13,14] and β-(BEDT-TTF)$_2PF_6$[15] crystals is of the same order at room temperature. Transverse intermolecular S...S contacts in the latter crystals are still shorter than in (BEDT-TTF)$_2I_3$ and are equal to 3.34-3.35 and 3.44 - 3.52 Å, respectively.[10,15]

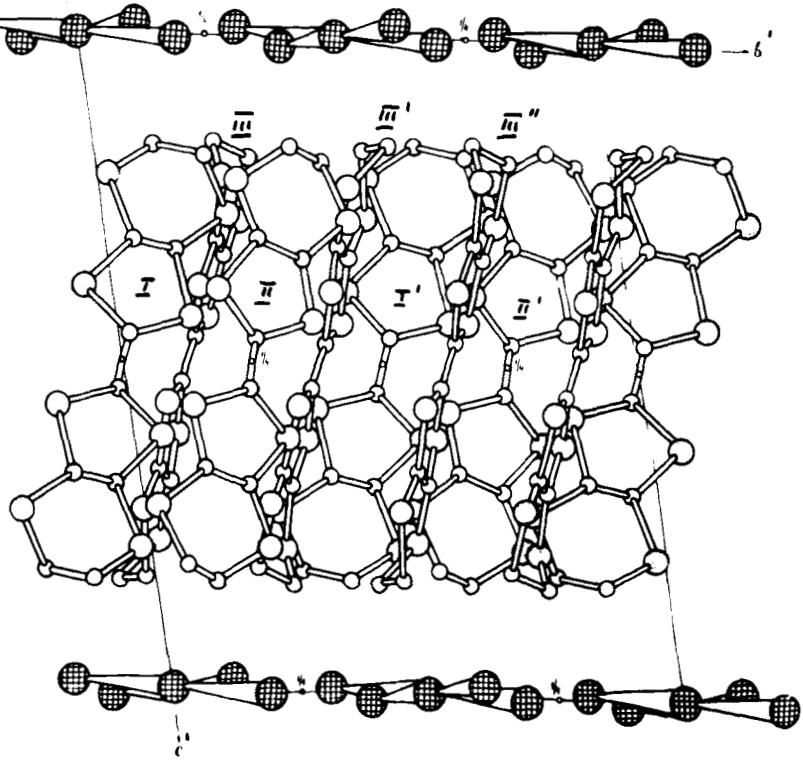

FIGURE 7 (BEDT-TTF)$_2I_3$ (α). The structure projection along a' diagonal (a' = a + b).

The principal differences of β and α crystals are revealed in the internal structure of their BEDT-TTF layers. All the BEDT-TTF molecules in the layer of β are parallel and there is a sufficient overlapping between the stacks (Figure 6 a). As to α, the BEDT-TTF molecules occupying general positions (III,III') (Figure 5) form one stack with a rather weak overlapping (Figure 6 b). Centrosymmetric molecules I,II form an otherwise oriented stack with approximately the same overlapping. This is confirmed by the projection of structure α along diagonal a' (Figure 7).

To make the part concerning the $(BEDT\text{-}TTF)_2I_3$ α and β crystals complete, it is necessary to mention that later these crystals were obtained not only by electrocrystallization, but also in chemical oxidation of BEDT-TTF with Bu_4NI_3 in $C_2H_3Cl_3$ or with I_2 in benzonitrile.

Now a few words about other compounds in the (BEDT-TTF)-I system. There have been obtained two other BEDT-TTF cation-radical salts (γ and δ) in the reaction of electrochemical synthesis in $C_2H_3Cl_3$ at high current densities. One of the salts, namely δ, has a metal-insulatir transition near 130 K, the other salt, γ, experiences a superconducting transition at $T_c = 2.5$ K.[8]

The X-ray study of crystals δ showed them to be a 1:1 cation-radical salt $(BEDT\text{-}TTF)I_3$. The projection of the structure of δ along a-direction is pictured in Figure 8. As seen, it has mixed cation-anion layers parallel to ab-plane, alternating with the layers of I_3^- anions. Two of four crystallographically independent BEDT-TTF are situated on the twofold axis, the other two occupying general positions.

Figure 9 shows the projection of γ-structure along a-direction. It should be taken into account that the above crystal data for γ (Table) relate to some average crystal structure only. Besides, there is some different crystal phase. This fact is supported by the presence of additional 00l-Bragg reflections and diffuse streacks in the okl-Weissenberg photograph, the latter corresponding to the incommesurate b-period in γ. It might be the phase which is responsible for superconductivity in these crystals.[8] This aspect requires further special elucidation.

Finally, quite recently one more superconducting ε-crystals with $T_c \sim 2.5$ K have been isolated in the reaction of chemical oxidation of BEDT-TTF by I_2. The

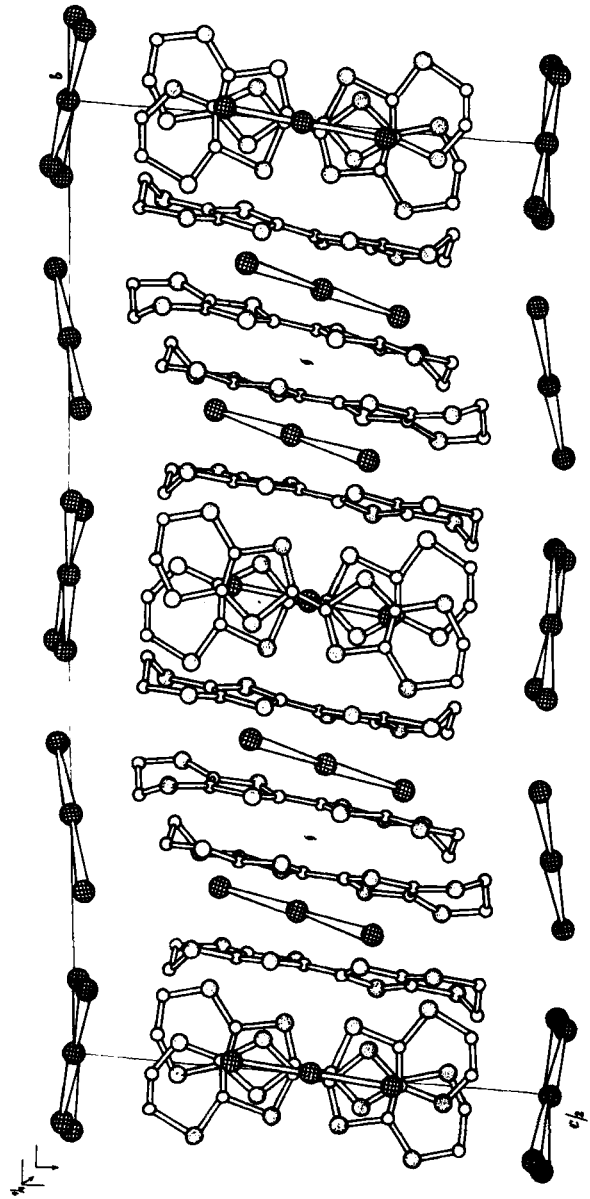

FIGURE 8 (BEDT-TTF)I_3 (δ). The structure projection along a.

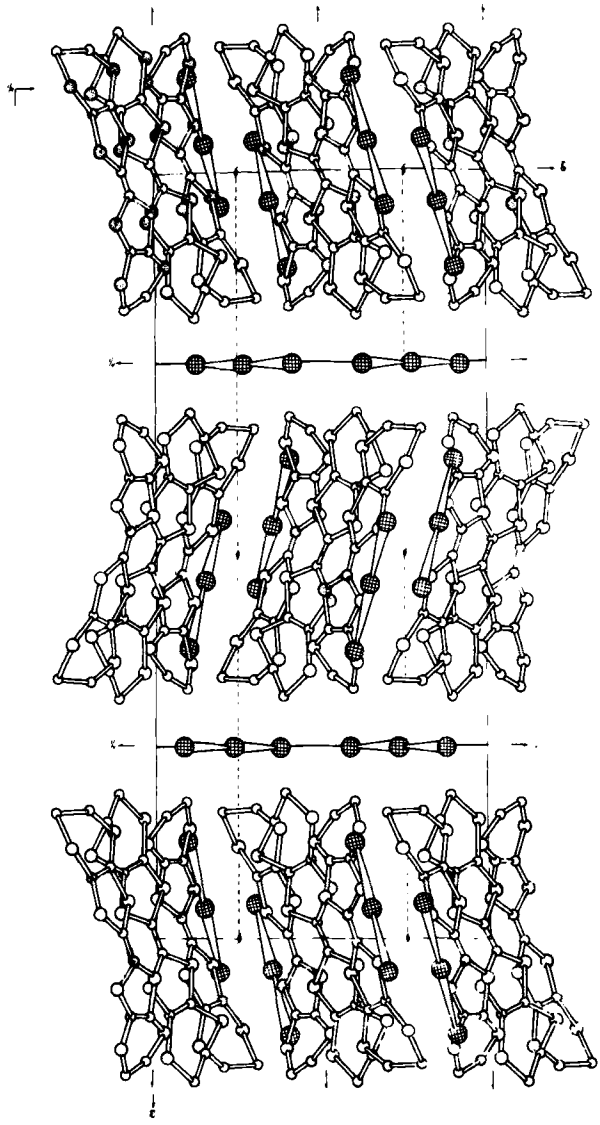

FIGURE 9 $(BEDT\text{-}TTF)_3(I_3)_{2.5}$ (Y). The structure projection along a.

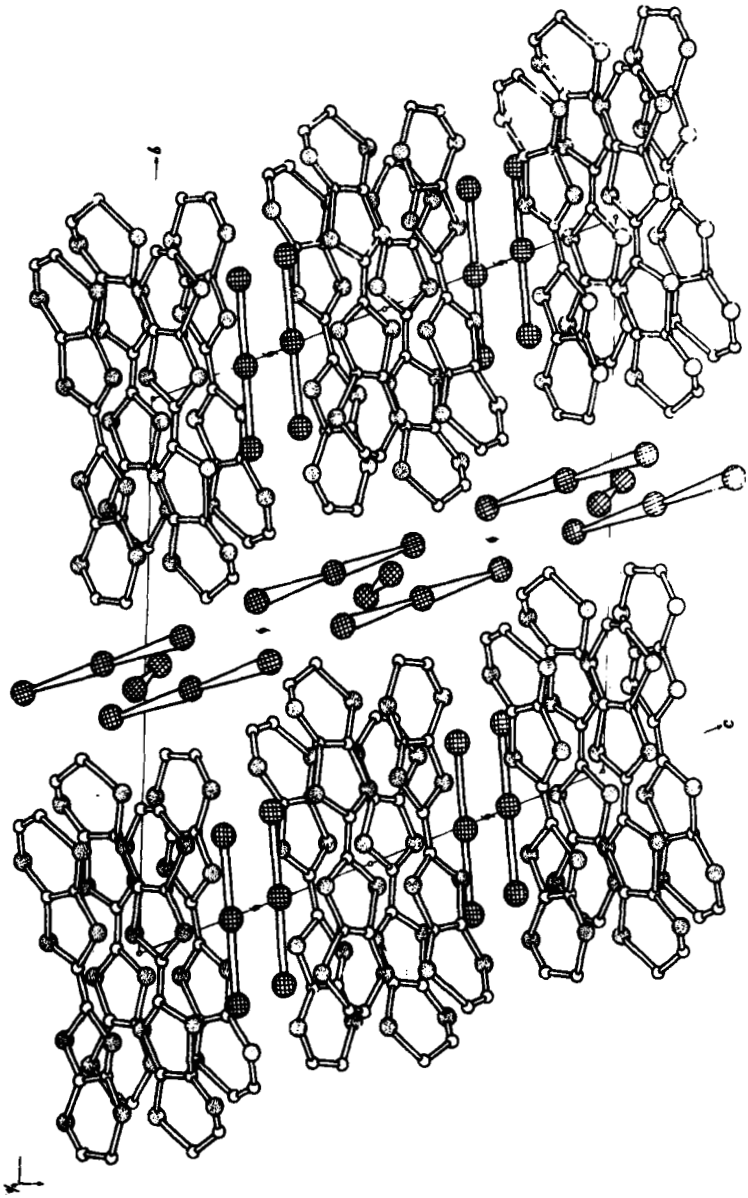

FIGURE 10 $(BEDT\text{-}TTF)_2I_3(I_8)_{0.5}$ (Σ). The structure projection along a.

temperature dependence of the resistivity and the superconducting transition temperature of crystals γ and ε are rather close. Though the X-ray analysis shows them to be different crystals. Figure 10 demonstrates the [001]-projection of ε-structure.

Thus, a number of new organic metals have been obtained in the (BEDT-TTF)-I system. It was found that some of them are superconductors at ambient pressure and T_c = 1.5-3 K.[6-8,16] These are the first ambient-pressure organic superconductors based on sulphur but not selenium compounds.

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