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Crystal Structure of the Mixed-Stacked Salt of Bis(ethylenedithio)-tetrathiafulvalene (BEDT-TTF) and Tetracyanoquinodimethane (TCNQ)

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Synopsis. The crystal structure of the monoclinic form of (BEDT-TTF)(TCNQ) is determined by X-ray analysis. The donor (BEDT-TTF) and the acceptor (TCNQ) molecules are planar and form alternating stacks.

Recently the discoveries of superconductivity have aroused much interest in BEDT-TTF complexes. Although the organic superconductors based on BEDT-TTF have been found among the salts with inorganic anions such as ReO_4^-, I_3^-, IBr_2^-, and AuI_2^-,[1] the conventional type of charge-transfer complex (BEDT-TTF)(TCNQ) was already prepared as early as 1978 when BEDT-TTF was first synthesized,[2] and this complex has been reported to be highly conductive by the measurements on compressed samples.[2,3] On the way to characterize this complex by means of the X-ray analysis and the measurements of physical properties by using single crystals, we found two different types of crystals: The monoclinic form and the triclinic form. The triclinic form of (BEDT-TTF)(TCNQ) is composed of segregated stacks, where TCNQ molecules are stacked face to face, while BEDT-TTF molecules are arranged side by side along the TCNQ stacks. This complex shows comparatively high conductivity and undergoes a characteristic metal-insulator transition around room temperature.[4] In the present paper we report the crystal structure of the other form, the monoclinic form of (BEDT-TTF)(TCNQ).

Experimental

Single crystals for structure analysis were obtained by the direct reaction of the donor and the acceptor in various organic solvent.[4] The donor and the acceptor were dissolved together in a hot organic solvent such as 1,1,1- and 1,1,2-trichloroethane, 1,2-dichloroethane, and THF, and the solution was allowed to evaporate at room temperature. By keeping for several weeks, black crystals of the complex in the form of elongated plates were grown. The triclinic form was obtained together with the monoclinic form from the same solution, and it was difficult to control reaction conditions so as to obtain only one form. Since these two forms were quite similar in shape, they were only distinguished by X-ray investigations.

Crystal Data. $C_{22}H_{12}N_4S_8$, F.W. 588.89, monoclinic, space group $P2_1/n$, a=23.897(4), b=7.327(2), c=7.053(2) Å, β=98.37(2), U=1221.8(5) Å^3, Z=2, D_x=1.601 gcm^{-1}, and μ(Mo $K\alpha$)=7.23 cm^{-1}. Intensity data were measured by the θ—2θ scan technique on a Rigaku AFC-5R automated four-circle diffractometer with graphite-monochromatized Mo $K\alpha$ radiation ($2\theta<60°$) and corrected for usual Lorentz and polarization effects, but not for the absorption. The structure was solved by the direct method and refined by the block-diagonal least-squares procedure to an R value of 0.052, by using 2294 independent reflections ($|F_o|>3\sigma(|F_o|)$). Anisotropic thermal parameters were adopted for all non-hydrogen atoms, and the hydrogen atoms were refined isotropically.

Results and Discussion

The atomic coordinates are listed in Table 1.[5] The crystal sturcture is shown in Fig. 1. The donors and the acceptors are stacked alternately along the b axis (the crystal long axis). Each molecule is present on an inversion center. The donor and the acceptor molecules are planar (see Fig. 1). As shown in Table 2, the planarity of BEDT-TTF is as good as those observed in the BEDT-TTF salts with various inorganic anions; the deviation of each atom from the optimal plane is within 0.04 Å except the terminal ethylene groups. This contrasts with the nonplanar structure of the neutral molecule.[6]

It is noteworthy that BEDT-TTF and TCNQ form either segregated (the triclinic form) or mixed (the monoclinic form) stacks with the same 1:1 composition. This is largely related to the similar molecular size. The rectangle of the outer sulfur atoms of BEDT-TTF, 9.6×3.7=36 Å^2 has almost the same size as that of TCNQ, 8.5×4.1=35 Å^2. In this context, the terminal ethylene group of BEDT-TTF plays an exceptional role, because there is no overlap between this part and TCNQ (Fig. 1) due to the steric repulsion of this out-of-plane aliphatic moiety.

Table 1. Atomic Parameters (×10^4) of the Monoclinic (BEDT-TTF)(TCNQ)

Atom	x	y	z	B_{eq}
S (1)	4503 (1)	383 (1)	2357 (1)	3.4
S (2)	4241 (1)	983 (1)	−1821 (1)	3.1
S (3)	3384 (1)	1545 (2)	3196 (1)	4.3
S (4)	3091 (1)	2329 (1)	−1795 (1)	3.7
C (1)	4737 (1)	284 (4)	116 (4)	2.8
C (2)	3825 (1)	1222 (5)	1452 (5)	2.9
C (3)	3710 (1)	1518 (4)	−424 (4)	2.7
C (4)	2873 (2)	3064 (6)	1929 (6)	4.6
C (5)	2619 (1)	2391 (6)	−11 (6)	4.7
C (6)	427 (1)	500 (5)	3919 (4)	3.0
C (7)	−63 (1)	−158 (5)	3003 (4)	3.0
C (8)	516 (1)	698 (4)	5968 (4)	2.6
C (9)	1019 (1)	1362 (4)	6915 (4)	2.7
C (10)	1479 (1)	1938 (4)	5951 (4)	2.8
C (11)	1126 (1)	1495 (5)	8964 (5)	3.3
N (1)	1852 (1)	2407 (4)	5242 (4)	3.8
N (2)	1219 (1)	1579 (5)	10587 (4)	5.0

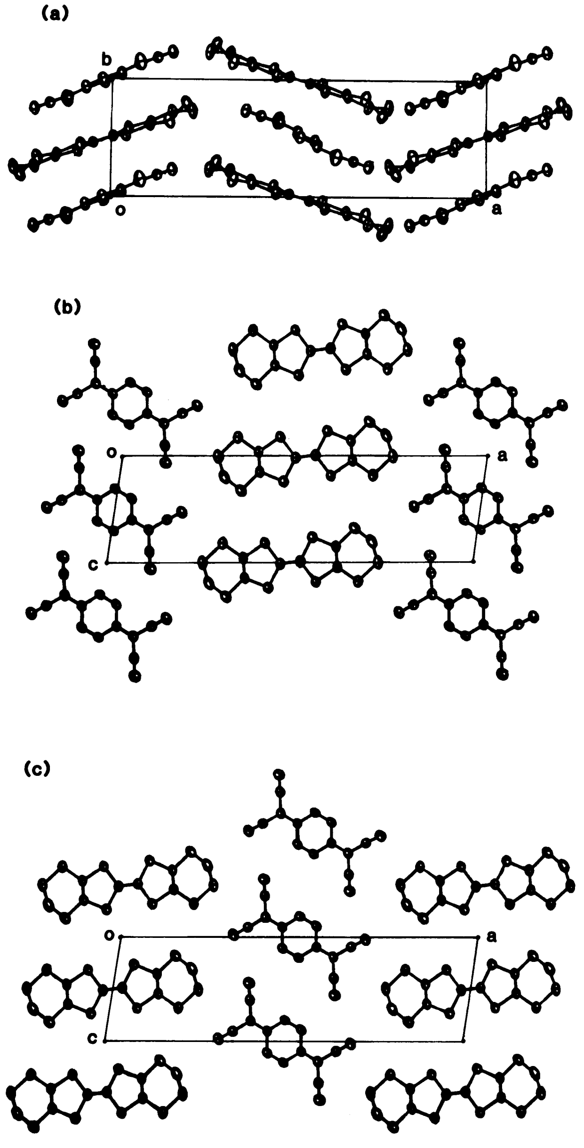

Fig. 1. Crystal structure of the monoclinic (BEDT-TTF)(TCNQ).
(a) Projection on the ab plane. (b) Projection along the b axis, the molecules on the $y=0$ inversion centers and (c) on the $y=0.5$ inversion centers.

Table 2. Least Squares Planes and Deviations (Å); X, Y, Z are Coordinates (Å) Referred to the Orthogonal Axes a, b, and c*

(a) TTF skeleton of BEDT-TTF					
$0.3267X+0.9372Y+0.1219Z=3.4333$					
S (1)	0.004	C (2)	0.004	S (4)	−0.015
S (2)	0.011	C (3)	−0.013	C (4)	−0.542
C (1)	0.004	S (3)	0.037	C (5)	0.219
(b) TCNQ					
$0.3684X-0.9276Y+0.0624Z=0.0284$					
C (6)	−0.030	C (9)	0.018	N (1)	0.004
C (7)	−0.041	C (10)	0.009	N (2)	−0.032
C (8)	0.015	C (11)	0.002		

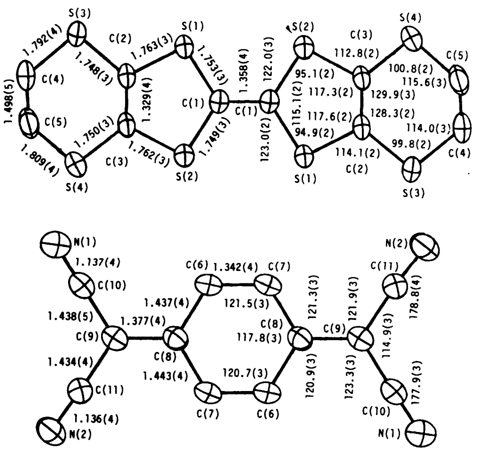

Fig. 2. Molecular geometry of BEDT-TTF and TCNQ.

Table 3. A Comparison of the Averaged Bond Lengths (mmm Molecular Symmetry) of BEDT-TTF and TCNQ with Those of the Neutral Species, BEDT-TTF$^{+1/2}$ in α-(BEDT-TTF)$_2$PF$_6$, and TCNQ$^{-1/2}$ in (Ph$_4$P)(TCNQ)$_2$ and (TMPD)(TCNQ)$_2$[6–8)]

	BEDT-TTF^0	Present Complex	BEDT-TTF$^{+1/2}$
C (1) - C (1)	1.319	1.358	1.365
C (1) - S (1)	1.757	1.751	1.740
C (2) - S (1)	1.754	1.763	1.750
C (2) - C (3)	1.332	1.329	1.345
	TCNQ^0	Present Complex	TCNQ$^{-1/2}$
C (6) - C (7)	1.346	1.342	1.353
C (6) - C (8)	1.448	1.440	1.434
C (8) - C (9)	1.374	1.377	1.396
C (9) - C (10)	1.441	1.434	1.428
C (10) - N (1)	1.14	1.14	1.17

The molecular geometry is depicted in Fig. 2. In order to estimate the degree of charge transfer, η, the molecular geometries of the constituents are analyzed in comparison with the molecular geometries in which the degrees of charge transfer are evident from their composition (Table 3). As for BEDT-TTF, the central C=C bond length and the C(1)–S(1) bond length are between those of η=0 and η=1/2 species. On the other hand, since the population of the LUMO of TCNQ is largest on C(8) and C(9),[9)] the bond lengths associated with these atoms are sensitive to η; these bond lengths are also between η=0 and η=1/2. As a whole, we can conclude the degree of charge transfer to be between η=0 and η=1/2, probably about η=0.2—0.3.

The electrical resistivity measured by the usual four-probe method is in the order of 10^6 Ωcm. Saito et al. have briefly mentioned two forms of (BEDT-TTF)(TCNQ); one affords a broad infrared spectrum and the other affords a sharp spectrum.[3)] The broad spectrum is considered to be that of the triclinic form, and is associated with its high conductivity. On the other hand, the sharp spectrum is that of the present low-conductive monoclinic form.

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