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Structural and Conducting Properties of (TTF)(DMeT-DCNQI)

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Synopsis. The title charge-transfer complex, where TTF is tetrathiafulvalene, and DMeT-DCNQI is 2,5-bis(methylthio)-*p*-benzoquinone bis(*N*-cyanoimine), crystallizes in triclinic space group $P\bar{1}$, a=15.447 (3), b=15.774 (3), c=3.834 (2) Å, α=96.96 (3), β=97.14 (3), γ=82.24 (2)°, V=913 (5) Å^3 and Z=2. The donor and acceptor molecules form segregated colums. This complex shows high electrical conductivity, 400 S cm^{-1} at room temperature, and undergoes a metal-semiconductor transition at around 130 K.

The discovery of metallic electrical conductivity in a copper salt of DCNQI (*p*-benzoquinone bis(*N*-cyanoimine)) has aroused much interest in anion radical salts of DCNQI's.[1] In these salts, DCNQI's work not only as acceptors but also as ligands, where the terminal nitrogen atoms coordinate to the metal atoms.

In order to explore the substituent dependence of the chemical and physical properties, we have recently synthesized a new DCNQI molecule, DMeT-DCNQI, where the 2- and 5-positions of DCNQI are substituted with methylthio groups.[2] Because the methylthio group is bulky, metal salts of DMeT-DCNQI show considerably different chemical and structural properties from the other DCNQI salts with ordinary substituents. In Ag$_{1.2}$(DMeT-DCNQI), a part of the Ag atoms are coordinated by the sulfur atoms of the methylthio groups and the inner nitrogen atoms of the *N*-cyanoimino groups.[2]

Because DCNQI's are good electron acceptors, they also form charge-transfer salts with organic electron donors such as TTF.[3-5] Structural studies of these charge-transfer salts are, however, not many. In the present work, we report X-ray crystal structure analysis, electrical conductivity, and thermoelectric power of (TTF)(DMeT-DCNQI).

Experimental

Hot acetonitrile solutions of TTF and DMeT-DCNQI[2] were mixed, and allowed to evaporate slowly in a desiccator (silica gel). Black needle-like tiny crystals were obtained.

A single crystal with approximate dimensions 0.7×0.04×0.05 mm^3 was mounted on a CAD-4 diffractometer for the X-ray analysis. Crystal data: $C_{16}H_{12}N_4S_6$, M=452.658, triclinic, space group $P\bar{1}$, a=15.447 (3), b=15.774 (3), c=3.834 (2) Å, α=96.96 (3), β=97.14 (3), γ=82.24 (2)°, V=913 (5) Å^3, Z=2, and D_c=1.647 g cm^{-3}. Data were collected at room temperature using graphite-monochromatized Mo $K\alpha$ (λ=0.71073 Å) radiation by the $\omega/2\theta$ scan technique in the region $2\theta<60°$. Absorption correction (μ(Mo $K\alpha$)=7.29 cm^{-1}) was not applied. Atomic scattering factors were taken from Ref. 6. The structure was solved according to the direct method.[7] Block-diagonal least squares refinement (UNICS III[8]) with anisotropic thermal parameters for all non-hydrogen atoms converged to R=0.052 and R_W=0.059 (weighting scheme $1/w=\sigma^2+(0.015\ |F_o|)^2$) for 1419 independent significant reflections ($|F_o|>3\sigma(F_o)$). Atomic parameters and thermal parameters for non-hydrogen atoms are given in Table 1.[9]

Table 1. Atomic Parameters for (TTF) (DMeT-DCNQI) (×10^4)

Atom	x	y	z	B_{eq}[a)]/Å^2
S(1)	3740(2)	650(2)	2916(8)	3.0
S(2)	5497(2)	1183(2)	4229(8)	2.8
S(3)	8741(2)	5649(2)	6467(8)	3.0
S(4)	10499(2)	6181(2)	7450(8)	2.8
S(5)	8693(2)	1621(2)	2485(7)	2.2
S(6)	6309(2)	3376(2)	7175(7)	2.2
C(1)	4832(6)	389(6)	4394(27)	2.2
C(2)	3849(7)	1680(7)	2049(31)	3.3
C(3)	4651(7)	1914(7)	2640(30)	3.2
C(4)	9830(7)	5386(6)	5829(26)	2.3
C(5)	8851(7)	6673(7)	8448(30)	3.3
C(6)	9661(7)	6901(7)	8839(31)	3.3
C(7)	7622(7)	1387(7)	453(29)	2.9
C(8)	9363(6)	708(6)	1050(25)	1.9
C(9)	9125(6)	56(6)	−1448(26)	2.0
C(10)	10294(6)	673(6)	2529(23)	1.6
C(11)	11330(7)	1305(7)	6438(26)	2.4
C(12)	7380(7)	3629(7)	6389(26)	3.0
C(13)	5621(6)	4298(6)	5951(24)	1.7
C(14)	5897(6)	4944(6)	4384(24)	1.6
C(15)	4715(6)	4339(6)	6583(24)	1.8
C(16)	3669(7)	3694(6)	8790(26)	2.2
N(1)	10497(5)	1318(5)	4926(21)	2.2
N(2)	12022(6)	1365(5)	7899(25)	4.0
N(3)	4499(5)	3683(5)	8137(20)	2.0
N(4)	2991(6)	3644(7)	9564(27)	4.2

a) $B_{eq}=4/3\Sigma\Sigma B_{ij}\boldsymbol{a}_i\cdot\boldsymbol{a}_j$.

The electrical conductivity was measured by the conventional four-probe method along the crystal long (c) axis. The electical contacts were made with gold paint. The thermoelectric power was measured along the crystal long (c) axis by the previously reported method.[10]

Results and Discussion

Atomic numbering scheme is shown in Fig. 1. There are two crystallographically independent TTF molecules (TTF-A and TTF-B) and two independent DCNQI molecules (DCNQI-A and DCNQI-B), all of which are located on inversion centers at (0.5, 0, 0.5), (1, 0.5, 0.5), (1, 0, 0), and (0.5, 0.5, 0.5), respectively. Both TTF and DCNQI molecules are planar; the deviation from the best plane is within 0.06 Å except the thiomethyl carbon of DCNQI, which deviates for 0.18 (1) Å from the molecular plane.

The intramolecular bond distances and angeles are listed in Table 2. The degree of charge transfer ρ can be estimated from the change of intramolecular bond distances of TTF;[11] the results in Table 2 indicate ρ to be 0.6—0.8. The degree of charge transfer can be also estimated from the shift of infrared absorption;[12] the C=N stretching frequency (KBr disk) is 1542 cm^{-1} for the neutral DMeT-DCNQI, 1499 cm^{-1} for the present

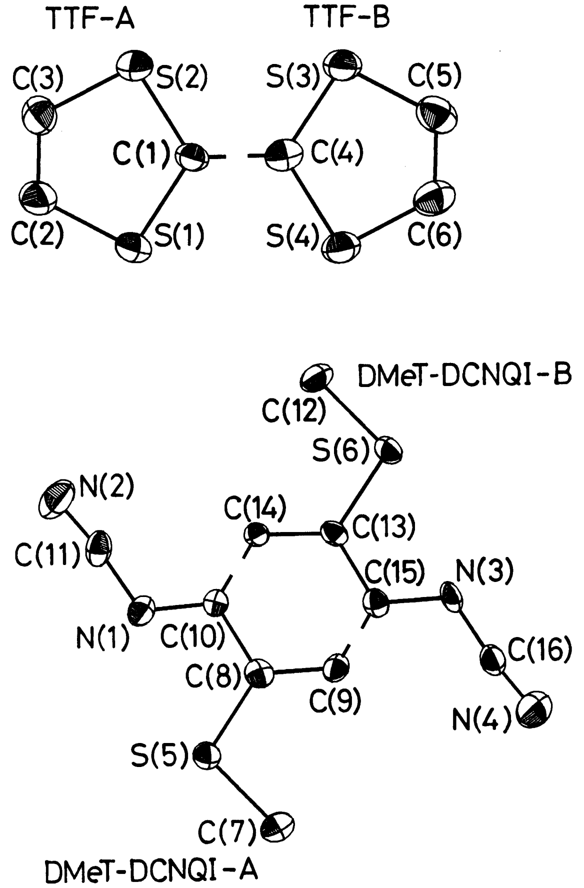

Fig. 1. ORTEP drawing of TTF and DMeT-DCNQI with atomic numbering.

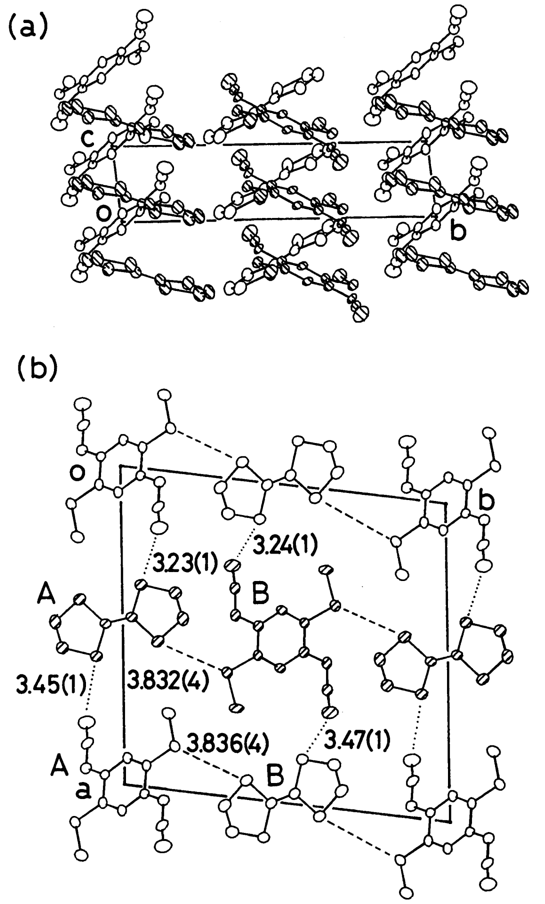

Fig. 2. Crystal structure projected along the *a* and *c* axes.

Table 2. Intramolecular Bond Distances (Å) and Angles (°)

TTF-A					
S(1)-C(1)	1.72(1)	S(1)-C(2)	1.73(1)	S(2)-C(1)	1.73(1)
S(2)-C(3)	1.73(1)	C(1)-C(1)	1.38(1)	C(2)-C(3)	1.32(2)
C(1)-S(1)-C(2)	95.4(4)	C(1)-S(2)-C(3)	94.7(5)		
S(1)-C(1)-S(2)	115.0(6)	S(1)-C(2)-C(3)	116.6(9)		
S(2)-C(3)-C(2)	118.2(9)				
TTF-B					
S(3)-C(4)	1.72(1)	S(3)-C(5)	1.72(1)	S(4)-C(4)	1.74(1)
S(4)-C(6)	1.70(1)	C(4)-C(4)	1.37(1)	C(5)-C(6)	1.33(2)
C(4)-S(3)-C(5)	95.5(5)	C(4)-S(4)-C(6)	94.3(5)		
S(3)-C(3)-S(4)	115.0(6)	S(3)-C(5)-C(6)	116.0(9)		
S(4)-C(6)-C(5)	119.3(9)				
DCNQI-A					
S(5)-C(7)	1.80(1)	S(5)-C(8)	1.73(1)	C(8)-C(9)	1.37(1)
C(8)-C(10)	1.48(1)	C(9)-C(10)	1.41(1)	C(10)-N(1)	1.33(1)
N(1)-C(11)	1.34(1)	C(11)-N(2)	1.15(2)		
C(7)-S(5)-C(8)	102.1(5)	S(5)-C(8)-C(9)	126.6(8)		
S(5)-C(8)-C(10)	115.3(7)	C(9)-C(8)-C(10)	118.0(9)		
C(8)-C(10)-N(1)	116.0(8)	C(10)-N(1)-C(11)	118.5(8)		
N(1)-C(11)-N(2)	173.8(12)				
DCNQI-B					
S(6)-C(12)	1.82(1)	S(6)-C(13)	1.76(1)	C(13)-C(14)	1.38(1)
C(13)-C(15)	1.44(1)	C(14)-C(15)	1.43(1)	C(15)-N(3)	1.35(1)
N(3)-C(16)	1.33(1)	C(16)-N(4)	1.14(2)		
C(12)-S(6)-C(13)	101.4(5)	S(6)-(13)-C(14)	124.1(7)		
S(6)-C(13)-C(15)	115.6(7)	C(14)-C(13)-C(15)	120.3(9)		
C(13)-C(15)-N(3)	116.7(8)	C(15)-N(3)-C(16)	119.0(8)		
N(3)-C(16)-N(4)	173.3(12)				

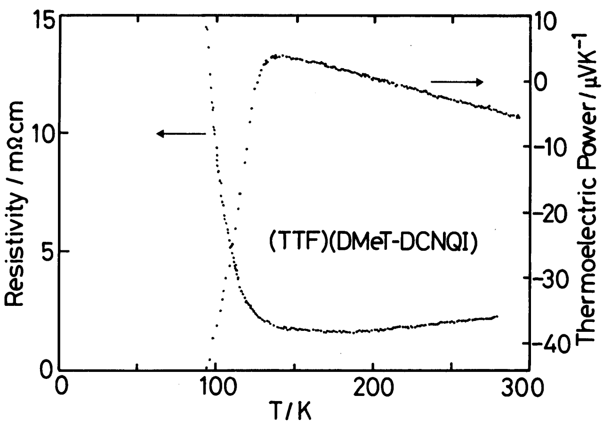

Fig. 3. Electrical resistivity and thermoelectric power.

complex, and 1454 cm^{-1} for $Ag_{1.2}$(DMeT-DCNQI). If one assumes a linear relation, ρ of the present complex is expected to be about 0.6.

The crystal structure is depicted in Fig. 2. The crystallographically independent molecules form independent segregated columns; the interplanar spacings of the TTF-A, TTF-B, DCNQI-A, DCNQI-B columns are 3.515 (3), 3.516 (3), 3.187 (4), and 3.181 (4) Å, respectively. These values are ordinary as these kinds of molecules. The mode of overlap is the usual bond-over-ring type. There are several short intercolomnar S–S and S–N distances which are shorter than the sum of the van der Waals radii; these distances are indicated in Fig. 2. Though these short contacts mediate intercolumnar interaction, the path of the conduction electron is expected to be essentially one-dimensional. The calculation of intermolecular overlap of the conduction molecular orbitals suggests that the intercolumnar intetaction is about one tenth of the intracolumnar interaction.[13]

The electrical resistivity and the thermoelectric power (Seebeck coefficient) are shown in Fig. 3. The conductivity is about 400 S cm^{-1} at room temperature, and is metal down to about 130 K, below which it becomes semiconducting. In view of the highly one-dimensional structure, this transition is presumably due to some one-dimensional instabilities. The thermoelectric power shows linear temperature dependence in the metallic region, but crosses zero at around 200 K. This is an evidence that both TTF and DCNQI columns contribute to the electric conduction. The metal-semiconductor transition is also clear in the thremoelectric power.

The present investigation of the structural and physical properties of (TTF)(DMeT-DCNQI) shows that DCNQI, as well as TCNQ (tetracyanoquinodimethane), can realize a highly-conducting organic metal in the form of an ordinary charge transfer complex.

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