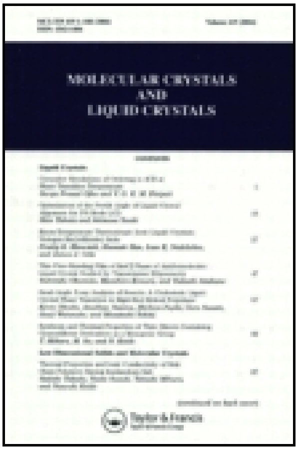

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# Approach to Organic Ferromagnetic Metal Using Novel Twin-Donors

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# APPROACH TO ORGANIC FERROMAGNETIC METAL USING NOVEL TWIN-DONORS

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Abstract Twin donors which have two BEDT-TTF units linked by alkanedithio bridge(s) have been prepared. Two types of radical ion salts of single methylenedithio-bridged donor 1 were obtained through electrocrystallization. Crystal A ($1 \cdot ClO_4$) exhibits antiferromagnetic interaction among phane-type conformers, while Crystal B ($1 \cdot (ClO_4)_{0.5}$) is semiconductor with an activation energy of $5 \times 10^{-2}$ eV. The radical ion salt obtained from double ethylenedithio-bridged donor 5 ($5 \cdot ClO_4$) is metallic down to 130K. The crystal structure is characterized by the presence of a unique three dimensional S•••S network.

## INTRODUCTION

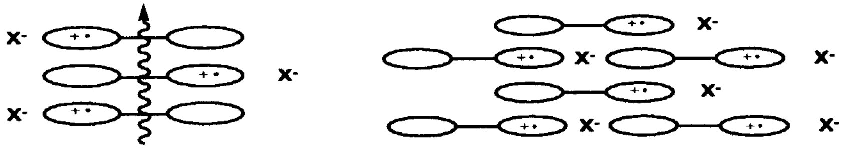
Physical properties of organic molecular crystals depend heavily on crystal structures and electronic features of constituent molecules. If molecular arrangements in crystals are well designed, one can realize organic conductors with ferromagnetic property[1]. In order to realize such a molecular system, we have prepared novel twin donors where two donor units are linked by alkanedithio bridge(s)[2]. Here we describe an approach to organic ferromagnetic and/or metallic molecular crystals using twin donors.

## DESIGN OF MOLECULAR AND CRYSTAL STRUCTURE OF TWIN DONORS

The prepared twin donors have two BEDT-TTF (ET) units linked by a methylene-, ethylene-, or propylene-dithio bridge(s)[3] .

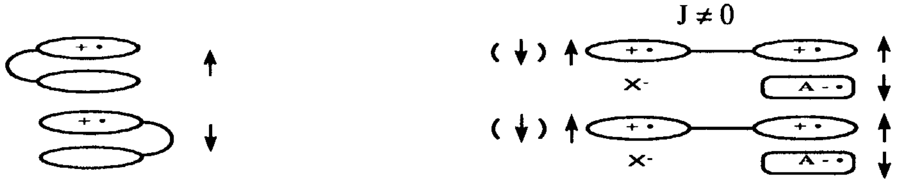
Structural and electronic features of twin donors are as follows. First, the presence of two donor units within a molecular provides the twin donor with multi-redox states. Second, oxidation potential or on-site Coulombic repulsion of the twin donor should show conformational dependence because intramolecular through bond or through space interaction between two donor units varies with their relative orientation. Third, conformational flexibility of twin donors will result in the versatility in molecular arrangement in crystals.

Some of the possible arrangements of radical ion salts of twin donors are schematically depicted in Figure 1. The donor takes a stretched conformation in arrangements type **a**, **b**, **d**, **e**, while it takes a folded one in type **c**.



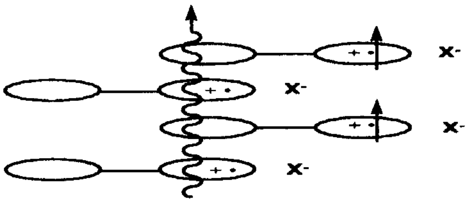
type **a**: uniform stack of stretched conformers : organic metal to be expected.

type **b**: an alternate stack of stretched conformers :two-dimensional organic metal to be expected.



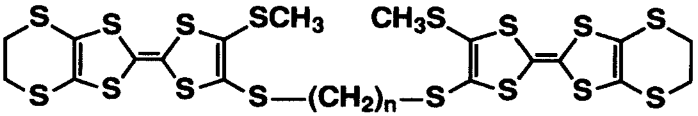
type **c**: uniform stack of folded conformers.

type **d**: an alternate DA column with donor units as a pendant group : organic ferromagnets to be expected.

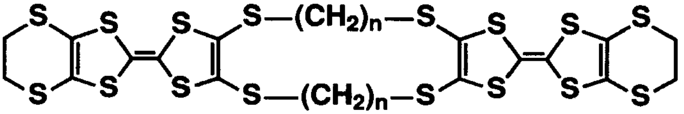


type **e**: a column structure with donor units as a pendant group : coexistence of conductivity and magnetism to be expected.

FIGURE 1 Schematic molecular arrangements of twin donors.



single bridged twin donor (SBCn) n=1 : 1 n=2 : 2 n=3 : 3

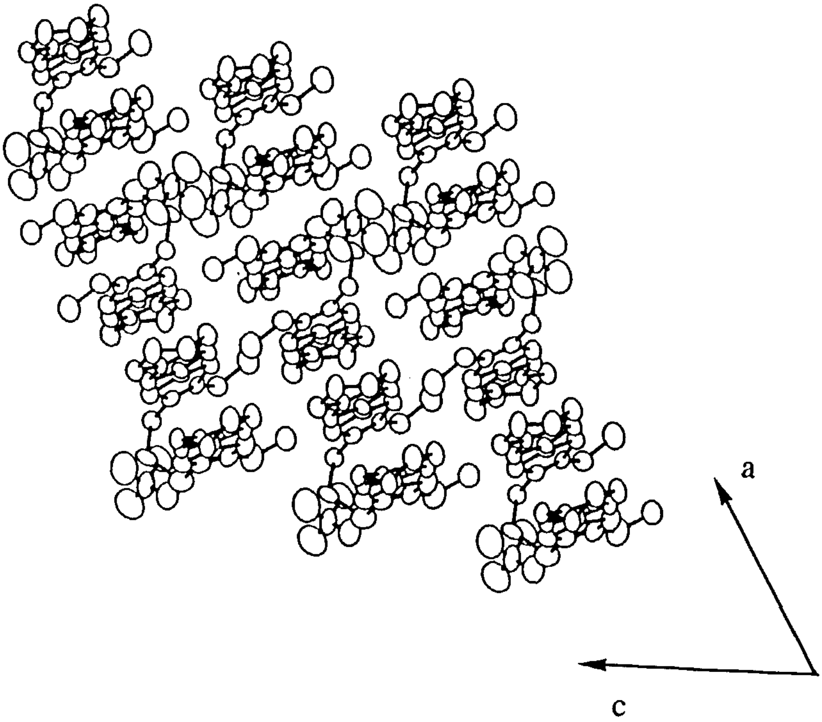


double bridged twin donor (DBCn) n=1 : 4 n=2 : 5 n=3 : 6

## STRUCTURE AND PROPERTY OF RADICAL ION SALTS OF SINGLE METHYLENEDITHIO-BRIDGED TWIN DONOR (1)

The donor ability of single or double bridged twin donors is almost the same as that of ET judged from cyclic voltammetric measurements. Electrocrystallization of 1 in the presence of n-$Bu_4NClO_4$ as an supporting electrolyte afforded two kinds of radical ion salts; Crystal A :black blocks, Crystal B: greenish black plates.

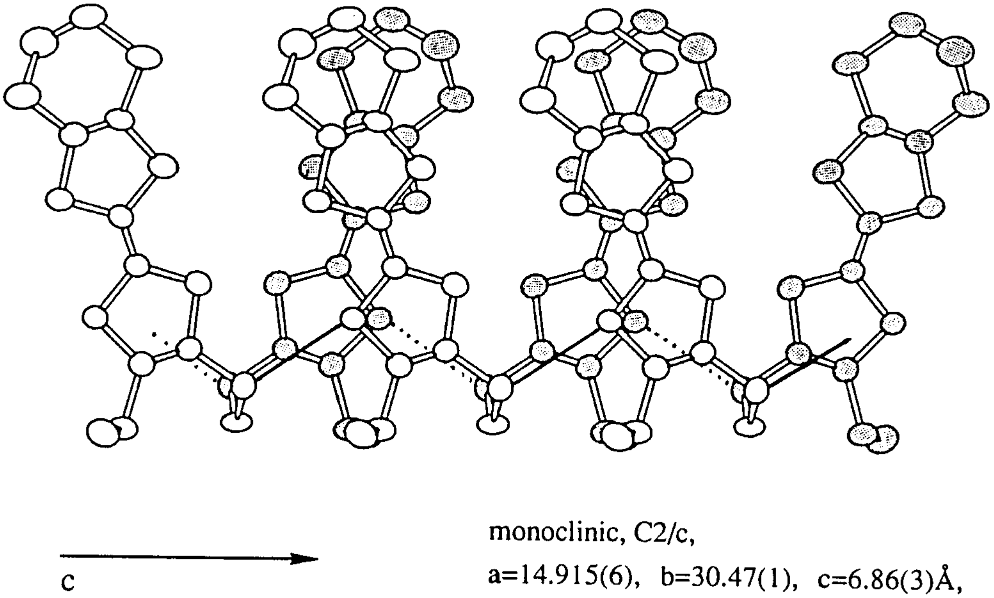
An X-ray analysis of crystal A (1•$ClO_4$) reveals that the cation radical of 1 ($1^{+\bullet}$) takes a phane-like conformation in crystals, it stacks in a column along a axis, although one can recognize a periodicity in the arrangement consisted of four twin donors (...DD•DD...) within the column (Figure 2). Namely type c in Figure 1 arrangement is realized in this salt. The shortest S•••S distance between donor units in the phane is 3.09Å, while that between phanes is 3.67Å. Therefore the radical ion is considered to be stabilized largely within the phane. In fact conductivity measured along c axis turns out to be very low $\sigma_{rt} = 10^{-8}$ $Scm^{-1}$. On the other hand, crystal A exhibits an interesting magnetic behavior. Temperature dependence of ESR signal intensities (g=2.0062) shows a thermal activation pattern, with a transition[4] at 150K. The magnetic behavior is well interpreted by the one-dimensional antiferromagnetic Heisenberg model. The temperature dependence of the susceptibility above 150K was interpreted by S-T model. An energy gap between singlet and triplet was determined to be 0.05eV, which is significantly large.



triclinic, $P\bar{1}$,
a=13.143(2), b=14.554(1), c=9.798(1)Å,
α=91.07(1) , β=102.86(1), γ=119.812(7)°,
V=1566.7(3)Å$^3$, R=0.082

FIGURE 2 Crystal structure of crystal A (1•$ClO_4$).

The composition of twin donor and anion in crystal B is 2:1 ( the ratio of donor unit to anion is 4:1). The donor takes a twist phane-like conformation in the crystal. The donor arranges side-by-side and forms an uniform column along c axis (Figure 3). The shortest S•••S contacts of 3.4Å are recognized in upper and lower edges of each donor units, which constitute two zig-zag conduction paths. The salts is a semiconductor ($\sigma_{rt}$ = 0.1 Scm$^{-1}$ ) with an activation energy of 5 × 10$^{-2}$ eV. The arrangement of the twin donor in this salt correspond to type **a** in Figure 1, although the stacking is side-by-side rather than face-to-face. The donor 1 also gives a CT complex with TCNQ. Its magnetic property is now under investigation.



monoclinic, C2/c,
a=14.915(6), b=30.47(1), c=6.86(3)Å,
β=70.08(4)°, V=3054(2)Å$^3$, R=0.083

FIGURE 3 Crystal structure of crystal B ($\underline{1}$•$(ClO_4)_{0.5}$). The shortest S•••S contacts for upper and lower paths are shown in straight or dotted lines, respectively. Atoms in lower part of $\underline{1}$ is shaded.

## STRUCTURE AND PROPERTY OF RADICAL ION SALT OF DOUBLE ETHYLENEDITHIO-BRIDGED TWIN DONOR(5)

If the donor units are doubly linked, larger intramolecular interaction should be guaranteed. Thus radical ion salt of double ethylenedithio-bridged donor $\underline{5}$ was prepared. The crystal structure of $\underline{5}$•$ClO_4$ is characterized by stackings of V-shaped conformers along c axis, donors in the adjacent stacks being inverted (Figure 4). The long axis of the donor is arranged parallel to *b* axis, and one can find short S•••S contacts (3.6 ~ 3.7Å) along *a* axis, which corresponds to side-by-side interaction among donors. Besides there are intramolecular S•••S contacts (3.34 ~ 3.43Å) between sulfur atoms at the foot of ethylene bridges. Thus the arrangement of $\underline{5}$ in crystals suggest the presence of a unique three-dimensional S•••S network[5]. The crystal structure is similar to type **b** in Figure 1. An additional intramolecular interaction increases the dimensionality. The crystal is metallic ($\sigma_{rt}$ = 5 Scm$^{-1}$) down to 130K.

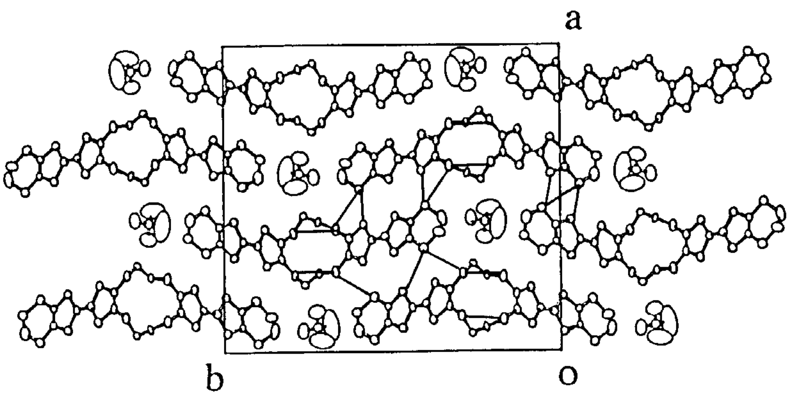


FIGURE 4 Crystal structure of 5•ClO$_4$. Short S•••S contacts are shown in straight lines.

## FUTURE SCOPE

Basing upon the success of preparating twin donor salts which have either conductive or magnetic property selectively, we now propose a design of twin donor salts with both conductive and ferromagnetic property. One of the donor units of the twin donor is stacked to form a conduction column, leaving the other as a holder of a local spin(type e in FIGURE 1). If a magnetic coupling is present between conduction electrons and localized ones, organic ferromagnetic metal should be achieved. The research along this line is in progress.

## ACKNOWLEDGMENT

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## REFERENCES

1. E. Dormann, M. J. Nowak, K. A. Williams, R. O. Augus, Jr., F. Wudl, J. Am. Chem. Soc., 109, 2549 (1987).
2. K. Bechgaard, K. Lerstrup, M. Jϕrgensen, I. Johannsen, J. Christensen, and J. Larsen, Mol. Cryst. Liq. Cryst., 181, 161 (1990); G. Rindorf, N. Thorup, K. Lerstrup, and K. Bechgaard, Acta Cryst., C 46, 695 (1990).
3. Preparation of twin donors (1~6) will be described elsewhere.
4. I.F.Shchegolev, Phys. stat. sol. (a), 12, 9 (1972).
5. R. Kato, H. Kobatyashi, T. Mori, and H .Inokuchi, Chem. Lett., 1987, 277.