Cyclohexylenedithio Annelated Bis-Fused TTF Donors and Their Conducting Salts

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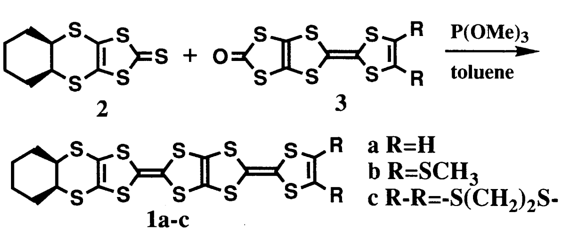
Bis-fused TTF(tetrathiafulvalene) derivatives with a cyclohexane ring **1a-c** have been synthesized. One of their radical-cation salts $(\mathbf{1b})_2Au(CN)_2$ exhibits high conductivity $\sigma_{rt} = 160$ Scm^{-1} and is metallic down to 120 K. Its structure consists of weakly dimerized columns with relatively small intercolumnar interactions.

Bis-fused TTF donors (or alternatively TTP(tetrathiapentalene) donors) have been afforded a large number of highly conducting radical-cation salts.[1] Their extended skeletons, however, largely reduce their solubilities in organic solvents; this is a great drawback in preparing their conducting salts. In addition, although many salts exhibit metallic conduction down to low temperatures, they do not show superconductivity except for $(DTEDT)_3Au(CN)_3$.[2] It has been, however, pointed out that moderate dimerization will contribute to superconductivity.[3] On the other hand it has been recently reported that introduction of bulky substituents increases the solubility but does not hurt the high conductivity.[4] So we have prepared TTP donors with a cyclohexane ring **1a-c** by expecting improvement of the solubility and enhancement of the degree of dimerization, by partially blocking the face-to-face interaction.



The target molecules were prepared by the phosphite-mediated cross coupling of **2**[5] and **3**.[1,6] Their solubilitites were somewhat improved in comparison with the corresponding ethylenedithio derivatives (those without the cyclohexane ring). As shown in Table 1, these donors showed four-step oxidations characteristic of the TTP donors.

Several radical-cation salts were grown by the electrochemical method (Table 2). Because some were obtained only as a polycrystalline form, the conductivities were not very high, but many salts showed metallic behavior at room temperature. For example the temperature dependence of the resistivity of $(\mathbf{1b})_2$ $Au(CN)_2$ is shown in Figure 1. This compound reproducibly showed a hysteretic M-I transition like many other TTP salts.[1]

Table 1. Redox potentials

Donor	E_1	E_2	E_3	E_4	E_2-E_1
1a	0.41	0.66	1.02		0.25
1b	0.50	0.69	0.91	1.14	0.19
1c	0.49	0.69	0.87	1.10	0.20
TTM-TTP[1]	0.48	0.67	0.89	1.01	0.19

vs. Ag/AgCl in Bu_4NPF_6/PhCN at a Pt working electrode. E_3 and E_4 of **1a** were not clearly separated.

Table 2. Composition and Conductivity of $(\mathbf{1})A_x$

Donor	Anion	Solvent	x[a]	σ_{rt}/S cm^{-1}	T_{MI}
1b	$Au(CN)_2$	THF	0.59(Au), 0.50(X)	150	120K
	I_3	THF	0.25(I)	1	160K
1c	ClO_4	THF	0.95(Cl)	0.6	I
	I_3	THF	0.33(I)	1.7	<120K

[a] Determined by the energy dispersion spectroscopy from the ratio of sulfur and the elements designated in the parentheses. X represents the value determined from the single crystal X-ray structure analysis.

X-ray single crystal structure analysis of $(\mathbf{1b})_2Au(CN)_2$ has been carried out.[7] The structure is so called β-type structure. A unit cell contains two donor molecules and one anion; a whole molecule of the donor is crystallographically independent, and located on a general position, and an anion is located on an inversion center. The refinement of the anion population showed no deficiency. Therefore 2 : 1 composition is concluded from the structure.

One thiomethyl carbon is located in the molecular plane (within 0.16 Å), but another carbon extends out of the plane. This structure is consistent with the partially oxidized donor. As shown in Figures 2 and 3 the cyclohexane ring is considerably tilted from the molecular plane. The cyclohexane rings are incorporated in the anion layers, and construct the insulating layer together with the anions.

The donors form a stack along the a axis. In the stack the cyclohexane rings are arranged alternately at the opposite ends of the donors, so there is no orientational disorder. Two intrachain overlap modes are characterized by the slip along the

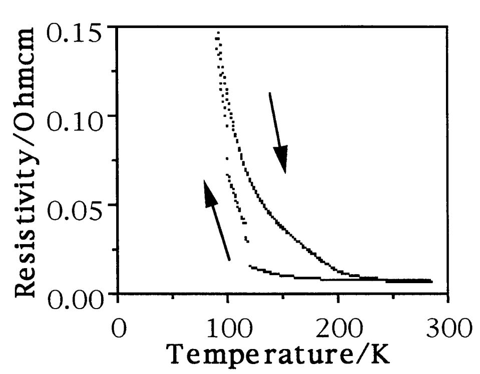


Figure 1. Electrical resistivity of $(\mathbf{1b})_2Au(CN)_2$. The activation energy in the semiconducting region is 0.028 eV.

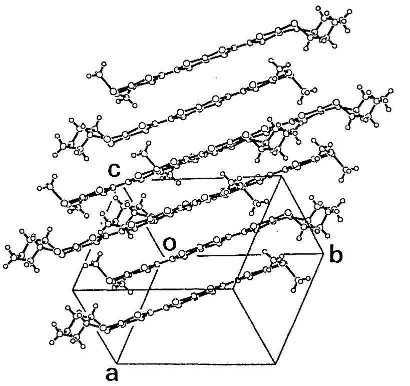


Figure 2. Crystal structure of $(\mathbf{1b})_2Au(CN)_2$.

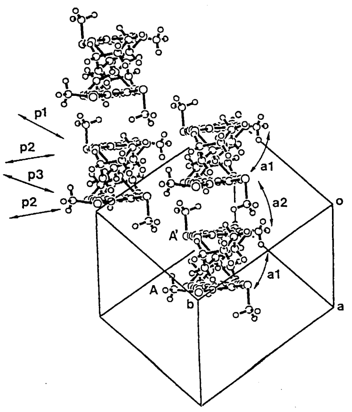


Figure 3. Donor arrangement of $(\mathbf{1b})_2Au(CN)_2$.

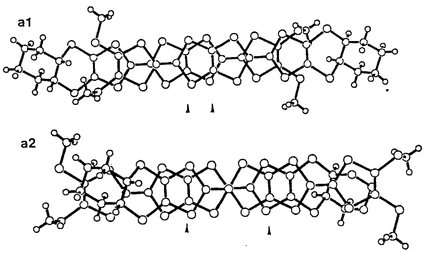


Figure 4. Overlap mode of $(\mathbf{1b})_2Au(CN)_2$.

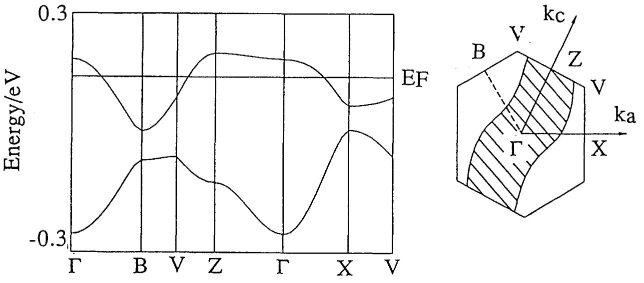


Figure 5. Energy band structure and Fermi surface of $(\mathbf{1b})_2Au(CN)_2$.

molecular long axis, D=1.9 Å for a1 and 4.9 Å for a2 (Figure 4). These values are somewhat larger than those of β-(BEDT-TTF)$_2$I$_3$ (1.5 Å and 3.8 Å), β-(BEDT-TTP)$_2$I$_3$ (1.8 Å and 4.4 Å), and β-(EP-TTP)$_2$I$_3$ (1.9 Å and 4.7 Å).[1] Overlap integrals of the HOMO are a1=11.3, a2=7.9, p1=1.2, p2=1.8, and p3=1.6 x10^{-3}.[8] The small difference of a1 and a2 indicates the comparatively small dimerization. The interchain overlap is about one sixth of the intrachain overlap, so that the one-dimensionality is relatively high. As shown in Figure 5, energy band and Fermi surface are calculated from the above overlap integrals. The energy band is basically one-dimensional along the a axis.

In conclusion we have prepared TTP donors having a cyclohexane ring; as expected, their solubilities are improved and they have made metallic radical-cation salts. Detailed investigation of the crystal and electronic structures of $(\mathbf{1b})_2Au(CN)_2$ has, however, showed that unfortunately the dimerization is decreased and the one-dimensional anisotropy is increased.

References and Notes

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6 **1a**: 34% yield; Mp 227 °C (dec.); ^{1}H NMR (δ in CDCl$_3$-CS$_2$) 1.43 (s, 2H), 1.7 (s, 2H), 2.0 (d, 4H), 3.58 (d, 2H), 6.32 (s, 2H). **1b**: 24% yield; Mp 209 °C (dec.); ^{1}H NMR 1.45 (s, 2H), 1.71 (s, 2H), 1.92 (d, 4H), 2.41 (s, 6H), 3.57 (d, 2H). **1c**: 20% yield; Mp 251°C (dec.); ^{1}H NMR 1.4 (s, 2H), 1.7 (s, 2H), 1.9 (d, 4H), 3.27 (s, 4H), 3.54 (d, 2H).

7 Crystal data of $(\mathbf{1b})_2Au(CN)_2$: F_w=1851.4, triclinic, space group $P\bar{1}$, a= 9.77(1), b=17.15(1), c=8.87(1) Å, α=83.73 (8), β=116.83 (6), γ=106.37(6) °, Z=1, ρ_{calc}=2.419 g cm^{-3}, and V=1271(5) Å^3. The final R=0.062 (R_w=0.079) for independent 1954 reflections (I>5σ(I)).

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