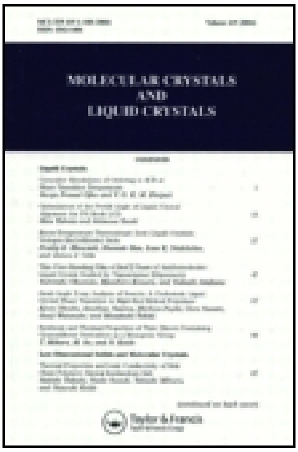

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Synthesis and Properties of π-Extended TTF Analogues and Their Cation Radical and Dication Salts

Yoshiro Yamashita [a], Masaaki Tomura [b], Mikio Uruichi [b] & Kyuya Yakushi [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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Synthesis and Properties of π-Extended TTF Analogues and Their Cation Radical and Dication Salts

YOSHIRO YAMASHITA[a], MASAAKI TOMURA[b],
MIKIO URUICHI[b] and KYUYA YAKUSHI[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 and*
[b]*Institute for Molecular Science, Myodaiji, Okazaki 444-8585, Japan*

Abstract New bis(1,3-dithiole) electron donors containing a cyclohexene unit were prepared using a Wittig-Honer reaction and a cycloreversion reaction. The tetramethyl derivative afforded the highly conductive cation radical salts as single crystals whose unusual crystal structures were revealed by X-ray analysis.

Keywords: TTF, electron donor, cation radical salts, extended conjugation, crystal structure

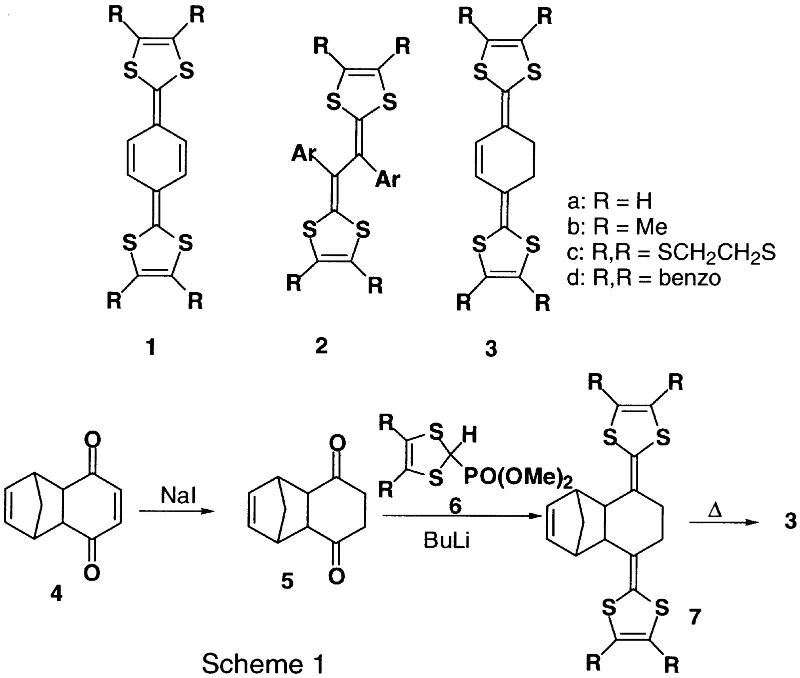
INTRODUCTION

Reduction of on-site Coulombic repulsion is important for design of component molecules affording organic conductors [1]. Extension of π-conjugation is one of the most effective method to reduce Coulombic repulsion [2]. For this purpose we have prepared tetrathiafulvalene (TTF) analogues **1** and **2** [3,4]. Quinoid compounds **1** are very strong electron donors [3] and the analogues containing a fused-thiadiazole ring afforded metallic cation radical salts [5]. TTF vinylogues **2** bearing substituents at the vinyl positions are generally non-planar due to the steric interactions between the substituents and the 1,3-dithiole parts [6]. However, we have recently found that the derivatives with *o*-substituted phenyl groups have planar geometry at the cation radical states where the phenyl substituents are twisted from the π-conjugated framework to give unusual crystal structures such as two-dimensional stacking [4]. As an extension of these works, we have now designed TTF analogues **3** with a cis-fixed double bond, which are dihydro compounds of strong electron donors **1**. The parent molecule (R = H) is known [7], but its cation radical salts have not been reported. We report here the preparation and properties of the derivatives of **3**, and their cation radical salts.

RESULTS AND DISCUSSION

The new electron donors **3b-d** were prepared according to the method shown in Scheme 1. The key point of the synthesis is the protection of the double bond of the six-membered ring. For this purpose, the double bond was protected by cyclopentadiene which was removed at the final stage. The ketone **5** was obtained by selective reduction of the cyclopentadiene adduct **4** with sodium iodide in acetone [8]. A Wittig-Horner reaction of **4** with the corresponding phosphonate esters **6** afforded bis(1,3-dithiole) compounds **7**. Cycloreversion reaction occurred to give the desired compounds **3** at around 200 °C.

The oxidation potentials of the new donors **3b-d** measured by cyclic voltammetry (CV) are shown in Table 1. The parent compound **3a** underwent two-electron oxidation at one-stage [7]. However, the new donors **3b-d** show two stage one-electron oxidation waves. The CV of **3b** is depicted in Figure 1. The differences between the first and second oxidation potentials in them are much smaller than that for TTF, indicating that on-site Coulombic repulsion is decreased in them.



Scheme 1

TABLE I Oxidation potentials of donors.

Donor	E_1	E_2	ΔE
3b	0.18	0.29	0.11
3c	0.45	0.53	0.08
3d	0.36	0.42	0.06
TTF	0.35	0.79	0.44

V vs. SCE, 0.1 mol dm^{-3} Bu_4NPF_6 in PhCN, Pt electrode, scan rate 100 mV s^{-1}.

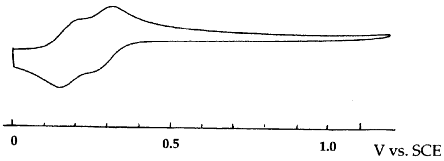


FIGURE 1 Cyclic voltammogram of **3b**.

The donor **3b** gave two cation radical salts [(**3b**)$_2$·PF$_6$ and (**3b**)$_2$·AsF$_6$] as single crystals when electrochemically oxidized in chlorobenzene. The molar ratios were determined on the basis of elemental analyses. The salts exhibit good conductivities at room temperature [(**3b**)$_2$·PF$_6$; 10 Scm^{-1} and (**3b**)$_2$·AsF$_6$; 6 Scm^{-1}] which are almost constant to ca. 270 K and then rapidly decrease. The dication salts were prepared as powders when **3b**-**d** were reacted with tris(4-bromophenyl)aminium hexachloroantimonate. However, the single crystals have not been obtained.

The X-ray crystal analyses of the cation radical salts revealed their unique structures.† The two crystals are isomorphous, and so only the PF$_6$ crystal is discussed here. The molecular structure of the donor molecule is shown in Figure 2a. The central six-membered ring is disordered, and the bond lengths shown in Figure 2a are between the double bond and single bond. The planar molecules are stacked according to the manner shown in Figure 2b, which is similar to those of the TMTSF salts. The PF$_6$ anions are located between the methyl groups. No short contact exists between the columns, indicating a one-dimensional structure. The stacking mode can be seen in Figure 2c, where a zigzag type stacking is depicted. The distances between the molecules are almost the same (3.66 and 3.67 Å) although this is crystallographycally not uniform. The distances are longer than those in TMTTF or TMTSF salts. This is attributed to the steric interactions caused by the methylene protons. The weak intermolecular interactions suggest that these are strong correlation systems.

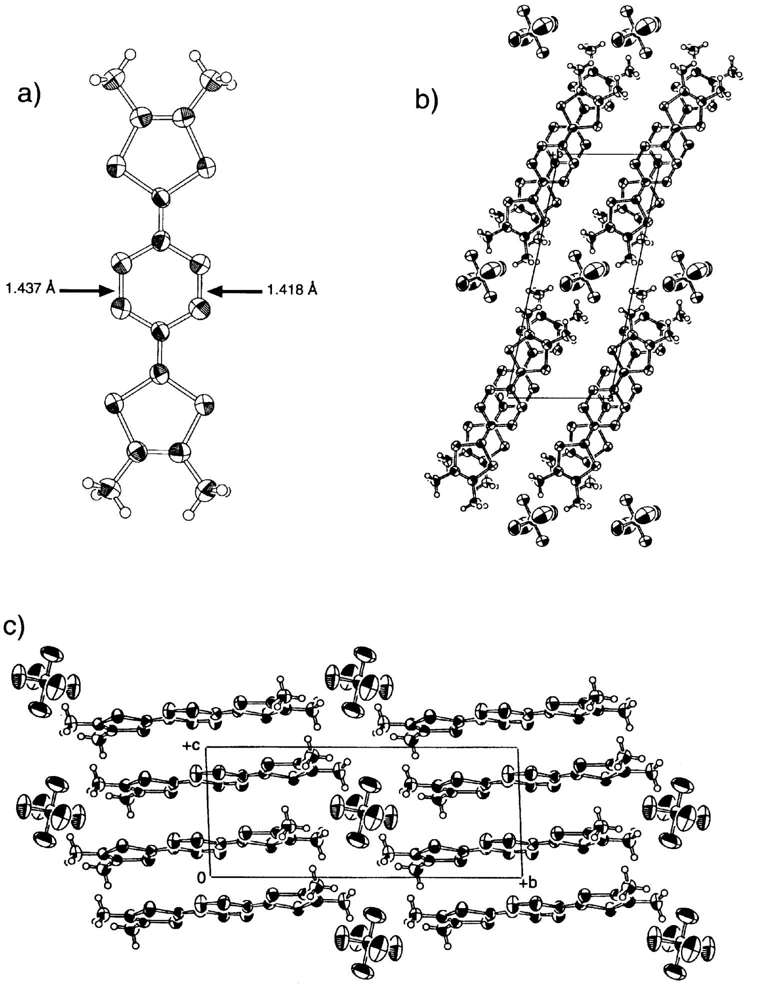


FIGURE 2 Crystal structure of $(\mathbf{3b})_2PF_6$. (a) Molecular structure, (b) top view, and (c) side view.

†Crystal data for $(\mathbf{3b})_2 \cdot PF_6$: $C_{32}H_{36}F_6PS_8$, M = 822.09, triclinic, space group P-1; a = 7.4744(5), b = 17.217(1), c = 7.3515(7) Å, α = 95.936(6), β = 107.152(6), γ = 77.098(5)°, V = 880.4(1) Å^3, R = 0.095, G.O.F = 1.00.,

Crystal data for $(\mathbf{3b})_2 \cdot AsF_6$: $C_{32}H_{36}F_6AsS_8$, M = 866.04, triclinic, space group P-1; a = 7.533(9), b = 17.329(11), c = 7.373(3) Å, α = 91.17(4), β = 106.86(4), γ = 78.12(8)°, V = 901(1) Å^3, R = 0.047, G.O.F = 0.87.

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