

2,2'-(2,5-DIHYDROTHIOPHENE-2,5-DIYLIDENE)BIS(1,3-DITHIOLE) DERIVATIVES:
NEW EXTENDED ONE-ELECTRON DONORS AND THEIR ELECTROCONDUCTIVE COMPLEXES

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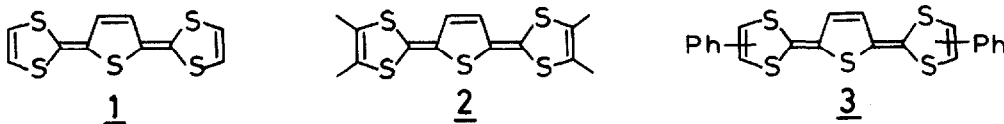
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Summary: The tetramethyl and diphenyl derivatives of 2,2'-(2,5-dihydrothiophene-2,5-diylidene)bis(1,3-dithiole) have been isolated as their dication salts, which gave stable radical cations by one-electron reduction. The complexes of new donors with tetracyanoquinodimethan (TCNQ) and iodine showed comparatively high electroconductivities.

Active investigation has been continuing toward the synthesis of a variety of organic π -donors to find out the important factors closely relating to high electroconductivity of their molecular complexes.¹ In these efforts conjugation extended-type of several tetrathiafulvalene (TTF) or dibenzotetrathiafulvalene (DBTTF) analogues² in which a sp^2 -carbon chain or a benzoquinonoid ring is inserted between the two 1,3-dithiole rings, have been so far synthesized in order to minimize the Coulomb repulsion in the dication state and the lowest electron transfer excitation energy between adjacent molecules in the stacks.^{3,4,5} Nonetheless such extended donors tend to be oxidized to unstable radical cations, not forming highly conductive complexes,⁶ and hence the structural features of their complexes in connection with the conductivity have not been fully investigated.

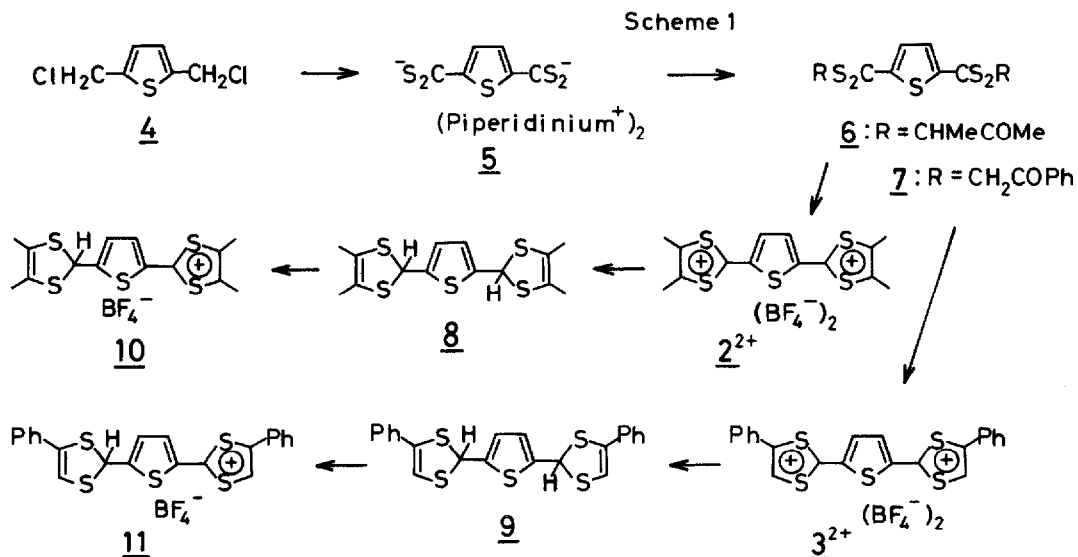
A new donor, 2,2'-(2,5-dihydrothiophene-2,5-diylidene)bis(1,3-dithiole) (DTBBDT: 1) now seems to have several advantages in forming highly conductive complexes, since a) the radical cation $\underline{1}^{\cdot+}$ as well as dication $\underline{1}^{2+}$ are expected to be stabilized by the strong conjugation between the central sulfur atom and the terminal 1,3-dithioly radical or 1,3-ditholium ion, and consequently, b) the rotation about the intercyclic bonds must be difficult to occur⁷ and each ring could exist in a coplanar conformation through the whole electron transfer process. Additionally, c) the on-site Coulomb repulsive energy must be less in $\underline{1}^{2+}$ than TTF^{2+} , and d) the aromatic sextet of thiophene ring is created upon oxidation.⁸

With these in mind, we have now synthesized tetramethyl (TM-DTBBDT: 2) and diphenyl (DP-DTBBDT: 3) derivatives of 1 in their dication forms, which compose of a reversible two-stage one-electron redox system between dications and neutral species. Actually the complexes of 2 with TCNQ and iodine showed markedly high conductivity.



Dications $\underline{2}^{2+}$ and $\underline{3}^{2+}$ have been synthesized by an analogous route to Ueno et al.^{2a} and Bryce et al.,^{2e,8} as outlined in Scheme 1. 2,5-Bis(chloromethyl)thiophene (4),⁹ when allowed to react with sulfur and sodium methoxide, yielded sodium bis(dithiocarboxylate) which was isolated as a stable dipiperidinium salt 5. Alkylation of 5 with 3-chloro-2-butanone gave

bis(dithioester) 6 which, upon dissolving in conc. sulfuric acid at 0 °C and then treating with a mixture of fluoroboric acid and acetic anhydride, afforded desired $\underline{2}^{2+}$ as a bistetrafluoroborate salt. When 5 was alkylated with bromoacetophenone, diester 7 was readily obtained. The conversion of 7 to $\underline{3}^{2+}$ by using cyclization and subsequent dehydration was performed by the same procedure as for the preparation of $\underline{2}^{2+}$. These dications $\underline{2}^{2+}$ and $\underline{3}^{2+}$ (Table II) are stable in solid state and in solution of dry aprotic solvents. Sodium borohydride reduction of $\underline{2}^{2+}$ and $\underline{3}^{2+}$ gave dihydro derivatives 8 and 9 which upon reaction with trityl fluoroborate afforded monocations 10 and 11, respectively.¹⁰



When 10 and 11 were deprotonated with an excess of triethylamine, orange precipitates assumed to be 2 and 3, respectively, were produced which are so air-sensitive that the isolation in a solid state is unsuccessful at the present stage. The NMR chemical shifts of the thiophene ring protons and carbons of the dications $\underline{2}^{2+}$ and $\underline{3}^{2+}$ appeared at lower field by 1.02 - 1.27 and 11.5 - 12.4 ppm respectively than those of thiophene itself. Moreover, the radical cations $\underline{2}^{\cdot+}$ and $\underline{3}^{\cdot+}$ exhibit smaller *g* and hfsc values than those of TTF radical cation in the ESR spectra.¹¹ These results support the pronounced distribution of the positive charge or the unpaired electron over the thiophene ring, providing a partial double bond character for the intercyclic bonds of $\underline{2}^{\cdot+}$, $\underline{3}^{\cdot+}$, $\underline{2}^{2+}$, and $\underline{3}^{2+}$, i.e., three rings of these species would exist in a good coplanar conformation both in solution and in solid state.

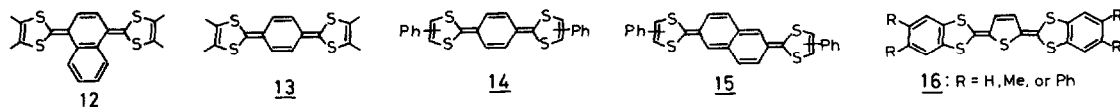
Actually, the cyclic voltammograms of $\underline{2}^{2+}$ and $\underline{3}^{2+}$ display two reversible one-electron couples from which the half-wave oxidation potentials of 2 and 3 are determined and listed in Table I together with the corresponding ΔE ($E_2^{\text{ox}} - E_1^{\text{ox}}$) and semiquinone formation constant $\log K_{\text{sem}}$. The first oxidation potentials of 2 and 3 are lower by about 0.3 V than that of TTF, revealing that the thienoquinonoidal extension brings about an increase in donor ability in this order. The diminished on-site Coulomb repulsion in the dication state is shown by the smaller ΔE values for 2 and 3 as compared with TTF. In accord with the above-mentioned view on the coplanarity of the radical cations, $\underline{2}^{\cdot+}$ and $\underline{3}^{\cdot+}$ are thermodynamically stable as is demonstrated by the relatively larger $\log K_{\text{sem}}$ values for 2 and 3 compared with $\underline{12}^{2g}$ and other donors extended with a benzo- or naphthoquinonoid structure.^{2a,b}

A charge-transfer complex of 2 with TCNQ was obtained by methathesis reaction of 2²⁺ with lithium salt of TCNQ, whereas no 3-TCNQ complex was isolated from 3²⁺. Dark violet 2- and 3-DDQ complexes were obtained on treatment of 8 and 9 with DDQ respectively. 2- and 3-Iodine complexes¹⁰ were isolated as black powders from the reaction of 2²⁺ and 3²⁺ with lithium iodide in acetonitrile. Stoichiometries determined from the elemental analyses and conductivities measured on their compressed pellets are listed in Table I.

Table I. Electrochemical properties of donors (2, 3, and 12) and electrical conductivities of their complexes with TCNQ, DDQ, and iodine.

Donor	Electrochemical property ^a				Electric conductivity $\rho/\Omega \text{ cm}$		
	E_1^{OX}/V	E_2^{OX}/V	$\Delta E (E_2^{\text{OX}} - E_1^{\text{OX}})$	$\log K_{\text{sem}}$	TCNQ D:A=1:2	DDQ D:A=1:2	I_x D:A=1:2
<u>2</u>	+0.04	+0.31	+0.27	4.66	80	7.8×10^6	8.2
<u>3</u>	+0.09	+0.40	+0.31	5.50	—	7.1×10^6	300 ^c
<u>12</u> ^b	+0.03 (2e)		≈ 0	≈ 0	$>10^3$	—	—

a: 0.1 mol dm⁻³ Bu₄NClO₄ in CH₂Cl₂; scan rate 50 mV/s; V vs SCE. b: Ag/AgCl. c: D:A=1:1



Noticeably the complex 2·(TCNQ)₂ showed more than 10 times higher conductivity than 12·(TCNQ)_{2.4}^{2g} and 13·(TCNQ)₂^{2a}. The complexes 2·(I)₂ and 3·(I)₁ showed 10⁵ - 10³ times higher conductivities than 14·(I)_{2.8}^{2a} and 15·(I)₂^{2e}. These facts suggest that the coplanarity, uniform conformation, and thermodynamic stability of the open-shell and closed-shell molecules play a very important role also in extended donors in allowing maximum overlap of the wave functions and in lowering the activation energy, both of which bring about the maximum electron density at the Fermi level. The activation energies for 2·(TCNQ)₂ and 2·(I)₂ will be examined soon. The relatively lower conductivity of 3·(I)₁ compared with that of 2·(I)₂ would be ascribed to the steric crowding of the phenyl groups which would disturb to form a uniform stack.

DTBBDT's 16 having $E_1^{\text{OX}} = +0.34 - +0.28 \text{ V}$ have been reported by us to form simple 1:1 complexes with TCNQ and DDQ,¹² whereas DTBBDT's 2 and 3 have now been revealed to form 1:2 complexes. DTBBDT's 2 and 3 are thus supposed to be too much electron donating to form 1:1 complexes with TCNQ. The 2·(TCNQ)₂ appears to be in a partial CT condition with mixed valence since the complex exhibits high conductivity and shows two CN stretching absorptions at 2170 and 2190 cm⁻¹ in the IR spectrum.^{13,14} On the other hand the complexes 2·(DDQ)₂ and 3·(DDQ)₂ are supposed to be Mott-type insulators¹⁵ in complete charge transfer conditions since they showed no carbonyl band in the IR spectra.¹⁴ The 2·(I)₂¹⁴ showed very high conductivity which is, as far as we know, the highest record of the values for the complexes of conjugation extended-type of TTF and DBTTF with iodine reported so far.

Few donors having chalcogen atom(s) at the central part of TTF have recently been synthesized,¹⁶ however their complexation has never been reported. Therefore the high complexation ability of DTBBDT's is noteworthy. Further efforts are being continued to synthesize other derivatives of DTBBDT having slightly higher E_1^{OX} than 2 and 3 in order to form 1:1 complexes with TCNQ in partial CT conditions.

Table II. Physical and spectroscopic data of bistetrafluoroborate of 2^{2+} and 3^{2+} .

Compd.	mp (°C)	$^1\text{H-NMR}$	$^{13}\text{C-NMR}$	UV-VIS λ max (MeCN) nm (log ϵ)
		$\delta(\text{CF}_3\text{CO}_2\text{D})$	$\delta(\text{CF}_3\text{CO}_2\text{D})$	
2^{2+}	238-239	2.82 (Me)	137.7 (C-3,4), 139.9 (C-4',5')	221 (3.80), 267 (3.71)
		8.12 (H-3,4)	154.6 (C-2,5), 181.5 (C-2')	337 (3.57), 476 (4.43)
3^{2+}	234-236	8.96 (H-3')	138.6 (C-3,4), 135.6 & 140.7 (C-4',5')	254 (4.40)
		8.37 (H-3,4)	164.8 (C-2,5), 185.4 (C-2')	340 (3.80), 500 (4.42)

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- All new compounds gave satisfactory elemental analyses and spectroscopic data supporting their structures; **5**: a dark yellow powder, mp 146-148 °C; **6**: violet needles, mp 158-160 °C; **7**: yellow needles, mp 224-226 °C; **8**: dark red needles, mp 78-79 °C; **9**: an orange viscous oil; **10**: a dark green powder, mp 224-226 °C; **11**: a brown powder, mp 208-211 °C. $2 \cdot (\text{TCNQ})_2$: mp > 220 °C, VIS (MeCN) λ max 395, 406, 419, 481, 688, 820, 935 nm; $2 \cdot (\text{DDQ})_2$: mp 167-169 °C, VIS (MeCN) λ max 348, 428, 668, 800, 938 nm; $3 \cdot (\text{DDQ})_2$: mp 188-192 °C, VIS (MeCN) λ max 347, 503, 676, 787, 928 nm; $2 \cdot (\text{I})_2$: mp 208-211 °C, VIS (MeCN) λ max 476, 668, 790, 930 nm; $3 \cdot (\text{I})_1$: mp 233-236 °C, VIS (MeCN) λ max 482, 678, 800, 938 nm.
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