The Crystal Structure of a Charge-Transfer Complex of Tetrakis(methylthio)-tetrathiafulvalenium Dibromoiodate, TMT-TTF·IBr₂

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(Received July 23, 1987)

Synopsis. The crystal structure of the title complex, a semiconductor, has been determined. The space group is $P2_1/n$, with a=8.207(3), b=11.537(4), and c=21.804(12) Å, β=91.88(5)°, and Z=4. The donor cations assume dimer structures with short intermolecular S⋯S contacts of 3.43, 3.53, and 3.60 Å.

It has been proposed that two-dimensional electrical properties of a superconductor β-(BEDT-TTF)₂I₃ (BEDT-TTF=bis(ethylenedithio)tetrathiafulvalene) and its related compounds derive from the four outer sulfur atoms attached to the tetrathiafulvalene (TTF) skeleton.[1] Tetrakis(alkylthio)-substituted TTFs have also similar sulfur atoms, and the influence of alkyl groups on the dimensionality of the electronic systems has been investigated.[2] Wu and Zheng[3] reported of an X-ray analysis of the title compound, but no precise crystal structure was given. Here the present authors report its crystal structure and electrical properties.

Experimental

Black plates of TMT-TTF·IBr₂ were obtained by electrochemical oxidation[4] (at a constant current of 1 μA under nitrogen stream at 20 °C) from a 60 ml chlorobenzene solution containing 0.13 mmol of TMT-TTF and 0.26 mmol of tetrabutylammonium dibromoiodate. The electrical resistivity of single crystal was measured along the a axis by the four-probe method.

A crystal, with 10 faces, of 0.34×0.50×0.23 mm was mounted on a Rigaku AFC-4 four-circle diffractometer. Intensity data were collected at room temperature by using Mo $K\alpha$ radiation (λ=0.71069 Å, graphite monochromated) in the 2θ-ω scan mode with a scan width of $\Delta\omega$=(1.0+0.5 tan θ)° and a scan speed of 4.0° min⁻¹ over the range of 2θ values from 3° up to 55°. Intensities of 5084 reflections were collected and 3147 independent reflections ($|F_o| \geqq 3\sigma(|F_o|)$) were obtained. Three standards measured every 50 reflections showed no significant X-ray damage or crystal decay. Absorption correction following the method of Busing and Levy[5] was applied.

Crystal Data. C₁₀H₁₂S₈·IBr₂: FW=675.43; monoclinic; space group $P2_1/n$; a=8.207(3), b=11.537(4), and c=21.804(12) Å and β=91.88(5)°; U=2063(2) Å³; D_c=2.17 g cm⁻³ for Z=4; μ(Mo $K\alpha$)=64.4 cm⁻¹.

Structure Analysis and Refinement. The structure was solved by use of the Monte Carlo method.[6] Anisotropic thermal parameters were assumed for all non-hydrogen atoms. Hydrogen atoms were not located. The final full-matrix least-squares refinement for 3147 independent reflections led to the R value of 0.069 and the R_w value of 0.083 in conjunction with the weighting scheme of w=(0.011 $|F_o|^2 - |F_o| + 20)^{-1}$. The atomic scattering factors were taken from the International Tables for X-Ray Crystallography (1974). All the computations were carried out on a FACOM M-380 computer using the UNICS III system.[7]

Results and Discussion

The final atomic parameters of the non-hydrogen atoms are given in Table 1.[8] Wu and Zheng[3] reported that the crystal belongs to the monoclinic space group of $P2_1$ with a=8.21, b=11.56, and c=21.85 Å and β=92.1°. The lattice constants of our result are similar to those reported but the space group is different. Figure 1 shows the projection along the a axis. The
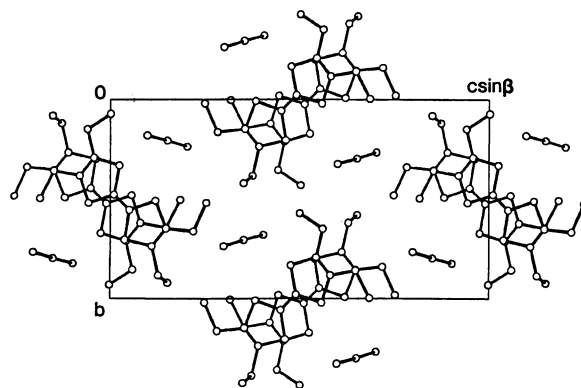

Fig. 1. Crystal structure projected along the a axis.[9]

Table 1. Fractional Atomic Coordinates/×10⁴ and Equivalent Isotropic Thermal Parameters, with Estimated Standard Deviations in Parentheses

| Atom	x	y	z	$B_{eq}/$Å²
I	1040(1)	2040(1)	1497(0.3)	3.91(0.02)
Br(1)	−1860(2)	2358(1)	2019(1)	5.21(0.04)
Br(2)	3974(2)	1778(1)	979(1)	5.48(0.04)
S(1)	1456(3)	2979(2)	−386(1)	3.83(0.06)
S(2)	618(3)	4918(2)	−1188(1)	3.59(0.06)
S(3)	192(4)	1180(2)	−1268(1)	4.52(0.08)
S(4)	−842(4)	3385(3)	−2181(1)	4.80(0.08)
S(5)	3282(3)	4804(2)	569(1)	3.70(0.06)
S(6)	2288(3)	6696(2)	−247(1)	3.60(0.06)
S(7)	5012(4)	6427(3)	1468(1)	4.57(0.07)
S(8)	3730(4)	8530(2)	595(1)	4.51(0.07)
C(1)	552(13)	2648(10)	−1096(5)	4.1(0.3)
C(2)	141(13)	3531(8)	−1466(5)	3.5(0.2)
C(3)	2214(17)	807(10)	−1504(6)	5.3(0.3)
C(4)	−516(18)	4803(11)	−2520(5)	5.8(0.4)
C(5)	3855(12)	6193(9)	798(4)	3.6(0.2)
C(6)	3349(13)	7093(9)	422(5)	3.8(0.2)
C(7)	5019(17)	5037(11)	1839(6)	5.7(0.4)
C(8)	2624(17)	9287(9)	−15(6)	5.3(0.3)
C(9)	1531(12)	4447(9)	−509(4)	3.5(0.2)
C(10)	2292(12)	5227(8)	−106(4)	3.3(0.2)
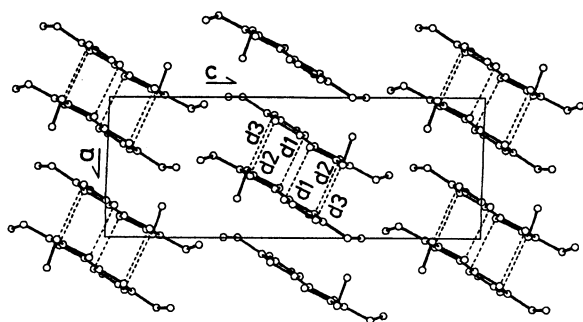
Fig. 2.   The packing motif of TMT-TTF molecules projected along the b axis. The S···S contacts of $d1=3.431(4)$ (S(1)···S(6)), $d2=3.529(4)$ (S(2)···S(5)), and $d3=3.598(4)$ (S(3)···S(8)) shorter than the van der Waals distance of 3.7 Å are indicated.
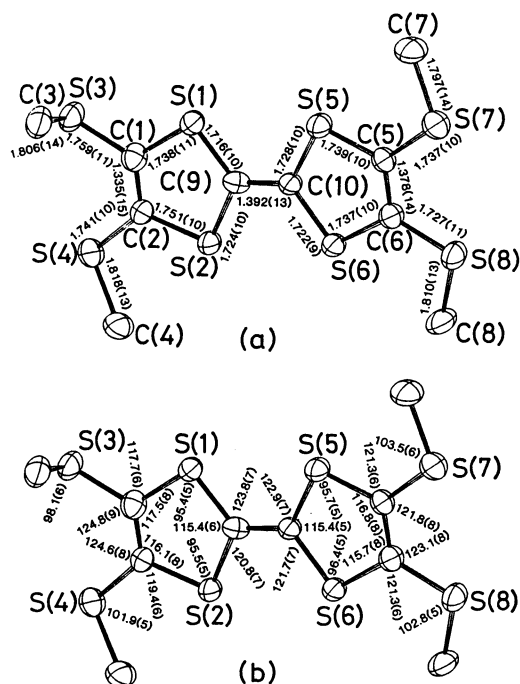

Fig. 3.   Molecular structure[12] of TMT-TTF with the numbering system for the non-hydrogen atoms and the bond distances(Å) (a), and the bond angles(°) (b). Thermal ellipsoids are drawn at 40% probability. Bond distances of IBr₂ molecule are 2.698(2) Å and 2.711(2) Å for I-Br(1) and I-Br(2), respectively, and Br(1)-I-Br(2) bond angle is 178.5(1)°.

umns prevent the intermolecular interaction between the donor columns. As shown in Fig. 2, the donor molecules TMT-TTF's face each other to assume a dimeric structure around the inversion center at (0, 1/2, 0) and (1/2, 0, 1/2), with close S···S contacts of $d1=3.431(4)$ (S(1)···S(6)), $d2=3.529(4)$ (S(2)···S(5)), and $d3=3.598(4)$ (S(3)···S(8)), all shorter than the van der Waals distance of 3.7 Å. No close S···S contacts are found between the adjacent dimers. The bond lengths and angles of the TMT-TTF molecule are shown in Fig. 3 along with the molecular structure. It has been demonstrated that central C=C bond lengths of TTF analogues in charge-transfer complexes correlate well to the degree of charge transfer (ρ).[13] Katayama et al.[10] estimated the ρ value of the (TMT-TTF)(HCBD) complex to be 0.4—0.6 since the central C=C bond length of 1.382(6) Å is almost the mean value between 1.348(5) Å of the neutral TMT-TTF molecule ($\rho \equiv 0$) and 1.438(12) Å of the (TMT-TTF)(AsF₆) complex ($\rho \equiv 1$). In the present complex, however, the corresponding C=C length of 1.392(13) Å (C(9)-C(10)) is shorter than the value for the complete charge transfer ($\rho=1$) as expected from the chemical stoichiometry of donor TMT-TTF and acceptor IBr₂⁻. This discrepancy is a subject for future study. The TMT-TTF molecule moiety without the terminal four methyl groups is nearly planar but slightly folded, possibly due to the dimer formation; the inner S···S contacts are shorter than the outer S···S contacts as mentioned above. The best-fit planes defined by S(1), S(2), S(3), S(4), C(1), and C(2) (plane I), S(5), S(6), S(7), S(8), C(5), and C(6) (plane II), and S(1), S(2), S(5), S(6), C(9), and C(10) (plane III) have dihedral angles of 175.2(1)° for planes I and III and 177.7(1)° for planes II and III. The three methyl groups (C(4), C(7), and C(8)) are not so much displaced from the molecular plane and the other one (C(3)) is almost normal to the plane, which may block the interdimer interactions.

The temperature dependence of the electrical resistivity along the a axis was also measured. The resistivity increases as temperature decreases, which indicates that this crystal is semiconductive ($\rho=1\times10^7$ Ω cm and activation energy $E=5.0$ eV at room temperature). The observed high resistivity and large activation energy are consistent with the poor interdimer interactions.

unit cell contains four TMT-TTF's and four IBr₂'s in general positions. They are stacked in segregated columns extending along the a axis. In the case of other TMT-TTF complexes such as (TMT-TTF)-(HCBD)[10] (HCBD=hexacyanobutadiene) and (TMT-TTF)I₂.₄₇[11] complexes, the stacks of donor TMT-TTF's and those of acceptors form alternate sheets, and the donor TMT-TTF's are aligned almost in the direction of their long axis. In the present complex the crystal does not possess such sheet structures, and the long axis of the TMT-TTF molecule in the position of (x, y, z) is almost perpendicular to those of the molecules in the position of ($1/2-x$, $1/2+y$, $1/2-z$). The extended terminal methyl groups and the anion col-

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