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Synthesis, structure and properties of a novel trisulfide double-bridged TTF dimer

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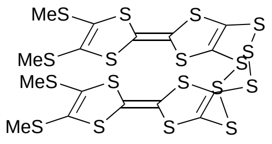
We have synthesized novel trisulfide-bridged tetrathiafulvalene (TTF) dimer molecule in which two TTF moieties are connected to each other by two trisulfide chains. X-Ray crystal structure analysis reveals that the molecule has a unique cyclophane-like U-shape structure. The structure of the ClO_4 salt is also described.

Research towards new donors for organic conductors based on the tetrathiafulvalene (TTF) framework has been actively pursued since the discovery of the metallic TTF–tetracyanoquinodimethane complex.[1] Among them, the synthesis of tetrathiafulvalenophane was first reported in 1980 and extensively developed in the 1990s because of its unusual molecular structure and interesting intramolecular interaction.[2,3] In particular several of these compounds have molecular structures like the dimeric structure of the coventional conducting salts such as the κ-type bis(ethylenedithio)–TTF salts,[4] which is related to the strong electron correlation system and Mott insulating state. However they often have a largely dislocated structure in the transverse direction because of the flexibility of the polymethylene chains which connect the two TTF moieties and this situation may weaken the interplanar interaction. With this in mind we focused on a polysulfide chain as a bridging chain because it has a more rigid framework than that of the polymethylene chain, and large interplanar interaction between two TTF moieties may be achieved in a dimer.



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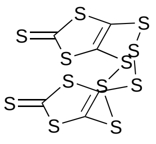

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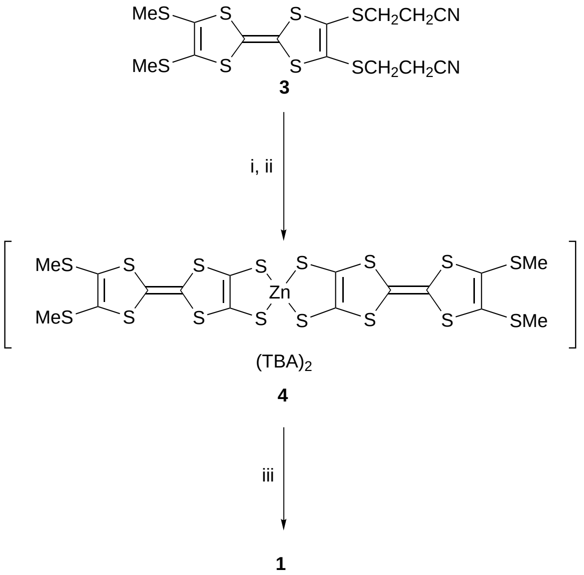
Furthermore it is expected to show the intermolecular interaction through the sulfur–sulfur contacts between the polysulfide chains. The trisulfide double-bridged molecule **2** has been reported as the 1,3-dithiole-2-thione derivative,[5] however, no TTF analog has been prepared so far. In this communication we report the synthesis and structure of a novel cyclophane-like trisulfide-bridged TTF dimer **1** in which two TTF moieties are connected to each other by two trisulfide chains. We also describe the structure and property of its dicationic ClO_4 salt.

Usually the synthesis of TTF derivatives is carried out by the phosphite mediated coupling reaction of thione or ketone precursors. However the bis(1,3-dithiole-2-thione) analog **2** was reported to react with trimethyl phosphite to yield the thiophosphonate.[5] Therefore we can not obtain the TTF dimer **1** by the cross-coupling reaction. Thus the synthesis of TTF dimer **1** was performed according to Scheme 1. 4,5-Bis(2′-cyanoethylthio)-4″,5″-bis(methylthio)-TTF **3**[6] was hydrolyzed with 28 wt% methanol solution of sodium methoxide in dry acetonitrile–methanol at room temperature and successively treated with zinc chloride and tetra-*n*-butylammonium bromide to generate the corresponding zinc dithiolene complex **4**, which was finally reacted with sulfur dichloride in dry acetonitrile at 55 °C. The resultant precipitates were filtered and washed with methanol. The crude product was purified by column chromatography (silica gel, carbon disulfide) and recrystallized from chlorobenzene to afford air-stable black plate-like crystals in 17% yield.† X-Ray crystal structure analysis‡ revealed that the TTF dimer **1** has a cyclophane-like U-shape structure (Fig. 1). Each of the two TTF moieties has a planar but slightly bent structure with dihedral angles of 16.4 and 24.1°. They stack in a ring-over-bond overlap mode with an intradimer interplanar distance of 3.86 Å. TTF dimers form sheet-like structures in the crystal which resemble the dimerized stacking structure in conducting sheets. The electrochemical properties were investigated by cyclic voltammetry. As shown in Fig. 2, the TTF dimer shows two pairs of reversible one-electron redox waves (+0.57 and 0.67 V *vs.* Ag/AgCl in PhCN) and one pair of reversible two-electron redox waves



Scheme 1 *Reagents and conditions:* i, 28 wt% sodium methoxide in methanol (2 equiv.), dry CH_3CN–MeOH (5 : 1, v/v), room temperature, 10 min; ii, zinc(II) chloride (0.5 equiv.), tetra-*n*-butylammonium bromide (1 equiv.), iii, SCl_2 (1 equiv.), dry CH_3CN, 55 °C, 2 h

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† Mp 144–145 °C (decomp.); ^1H NMR (270 MHz, carbon disulfide, $[^2H_6]$benzene): δ 2.27 (12H, s); Calc. for $C_{16}H_{12}S_{18}$: C, 24.60; H, 1.55%. Found: C, 24.95; H, 1.82%.

‡ Crystal data for **1**: $C_{16}H_{12}S_{18}$, $M = 781.35$, monoclinic, space group $C2/c$, $a = 12.597(8)$, $b = 10.62(1)$, $c = 44.867(9)$ Å, $\beta = 91.93(4)°$, $V = 5996(7)$ Å^3, $Z = 8$, μ(Mo–Kα) = 13.03 cm^{-1}. The total number of independent reflections measured at room temperature was 6335, of which 1478 were considered to be observed [$I > 3.00\sigma(I)$]. The structure was refined by full-matrix least squares to $R = 0.054$, $R_w = 0.046$. Full crystallographic details, excluding structure factors, have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, *J. Mater. Chem.*, 1998, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 1145/83.

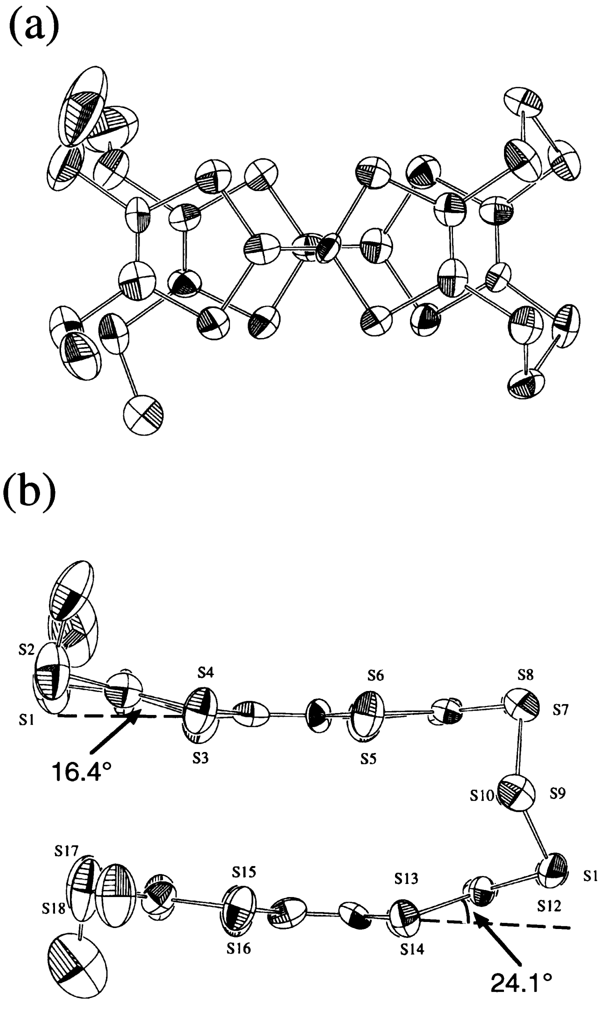

Fig. 1 Molecular structure of **1**: (*a*) top view and (*b*) side view

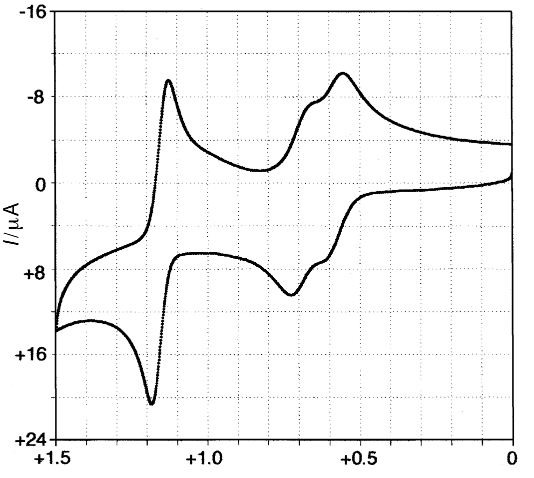

Fig. 2 Cyclic voltammogram of **1** under the following conditions: Bu_4NPF_6 0.1 mol dm^{-3} in PhCN, Pt electrode, 20 °C, scan rate 50 mV s^{-1}, E *vs.* Ag/AgCl

(+1.15 V). The first oxidation potential is slightly high compared to that of BEDT–TTF (0.53 V). The first and second oxidation processes are separated by an interval of 0.1 V, suggesting the existence of intradimer interactions between two TTF moieties. The preparation of cation radical salts was performed in THF by electrochemical oxidation, and the structure of the ClO_4 salt obtained was revealed by X-ray

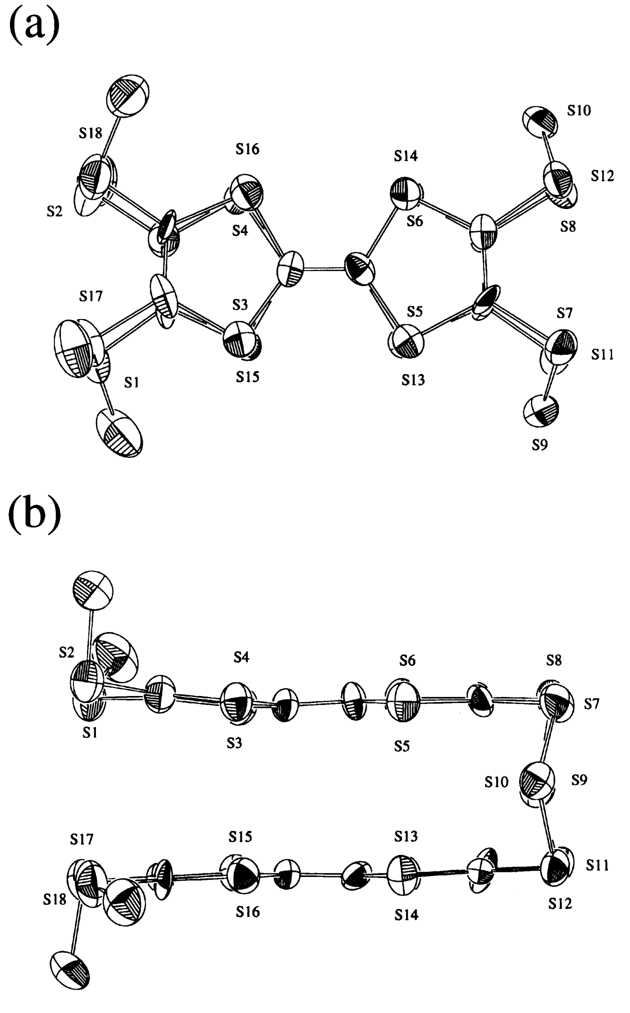

Fig. 3 Molecular structure of dicationic donor molecule $\mathbf{1}^{2+}$ in the ClO_4 salt: (*a*) top view and (*b*) side view

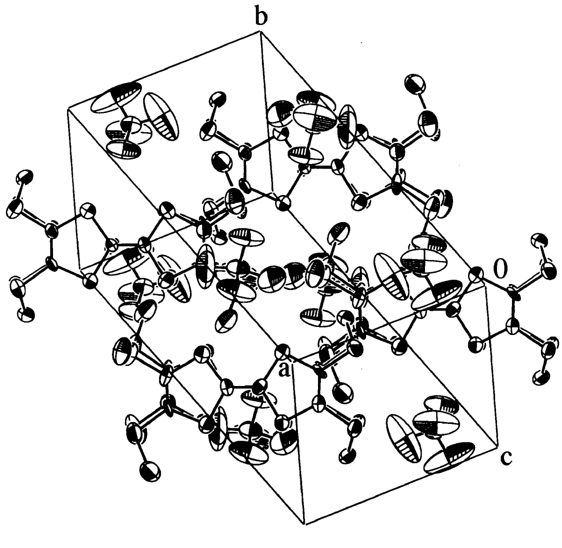

Fig. 4 Crystal structure of $\mathbf{1}{\cdot}(ClO_4)_2$. One ClO_4 anion is pentahedrally disordered.

crystal structure analysis.§ Unfortunately the composition of

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§ Crystal data for the ClO_4 salt: $C_{16}H_{12}S_{18}Cl_2O_8$, $M = 980.25$, triclinic, space group $P\bar{1}$, $a = 11.348(2)$, $b = 20.044(7)$, $c = 8.053(2)$ Å, $\alpha = 94.77(2)$, $\beta = 99.30(1)$, $\gamma = 106.21(2)°$, $V = 1719.9(9)$ Å^3, $Z = 2$, μ(Mo–Kα) = 13.23 cm^{-1}. The total number of independent reflections measured at room temperature was 3305, of which 1669 were considered to be observed [$I > 3.00\sigma(I)$]. The structure was refined by full-matrix least squares to $R = 0.042$, $R_w = 0.041$.

the ClO_4 salt is 1:2 (donor:anion) and the donors are in the dicationic state (*i.e.* each TTF is present as the radical cation species). Fig. 3 shows the molecular structure of the dicationic TTF dimer. The TTF moieties have a planar structure and eclipse each other almost perfectly with a comparatively short interplanar distance of 3.39 Å compared to that of the neutral one (3.86 Å). Each pair of adjacent dimers is almost separated by the counter anions and the interaction between donors exists only through the sulfur atoms of methylthio groups in the direction of the molecular long axis (Fig. 4). The electrical properties of this ClO_4 salt were measured; it appeared to be an insulator because of the dicationic state of the donors and its mixed stacking crystal structure. Preparation of other derivatives of **1** and other conducting salts is in progress.

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