CHEMISTRY LETTERS, pp. 2321-2324 1992.

Methylthio Substituted 2,5-Bis(1',3'-dithiol-2'-ylidene)-1,3,4,6-tetrathiapentalene. A Bis-Fused Tetrathiafulvalene

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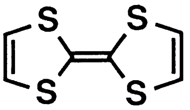
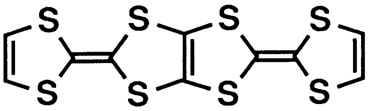
Synthesis of the title compound (**1**), and its molecular structure determined by X-ray crystallographic analysis, and electrochemical property investigated by cyclic voltammetry are described. Several cation radical salts of **1** have been prepared by electrochemical oxidation method, and their electrical properties are also presented.

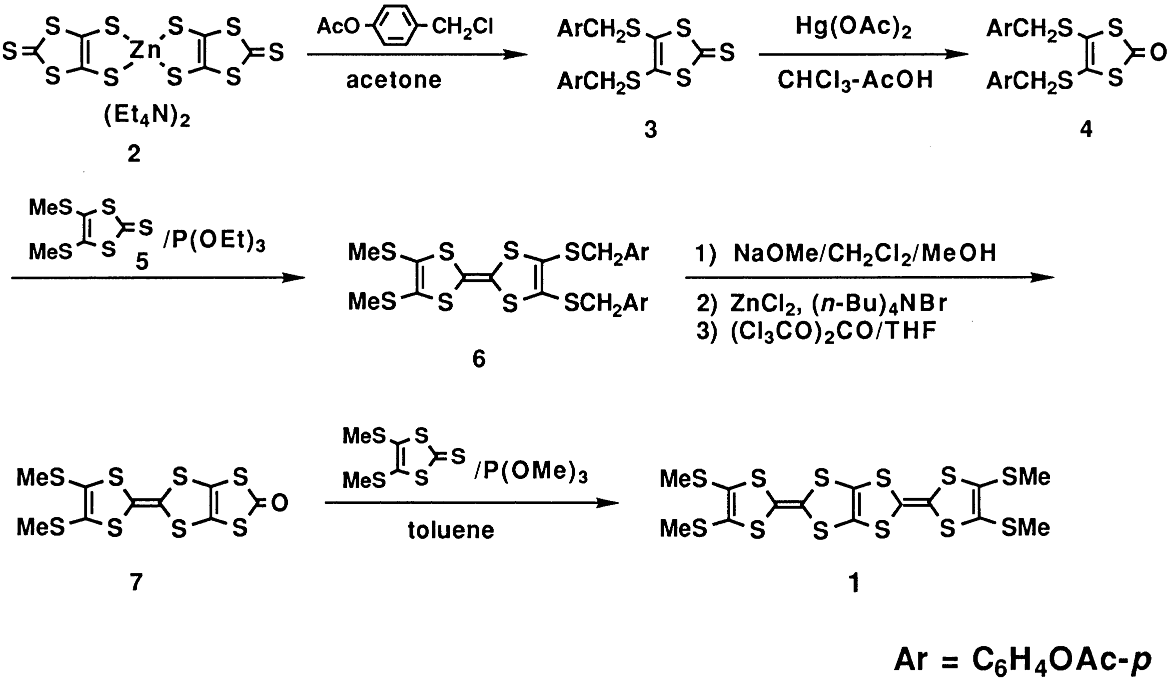
Recently synthesis of new π-electron donors designed by modification of tetrathiafulvalene (TTF) has received current attentions because TTF and its derivatives have yielded most of organic metals and organic superconductors.1-4) The importance of two strategies have been recognized for modification on TTF skeleton. One is to increase dimensionality in the cation radical salts introducted of alkylchalcogeno substituents on TTF and/or replaced of sulfur atoms in TTF with the larger chalcogenides such as selenium or tellurium.2) The other is to decrease on-site Coulombic repulsion in the dication states realized by extension of π-conjugation or by linkage of two TTF units.3,4) In this context design and preparation of donor molecules satisfying both guiding principles mentioned above is of considerable interest. 2,5-Bis(1',3'-dithiol-2'-ylidene)-1,3,4,6-tetrathiapentalene (BDT-TTP), a bis-fused TTF, is one of the most promising donors. Thus, on-site Coulombic repulsion in its dication is expected to decrease if two positive charges delocalize over two TTF units. Furthermore, considering arrangement of sulfur atoms in BDT-TTP, it is also expected to show two-dimensional conductive behavior through intermolecular S•••S contacts in its cation radical salts.5) Although BDT-TTP's substituted with strongly electron-withdrawing cyano or trifluoromethyl groups have been already prepared,6) there was no report on the details of their structure and properties, especially redox behavior and preparation of conducting solids using them. Herein we describe synthesis, structure and electrochemical properties of a new BDT-TTP substituted with more strongly electron-donating methylthio groups (**1**), and electrical properties of its cation radical salts.



TTF



BDT-TTP



Scheme 1.

The synthesis of **1** was achieved as shown in Scheme 1.7) Treatment of bis(tetraethylammonium) salt of $Zn(dmit)_2$ complex (**2**) with *p*-acetoxybenzylchloride (4.8 equiv.) in refluxing acetone gave 4,5-bis(*p*-acetoxybenzylthio)-1,3-dithiole-2-thione (**3**) in 95% yield, which was quantitatively converted to the corresponding ketone (**4**) by the reaction with mercury(II) acetate (1.5 equiv.) in chloroform-acetic acid (3 : 1, v/v). The ketone **4** and 4,5-bis(methylthio)-1,3-dithiole-2-thione (**5**, 2 equiv.) were cross-coupled in neat triethylphosphite at 110 °C to afford an unsymmetrical TTF (**6**) in 62% yield.8) The compound **6** was allowed to react with excess sodium methoxide in dichloromethane-methanol (1 : 4, v/v) at room temperature, followed by treatment with zinc chloride and tetra-*n*-butylammonium bromide, and then with an excess of triphosgen in THF at -78 °C to provide a TTF fused 1,3-dithiol-2-one (**7**, yield 54%).9,10) By the cross-coupling reaction of **7** and **5** (2 equiv.) with a large excess of trimethylphosphite in refluxing toluene was obtained the target **1** as stable reddish orange plates in 35% yield.11). The cyclic voltammogram of **1** in benzonitirile exhibited four pairs of redox waves at +0.53, +0.72, +0.99 and +1.11 V (vs. SCE).12) Comparison of redox potentials with those of tetrakis(methylthio)-TTF (**8**, +0.51, +0.78 V) measured under the identical conditions revealed that E_1 values of the both donors were almost equal, and that ΔE (= E_2 - E_1) value of **1** was smaller by 0.08 V than that of **8**, suggesting that on-site Coulombic repulsion in the dication state of **1** decreased due to delocalization of two positive charges over the bis-fused TTF skeleton as expected.

A single crystal of **1** was obtained by recrystallization from carbon disulfide-toluene, and the molecular structure was determined by X-ray diffractional analysis.13) As shown in Fig. 1, the molecule **1** is almost planar except for methyl groups which are bent nearly perpendicular to the BDT-TTP plane, and the point of symmetry around the midpoint of the C5-C15 bond lies on an inversion point in the crystal. This result is in a striking con-

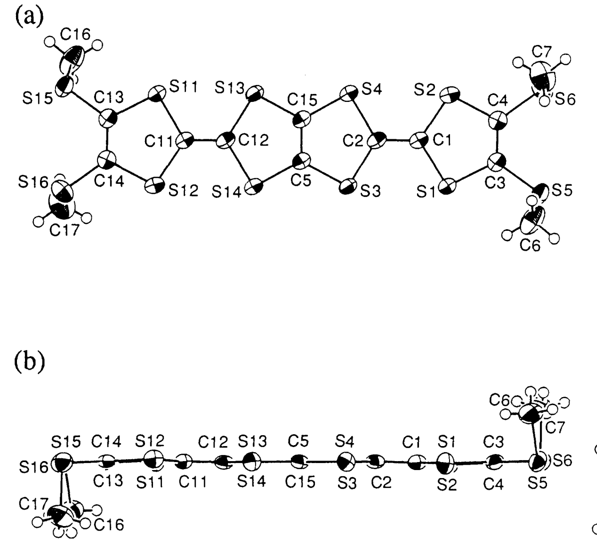


Fig. 1. Molecular structure of **1** (a) and the side view (b).

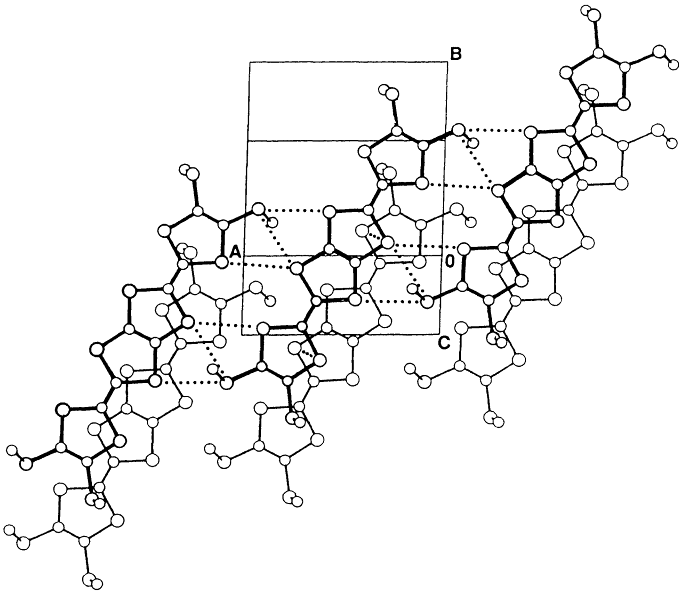


Fig. 2. Crystal structure of **1** showing close intermolecular contacts with dotted lines.

trast to that of **8**, which adopts non-planar tub conformation and all methylthio groups are bent upward.[14] The crystal of **1** consists of both sheet-like networks and stacking columns through intermolecular S•••S contacts within van der Waals radii (3.70 Å), the shortest one being 3.447(2) Å (see Fig. 2).

Several cation radical salts of **1** were prepared by electrochemical oxidation using the corresponding tetra-*n*-butylammonium salts as the electrolytes. Their electrical properties are summarized in Table 1. The room temperature conductivities (σ_{rt}) of ClO_4^- and PF_6^- salts were not so high values of 2.0 and 2.8×10^{-3} S cm^{-1}, respectively, both of which showed semiconductive behavior with the respective activation energies (E_a) of 0.13-0.19 and 0.14 eV. On the contrary, I_3^- salt exhibited very high electrical conductivities of 630 S cm^{-1} at room temperature. This salt showed metallic conductive behavior, and metal-semiconductor transition occurred around 230 K. We are currently investigating the preparation of superior quality single crystals of these salts suitable for X-ray diffractional analysis.

Table 1. Electrical Properties of Cation Radical Salts of **1**

Anion	Solvent [a)]	Form	D:A [c)]	σ_{rt} / S cm^{-1} [d)]	E_a / eV
ClO_4^-	THF	black needles	1:1	2.0	0.13-0.19
PF_6^-	THF	black plates	3:2	2.8×10^{-3}	0.14
I_3^-	TCE [b)]	black needles	1:1	630	metallic, $T_{MI} \approx 230$ K

a) All the solvents contain 10% (v/v) EtOH. b) TCE = 1,1,2-trichloroethane. c) Determined based on measurements of energy dispersion spectroscopy (EDS). d) Measured by four-probe method.

We are deeply thankful to Dr. H. Mori (International Superconductivity Technology Center) for measurements of EDS. One of the authors (Y. M.) is indebted to the Yazaki Memorial Foundation for Science and Technology for support of this work.

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5) A simple Hückel MO calculational results revealed that LCAO coefficients of all sulfur atoms in the HOMO of BDT-TTP are in the same phases, suggesting that bonding intermolecular interaction is expected to exist between adjacent BDT-TTP molecules in the donor sheet of cation radical salts.
6) R. R. Schumaker and E. M. Engler, *J. Am. Chem. Soc.*, **102**, 6652 (1980).
7) The synthetic method for the preparation of the known BDT-TTP's could not be applicable to our target.
8) Since the completion of our work we have learned that compound **6** has been prepared by Kilburn et al. using a similar methodology; C. Gemmell, J. D. Kilburn, H. Uech, and A. E. Underhill, *Tetrahedron Lett.*, **33**, 3923 (1992).
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10) When zinc chloride was not used in this reaction, cleavage of two *p*-acetoxybenzylthio groups did not adequately proceed, and the yield of **7** decreased less than 20%.
11) **1a**: Mp 192 - 193 °C. IR (KBr) 2915, 1427, 1417, 961 cm^{-1}. UV ($CHCl_3$, nm) λ_{max} (log ε) 385 (sh, 3.82), 325 (4.51), 288 (sh, 4.42). ^1H NMR (δ in CS_2-$CDCl_3$) 2.41 (s). Mass *m*/z 564 (M^+)
12) The cyclic voltammetries of **1** and **8** were performed in benzonitrile containing 0.1 mol dm^{-3} $(n\text{-Bu})_4NClO_4$ as an electrolyte by use of Pt working and counter electrodes and a standard SCE reference electrode at 25 °C (scan rate, 50 mV s^{-1}).
13) Crystal data for **1a**: $C_{14}H_{12}S_{12}$, F_w, 564.96, triclinic, space group $P\bar{1}$, a = 9.201 (1), b = 12.144(2), c = 5.1172(8) Å, α = 94.74(1), β = 98.36(1), γ = 101.36(1)°, V = 550.9 (1) Å^3, Z = 1, D_{calcd} = 1.70 g/cm^3, R = 0.035 for 1192 observed reflections.
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(Received August 26, 1992)