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PREPARATION AND ELECTRICAL PROPERTIES OF RADICAL CATION SALTS BASED ON 1,3-DITHIANE DERIVATIVES*

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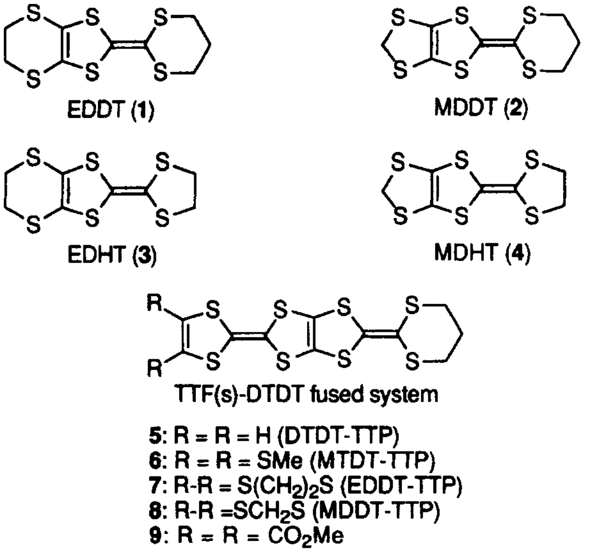
Abstract Preparation of radical cation salts based on 1,3-dithiane derivatives (**1**,**2** and **5**-**8**) was investigated. Although attempts to prepare stable radical cation salts derived from **1** and **2** were unsuccessful, various radical cation salts composed of TTF (tetrathiafulvalene) derivatives fused with a 2-(1,3-dithiol-2-ylidene)-1,3-dithiane (DTDT) unit (**5**-**8**) were formed with ease by electrochemical oxidation. Several radical cation salts of **6**-**8** exhibited metallic conducting behaviors on a single crystal or compressed pellets.

Keywords: 1,3-Dithiane derivatives, TTF derivatives, radical cation salts, conducting behaviors, organic metals

INTRODUCTION

Previously we reported the synthesis of 1,3-dithiane derivatives such as 2-(4,5-ethylenedithio-1,3-dithiol-2-ylidene)-1,3-dithiane [EDDT (**1**), Fig. 1] and TTFs[1]-DTDT fused donors (**6**-**8**).[2] Despite the development of new organic conductors based on radical cation salts of analogous TTF derivatives, *i.e.*, EDHT [(ethylenedithio)-dihydrotetrathiafulvalene, **3**],[3] MDHT [(methylenedithio)dihydrotetrathiafulvalene, **4**],[3] and TTF(s)-fused systems,[4] studies on the electrochemical properties and electrical conductivities of radical cation salts prepared from 1,3-dithiane derivatives, which are regarded as modifications of the TTF derivative with a trimethylene group,[5] have not been reported. In the present paper, we disclose the synthesis of two new 1,3-dithiane derivatives (**2** and **5**), the electrochemical properties of **1**,**2** and **5**-**7** by cyclic voltammograms (CVs), and the preparation of radical cation salts by use of **1**,**2** and **5**-**8**[6] as new electron donors. Also, we describe the conducting behavior of radical cation salts based on TTF(s)-DTDT fused donors (**5**-**8**).

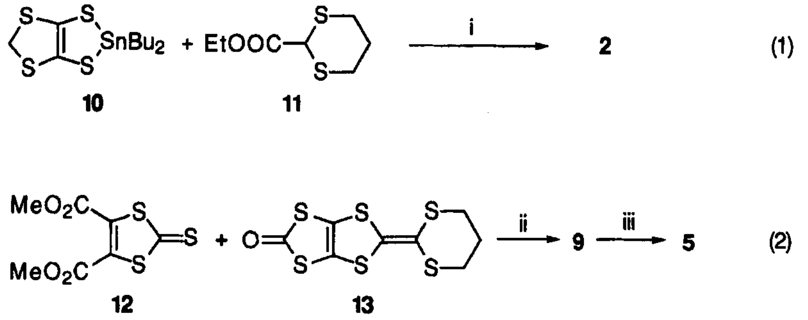


5: R = R = H (DTDT-TTP)
6: R = R = SMe (MTDT-TTP)
7: R-R = $S(CH_2)_2S$ (EDDT-TTP)
8: R-R = SCH_2S (MDDT-TTP)
9: R = R = CO_2Me

FIGURE 1 1,3-Dithiane derivatives and dihydrotetrathiafulvalene derivatives.

SYNTHESIS OF NEW 1,3-DITHIANE DERIVATIVES

Similarly to the synthesis of EDDT (**1**) via the Me_3Al-promoted reaction,[1] reaction of organotin thiolate **10** with ester **11** in the presence of trimethylaluminium gave 2-(4,5-methylenedithio-1,3-dithiol-2-ylidene)-1,3-dithiane [MDDT (**2**)][7] in 12% yield after column chromatography on silica gel followed by recrystallization from dichloromethane-pentane (Eq. 1, Scheme 1). Synthesis of DTDT-TTP (**5**) was carried out as shown in Eq. 2. Cross-coupling reaction of the ketone **13**[1] with 4,5-bis(methoxycarbonyl)-1,3-dithiole-2-thione (**12**, 2 equiv) in trimethyl phosphite-toluene (v/v = 1:1) under reflux gave **9** in 85% yield based on **13**. Demethoxycarbonylation of **9** was performed by treatment with an excess of lithium bromide hydrate in hexamethylphosphoramide (HMPA) at 90-110 °C. Purification with silica gel column chromatography followed by recrystallization from carbon disulfide gave the desired product **5**[8] in 26% yield.



Reagent and Conditions: i) Me_3Al in CH_2Cl_2, -78 °C → room temperature, overnight; ii) $(MeO)_3P$ in toluene, reflux, 2 h; iii) $LiBr{\bullet}H_2O$ (10 equiv) in HMPA, 90 °C, 1 h, 110 °C, 1h.

SCHEME 1 Synthesis of 1,3-dithiane derivatives **2** and **5**.

ELECTROCHEMICAL PROPERTIES

Electrochemical properties of 1,3-dithiane derivatives **1**,**2** and **5**-**7** were studied by CVs, and the results are summarized in Table 1. The measurement of each CV was carried out in benzonitrile containing 0.1 M tetra-*n*-butylammonium perchlorate as a supporting electrolyte under nitrogen at room temperature by use of platinum working and counter electrodes, and a saturated calomel electrode (SCE) as reference electrode (scan rate: 50 mV/s). A satisfactory CV of MDDT-TTP (**8**) could not be obtained due to its insolubility in benzonitrile. The CVs of EDDT (**1**) and MDDT (**2**) showed two pairs of reversible redox waves, indicating the existence of two pairs of single electron redox processes. On the other hand, the CVs of TTF(s)-DTDT fused donors (**5**-**7**) consisted of three pairs of single electron redox waves; the redox processes were all reversible. In a series of TTF(s)-DTDT fused donors (**5**-**7**), the E_1 value of the parent TTF-DTDT fused donor **5** was lower than those of TTFs-DTDT fused donors **6** and **7**, whereas the ΔE (E_2 - E_1) value of **5** was larger than those of **6** and **7**. In addition, while the E_1 value of EDDT-

TABLE 1 Cyclic voltammograms of 1,3-dithiane derivatives.

Compound	E_1	E_2	E_3	ΔE (E_2-E_1)
EDDT (**1**)	0.69	0.99		0.30
MDDT (**2**)	0.67	1.06		0.39
DTDT-TTP (**5**)	0.60	0.98	1.41	0.38
MTDT-TTP (**6**)	0.65	0.86	1.21	0.21
EDDT-TTP (**7**)	0.69	0.88	1.22	0.19

TTP (**7**) was equal to that of EDDT (**1**) in spite of the insertion of a tetrathiapentalene unit into the central C=C bond of EDDT, the ΔE value of **7** was smaller by 0.11 V than that of **1**, suggesting that on-site Coulombic repulsion in the dication state of EDDT-TTP (**7**) is decreased by the introduction of a tetrathiapentalene unit.

FORMATION AND CONDUCTING BEHAVIOR OF RADICAL CATION SALTS

Reaction of EDDT (**1**) with TCNQ (tetracyanoquinodimethane) in acetonitrile gave only a trace amount of the TCNQ complex. Furthermore, preparation of the EDDT (**1**) salts with I_3^-, BF_4^-, ClO_4^-, PF_6^-, and AsF_6^- by electrocrystallization in chlorobenzene containing the corresponding tetrabutylammonium salts with a controlled current[9] under nitrogen was not successful. Also, under similar electrochemical oxidation conditions in chlorobenzene or 1,1,2-trichloroethane (TCE), the MDDT (**2**) salts with I_3^-, AuI_2^-, ClO_4^-, and PF_6^- were could not be obtained. These results are in marked contrast to the easy accessibility of the stable EDHT (**3**)- and MDHT (**4**)-based salts. The π-electron system of EDDT (**1**) and MDDT (**2**) is the same as that of EDHT (**3**) and MDHT (**4**), and the E_1 values of the former are almost comparable to those of the latter [0.64 V, 0.64 V, 0.63 V, and 0.60 V vs. SCE in acetonitrile for EDDT (**1**), MDDT (**2**), EDHT (**3**), and MDHT (**4**)]. Consequently, the radical cation of EDDT (**1**) or MDDT (**2**) most probably is generated in the course of the electrochemical oxidation, but the structural flexibility of a trimethylene group in EDDT (**1**) or MDDT (**2**) appears to prevent the formation of stable radical cation salts with the anions examined.

Next, we investigated the crystal growth of radical cation salts by use of TTF(s)-DTDT fused donors **5**-**8**. Although single crystals of the TCNQ complexes with DTDT-TTP (**5**) and MTDT-TTP (**6**) could not be prepared by treatment of TCNQ with **5** and **6** in TCE at room temperature followed by recrystallization of the resulting black solid from TCE by allowing it to cool slowly, these TCNQ complexes were obtained as powders. Under the same reaction conditions, however, EDDT-TTP (**7**) failed to form its TCNQ complex even under prolonged reaction time. On the other hand, radical cation salts of **5**-**8** with various anions were readily obtainable by electrochemical oxidation in TCE under the same conditions as employed in the attempt to prepare the EDDT (**1**) or MDDT (**2**) salts.

Table 2 summarizes the composition and conducting behavior of the resulting radical cation salts. DTDT-TTF (**5**) produced conducting salts with TCNQ, I_3^-, AuI_2^-, ClO_4^-, and AsF_6^-, whose room temperature conductivities on compressed pellets were 10^{-1}-10^0 S cm^{-1}. While all of their resistivities indicated semiconductive temperature dependences, the activation energy (Ea) of the salt with TCNQ was very small (27 meV),

TABLE 2 Conducting behavior of radical cation salts.

Donor	Acceptor	D : A[a]	σ_{rt} / S cm^{-1} [b]
5	TCNQ	5 : 4	7.8 [c] (Ea = 27 meV)
	I_3	2 : 1	0.85 [c] (Ea = 44 meV)
	AuI_2	2 : 1	1.9 [c] (Ea = 49 meV)
	ClO_4	- [d]	2.0 [c] (Ea = 120 meV)
	AsF_6	5 : 3	1.2 [c] (Ea = 74 meV)
6	TCNQ	5 : 4	13 [c] (Ea = 92 meV)
	I_3	3 : 2	3.9 [c] (Ea = 45 meV)
	AuI_2	2 : 1	710 [e] (metallic down to 250 K)
	ClO_4	- [d]	0.46 [e] (Ea = 100 meV)
	AsF_6	3 : 2	11 [e] (Ea = 79 meV)
7	I_3	2 : 1	1.1 [c] (Ea = 34 meV)
	AuI_2	2 : 1	36 [c] (metallic down to 165 K)
	BF_4	2 : 1	52 [c] (metallic down to 170 K)
	ClO_4	- [d]	21 [c] (metallic down to 125 K)
	PF_6	2 : 1	44 [c] (metallic down to 60 K)
	AsF_6	3 : 2	12 [c] (metallic down to 95 K)
8	AuI_2	2 : 1	71 [c] (metallic down to 215 K)
	ClO_4	- [d]	0.018 [c] (Ea = 190 meV)
	AsF_6	1 : 1	0.037 [c] (Ea = 140 meV)

[a] Determined by elemental analysis.
[b] Room temperature conductivity measured by a four-probe technique.
[c] Measured on a compressed pellet.
[d] Not determined because this complex may explode during analysis.
[e] Measured on a single crystal.

suggesting that its single crystal can be expected to show metallic conducting behavior. Among the MTDT-TTP (**6**) salts, (MTDT-TTP)$_2$AuI$_2$ showed high room temperature conductivity (710 S cm^{-1}) on a single crystal, and the temperature dependence of its resistivities revealed that it was metallic around room temperature in the cooling and heating runs (Fig. 2). The other MTDT-TTP (**6**) salts were semiconductors on compressed pellets or single crystals, but the Ea value of the salt with I_3^- was relatively small (45 meV). In contrast, all of the EDDT-TTP (**7**) salts so far prepared, except for the salt with I_3^-, exhibited high conductivity (10^1 S cm^{-1}) at room temperature despite the fact that the measurements were taken on compressed pellets, and their resistivities showed metallic temperature dependences down to 60-170 K, below which they increased in arcs. Thus, we examined the preparation of single crystals of the EDDT-TTP (**7**) salts with ClO_4^- and AsF_6^- by changing the solvent used for electrocrystallization from TCE to chlorobenzene or THF. However, their single crystals with good qualities suitable for measurements of exact electrical resistivities at low temperature and X-ray diffractional analyses could not be obtained. Further investigation on the crystal growth of the EDDT-TTP (**7**) salts is in progress. As for the conducting behavior of the MDDT-TTP (**8**) salts, the salt with AuI_2^- exhibited metallic conducting property with a metal to semiconductor transition on a compressed pellet, and the salts with ClO_4^- and AsF_6^- showed semiconducting behavior with relatively high Ea values (190 and 140 meV, respectively).

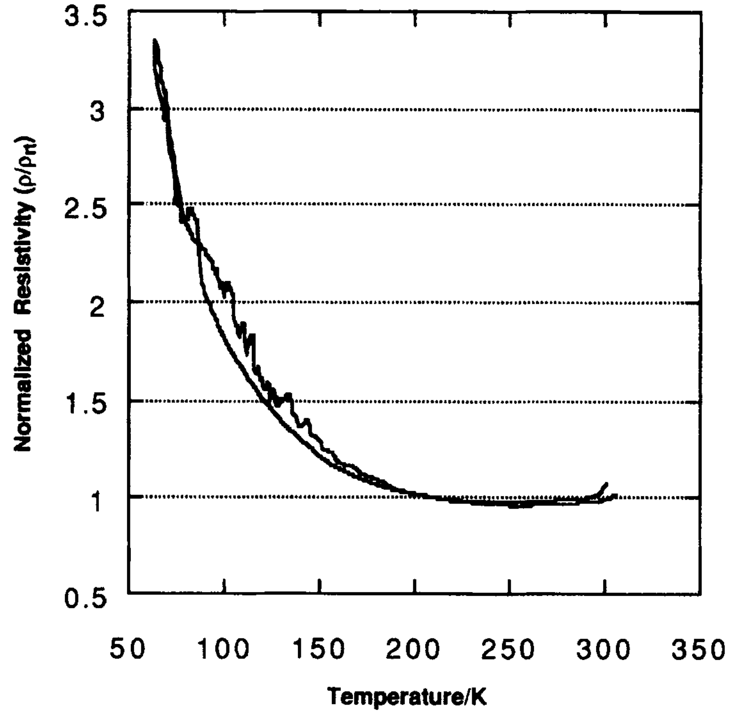


FIGURE 2 Temperature dependance of resistivities of $(MTDT\text{-}TTP)_2AuI_2$.

Conclusion

Recent studies on the radical cation salts derived from bis-fused TTF and its derivatives[10] have pointed out that the insertion of a tetrathiapentalene unit into the central C=C bond of TTF or TTF derivatives is a very promising molecular design for the development of new π-electron donors which produce organic metals stable at low temperatures. Meanwhile, the present work has suggested that the above molecular design is applicable to the DTDT derivatives, such as EDDT and MDDT, whose stable radical cation salts are by no means easy to obtain. Alternatively, it may be noted that the fusion of a 2-(1,3-dithiol-2-

ylidene)-1,3-dithiane unit onto TTF derivatives becomes one important molecular substructure of π-electron donors leading to metallic radical cation salts.

REFERENCES AND NOTES

*Dedicated, with all best wishes, to Professor Yusei Maruyama and Professor Fumio Ogura on the occasion of their retirement.

1. TTFs, used here as an abbreviation, means tetrathiafulvalenes, and does not indicate the plural form of TTF.
2. J. Yamada, S. Satoki, S. Mishima, N. Akashi, K. Takahashi, N. Masuda, Y. Nishimoto, S. Takasaki and H. Anzai, J. Org. Chem., 61, 3987 (1996).
3. J. Yamada, S. Takasaki, M. Kobayashi, H. Anzai, N. Tajima, M. Tamura, Y. Nishio and K. Kajita, Chem. Lett., 1069 (1995).
4. Y. Misaki, H. Fujiwara and T. Yamabe J. Org. Chem., 61, 3650 (1996) and references therein.
5. For conducting properties of radical cation salts prepared from other TTF derivatives with one or two trimethylene groups, see: a) R. Kato, T. Mori, A. Kobayashi, Y. Sasaki and H. Kobayashi, Chem. Lett., 781 (1984); b) T. Mori, A. Kobayashi, Y. Sasaki, R. Kato and H. Kobayashi, Chem. Lett., 1335 (1984); c) T. Mori, Y. Misaki and T. Yamabe, Bull. Chem. Soc. Jpn., 67, 3187 (1994); d) K. Takahashi and T. Ise, Chem. Lett., 77 (1995).
6. Abbreviations: DTDT-TTP, 2-(1',3'-dithiol-2'-ylidene)-5-(1",3"-dithian-2"-ylidene)-1,3,4,6-tetrathiapentalene; MTDT-TTP, 2-[4',5'-bis(methylthio)-1',3'-dithiol-2'-ylidene]-5-(1",3"-dithian-2"-ylidene)-1,3,4,6-tetrathiapentalene; EDDT-TTP, 2-[4',5'-(ethylenedithio)-1',3'-dithiol-2'-ylidene]-5-(1",3"-dithian-2"-ylidene)-1,3,4,6-tetrathiapentalene; MDDT-TTP, 2-[4',5'-(methylenedithio)-1',3'-dithiol-2'-ylidene]-5-(1",3"-dithian-2"-ylidene)-1,3,4,6-tetrathiapentalene.
7. Compound **2**: brownish-yellow powder, mp 180 °C (decomp); ^{1}H NMR (400MHz, $CDCl_3$) δ 2.19 (m, 2 H), 2.87 (m, 4 H), 4.87 (s, 2 H); MS m/z (% relative intensity) 298 (M^++2, 28), 296 (100, M^+), 224 (17), 222 (73), 88 (65); HRMS (EI) m/z 295.8952. Calcd for $C_8H_8S_6$ m/z 295.8950.
8. Compound **5**: orange powder, mp 177 °C (decomp); ^{1}H NMR (400MHz, $CDCl_3$-CS_2) δ 2.20 (m, 2 H), 2.89 (m, 4 H), 6.35 (s, 2 H); MS m/z (% relative intensity) 398 (M^++2, 58), 396 (100, M^+), 324 (12), 322 (38), 146 (53); HRMS (EI) m/z 395.8375. Calcd for $C_{11}H_8S_8$ m/z 395.8392.
9. H. Anzai, J. M. Delrieu, S. Takasaki, S. Nakatsuji and J. Yamada, J. Crystal Growth, 154, 145 (1995).
10. Y. Misaki, K. Kawakami, H. Fujiwara, T. Yamabe, T. Mori, H. Mori and S. Tanaka, Chem. Lett., 1125 (1995), and references therein.