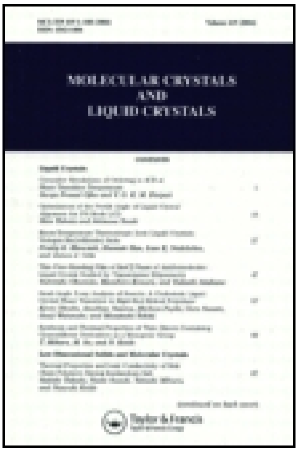

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Characteristics of Molecular-Based Conductors Prepared by Twin Donors with a Hydrogen-Bonded Counter Ion System

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CHARACTERISTICS OF MOLECULAR-BASED CONDUCTORS PREPARED BY TWIN DONORS WITH A HYDROGEN-BONDED COUNTER ION SYSTEM

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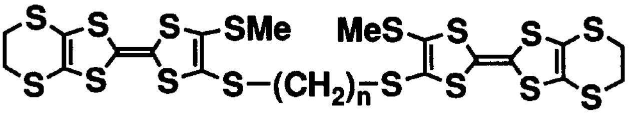
Abstract In order to realize a molecular-based conductor exhibiting three-dimensional intermolecular interaction, twin donors (**1** ~ **4**) have been designed. Electrocrystallization of the twin donor **1** gave three types of crystals (α-, β-, and β'-types). The crystal of α-type is composed of a pseudo cyclophane-shaped donor with 2:1 stoichiometry ($\mathbf{1}_2 \cdot X$, $X = PF_6^-$, BF_4^-, I_3^-, ClO_4^-), exhibiting a semiconducting character ($Ea = 5 \times 10^{-2}$ eV). The crystal of β-type is obtained as another morphology of ClO_4^- salts. The structure of the donor is a cyclophane-shape with short intramolecular S···S distances. Insulating character of the salts can be rationalized mainly by the remote intermolecular S···S distances. On the other hand, $\mathbf{1} \cdot Cl \cdot (H_2O)_x$ salts (β'-type) shows a metallic conductivity. The difference in crystal structures between β and β'-type salts may be explained by introduction of a polymeric hydrogen-bonded counter ion system.

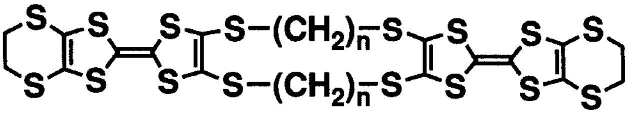
INTRODUCTION

Construction of an exotic electronic structure of molecular conductors is the current interest in materials science.[1] A donor molecule which has isotropic intermolecular interaction is one of the targets along this line.[2] C_{60} is an ideal compound in this respect.[3] Since we are interested in preparing a donor of a brick-like shape, twin donors (**1** ~ **4**), where two donor units are connected with an alkyldithio chain or a thiacrown ring, have been designed.[4] When the twin donor is singly oxidized, it is expected to form a cyclophane-shaped structure in order to stabilize the cation radical intramolecularly. The cyclophane-shaped donor may have a possibility to exhibit three-dimensional intermolecular interaction because of the presence of sulfur atoms at the periphery of the brick-shaped donor molecule. This species can also be regarded as a model for the mixed-valent state at the molecular level, provided that rapid exchange of a positive charge occurs between two donor units.

We report here what kind of crystal structures of ion radical salts will appear based on characteristic conformations of twin donors, and how the alignment of donors can be regulated by the oxidation state of donors or by arrangement of the counter ion system.



1 : n = 1 **2** : n = 2 **3** : n = 3



4 : n = 2

EXPERIMENTALS

Synthesis of twin donor **1** was described elsewhere.[4b] Half-wave oxidation potentials of twin donor **1**, $E_{1/2}$ vs. Ag/AgCl, were measured by cyclic voltammetry in dichloromethane in the presence of tetra-n-butylammonium perchlorate as an electrolyte with a scanning rate of 200 mVs^{-1}. Single crystals of **1**·X were grown by electrochemical oxidation (0.5 - 3 μA) of **1** (10.0mg, 0.0132mmol) in the presence of $n\text{-}Bu_4N\cdot X$ (~60 mg) as supporting electrolyte with a platinum electrode (5 mm ϕ) in a 20 ml H-typed cell.

The electric conductivity was measured by a four probe method. Along the long axis of the sample, gold wires (25μm ϕ) were attached to the sample with gold paste as a contact. The sample was fixed in a chamber in a homemade cryostat and was cooled slowly. The temperature was measured by using an Au-Fe-Chromel thermocouple.

Data collections for X-ray crystal structure analyses were performed at ambient temperature on a Rigaku AFC-5 four-circle diffractometer by using graphite monochromated Mo Kα radiation. Structures were solved by direct methods and refined by a block diagonal least-square refinement.

RESULT AND DISCUSSION

Cyclic voltammogram of **1** showed reversible potential waves of the first and second redox processes; $E^1_{1/2}$ = 0.47 V, $E^2_{1/2}$ = 0.55 V. The splitting of the waves indicates that two TTF moieties interact in terms of a through-bond and/or through-space mechanism. The results suggest that the donor ability of twin donor **1** is practically the same as that of BEDT-TTF ($E_{1/2}$ = 0.52 V, measured under the same condition), except for the presence of intramolecular electronic interaction.

TABLE I. Conditions of electrocrystallization of twin donor **1**.

Counter Anion (X^-)	Solvent	Electric Current (μA)	Crystal Structure
PF_6^-	1,1,2-TCE:THF=1:1	0.5~3	α
BF_4^-	PhCl	0.5	α
I_3^-	1,1,2-TCE:EtOH=9:1	*	α
ClO_4^-	THF:CH_2Cl_2=1:1	0.5	α, β
Cl^-	$CH_2Cl_2(H_2O)$	0.5	β'

* a diffusion method was applied

Conditions of electrocrystallization for various counter anions and types of crystal structures obtained under each condition are listed in TABLE I. Twin donor **1** with a methylenedithio chain afforded a hexafluorophosphate salt $\mathbf{1}_2\cdot PF_6$ (α-type, greenish black needles) by using n-$Bu_4N\cdot PF_6$ as a supporting electrolyte. In the α-typed crystal, the structure of the donor is a pseudocyclophane-shape (FIGURE 1a). Namely one of the donor units of the cyclophane-shaped conformer is turned over and rotated slightly through bond rotations of the methylenedithio chain: the conformation of the methylenedithio group (S-C, C-S bonds) is (+sc), (+sc). The pseudocyclophane-shaped conformers are arranged side-by-side in a one-dimensional array, and they have a short intermolecular S···S distance of 3.4 Å between upper or lower edges of each donor units along the *c* axis (FIGURE 1b). The result suggests that the oxidized donor is stabilized intermolecularly in the α-typed salt rather than be stabilized intramolecularly by forming the cyclophane-shaped conformer. The α-salt is a semiconductor (σ_{rt} = 0.15 Scm^{-1}) down to 100 K with an activation energy of 5×10^{-2} eV. The 2:1 ratio of donor and counter ion means that the ratio of donor units and counter ion is 4:1. The counter ions are located on the C_2 symmetry axis of the donor (FIGURE 1b). There are two occupying sites for the counter ion. Since these two sites are so closely located that only one counter ion can occupy the site, leaving the other empty. This situation rationalizes the unusual ratio and the disordered arrangement of counter ions along the *c* axis. Ion radical salts obtained by using counter ions, such as BF_4^-, I_3^-, are found to be classified as the α-type as well, exhibiting a similar conducing property.

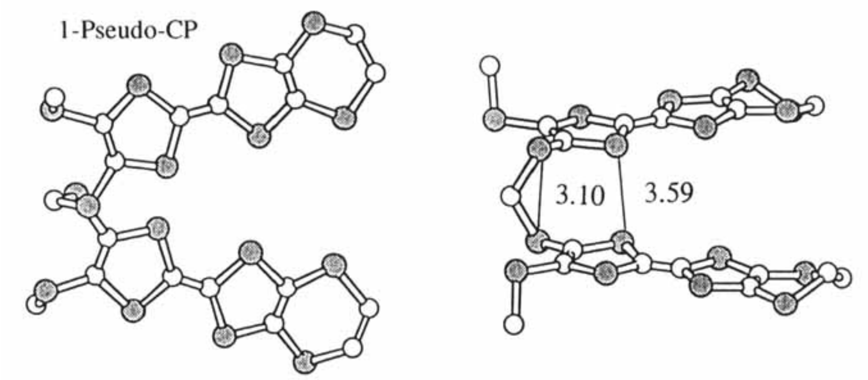


FIGURE 1a Molecular structure of $\mathbf{1}_2$·PF_6. Intramolecular S···S distances are also shown.

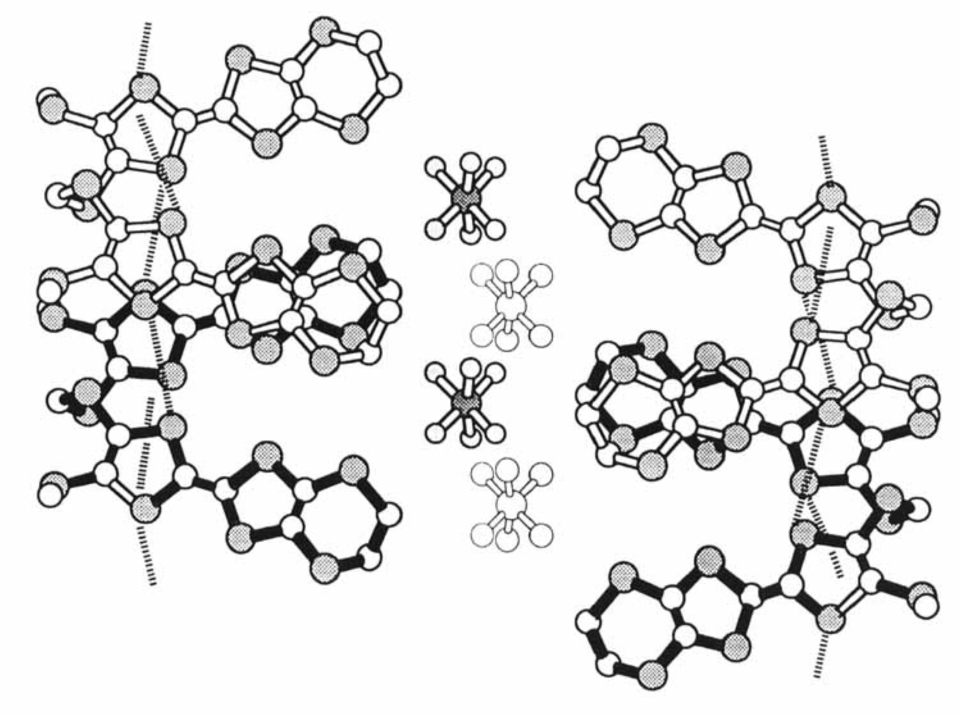


FIGURE 1b Crystal structure of $\mathbf{1}_2$·PF_6. S···S contacts of 3.4Å are shown by dotted lines. Atoms of PF_6^- located in one of the possible sites are shown by shaded balls, while those in another site is shown by white balls.

Twin donor **1** afforded the other type of an ion radical salt (β-type, **1**·ClO_4, black blocks) together with an α-type salt ($\mathbf{1}_2$·ClO_4) when ClO_4^- was selected as a counter ion. In the β-type crystal, the structure of twin donor **1** is a cyclophane-shape in which two donor units are overlapped thoroughly: the conformation of the methylenedithio group (S-C, C-S bonds) is assigned to be (+sc), (-sc) (FIGURE 2a). The two donor units are inclined by 8.6 degrees and S···S distances are longer at the methylthio side in order to avoid the steric hindrance. The interplanar distance between donor units, defined by four sulfur atoms attached to the central C=C bond, is 3.65 Å. The cyclophane-shaped conformers are stacked in a dimeric columnar structure along the (101) direction. The intermolecular S···S contacts along this direction is longer than 3.65 Å. On the other hand, donors form a one-dimensional chain along the *b* axis structurally (FIGURE 2b). The effective electronic interaction along this direction, however, is limited within a dimer through S···S contacts (3.42 Å) between sulfur atoms of the ethylenedithio groups of neighboring donors, although another S···S contacts (3.46 Å) are recognized between sulfur atoms of the methylthio groups of facing donors. Perchlorate ions are located by the side of the ethylenedithio groups. Since most of the intermolecular S···S distances are considerably longer than intramolecular ones, an unpaired electron of the ion radical species is considered to be localized within the dimeric pair. The nearly insulating property (σ_{rt} = 1×10^{-8} Scm^{-1}) of the salt is consistent with the crystal structure. Appearance of the cyclophane-shaped conformer may be rationalized in terms of intramolecular stabilization of the singly-oxidized twin donor. The packing of the conformers, however, is not appropriate for achieving a metallic conductivity, because of rather remote intermolecular distances.

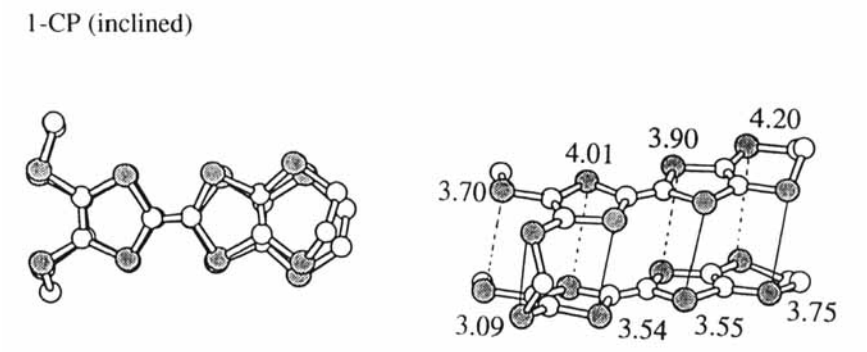


FIGURE 2a Molecular structure of **1**·ClO_4 . Intermolecular S···S distances are also shown.

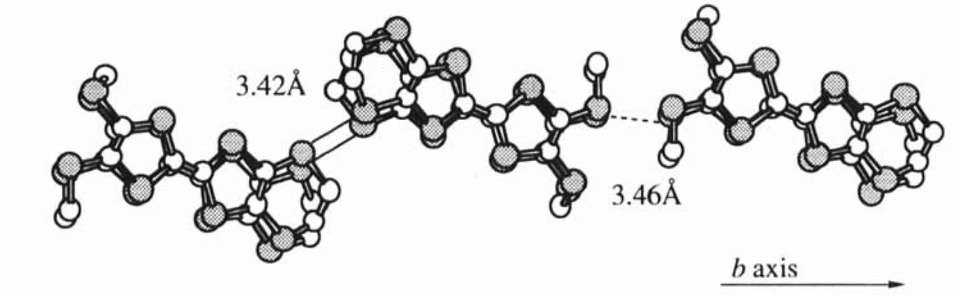


FIGURE 2b Crystal structure of **1**·ClO_4.
Intermolecular S···S distances are also shown.

We tried therefore to construct a polymeric counter ion system, especially utilizing intermolecular hydrogen bonds, in order to improve the alignment cyclophane-shaped donors.[5] When electrocrystallization of **1** was performed by using n-Bu_4N·Cl in the presence of an aliquot of water, an ion radical salt (β'-type, **1**·Cl·$(H_2O)_x$, black blocks) was obtained. The structure of the donor is close to the ClO_4^- salts of the β-type, although the longitudinal axis of two donor units are twisted slightly due to the steric repulsion (FIGURE 3a).

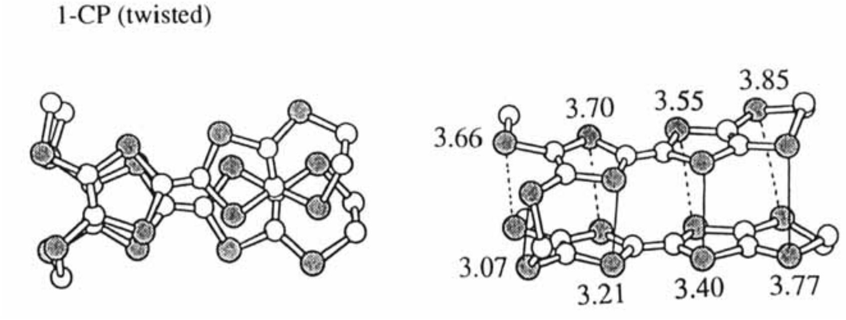


FIGURE 3a Molecular structure of **1**·ClO_4. Intramolecular S···S distances are also shown .

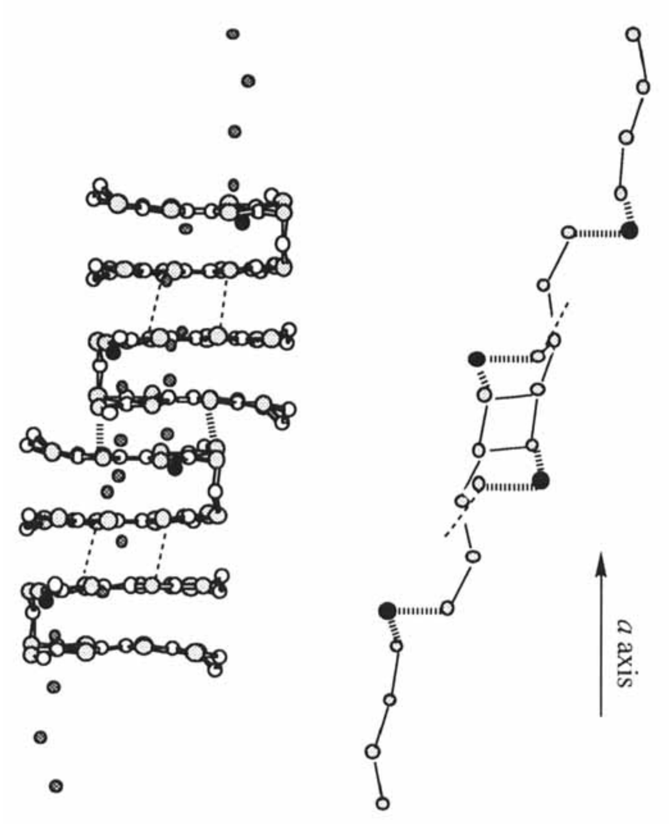


FIGURE 3b (left) Crystal structure of **1**·Cl·(H_2O)$_x$ along the *a* axis. Intermolecular S···S distances (3.56 Å) are shown by dotted lines, and those for 3.76 Å by broken lines.

(right) Polymeric hydrogen-bonded scheme incorporating chloride ions. Hydrogen bonds between chloride ions (●) and water molecules (◍) are shown by dotted lines (Cl···O distances are 3.08 Å, 3.22 Å), and hydrogen bonds between water molecules (O···O distances are 2.8 Å ~ 3.1 Å) are shown by solid lines.

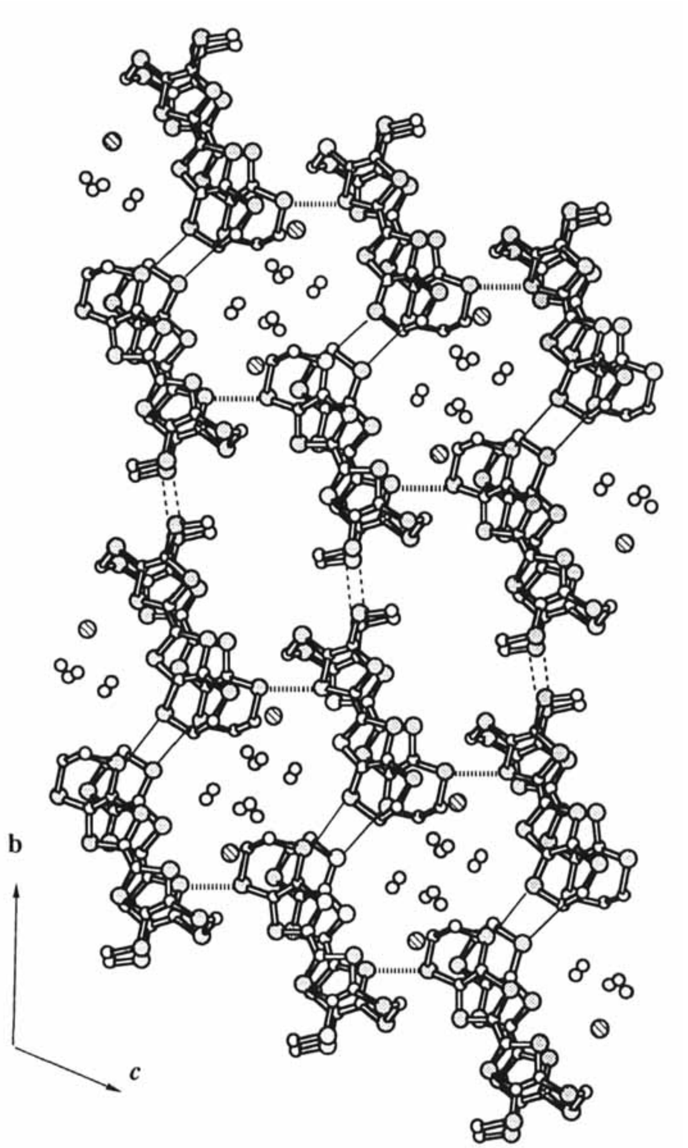


FIGURE 3c Crystal structure of **1**·Cl·$(H_2O)_x$ viewed normal to the *bc* plane. Dotted lines indicate S···S contacts of 3.31 Å along the *c* axis, solid lines indicate S···S contacts of 3.58 Å between ethylenedithio groups, and broken lines for S···S contacts of 3.31 Å between methylthio groups.

The crystal packing is also similar to the ClO_4^- salt. The cyclophane-shaped conformers are stacked along the *a* axis. The arrangement of donors, however, is dimerized along this direction, and the S···S contacts are longer than 3.56 Å within a dimer and interdimer S···S contacts are longer than 3.74 Å (FIGURE 3b). The arrangement of donors viewed normal to the *bc* plane is depicted in FIGURE 3c. The cyclophane-shaped conformers are aligned along the direction of the *b* axis, and they have side-by-side contacts along the *c* axis, forming "molecular stairs". Making a sharp contrast with the perchlorate salt, there are three kinds of intermolecular S···S contacts in the *bc* plane. First, the close S···S contacts (3.31 Å) exist along the *c* axis between the sulfur atom in the ethylenedithio group of the lower donor unit and that in the TTF moiety of the upper donor unit of the adjacent donor. Second, dual S···S contacts (3.58 Å) are observed along the *b* axis between sulfur atoms of the ethylenedithio groups between neighboring donors. Third, dual S···S contacts (3.31 Å) are also recognized between methylthio groups of the facing two donors. Reflecting the tight packing of the salt, it exhibits a metallic conductivity and undergoes a M-I transition at 170 K. The ratio of donor and counter ion is 1:1 and the salt contains several water molecules. The preliminary structure of the hydrogen-bonded counter ion system is shown in FIGURE 3b. The chloride ion is hydrogen-bonded with water molecules, with Cl···O distances of 3.08 Å, 3.22 Å . Water molecules are also connected by hydrogen-bonds (O···O distances are 2.8 ~ 3.1 Å) each other, forming two arrays of a one-dimensional chain. Since weak hydrogen bonds (3.1 Å) are also recognized between these two arrays, the hydrogen bond scheme is a ladder-like structure, incorporating chloride ions. It is to be noted that introduction of the polymeric counter ion system induces tight side-by-side interaction among donor molecules.

In summary, unconventional crystal structures of radical ion salts were obtained by newly designed twin donor **1**. Since physical properties of the salt is largely dependent on the conformation of the donor molecule, slight conformational change may modulate the conductive property efficiently. Besides, in the salts of **1**·Cl·$(H_2O)_x$ the polymeric counter ion system was recognized. Any change in the hydrogen bonding scheme may affect the position of the counter ions, which should cause a drastic effect on the transport properties.[6] It may be interesting to examine how physical properties can be modulated when reversible dynamic processes take place in the counter ion system.

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