The Crystal Structure of a New Charge-Transfer Complex of Hexamethylenetetrathiafulvalene with Triiodide, HMTTF·I_3[1]

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Synopsis. The crystal structure of bis(trimethylene)tetrathiafulvalenium triiodide (hexamethylenetetrathiafulvalenium triiodide) has been determined. The space group is $P\bar{1}$, with a=7.973 (2), b=11.849 (3), c=14.412 (4) Å, α=82.86 (2), β=89.13 (3), γ=95.85 (2)°, and Z=3. The crystal has intermolecular S...S contacts 3.36 and 3.37 Å shorter than the van der Waals distance of 3.7 Å.

Recent attention paid to organic charge-transfer complexes has demonstrated the possibility of their application to new electronic materials because of their large electronic anisotropy and/or conductivity. A series of complexes of bis(trimethylene)tetrathiafulvalene (hexamethylenetetrathiafulvalene[2]; HMTTF) has been one of the candidates for organic metals since the discovery of HMTTF·TCNQ.[2] The present authors have attempted the electrocrystallization of HMTTF salts with I_3^-, ClO_4^-, and PF_6^-; they have obtained single crystals of HMTTF·I_3 for the first time. Here, the crystal structure and the electrical properties will be reported.

Experimental

Black plates of HMTTF·I_3 were obtained by electrochemical oxidation (at a constant current of 1 μA under nitrogen at 20 °C) from a 80-ml THF solution containing 0.091 mmol of HMTTF and 0.27 mmol of tetrabutylammonium triiodide.[3] The electrical resistivity of the single crystal was measured along the long axis (a axis) by the four-terminal method. The cell dimensions and diffraction intensities were measured on a Rigaku AFC-4 four-circle diffractometer by using graphite monochromated Mo$K\alpha$ radiation (λ= 0.71069 Å) at room temperature. 3998 independent reflections with 2θ values from 3° up to 55° ($|F_o|\geqq 3\sigma(|F_o|)$) were used for the analysis.

Crystal Data: $C_{12}H_{12}S_4\cdot I_3$; FW=665.20; triclinic; space group, $P\bar{1}$; Z=3; a=7.973 (2), b=11.849 (3), c=14.412 (4) Å, α=82.86 (2), β=89.13 (3), γ=95.85 (2)°, U=1343.4 (6) Å^3; D_{obsd}=2.5, D_{calcd}=2.48 gcm^{-3}; μ(Mo $K\alpha$)=55.10 (cm^{-1}). The structure was solved by the use of the *MULTAN* 78 program.[4] The structural parameters were refined by a block-diagonal least-squares method. The hydrogen atoms were placed at the calculated positions.[5] All the computations were carried out on a FACOM M-380 computer using the *UNICS* III system.[6] The final refinement after the absorption correction led to the R value of 0.045. The possibility of another space group, $P1$, was excluded because the I-I bond distance of the I_3 anion on the inversion center was unacceptably prolonged (3.40 Å).

Results and Discussion

The final atomic coordinates of the non-hydrogen atoms are given in Table 1.[7] An *ORTEP*[8] projection of the crystal structure along the a axis is shown in Fig. 1. The unit cell contains three HMTTF (A, B, B′) and three I_3. One HMTTF (A) and one I_3 have their centers of mass on the crystallographic inversion center. Two I_3 anions are aligned almost parallel to the c axis, and the other one is aligned almost parallel to the b axis. These two types of I_3 anions are alternately stacked along the c axis. The anisotropic temperature factors of the I_3 anion on the inversion center are quite large, indicating that the I_3 anion is probably disordered. Figure 2 shows the bond distances in the HMTTF molecules. In the case of tetrathiafulvalene (TTF) salts,[9] oxidation is accompanied by a lengthening of

Table 1. Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Thermal Parameters, with Estimated Standard Deviations in Parentheses

	x	y	z	B_{eq}/Å^2
I1A	814(2)	2451(2)	125(1)	8.67(0.05)
I2A	0(0)	0(0)	0(0)	6.94(0.05)
I1B	286(1)	1947(1)	7068(1)	3.73(0.02)
I2B	378(1)	2249(1)	5010(1)	3.14(0.02)
I3B	597(1)	2526(1)	2972(1)	3.70(0.02)
S1A	3078(3)	−306(3)	−3882(2)	3.17(0.07)
S2A	6763(3)	−41(3)	−3860(2)	3.16(0.07)
S1B	4699(4)	2896(2)	−3812(2)	3.52(0.07)
S2B	7596(3)	4615(3)	−3768(2)	3.71(0.08)
S3B	4885(4)	3249(3)	−6059(2)	3.71(0.08)
S4B	7796(3)	4965(3)	−6042(2)	3.63(0.07)
C1A	4962(11)	−63(8)	−4510(6)	2.1(0.2)
C2A	5681(13)	−290(9)	−2788(6)	2.9(0.3)
C3A	6368(16)	−405(12)	−1831(8)	4.4(0.4)
C4A	4729(16)	−608(10)	−1200(7)	3.8(0.3)
C5A	3192(17)	−599(12)	−1847(8)	4.6(0.4)
C6A	4001(12)	−418(8)	−2797(6)	2.5(0.2)
C1B	6220(12)	3848(9)	−4432(8)	3.0(0.3)
C2B	6773(13)	3918(10)	−2708(8)	3.4(0.3)
C3B	7412(16)	3979(12)	−1729(10)	4.9(0.4)
C4B	6113(19)	3119(15)	−1133(10)	6.0(0.5)
C5B	4898(16)	2553(10)	−1785(9)	4.2(0.3)
C6B	5445(14)	3134(9)	−2723(8)	3.2(0.3)
C7B	6291(12)	4000(9)	−5398(7)	2.9(0.3)
C8B	7160(13)	4591(10)	−7126(8)	3.4(0.3)
C9B	7956(18)	4979(12)	−8071(9)	4.9(0.4)
C10B	6799(20)	4306(15)	−8694(11)	6.5(0.5)
C11B	5428(18)	3558(11)	−8081(10)	5.0(0.4)
C12B	5837(14)	3813(9)	−7127(8)	3.3(0.3)

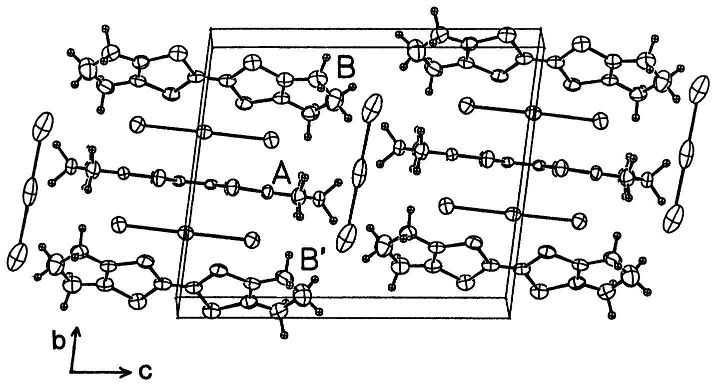

Fig. 1. ORTEP projection of the crystal structure of HMTTF·I_3 on the bc plane. Thermal ellipsoids for non-hydrogen atoms are at 40% probability.

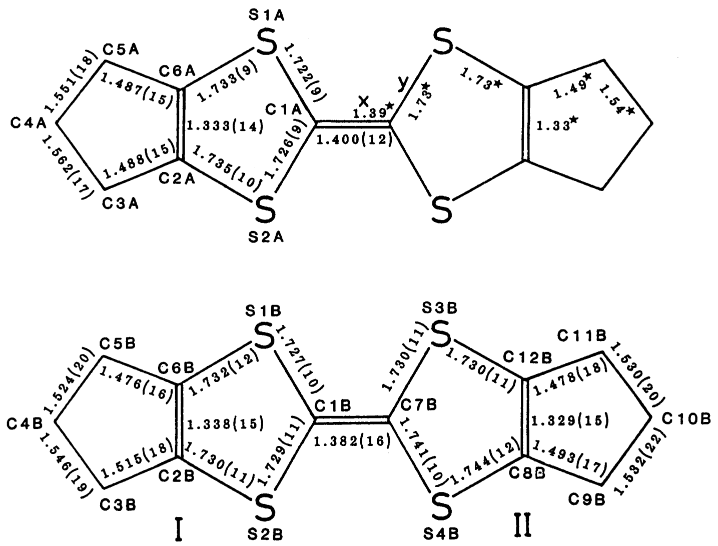

Fig. 2. Numbering system for the non-hydrogen atoms and the bond distances (Å) in the HMTTF molecules. The average distances are indicated at the right side of A with star at shoulder.

the exocyclic double bond (x) and a shortening of the contacts between the two carbon atoms involved in the exocyclic double bond and the sulfur atoms (y). It is impossible to compare the bond distances of HMTTF·I_3 with those of the neutral HMTTF molecule, for the single crystal of the HMTTF has not yet been obtained. The distances of x (1.39 Å) and y (1.73 Å) of HMTTF·I_3, however, agree with the corresponding distances of TTF·I_3 (x, 1.382 (7) Å and y, 1.719 (8) Å). Molecule A is almost planar, within the deviations of 0.05 Å. In Molecule B, both rings I (S1B-C1B-S2-B-C2B-C3B-C4B-C5B-C6B) and II (S3B-C7B-S4B-C8B-C9B-C10B-C11B-C12B) are almost planar, within deviations of 0.08 Å. However, the least-square plane of Molecule B, as a whole, has a deviation of 0.31 Å (C10B); that is, B is slightly folded (8.7°) at the central double bond (C1B—C7B). Figure 3 shows the projection along the c axis. The least-square planes of Molecules A and B have a dihedral angle of 38.0°. The enantiomers B and B′ are parallel and facing to each other, with close S...S contacts of 3.355 (4) and 3.366

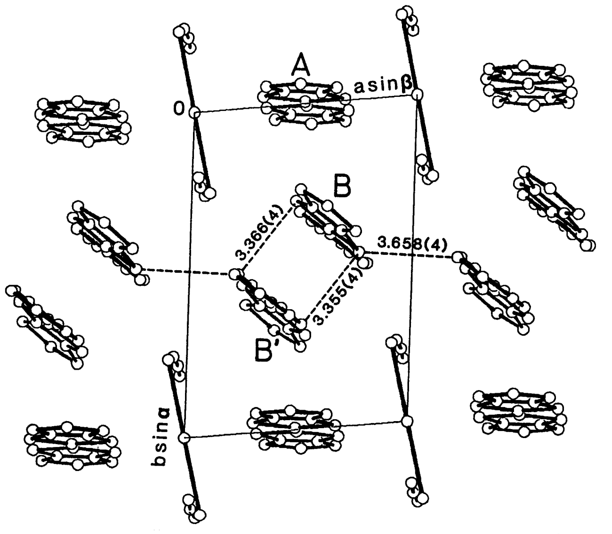

Fig. 3. Crystal structure projected along the c axis. Close intermolecular S···S contacts (Å) are indicated.

(4) Å shorter than the van der Waals distance of 3.7 Å, which may cause the foldings of Molecules B (and B′) described above. A slightly close S ... S contact of 3.658 (4) Å is also found between B and B′ in adjacent cells, but no sufficient overlapping of π-electrons can be expected. No other close S ... S contacts are found around Molecules B and B′ nor around Molecule A.

The temperature dependence of the electrical resistivity along the a axis was also measured. The resistivity increases as the temperature decreases (ρ=3.7×10^5 Ωcm and activation energy K=0.32 eV at 300 K);$^{10)}$ that is, this crystal is semiconductive, which is consistent with the molecular stacking along the a axis.

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