

## 4,7-Bis(1,3-dithiol-2-ylidene)-4,7-dihydro-2,1,3-benzothiadiazoles.

## A Novel Type of Electron Donors Affording Organic Metals

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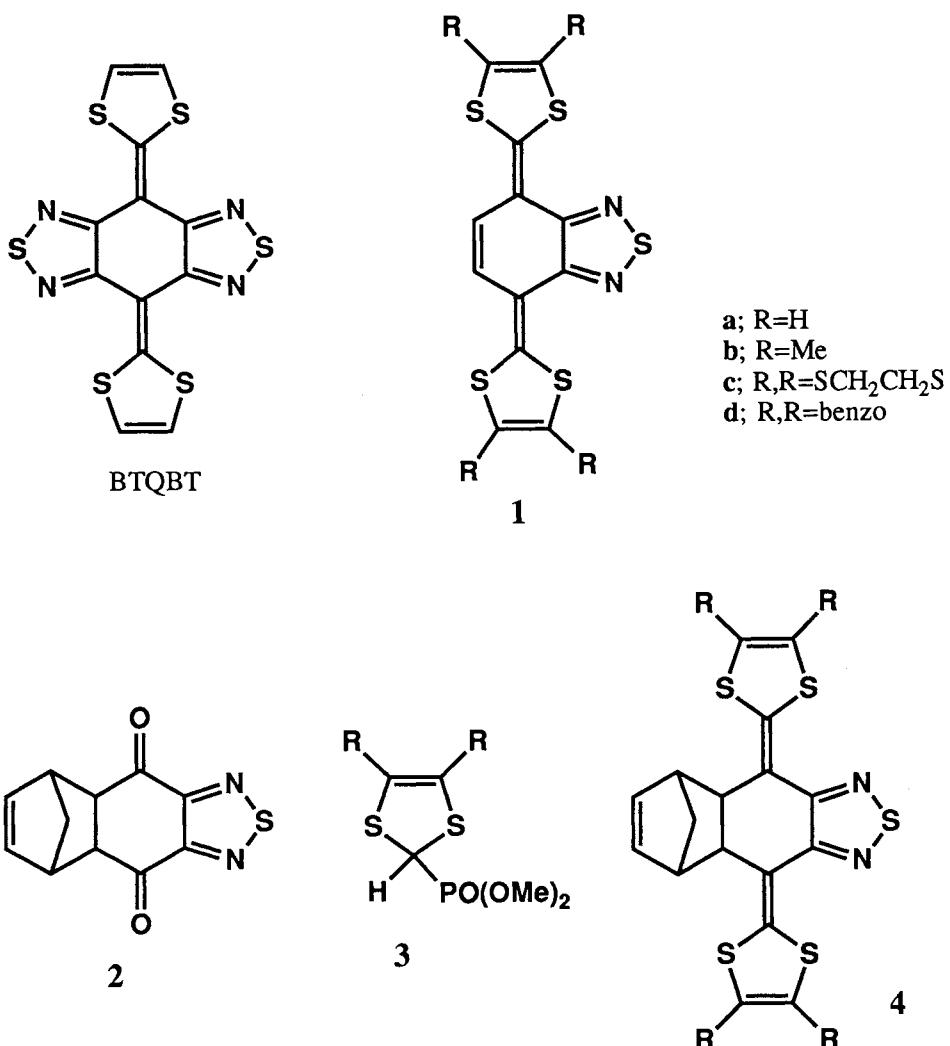
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The title compounds, tetrathiafulvalene (TTF) analogues with a quinoid structure fused with a 1,2,5-thiadiazole ring, are strong electron donors, and the tetramethyl derivative gave highly conductive cation radical salts showing metallic temperature dependence down to 100 K.

Electron acceptors containing fused-1,2,5-thiadiazole rings show interesting physical properties due to the strong intermolecular interactions by heteroatom contacts as well as the extended  $\pi$ -conjugation leading to decreased Coulombic repulsion.<sup>1)</sup> Electron donors containing such heterocycles are also of interest due to high polarizability as well as the above advantages although electron-donating properties are diminished by the introduction of electron-withdrawing heterocycles.<sup>2)</sup> We have recently prepared bis[1,2,5]thiadiazolo-*p*-quinobis(1,3-dithiole)(BTQBT),<sup>3)</sup> which has a skeleton of 2,2'-*p*-quinobis(1,3-dithiole).<sup>4)</sup> However, BTQBT could not be used as a donor giving organic conductors due to its low solubility although it showed an unusually high conductivity as a single component.<sup>3)</sup> We have now prepared title compounds **1** containing one fused-1,2,5-thiadiazole ring and investigated their properties including those of the charge-transfer complexes and cation-radical salts.

The donors **1a-d** were synthesized by the following method. 2,1,3-Benzothiadiazole-4,7-dione<sup>5)</sup> was reacted with cyclopentadiene to give **2**. A Wittig-Horner reaction of **2** with phosphonate esters **3**<sup>6)</sup> in the presence of BuLi afforded bis(1,3-dithiole) compounds **4a-d** in 22, 72, 75, and 92% yields, respectively. Thermolysis of **4a-d** at 180 °C under reduced pressure led to the quantitative formation of **1a-d** (**1a**, mp 297-298 °C; **1b**, decomp. 330 °C; **1c**, mp >400 °C; **1d**, mp 409-410 °C). The donor **1c** is interesting as a vinylogue of bis(ethylenedithio)tetrathiafulvalene (BEDT-TTF)<sup>7)</sup> which is the most important donor for organic superconductors. The new donors **1a-d** are air-stable violet solids. The absorptions of **1b** and **1c** containing electron-donating substituents are red-shifted compared with that of **1a** as shown in Table 1, suggesting that **1** are polarized by charge transfer from the 1,3-dithiole part to the electron withdrawing thiadiazole part.

The oxidation potentials of the donors **1a-d** measured by cyclic voltammetry are shown in Table 1. They show two reversible one-electron oxidation waves. The values for **1a-c** are lower than those for TTF, indicating that they are stronger donors than TTF although they contain an electron-withdrawing heterocycle. The high electron-donating ability is attributed to the quinoid structure. The differences between the first and second oxidation potentials are smaller than that for TTF, indicating that on-site Coulombic repulsion in **1** is decreased due to the extended  $\pi$ -conjugation.

Table 1. Oxidation potentials<sup>a)</sup> and absorption maxima of donors

Donor	<i>E</i> <sub>1</sub>	<i>E</i> <sub>2</sub>	$\Delta E$	$\lambda_{\text{max}}/\text{nm} (\log \epsilon)^{\text{b)}$
<b>1a</b>	+0.36	+0.53	0.17	494(4.75), 464(4.65)
<b>1b</b>	+0.30	+0.48	0.18	507(4.75), 478(4.65)
<b>1c</b>	+0.45	+0.60	0.15	511(4.70), 480(4.57)
<b>1d</b>	+0.54	+0.70	0.16	482, 454
TTF	+0.46	+0.87	0.41	319(4.11), 309(4.12)

a) 0.1 mol dm<sup>-3</sup> Bu<sub>4</sub>NClO<sub>4</sub> in C<sub>6</sub>H<sub>5</sub>CN, Pt electrode, scan rate 100 mV s<sup>-1</sup>,

V vs. S.C.E. b) In CH<sub>2</sub>Cl<sub>2</sub>.

The X-ray structural analysis of **1d** revealed that the molecule is almost planar and the intramolecular distances between the S of the dithiole and the N of the thiadiazole (2.81 and 2.83 Å) are shorter than the sum of the van der Waals distances (3.35 Å) as shown in Fig. 1.<sup>8)</sup> The similar short contact is found in BTQBT (2.78 Å). The molecules are uniformly stacked along the c axis with the intermolecular distance of 3.50 Å. This crystal exhibited an electrical conductivity of  $1.2 \times 10^{-8} \text{ S cm}^{-1}$  as a single crystal, which was measured along the stacking direction at room temperature. The temperature dependence of the conductivity showed a semi-conductive behaviour with  $Ea$  of 0.40 eV. The conductivity is lower than that of BTQBT, but higher than those of usual organic compounds.<sup>9)</sup>

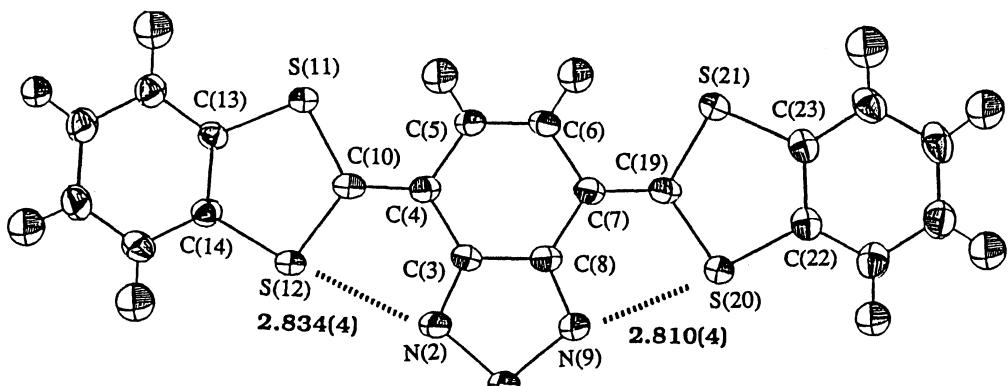


Fig. 1. Structure of **1d**: selected bond lengths (Å):  
 S(1)-N(2) 1.641(4); N(2)-C(3) 1.330(5); C(3)-C(4) 1.451(6); C(3)-C(8) 1.438(6); C(4)-C(5) 1.454(6); C(5)-C(6) 1.348(6); C(6)-C(7) 1.454(6); C(7)-C(8) 1.451(6); C(8)-N(9) 1.333(5); N(9)-S(1) 1.638(4); C(4)-C(10) 1.361(6); C(10)-S(11) 1.756(4); S(11)-C(13) 1.746(4); C(13)-C(14) 1.393(6); C(14)-S(12) 1.761(4); S(12)-C(10) 1.746(4); C(7)-C(19) 1.365(6); C(19)-S(20) 1.751(4); S(20)-C(22) 1.754(4); C(22)-C(23) 1.405(6); C(23)-S(21) 1.745(4); S(21)-C(19) 1.754(4).

Table 2. The properties of cation radical salts of **1b**

Anion	Molar ratio <sup>a)</sup>	$\sigma/\text{S cm}^{-1}$ b)	$Ea/\text{eV}$
$\text{ClO}_4$	2:1	16	0.046
$\text{BF}_4$	2:1	23	0.032
$\text{ReO}_4$	1:1	$4.3 \times 10^{-2}$	0.14
$\text{PF}_6$	2:1	110	
$\text{AsF}_6$	2:1	68	

a) Determined on the basis of elemental analyses. b) Determined by a four-probe technique on single crystals at room temperature.

The donor **1b** gave a highly conductive TCNQ complex [ $\sigma=0.56 \text{ S cm}^{-1}$  as a compaction pellet, D:A=3:2]. In addition, **1b** gave cation radical salts by an electrochemical oxidation. The properties are summarized in Table 2. The molar ratios are 2:1 (donor:salt) except for the  $\text{ReO}_4$  salt whose conductivity is poorer than those of other salts. Although the  $\text{ClO}_4$  and  $\text{BF}_4$  salts exhibited high conductivities, the temperature dependence showed semiconductive behaviours with small activation energies. On the other hand, the  $\text{PF}_6$  salt showed metallic temperature dependence down to 100 K as shown in Fig. 2. The  $\text{AsF}_6$  salt was also metallic down to 100 K. X-Ray structural analyses of these salts to clarify the differences depending on counter anions are

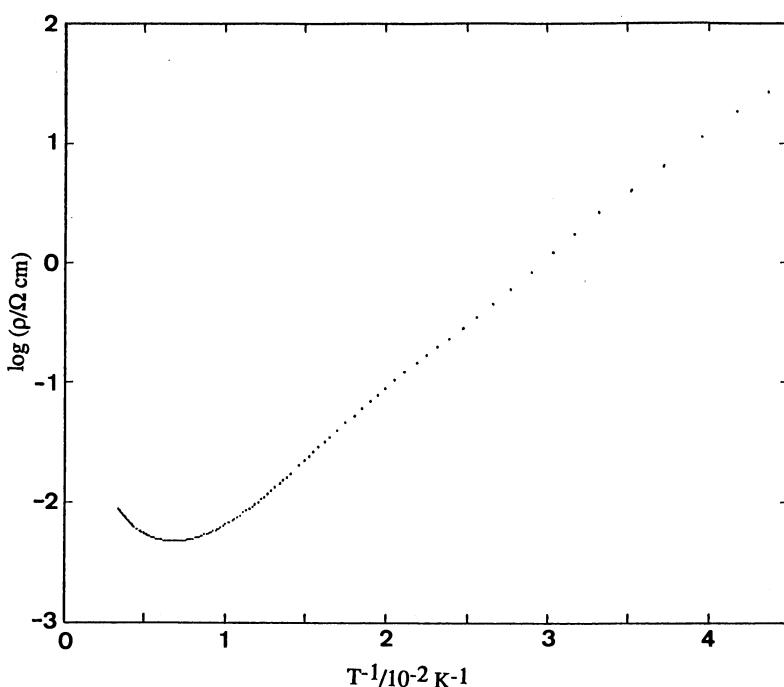


Fig. 2. Temperature dependence of electrical resistivity of  $(1b)_2PF_6$ .

now in progress.

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- 8) Crystal data for **1d**:  $C_{20}H_{10}N_2S_5$ ,  $M=438.60$ , orthorhombic, space group  $P2_12_12_1$ ,  $a=11.832(1)$ ,  $b=38.260(3)$ ,  $3.883(1)$  Å,  $V=1757.7(2)$  Å<sup>3</sup>,  $Z=4$ ,  $D_C=1.66$  g cm<sup>-3</sup>. The final  $R$  value is 3.65% for 1815 reflections with  $|F_O| > 3\sigma|F_O|$ .
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