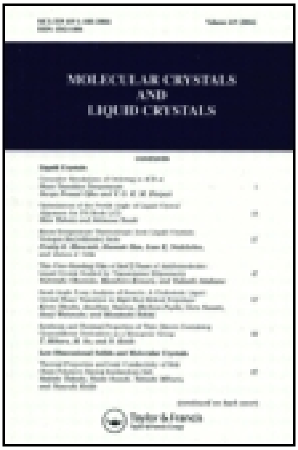

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Non-planar bedt-ttf derivatives fused with tetrahydrofuran rings affording cation radical salts with unusual crystal structures

Yoshiro Yamashita [a], Masaaki Tomura [b] & Kenichi Imaeda [b]

[a] Department of Electronic Chemistry, Interdisciplinary Graduate School of Science and Engineering, Tokyo Institute of Technology, 4259 Nagatsuta-cho, Midori-ku, Yokohama, 226-8502, Japan

[b] Institute for Molecular Science, Myodaiji, Okazaki, 444-8585, Japan

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NON-PLANAR BEDT-TTF DERIVATIVES FUSED WITH TETRAHYDROFURAN RINGS AFFORDING CATION RADICAL SALTS WITH UNUSUAL CRYSTAL STRUCTURES

*Yoshiro Yamashita**
Department of Electronic Chemistry, Interdisciplinary Graduate School of Science and Engineering, Tokyo Institute of Technology, 4259 Nagatsuta-cho, Midori-ku, Yokohama 226-8502, Japan

Masaaki Tomura and Kenichi Imaeda
Institute for Molecular Science, Myodaiji, Okazaki 444-8585, Japan

The title non-planar electron donors were prepared by the several steps involving the addition reaction of oligo(1,3-dithiole-trithione) with 2,5-dihydrofuran. They afforded the cation radical salts as single crystals whose unusual crystal structures were revealed by X-ray analysis.

Keywords: BEDT-TTF; electron donor; cation radical salts; non-planar molecule; crystal structure

INTRODUCTION

Organic conductors are usually composed of planar molecules since they are favorable for a face-to-face packing [1]. It has recently been reported, however, that non-planar electron donors afford organic conductors having two-dimensional character where intermolecular interactions within a stack are weakened by steric hindrance resulting in increase of dimensionality [2]. Furthermore, unusual crystal structures have been formed from non-planar molecules to avoid steric interactions [3]. Three-component conductors have also been prepared from non-planar molecules by inclusion of solvent molecules [4]. Therefore, non-planar molecules are promising candidates for components of a novel type of conducting materials. With this in mind, we have now designed new electron donors **1**

*Corresponding author. E-mail: yoshihiro@echem.titech.ac.jp and **2** where tetrahydrofuran (THF) rings are fused to bis(ethylenedithio)-TTF (BEDT-TTF) which produces many superconductors [5]. We report here unusual crystal structures of the cation radical salts of **2**.

RESULTS AND DISCUSSION

The new electron donors **1** and **2** were prepared as follows. First, a 1,3-dithiole-2-thione derivative **3** was synthesized by the addition reaction of oligo(1,3-dithiole-2,4,5-trithione) **5** [6] with 2,5-dihydrofuran in dioxane at 90°C. The thione **3** was converted to the ketone **4** by oxidation with $Hg(OAc)_2$. The BEDT-TTF derivative **1** was obtained by the self-coupling reaction of **4** in $P(OEt)_3$ at 120°C in 75% yield. On the other hand, the derivative **2** was obtained by the cross coupling reaction of **4** with thione **6** in 32% yield under the above conditions. Although the reaction produced a mixture of **1**, **2** and BEDT-TTF, the presence of the oxygen atom in the THF ring makes the separation of **2** from **1** and BEDT-TTF easy by column chromatography on alumina.

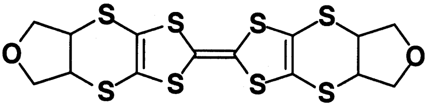
The oxidation potentials of the new donors **1** and **2** were measured by cyclic voltammetry [7]. They show two reversible one-electron oxidation waves (**1;** 0.60, 0.91 V *vs*. SCE, **2;** 0.55, 0.88 V *vs*. SCE). Introduction of a THF ring shifts the oxidation potentials a little more positive compared with those of BEDT-TTF (0.50, 0.85 V *vs*. SCE). This is probably due to the electronegative oxygen atom since a cyclopentadiene-fused derivative **7**[8] shows the same oxidation potentials as BEDT-TTF. The differences between the first and second oxidation potentials in **1** and **2** are a little smaller than that for BEDT-TTF, indicating that on-site Coulombic repulsion is a little decreased in them.

The donor **2** gave two cation radical salts [$\mathbf{2}\cdot Au(CN)_2$ and $\mathbf{2}\cdot PF_6\cdot(PhCl)_{0.5}$] as single crystals when electrochemically oxidized in chlorobenzene. The molar ratios were determined on the basis of elemental analyses. The salts exhibit semiconducting behavior since they are 1:1 salts [$\mathbf{2}\cdot Au(CN)_2$: $\sigma_{rt} = 3 \times 10^{-3}\ S\,cm^{-1}$, $E_a = 0.20\ eV$; $\mathbf{2}\cdot PF_6\cdot(PhCl)_{0.5}$: $\sigma_{rt} = 5 \times 10^{-5}\ S\,cm^{-1}$, $E_a = 0.24\ eV$].

The X-ray crystal analyses of these salts revealed their unusual structures.[†] The crystal structure of $\mathbf{2}\cdot Au(CN)_2$ salt is shown in Figure 1.

[†] *Crystal data* for $\mathbf{2}\cdot Au(CN)_2$: $C_{14}H_{10}AuN_2OS_8$, $M = 675.69$, monoclinic, space group $C2/m$, $a = 10.3088(6)$, $b = 11.819(1)$, $c = 17.002(4)$ Å, $\beta = 102.1(1)°$, $V = 2025.3(6)$ Å^3, $Z = 4$, $D_c = 2.216\ g\,cm^{-3}$, 2171 independent reflections, 144 variables, $R_1 = 0.0688$ and $wR_2 = 0.1779$ for 1308 data with $I > 2\sigma(I)$.

Crystal data for $\mathbf{2}\cdot PF_6(PhCl)_{0.5}$: $C_{12}H_{10}F_6OPS_8(ClC_6H_5)_{0.5}$, $M = 627.93$, monoclinic, space group $P2/a$, $a = 16.023(3)$, $b = 8.3881(6)$, $c = 17.558(2)$ Å, $\beta = 106.11(2)°$, $V = 2267.2(5)$ Å^3, $Z = 4$, $D_c = 1.840\ g\,cm^{-3}$, 4620 independent reflections, 318 variables, $R_1 = 0.0747$ and $wR_2 = 0.1955$ for 2931 data with $I > 2\sigma(I)$.



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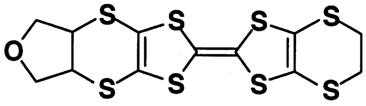

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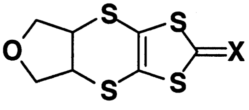
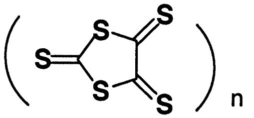


3 X = S
4 X = O



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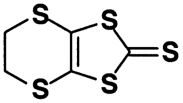

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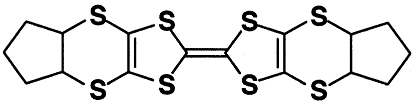

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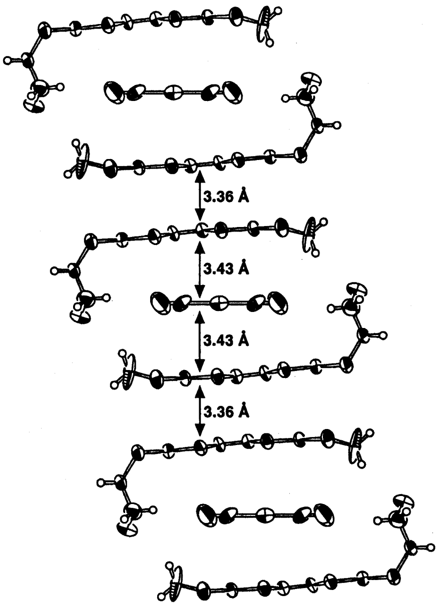

FIGURE 1 Crystal structure of **2**·Au$(CN)_2$ stacking along the a axis.

The donor molecule is non-planar and the cis-fused THF ring is like a hook where the dihedral angle between the planar TTF skeleton and the THF ring is 81.3°. One $Au(CN)_2$ anion is sandwiched between the donor molecules. The hooking part seems to play a role in including the anions. This sandwiched structure is stacked to give a column. The distances between the molecular planes (3.36–3.43 Å) are shown in Figure 1. Another $Au(CN)_2$ anion is located between the columns. The crystal structure of **2**$\cdot PF_6 \cdot (PhCl)_{0.5}$ is shown in Figure 2. The donor molecule has almost the same shape and bond lengths as those in the $Au(CN)_2$ salt. The dihedral angle between the TTF skeleton and the THF ring is 79.1°. The molecular arrangement is shown in Figure 2. Instead of a stacking structure, a complicated molecular network is observed. A prominent feature is that one neighboring molecule is highly leaned (77°). The molecules are combined by short S···S contacts as shown in Figure 2 to give a multi-dimensional structure. Solvent molecules are located between the layers of the donor

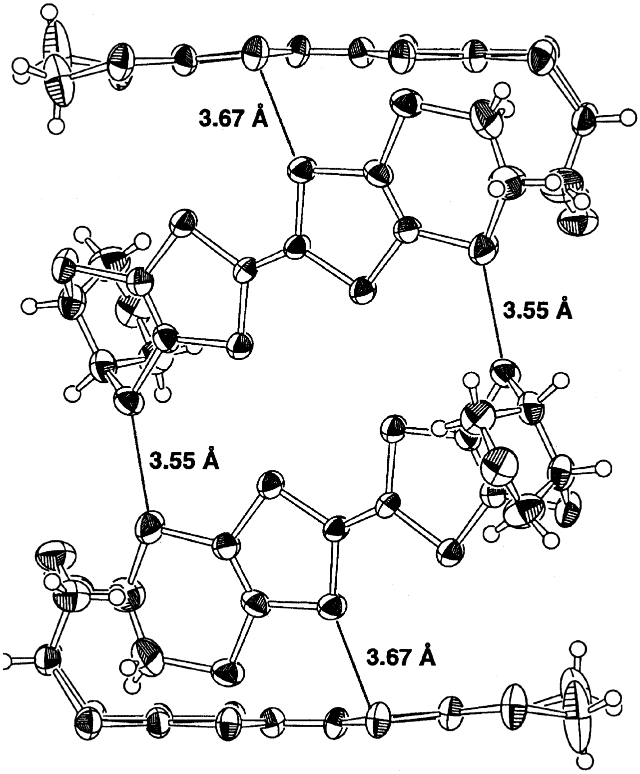

FIGURE 2 Crystal structure of **2**$\cdot PF_6 \cdot (PhCl)_{0.5}$.

molecules. These results indicate that unusual crystal structures of cation radical salts are derived from non-planar electron donors. Further studies are in progress to prepare other cation radical salts of these non-planar electron donors.

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