Crystal Structure of TTF·BTDA-TCNQ Complex. A New Type of CT Complex with an Inclusion Behavior and a Multi-Dimensional Structure

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(Received December 5, 1986)

The crystal structure of TTF·BTDA-TCNQ complex was determined by an X-ray diffraction method. The crystals are monoclinic, space group $P2_1/n$ with $a=9.660(1)$, $b=7.231(1)$, $c=14.628(2)$ Å, $\beta=91.31(1)°$, and $Z=2$. The structure was solved by the direct method and refined by the block-diagonal least-squares method to give an R value of 0.040 for non-zero 2620 reflections. The complex is nonionic and the molecules form equally spaced mixed stacks along the b axis. These stacks are connected by strong transverse interactions resulting in a three-dimensional structure. BTDA-TCNQ molecules make cavities by S-N≡C interactions in which TTF molecules are included. This complex is not a simple CT complex with mixed stacks but rather the one with some inclusion behavior.

Recently, we have reported the preparation[1)] and crystal structure[2)] of bis(1,2,5-thiadiazolo)tetracyanoquinodimethan (BTDA-TCNQ),[3)] which forms a two-dimensional "sheet-like network" by strong S-N≡C interactions in crystalline state. Thus, the charge-transfer complex or ion-radical salt of BTDA-TCNQ is proposed to exhibit a high-dimensional structure which could stabilize the metallic state[4)] and induce the electrical conductivity along the side-by-side directions. In the course of our examination for the CT complexes of BTDA-TCNQ, the donors with the larger size such as tetrathianaphthacene (TTN) and dimethyldihydrophenazine (DMPH) have been proved to give highly conductive complexes with BTDA-TCNQ.[5,6)] On the other hand, the CT complexes with tetrathiafulvalene (TTF) and its analogues exhibit very low electrical conductivities[5,6)] though TTF·TCNQ complex is a representative organic metal.[7)] We have succeeded in obtaining single crystals of TTF·BTDA-TCNQ.[8)] This report describes the structural analysis of the title complex from which the causes of the low conductivity are discussed.

Experimental

TTF·BTDA-TCNQ complex (decomp 247—248 °C) was prepared by a diffusion method in dichloromethane using an H-shaped tube. The molar ratio was determined to be 1 : 1 on the basis of the elemental analysis. Found: C, 41.26; H, 0.58; N, 20.69; S, 36.72%. Calcd for $C_{18}H_4N_8S_6$: C, 41.20; H, 0.77; N, 21.35; S, 36.68%. A platelike crystal with dimensions of 0.15×0.20×0.25 mm was used for the data collection on a Rigaku automated four-circle diffractometer (AFC-5), equipped with a rotating anode (50 kV, 200 mA), using graphite-monochromated MoK_α radiation ($\lambda=0.71069$ Å). Crystal data are as follows; $a=9.660(1)$, $b=7.231(1)$, $c=14.628(2)$ Å, $\beta=91.31(1)°$, $V=1021.5(4)$ Å^3, $P2_1/n$, $Z=2$, $D_{\mathrm{calcd}}=1.71$ g cm^{-3}. The ω—2θ scan mode with a scan rate of 4° min^{-1} was employed with the ω scan range $(1.0+0.5\tan\theta)°$. A total of 2915 reflections within $2\theta=55°$ was collected. No absorption correction was applied.

The structure was solved by the direct method using RANTAN81[9)] with some modification. The parameters of all the non-hydrogen atoms were refined by the block-diagonal least-squares method with the anisotropic temperature factors. Although the positions of hydrogen atoms were located by a difference Fourier map, the geometrically calculated ones were included in the refinement. The final R value ($R=\sum||F_o|-|F_c||/\sum|F_o|$) is 0.040 for 2620 non-zero reflections. The atomic coordinates are given in Table 1.

The atomic scattering factors from the International Tables for X-ray Crystallography[10)] were used. All the computation were carried out by an ACOS 1000 computer at Tohoku University using the applied library program of UNICSIII system.[11)]

Results and Discussion

Molecular Structure. Figures 1 and 2 show the thermal ellipsoids of the BTDA-TCNQ and TTF molecule, respectively. Since $Z=2$ in the space group $P2_1/n$, BTDA-TCNQ and TTF molecules are both restrictly related by a center of symmetry in the unit cell. Each molecule takes an almost planar conformation and the slight deviations of atoms from the

Table 1. Fractional Atomic Coordinates (×10^4) and Equivalent Temperature Factors (Å^2)

Atom	x	y	z	B_{eqv}[a)]
S 1	7057(1)	432(1)	3598(0)	3.1
N 1	7269(2)	870(3)	4676(1)	2.8
N 2	8594(2)	−271(3)	3356(1)	2.8
C 1	8587(2)	456(3)	4889(2)	2.3
C 2	9352(2)	−196(3)	4132(2)	2.3
C 3	9188(2)	722(3)	5806(2)	2.3
C 4	8467(2)	1391(3)	6520(2)	2.4
C 5	7001(2)	1786(3)	6498(2)	3.0
C 6	9067(2)	1764(3)	7411(2)	2.8
N 3	5863(2)	2097(4)	6589(2)	4.7
N 4	9404(2)	2130(4)	8140(2)	3.8
S 2	6862(1)	961(1)	9323(0)	2.9
S 3	6336(1)	−122(1)	11228(0)	2.9
C 7	8231(2)	1122(4)	10118(2)	3.4
C 8	7988(3)	636(4)	10961(2)	3.5
C 9	5667(2)	187(3)	10114(2)	2.4

a) $B_{\mathrm{eqv}}=(4/3)\sum_{ij}\beta_{ij}(a_i\cdot a_j)$.

Table 2. Comparison of Bond Lengths (Å) in BTDA-TCNQ

Bond	BTDA-TCNQ$^{\circ\,a)}$	BTDA-TCNQ$^{\overline{\cdot}\,b)}$	TTF complex
a	1.617(6)	1.614(4)	1.616(2)
b	1.330(4)	1.346(6)	1.338(3)
c	1.422(6)	1.443(5)	1.426(3)
d	1.457(6)	1.437(6)	1.462(3)
e	1.356(7)	1.390(6)	1.358(3)
f	1.438(6)	1.429(7)	1.442(3)
g	1.143(5)	1.140(6)	1.136(4)

a) Ref. 2. b) Ref. 20.

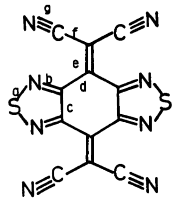
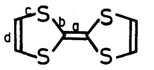


Table 3. Comparison of Bond Lengths (Å) in TTF

Bond	TTF$^{\circ\,a)}$	TTF$^{+\cdot\,b)}$	BTDA-TCNQ complex
a	1.349(3)	1.404(14)	1.352(3)
b	1.757(2)	1.713(9)	1.750(2)
c	1.730(2)	1.725(11)	1.743(3)
d	1.314(3)	1.306(16)	1.309(4)

a) Ref. 12. b) Ref. 13.



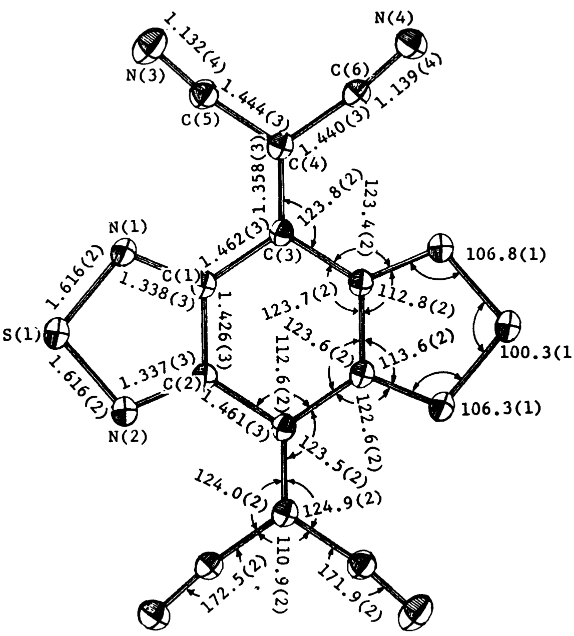


Fig. 1. ORTEP drawing of BTDA-TCNQ molecule with the bond lengths (l/Å) and bond angles (ϕ/°).

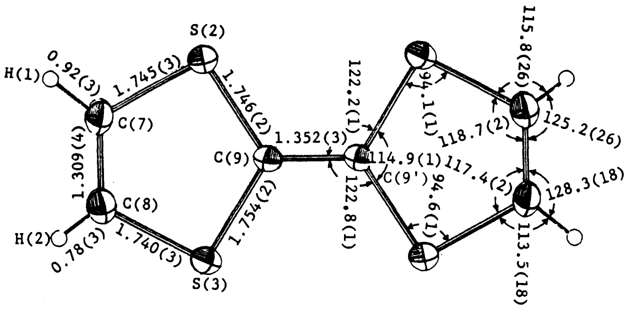


Fig. 2. ORTEP drawing of TTF molecule with the bond lengths (l/Å) and bond angles (ϕ/°).

molecular plane in BTDA-TCNQ indicate the twisting around the *exo*-methylene double bond (5.1°). Tables 2 and 3 show the comparisons of bond lengths of BTDA-TCNQ and TTF in the present complex with those in the neutral molecules or the ion-radical species. It is apparent that the present complex is nonionic as indicated by the degree of charge transfer (Z=0.06) estimated from the bond lengths of C(3)=C(4) (bond e) of BTDA-TCNQ and C(9)=C(9′) (bond a) of TTF.[14)]

Crystal Structure and Molecular Packing. Three views of the crystal structure are shown in Figs. 3—5. TTF and BTDA-TCNQ form a mixed stack with the equal space of 3.40 Å. This type of a mixed stacking is often observed in the CT complexes of TCNQ which exhibit low electrical conductivities.[15)] The low conductivity of the present complex can be attributed to this mixed stack formation as well as the small degree of the charge transfer from TTF to BTDA-TCNQ. The mixed stack formation is favored when the symmetry of HOMO of the donor is similar to that of LUMO of the acceptor.[15)] Thus, molecules tend to overlap in a "ring-double bond type"[16)] with a highly symmetrical superimposition so as to maximize the

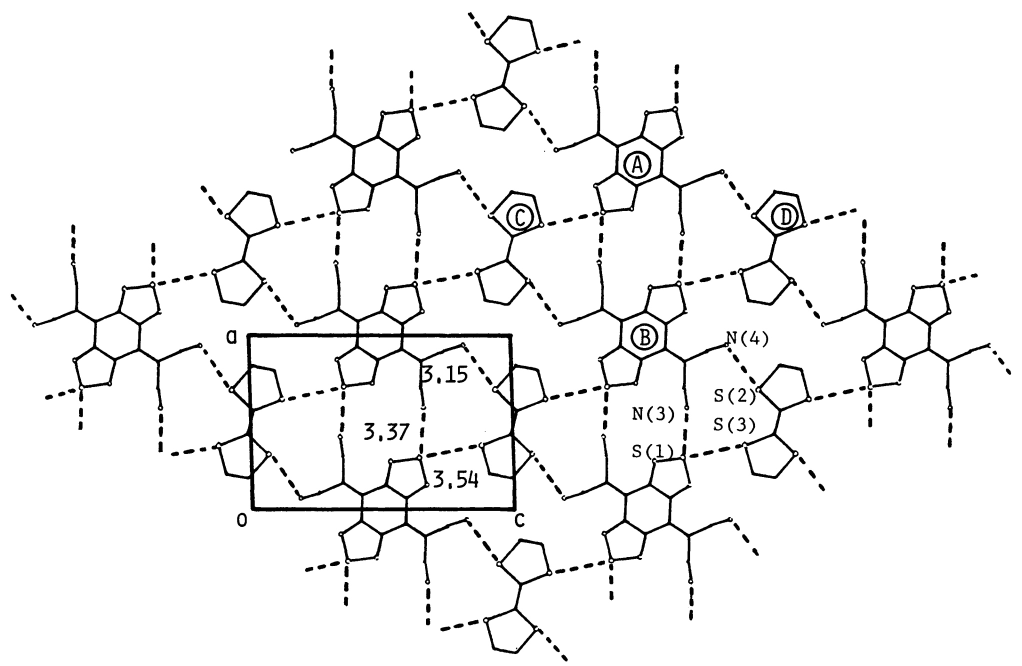


Fig. 3. "Sheet-like network" in the ac plane. S(1)-N(3)≡C(5) (3.37 Å), S(2)-N(4) (3.15 Å) and S(1)-S(3) (3.54 Å) interactions are indicated by broken line. Molecules A-D are related by the following symmetry operations: A (x,y,z and $2-x,-y,1-z$); B ($-1+x,y,z$ and $1-x,-y,1-z$); C ($x,y,-1+z$ and $1-x,-y,1-z$); D (x,y,z and $1-x,-y,2-z$).

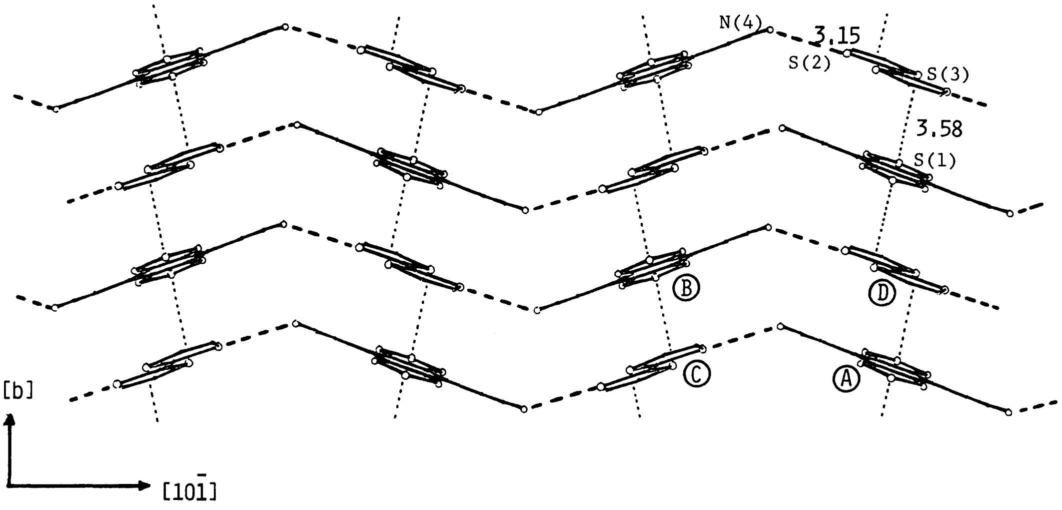


Fig. 4. Corrugation of the "sheet". The drawing of (10$\bar{1}$) plane. S(2)-N(4) (3.15 Å) interactions are indicated by broken line. S(1)-S(3) (3.58 Å) interactions along the b axis are indicated by dotted line. Molecules A—D are related by the following symmetry operations: A (x,y,z and $2-x,-y,1-z$); B ($-0.5+x,0.5-y,0.5+z$ and $1.5-x,0.5+y,1.5-z$); C (x,y,z and $1-x,-y,2-z$); D ($0.5+x,0.5-y,-0.5+z$ and $1.5-x,0.5+y,1.5-z$).

CT interaction in the mixed stacks. As shown in Fig. 6, the molecular overlapping of this complex is not such a type, but BTDA-TCNQ and TTF molecules are tightly connected by S(1)-S(3) (3.58 Å) and N(1)-S(3) (3.47 Å) interactions. These facts indicate that the mixed stacks in the present complex are formed by the direct interactions between heteroatoms rather than the charge-transfer interaction through the π-electron overlapping. Similar mode of overlapping is found in TTF·bis(1,2,5-thiadiazolo)benzoquinone[3] (1 : 1) complex and TTF·(1,2,5-thiadiazolo)naphthoquinone[3] (1 : 2) complex.[17]

The more interesting feature in the crystal is that the mixed stacks are connected by several transverse interactions resulting in the formation of a complicated three-dimensional network as a whole. In the ac plane perpendicular to the stacking b axis, the TTF and BTDA-TCNQ molecules form lines along the a axis and arranged alternately along the c axis. In this ac plane BTDA-TCNQ molecules are connected by weak S(1)-N(3)≡C(5) linkages (3.37 Å; molecules A and B in Fig. 3) and also connected by strong S(1)-S(3) (3.54 Å;

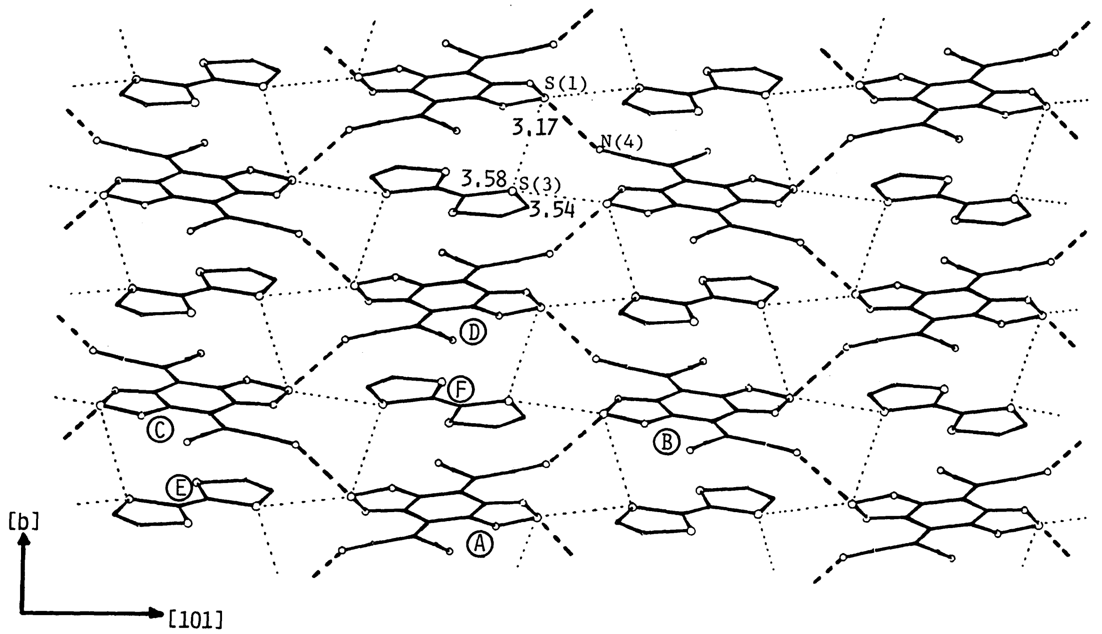


Fig. 5. Cavity formation of BTDA-TCNQ. The drawing of (101) plane. S(1)-N(4)≡C(6) (3.17 Å) interactions are indicated by broken line. S(1)-S(3) interactions along the b axis (3.58 Å) and along [101] direction (3.54 Å) are indicated by dotted line. Molecules A—F are related by the following symmetry operations: A (x,y,z and $2-x,-y,1-z$); B ($0.5+x,0.5-y,0.5+z$ and $2.5-x,0.5+y,1.5-z$); C ($-0.5+x,0.5-y,-0.5+z$ and $1.5-x,0.5+y,0.5-z$); D ($x,1+y,z$ and $2-x,1-y,1-z$); E ($x,y,z-1$ and $1-x,-y,1-z$); F ($0.5+x,0.5-y,-0.5+z$ and $1.5-x,0.5+y,1.5-z$).

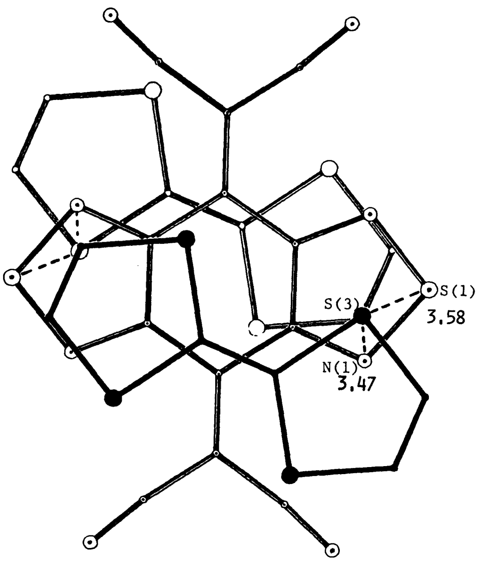


Fig. 6. Molecular overlapping of TTF and BTDA-TCNQ viewed perpendiculer to the molecular plane of BTDA-TCNQ. S(1)-S(3) (3.58 Å) and S(3)-N(1) (3.47 Å) interactions are indicated by broken line.

molecules A and C in Fig. 3) and S(2)-N(4)≡C(6) (3.15 Å; molecules A and D in Fig. 3) interactions along [101] and $[10\bar{1}]$ directions with TTF, thus forming a sheet-like network on this plane. Since the molecules incline ca. 20° from the ac plane,[18] this network is not coplanar but somewhat corrugated (Fig. 4). The more important finding is that there exist strong S(1)-N(4)≡C(6) interactions (3.17 Å; molecules A, B, C, and D in Fig. 5) along [111] and $[1\bar{1}1]$ directions. As a result, four BTDA-TCNQ molecules are connected to each other which surround a TTF molecule from top, bottom, and two sides. In other words, cavities which include TTF molecules are formed by BTDA-TCNQ molecules. This fact indicates that the present CT complex is more stabilized by the contribution of inclusion behavior. This inclusion behavior is also observed in the BTDA-TCNQ complexes with some aromatic hydrocarbons such as benzene.[19] It is suggested here that the present complex is not a simple CT complex with mixed stacks but rather the one with some inclusion behavior resulted from the multidimensional structure.

Conclusion

The crystal structure of TTF·BTDA-TCNQ complex does not exhibit a segregated columnar stack as found in TTF·TCNQ but a mixed stack resulting in the low electrical conductivity. However, the more important finding is the effects of the network formed by the strong interheteroatom interactions. It has been manifested in the anion-radical salts that the two-dimensional network of BTDA-TCNQ can enhance the electrical conductivity.[20] However, it is also true that these interactions can create the cavities leading to a mixed stack formation with the inclusion behavior for some CT complexes. In conclusion, it is suggested that a donor with a larger size and a relatively low oxidation potential which excludes the inclusion behavior observed in the present complex is needed in order to form a highly conductive CT complex with BTDA-TCNQ.

Tables of anisotropic thermal parameters, coordinates of hydrogen atoms, and observed and calculated structure factors are kept at the Chemical Society of Japan (Document No. 8740).

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