

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

## A Novel Type of Electron Donors Affording Organic Metals

Yoshiro YAMASHITA,\* Shoji TANAKA, Kenichi IMAEDA, Hiroo INOKUCHI, and Mizuka SANO†

Institute for Molecular Science, Myodaiji, Okazaki 444

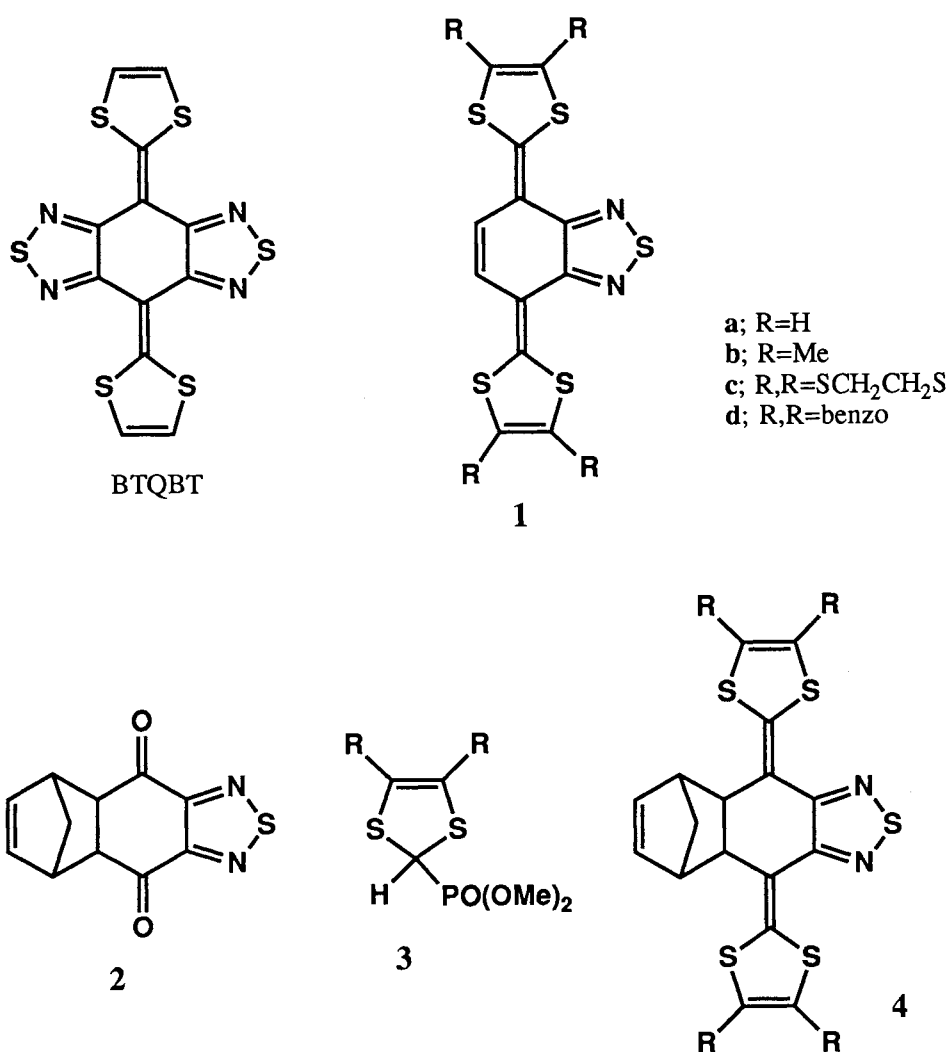
†Division of Natural Sciences, International Christian University, Mitaka, Tokyo 181

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	$E_1$	$E_2$	$\Delta E$	$\lambda_{\text{max}}/\text{nm}$ ( $\log \epsilon$ ) <sup>b)</sup>
<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  $E_a$  of 0.40 eV. The conductivity is lower than that of BTQBT, but higher than those of usual organic compounds.<sup>9)</sup>

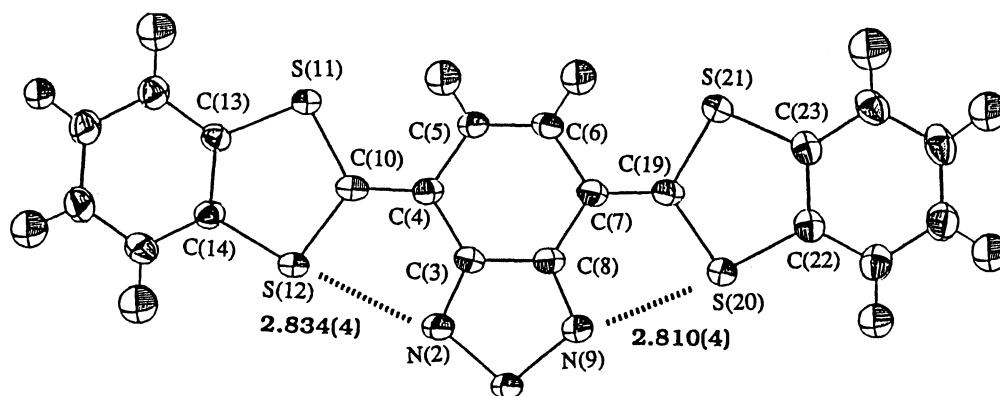


Fig. 1. Structure of **1d**: selected bond lengths (Å):

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>	$\sigma/\text{S cm}^{-1}$ <sup>b)</sup>	$E_a/\text{eV}$
ClO <sub>4</sub>	2:1	16	0.046
BF <sub>4</sub>	2:1	23	0.032
ReO <sub>4</sub>	1:1	$4.3 \times 10^{-2}$	0.14
PF <sub>6</sub>	2:1	110	
AsF <sub>6</sub>	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 ReO<sub>4</sub> salt whose conductivity is poorer than those of other salts. Although the ClO<sub>4</sub> and BF<sub>4</sub> salts exhibited high conductivities, the temperature dependence showed semiconductive behaviours with small activation energies. On the other hand, the PF<sub>6</sub> salt showed metallic temperature dependence down to 100 K as shown in Fig. 2. The AsF<sub>6</sub> salt was also metallic down to 100 K. X-Ray structural analyses of these salts to clarify the differences depending on counter anions are

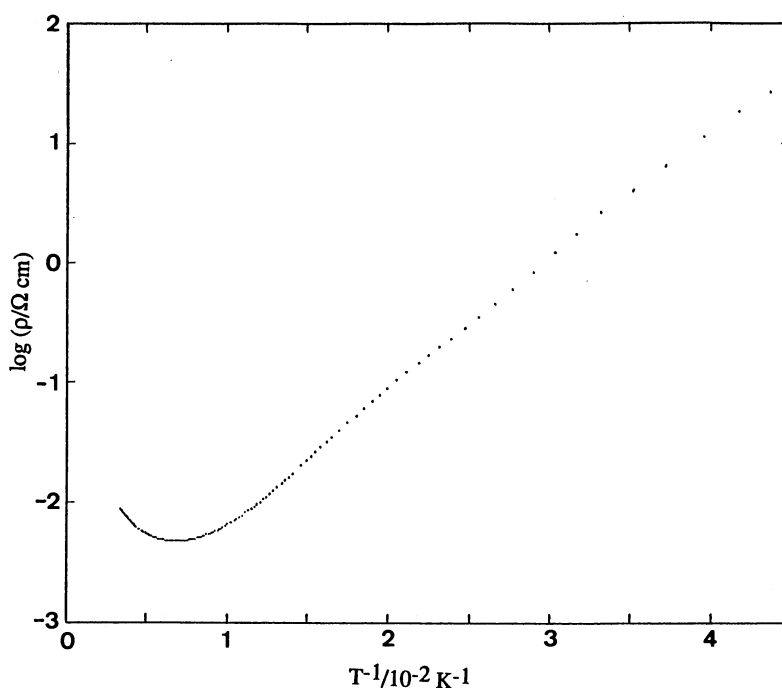


Fig. 2. Temperature dependence of electrical resistivity of **(1b)**<sub>2</sub>PF<sub>6</sub>.

now in progress.

This work was supported by the Grant-in-Aid for Scientific Research on Priority Areas No. 02230229 from the Ministry of Education, Science and Culture, Japan.

#### References

- 1) T. Suzuki, C. Kabuto, Y. Yamashita, T. Mukai, T. Miyashi, and G. Saito, *Bull. Chem. Soc. Jpn.*, **61**, 261 (1988); T. Suzuki, Y. Yamashita, C. Kabuto, and T. Miyashi, *J. Chem. Soc., Chem. Commun.*, **1989**, 1102.
- 2) Y. Yamashita and T. Miyashi, *Chem. Lett.*, **1988**, 661; Y. Yamashita, S. Tanaka, K. Imaeda, H. Inokuchi, and M. Sano, *J. Chem. Soc., Chem. Commun.*, **1991**, 1132.
- 3) Y. Yamashita, S. Tanaka, K. Imaeda, and H. Inokuchi, *Chem. Lett.*, **1991**, 1213.
- 4) Y. Yamashita, Y. Kobayashi, and T. Miyashi, *Angew. Chem., Int. Ed. Engl.*, **28**, 1052 (1989).
- 5) J. D. Warren, V. J. Lee, and R. B. Angier, *J. Heterocycl. Chem.*, **16**, 1617 (1979).
- 6) A. J. Moore and M. R. Bryce, *Synthesis*, **1991**, 26.
- 7) A. J. Moore, M. R. Bryce, D. J. Ando, and M. B. Hursthouse, *J. Chem. Soc., Chem. Commun.*, **1991**, 320; T. K. Hansen, M. V. Lakshmikantham, M. P. Cava, R. M. Metzger, and J. Becher, *J. Org. Chem.*, **56**, 2720 (1991).
- 8) Crystal data for **1d**: C<sub>20</sub>H<sub>10</sub>N<sub>2</sub>S<sub>5</sub>, M=438.60, orthorhombic, space group *P*2<sub>1</sub>2<sub>1</sub>2<sub>1</sub>, a=11.832(1), b=38.260(3), 3.883(1) Å, V=1757.7(2) Å<sup>3</sup>, Z=4, D<sub>c</sub>=1.66 g cm<sup>-3</sup>. The final R value is 3.65% for 1815 reflections with  $|F_o| > 3\sigma|F_o|$ .
- 9) K. Imaeda, T. Enoki, Z. Shi, P. Wu, N. Okada, H. Yamochi, G. Saito, and H. Inokuchi, *Bull. Chem. Soc. Jpn.*, **60**, 3163 (1987).

(Received November 14, 1991)