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Crystal Structure of 2,5-Bis(dicyanomethylene)-2,5-dihydrothieno[3,2-b]thiophene and Bis(ethylenedithio)tetrathiafulvalene Complex

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The crystal structure of 2,5-bis(dicyanomethylene)-2,5-dihydrothieno[3,2-b]thiophene and bis(ethylenedithio)tetrathiafulvalene complex showed a weak face to face interaction and sheet-like networks with intermolecular N···S and S···S interactions, and the shortest S···S contact is 3.48 Å between the acceptors.

Recent advances in the study on conducting organic solids have well established that the intermolecular heteroatom interactions are essential to enhance the dimensionality, which is useful to stabilize the metallic state against the metal-insulator transition of low-dimensional organic metals.$^{1)}$ We have recently reported the preparation of the condensed$^{2)}$ and the conjugated homologues$^{3)}$ of thiophene-TCNQ. Remarkable characteristics of these acceptors, though their electron affinities are as weak as thiophene-TCNQ, are the increase of polarizability and the decrease of on-site Coulomb repulsion. We have been interested in the crystal structure of their charge-transfer complexes, because significant intermolecular contacts between the sulfur atoms will be expected. In this letter, we report the crystal structure of the charge-transfer complex of 2,5-bis(dicyanomethylene)-2,5-dihydrothieno[3,2-b]thiophene (**1**) and 4,5:4'5'-bis-(ethylenedithio)tetrathiafulvalene (BEDT-TTF).

Black leaflets of charge-transfer complex were formed by the direct reaction of the acceptor and the donor in chlorobenzene, and single crystals for structure analysis were obtained by recrystallization from the same solvent.$^{4)}$ The intensities of X-ray diffraction were collected with a Rigaku automated diffractometer using Cu K_α radiation monochromatized with a graphite plate. We obtain 1969 independent diffractions which have intensities larger than the statistical counting error, and used all of them for analysis. The dimension of the crystal used in this measurement was 0.50×0.40×0.01 mm^3. The crystal belongs to the triclinic system with the space group, $P\bar{1}$, the lattice parameters being a=7.205(1), b=13.654(1), c=6.898(2) Å, α=91.76(1), β=103.85(2), γ=101.32(1)°, Z=1, and V=643.9(2) Å^3. The structure was solved by the direct method combined with the Monte-Carlo method$^{5)}$ for the selection of the initial set of phase. It was

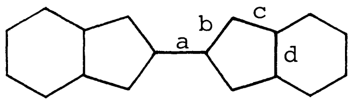
Table 1. Fractional atomic coordinates and equivalent temperature factors (Å^2)

	x(×10^4)	y(×10^4)	z(×10^4)	$B_{eq}$$^{a)}$		x(×10^4)	y(×10^4)	z(×10^4)	$B_{eq}$$^{a)}$
S1	646(2)	590(1)	2413(2)	3.7(1)	S10	4502(2)	9118(1)	2500(2)	3.6(1)
C2	870(7)	1594(4)	4156(7)	2.6(2)	C11	4715(7)	9518(4)	157(8)	2.8(2)
C3	487(8)	1287(4)	6068(8)	3.0(2)	S12	4184(2)	8546(1)	-1755(2)	3.4(1)
C4	-2(8)	259(4)	5936(7)	2.8(2)	C13	3568(7)	7579(4)	-242(8)	2.9(2)
C5	1398(8)	2559(4)	3690(8)	2.8(2)	C14	3718(8)	7841(4)	1675(8)	3.0(2)
C6	1684(8)	2765(4)	1747(9)	3.5(2)	S15	3271(3)	7086(1)	3577(2)	4.4(1)
N7	1869(8)	2899(4)	173(8)	4.8(2)	C16	2253(11)	5875(4)	2230(10)	5.1(2)
C8	1663(8)	3407(4)	5067(8)	3.2(2)	C17	3304(10)	5652(4)	639(9)	4.2(2)
N9	1897(8)	4108(4)	6123(7)	4.4(2)	S18	2842(2)	6375(1)	-1484(2)	3.6(1)

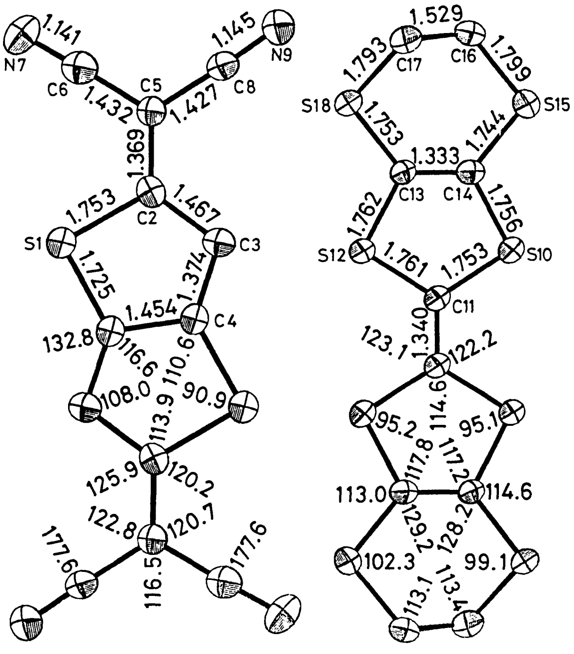
a) $B_{eq}=(4/3)\Sigma_{ij}\beta_{ij}(a_i \cdot a_j)$.

Table 2. A comparison of the mean bond lengths (Å) of BEDT-TTF

ρ$^{a)}$	a	b	c	d
0	1.31(1)	1.757(7)	1.754(8)	1.332(7)
1/2	1.365(4)	1.740(2)	1.750(2)	1.345(3)
*$^{b)}$	1.340(9)	1.757(6)	1.759(5)	1.333(8)



a) ρ=0:BEDT-TTF, ρ=1/2:α-(BEDT-TTF)$_2$PF$_6$, Ref. 7. b) Present complex.



1 BEDT-TTF

Fig. 1. Bond lengths and bond angles. Estimated standard deviations are 0.005-0.011 Å and 0.3-0.6° for lengths and angles, respectively.

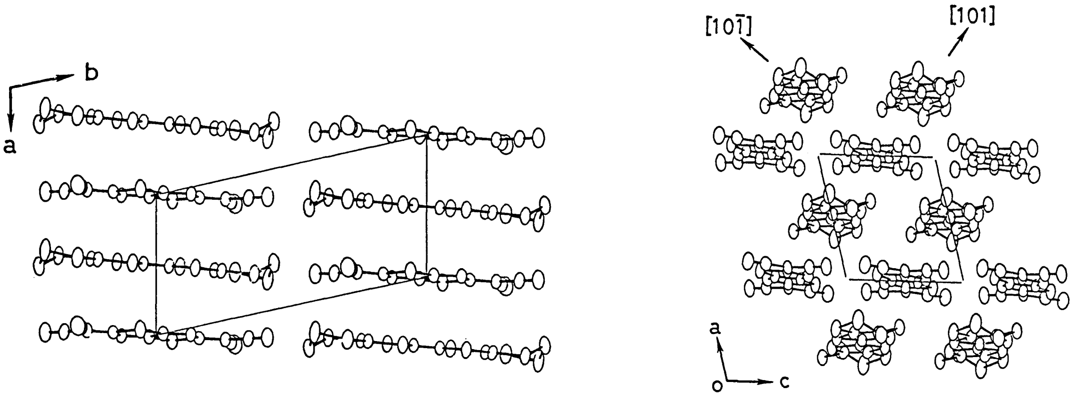
refined by the full-matrix least squares method after applying the absorption corrections. The final R value was 0.073.$^{6)}$

Each molecule is present on the crystallographic inversion center. The final atomic parameters are given in Table 1 and the molecular geometry is depicted in Fig. 1. Acceptor molecule **1** takes almost planar conformation; the largest deviation from the least squares plane is 0.057 Å for sulfur atoms. The planarity of BEDT-TTF molecule is similar to those observed in various BEDT-TTF salts with inorganic anions; the deviation of each atom from the optimal plane of TTF skeleton is within 0.03 Å except for the terminal ethylene groups. In order to estimate the degree of charge transfer, ρ, the bond lengths of the TTF moiety are compared with those of neutral and ρ=1/2 molecules (Table 2).$^{7)}$ The central C=C bond length of present complex is between those of ρ=0 and ρ=1/2 species. On the other hand, other C=C and C-S bond lengths are not significantly different from those with ρ=0. In addition, taking into account of the nitrile stretching frequency of present complex,4) we can conclude the degree of charge transfer to be very small.

Figure 2 shows the crystal structures. Though the acceptors and the donors are separately arranged along the a axis, the interplanar distances are as long as the length of this axis. Moreover, they are alternately arranged along [101] and [10$\bar{1}$] directions, but overlapping of the π-electron frameworks is hardly present (Fig. 3). Consequently, their face to face interaction may be effectively nil. The intermolecular S···S distances along these directions, 3.73 and 3.82 Å, are slightly longer than the sum of van der Waals radius (3.70 Å). The low conductivity of the present complex4) can be attributed to this weak face to face interaction as well as the small degree of the charge transfer.

In contrast, there are several intermolecular short contacts along transverse directions. In the (1$\bar{2}$0) plane, the acceptor and the donor are separately arranged side by side along the c axis and also arranged alternately along the long-molecular axis. As shown in Fig. 4, this complex forms sheet-like networks parallel to this plane with intermolecular N···S and S···S interactions. Molecule **1** and BEDT-TTF are connected with somewhat short N···S contact (3.33 Å) which is approximately equal to the van der Waals contact (3.35 Å). In side by side arrangement of BEDT-TTF, the outer sulfur atoms play an important role, that is, S···S distances between outer sulfur atoms and between outer and inner sulfur atoms are 3.64 and 3.59 Å, respectively, which are considerably short. That between inner sulfur atoms, however, is long; the shortest one is 3.98 Å. This structural feature is almost identical with that of various BEDT-TTF salts with inorganic anions8) and neutral BEDT-TTF.9) The most important finding is that there exist strong S···S interactions (3.48 Å) between acceptors. These strongly interacting sulfur atoms exist in the π-electron skeleton of acceptor molecule, in contrast with the situation of BEDT-TTF molecule. Thus, the π-electron frameworks of the acceptors are closely arranged along side by side direction.

Present studies suggest that the condensed and conjugated homologues of thiophene-TCNQ are potential acceptors which might form multi-dimensional



(a) (b)

Fig. 2. Crystal structures viewed (a) along the c axis and (b) approximately along the long axis of the molecule.

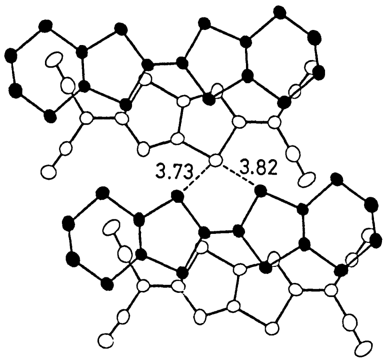


Fig. 3. The mode of the molecular overlap. The view direction is perpendicular to the molecular plane.

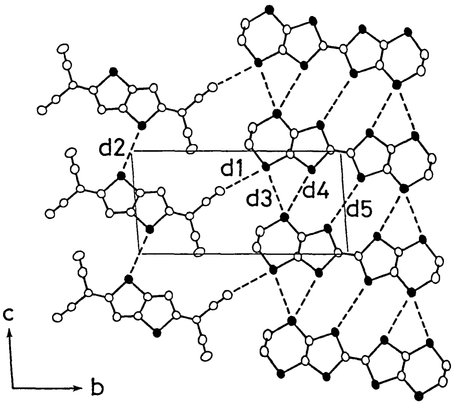


Fig. 4. Sheet-like networks in the [1$\bar{2}$0] plane. Some short contacts: d1=3.33, d2=3.48, d3=3.64, d4=3.59, and d5=3.98 Å.

molecular complexes.

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4) The molar ratio was determined to be 1:1 on the basis of the elemental analysis. The nitrile stretching frequency of this complex, 2223 cm^{-1}, was equal to that of neutral **1**, and the conductivity measured on a compressed pellet with a two-probe method was 6.9×10^{-10} $\text{S}\cdot\text{cm}^{-1}$.

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