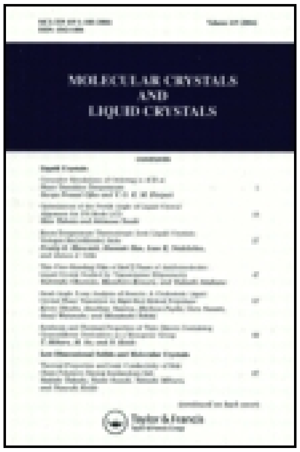

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COEXISTENCE OF ELECTRIC CONDUCTIVITY AND MAGNETISM IN THE ION-RADICAL SALTS OF A CROSS-CYCLOPHANE TWIN DONOR

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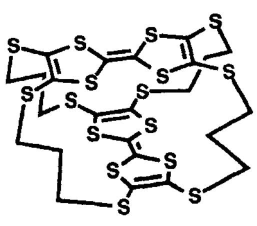
Abstract A *cross-cyclophane twin donor* (**1**) afforded ion-radical salts (**1**•Br•$(CHCl_2CH_2Cl)_2$) through electrocrystallization. Reflecting the molecular structure of the crossed-typed double-layered donor, orthogonal conduction paths were constructed through intermolecular S···S contacts at the bridge-head sulfur atoms of the upper or lower layer of donor units, respectively. The salt exhibits a semiconducting behavior ($\sigma_{rt}//a = 1.0 \times 10^{-2}$ Scm^{-1}, Ea//*a* = 0.75 eV, $\sigma_{rt}//c = 5.5 \times 10^{-3}$ Scm^{-1}). Judging from the temperature dependence of the magnetic susceptibility, magnetic behavior of the salt was basically paramagnetic, but it showed ferromagnetic interaction at lower temperatures.

INTRODUCTION

Construction of an exotic conduction path in organic molecular conductors may lead to a novel physical property[1]. Since intermolecular S···S contacts of sulfur-based donors are recognized as a conduction path in their ion-radical salts, design of a double-layered donor in which long axes of two TTF units are fixed in a crossed orientation should be of interest.[2, 3] Such a type of donor will be called as a *cross-cyclophane twin donor* (*X*-CPTD). Using *X*-CPTD orthogonal conduction paths may be constructed through intermolecular S···S contacts at sulfur atoms which are located at four corners of the rectangular donor units above and below, respectively. Besides if magnetic interaction operates when two holes are carried by one *X*-CPTD as dication-diradical species, the coexistence of conductivity and magnetism may be observed.

In this respect, we have designed and prepared *X*-CPTD (**1**) and constructed an ion-radical salt through electrocrystallization.

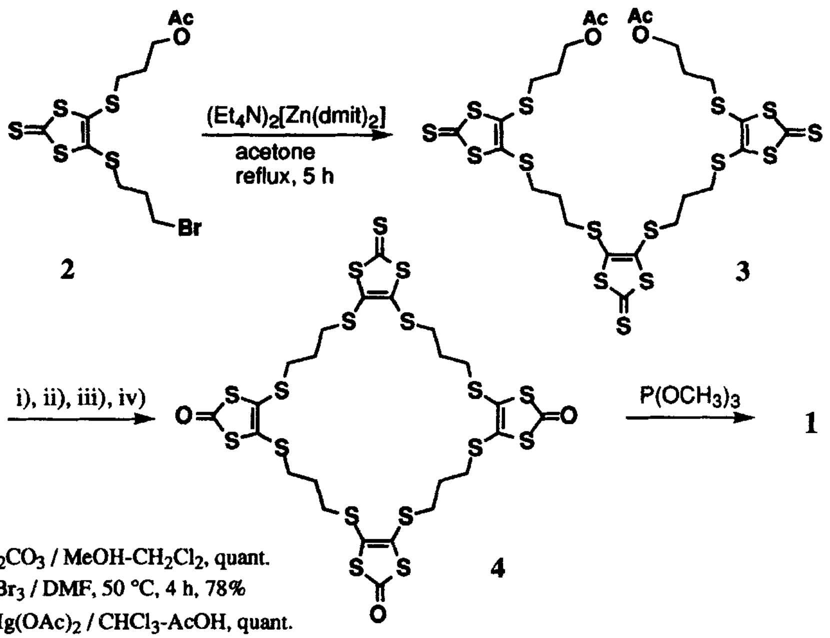


1

RESULTS AND DISCUSSION

Preparation of *X*-CPTD (**1**)

X-CPTD (**1**) with four trimethylenedithio chains was prepared along the following scheme 1.[4] Treatment of alkylated dmit (**2**) with zincate gave an acyclic trimer (**3**) in 80 % yield. After thions and terminal acetoxy groups of **3** were converted to ketones and bromines, respectively, the resulted acyclic trimer was then reacted with zincate to give the cyclic tetramer (**4**) in good yield. Intramolecular coupling of **4** by trimethylphosphite afforded the desired product **1** in 15 % yield.



i) K_2CO_3 / MeOH-CH_2Cl_2, quant.
ii) PBr_3 / DMF, 50 °C, 4 h, 78%
iii) $Hg(OAc)_2$ / $CHCl_3$-AcOH, quant.
iv) Zincate / acetone, reflux, 67%

SCHEME 1 Synthesis of *X*-CPTD (**1**)

Redox Potentials of *X*-CPTD (**1**)

Oxidation potentials of **1** were determined by cyclic voltammetry. There are four reversible redox waves and their half-wave oxidation potentials are listed in Table 1, together with those of BEDT-TTF as a reference.

TABLE 1 Redox Potentials

	$E_{1/2}^{1}$	$E_{1/2}^{2}$	$E_{1/2}^{3}$	$E_{1/2}^{4}$
BEDT-TTF	0.58	0.88	-	-
X-CPTD	0.64	0.77	1.07	1.18

Ag / AgCl : PhCN / 0.1 M-TBAP : 200 mV / sec

The donor ability of **1** was found to be almost the same as that of BEDT-TTF. The splitting between the first and second oxidation potentials is too small to be ascribed to the on-site Coulombic repulsion. It should be resulted from the electronic interaction between two donor units.

Preparation and X-ray Structure of Ion-Radical Salts of *X*-CPTD (**1**)

Ion-radical salts of donor **1** was prepared through galvanostatic electrocrystallization in 1,1,2-trichloroethane (TCE) solution, using tetra-n-butylammonium bromide as a supporting electrolyte. The chemical composition of the salt is determined by the elemental analysis to be **1**:Br:TCE = 1:1:2.[5] The crystal structure of the salt was revealed by X-ray crystallographic analysis.[6] The cyclophane donor molecules construct a sheet structure, and the donor sheets are stacked sliding by a half of the donor unit along the *a*-axis and the *b*-axis to form a cavity among them. Bromide anion and solvent molecules are incorporated in the cavity (Fig. 1). Since the location of the solvent molecules is heavily disordered, they are not shown in the Figure. There are intermolecular S···S contacts (3.6-3.8 Å) between sulfur atoms at the four corners of the donor units of the rectangular shape above and below, respectively. Since the long axes of the donor units are orthogonal each other, there are two orthogonal conduction paths: one is running from east to west and the other is running from north to south.

Conductive Property of *X*-CPTD (**1**) · Br (1,1,2-TCE)$_2$

Conductivity of the salt was measured by a four-probe method both along the *a*- or *b*-axis and *c*-axis. The conductivity at the room temperature was 1.0×10^{-2} S • cm^{-1} along the *a*- or *b*-axis and 5.5×10^{-3} S • cm^{-1} along the *c*-axis. The temperature dependence of conductivity indicates that the salt exhibits a semiconducting behavior. The activation energy along the *a*- or *b*-axis in the salt was estimated to be 0.75 eV from the *Arrhenius* plot.

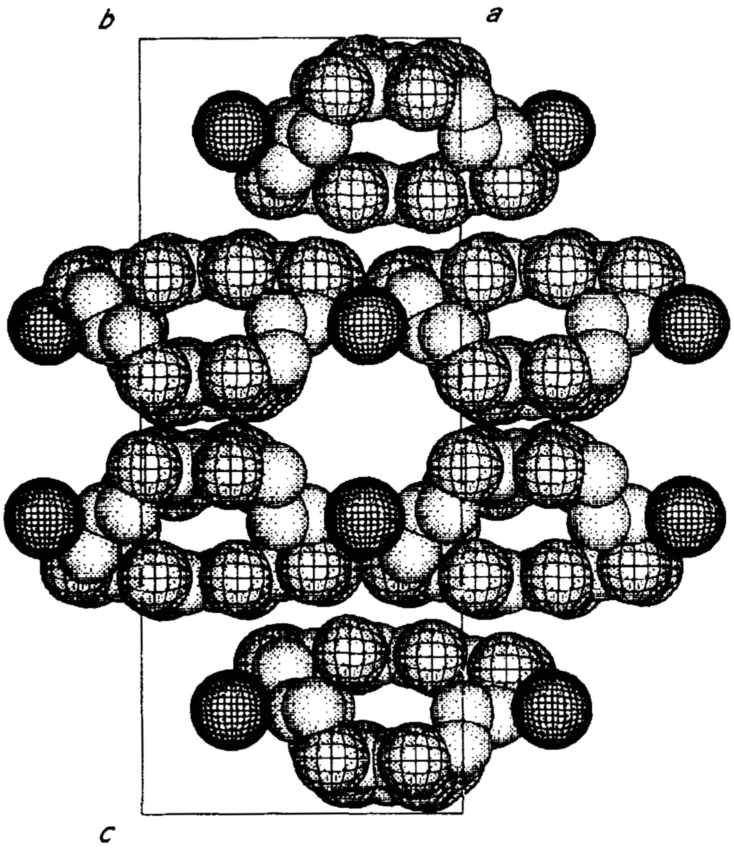


FIGURE 1 Crystal structure of (**1**)·Br(1,1,2-TCE):
A projected drawing along the *b*-axis. Since the solvent molecules are heavily disordered, they are not shown in the figure.

Magnetic Susceptibility of *X*-CPTD (1) · Br salt

Magnetic property of the single crystal of the salt was measured by a Faraday-type magnetic balance with increasing temperatures from 2 K to 300K. The χT value of the salt (0.375 emu·K·mol^{-1}) at room temperature shows that the each donor molecule carries one unpaired electron when the molecular weight was calculated according to the chemical formula determined by the elemental analysis. Temperature dependence of the χT value indicates that the salt is basically a paramagnet. The χT value was, however, found to show an increase at temperatures lower than 30 K, although a weak antiferromagnetic interaction was observed below 5 K (Fig 2).

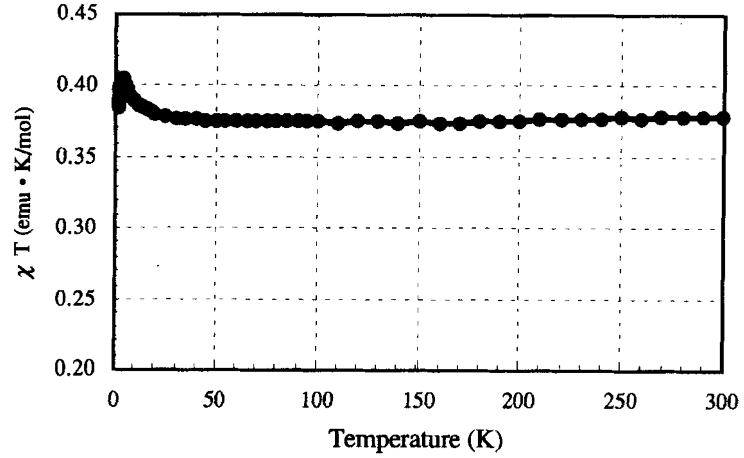
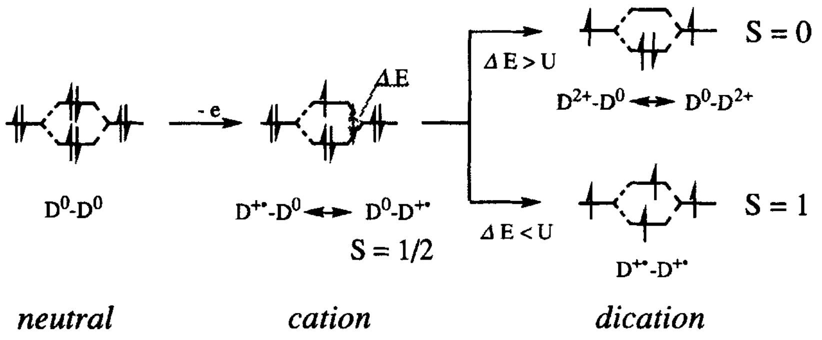


FIGURE 2 χT *vs* T plot of X-CPTD·Br

The ferromagnetic interaction (J= +0.13 K) will be derived either from the inter- or intramolecular origin. The latter case may occur if the dication-diradical species is formed through a disproportionation process between two cation-radicals, since the dication-diradical can exist as a ground state triplet species, judging from the following reasons. The result of CV measurement shows that the first oxidation process removes an electron from HOMO and the second oxidation occurs from NHOMO of the donor, because the on-site Coulombic repulsion is to be larger than the difference in orbital energies between HOMO and NHOMO (Scheme 2).[7] Thus the disproportionation may induce to form an open-shell dication-diradical instead of a closed-shell dication. Since the intra-planar distance (4.6 Å) of the cation-radical is considerably large, an effective electronic overlap can not occur between two donor units. Thus the antiferromagnetic interaction in the dication-diradical also be suppressed.



SCHEME 2 Oxidation States and Electric Structures of Twin Donor

CONCLUSION

Although the magnetic interaction observed in the ion-radical salt of *X*-CPTD has not been elucidated in detail, the coexistence of the conductivity and magnetism of the ion-radical salt composed of the *cross-cyclophane twin donor* is of great significance as an approach of organic conductive ferromagnets.[8] The investigation along this line is in progress in these laboratories.

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5 **1** · Br(1,1,2-TCE)$_2$: Anal. Calcd for $C_{28}H_{30}S_{16}BrCl_6$: C, 28.69; H, 2.58; S, 43.76; Cl, 18.15; Br, 6.82; N, 0. Found: C, 28.56; H, 2.60; S, 43.28; Cl, 18.31; Br, 6.76; N, 0.

6 Crystal Data of **1** · Br(1,1,2-TCE)$_2$: *Tetragonal*, Space group: $P4_1$, $a = 12.425(3)$, $c = 29.919(7)$ Å, $V = 4619(3)$ Å^3. $Z = 4$, $D_{cal} = 1.930$ g·cm^{-3}, R = 0.107, unique reflection data, 2384

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