(100 MHz, $CDCl_3$) δ = 152.17 (s, Ar-C).

Stoichiometry of CT Complexes and Determinations of Association Constants *K*. The stoichiometry of the CT complexes of **9**, **3b**, and **6** with TCNE in dichloromethane was found to be 1:1, employing the usual Job method.[19]

For the present situation (1:1 complexes, activity coefficients equal to unity) the association constant may be expressed in the following way on the molar scale (the index$_0$ represents initial concentration, A = acceptor, D = donor:

$$K = [AD]/[[A]_0 - [AD]] - [[D]_0 - [AD]]$$

When $[A]_0 \ll [D]_0$ this equation may be rewritten according to the classical expressions of Benesi–Hildebrand, Scott, or Scatchard. Foster points out[19] (after Deranleu[20]) that "if a termolecular complex is present, the effect on the curvature of the various plots is most marked in the case of the Scatchard plot". This is the reason why the "*Scatchard*" equation was employed in the present study: $A/[D]_0[A]_0 = (-K())/[A]_0 + K\epsilon$, where A is the absorbance of the complex at a given wavelength and for a given concentration for the acceptor A.

X-ray Crystal Structure Determination of Compound 6. The compound crystallizes in the noncentrosymmetric space group *Pc* with cell dimensions a = 8.381 (3), b = 10.288 (3), and c = 8.368 (2) Å, β = 116.38 (2)°, V = 646.4 Å^3 (at −95 °C), Z = 2. The near equality of the a and c axes allows the construction of a metrically orthorhombic cell, but the true symmetry is no higher than monoclinic (R_{int} 0.27 for orthorhombically merged "equivalents"). Data were collected on a Siemens four-circle diffractometer using Mo Kα radiation ($2\theta_{max}$ 55°, 1435 unique observed reflections). The structure was solved by direct methods and refined to R 0.032, R_w 0.037. H atoms were included using a riding model. Full details of the structure determination are available as supplementary material.

Acknowledgment. We are indebted to the DAAD (Germany) and the ANRT (France) for a PROCOPE grant. H.R.L. is grateful to the Alexander von Humboldt Foundation for financial support. We furthermore thank Dr. F. Fages for discussions and Ms Christina Antonius for assistance.

Registry No. 1, 103-16-2; **2**, 142746-15-4; **3a**, 86072-79-9; **3b**, 56207-34-2; **3b**·TCNE, 142746-22-3; **3b**·TCNQ, 142746-25-6; **4**, 150-76-5; **5**, 142746-16-5; **6**, 142746-17-6; **6**·TCNE, 142746-23-4; **6**·TCNQ, 142746-26-7; **7**, 142746-18-7; **8** (n = 3), 142746-19-8; **8** (n = 5), 142746-20-1; **8** (n = 7), 142746-21-2; **9**·TCNE, 19199-93-0; **9**·TCNQ, 142746-24-5; $Br(CH_2)_3Br$, 109-64-8.

Supplementary Material Available: Complete crystallographic details (8 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

Preparation and Properties of Bis[1,2,5]thiadiazolo-*p*-quinobis(1,3-dithiole) and Its Derivatives. Novel Organic Semiconductors

Yoshiro Yamashita,* Shoji Tanaka, Kenichi Imaeda, Hiroo Inokuchi, and Mizuka Sano†

Institute for Molecular Science, Myodaiji, Okazaki 444, Japan, and Division of Natural Sciences, International Christian University, Mitaka, Tokyo 181, Japan

Received May 18, 1992

Bis[1,2,5]thiadiazolo-*p*-quinobis(1,3-dithiole) (BTQBT) (**3a**) and its derivatives **3b–f** were prepared by using a Wittig–Horner reaction. The conductivity of BTQBT was good as a single component. The X-ray structural analysis reveals that the planar molecule forms a sheetlike network by short S---S contacts. The conductivities of the derivatives **3b–f** were poorer than that of BTQBT, indicating that the unique crystal structure of BTQBT is needed for the good conductivity. The selenadiazolo analogues **9a,b** were also prepared. The conductivities were a little higher than that of BTQBT due to the stronger intermolecular interactions caused by the selenium atom.

Recently, much attention has been focused on organic conductors, and a large number of organic metals have been reported.[1] Organic superconductors have also been prepared.[2] Those organic conductors are comprised of more than two components. However, multicomponent systems have disadvantages such as instability to air, solvent, or heat treatment. Therefore, it is important to develop single-component organic conductors from viewpoints of fundamental research as well as applied science.[3] It is also a challenging theme to prepare such molecules since usual organic compounds are good insulators as single components.

Some compounds have been designed to exhibit electrical conductivities as single components. For example, tetrathiafulvalene (TTF) derivatives **1a,b** containing long alkyl chains or methyltelluro substituents show conductivities of 10^{-5} S cm^{-1}, which are attributed to strong intermolecular interactions between adjacent molecules.[4,5] In the former case, the van der Waals attractive force among alkyl chains results in strong intermolecular interactions (fastener effect).[4] In the latter case, tellurium atom contacts provide a transport of electrons in the crystal.[5] Stable heterocyclic biradicals **2a** were recently found to show good conductivities. In this case the importance of intermolecular interactions based on selenium–selenium contacts for the good conductivities is pointed out since the corresponding sulfur analogues **2b**

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† International Christian University.

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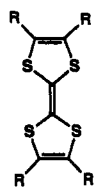
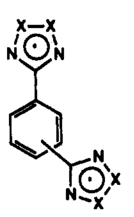
0022-3263/92/1957-5517$03.00/0

having isomorphous structures are insulators.[6] Another attempt for obtaining single component conductors is to synthesize a molecule containing both donor and acceptor units which are linked by σ-bonds.[7] Although several molecules were synthesized according to this idea, good conductivities have not been accomplished in these systems due to difficulties in controlling both molecular overlapping and degree of charge transfer.

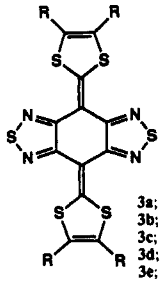
We have used fused-heterocycles to increase intermolecular interactions by heteroatom contacts and found that electron donors and acceptors containing fused 1,2,5-thiadiazole units show interesting properties.[8] In the continuation of these works we have designed bis[1,2,5]-thiadiazolo-*p*-quinobis(1,3-dithiole) (BTQBT) (**3a**) as a single-component organic semiconductor.[9] BTQBT has a skeleton of a very strong electron donor, 2,2′-*p*-quinobis(1,3-dithiole) (**4**)[10] and seems to have the following advantages in exhibiting a good conductivity as a single component. First, BTQBT is a symmetrical molecule and is expected to form a sheetlike network by heteroatom contacts. Second, intermolecular interactions along the stacking direction may be strengthened by interactions between the sulfur atoms in BTQBT. Third, BTQBT has an extended π-conjugation which is useful to decrease on-site Coulombic repulsion. Fourth, the molecule contains electron-donating 1,3-dithiole rings and electron-withdrawing thiadiazole rings, i.e., both donor and acceptor units, which may result in large polarization. Finally, introduction of substituents to the 1,3-dithiole rings of BTQBT is easy to give its various derivatives. We report here the preparation and properties of BTQBT and its derivatives.



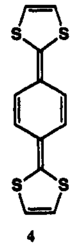
1a; R=S(CH$_2$)$_9$CH$_3$
1b; R=TeCH$_3$
1c; R=SCH$_3$



2a; X=Se
2b; X=S



3a; R=H (BTQBT)
3b; R=CH$_3$
3c; R=SCH$_3$
3d; R=SCH$_2$CH$_3$
3e; R,R=SCH$_2$CH$_2$S
3f; R,R=benzo



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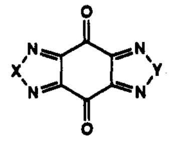
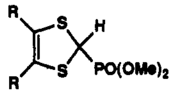
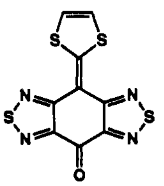


5a; X=Y=S
5b; X=S, Y=Se
5c; X=Y=Se



6a; R=H
6b; R=CH$_3$
6c; R=SCH$_3$
6d; R=SCH$_2$CH$_3$
6e; R,R=SCH$_2$CH$_2$S
6f; R,R=benzo



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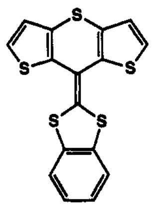

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Results and Discussion

BTQBT (**3a**) was synthesized by a Wittig–Horner reaction of 4*H*,8*H*-benzo[1,2-*c*:4,5-*c*′]bis[1,2,5]thiadiazole-4,8-dione (**5a**)[11] with a carbanion generated from phosphonate ester **6a**[10] in 48% yield. When an equal amount of **6a** was used in this reaction, ketone **7** was obtained as a dark violet solid in 40% yield. Introduction of substituents on the 1,3-dithiole rings was easily achieved by using substituted phosphonate esters **6**.[12] Thus, reactions of dione **5a** with the anions derived from phosphonate esters **6b–f** gave the corresponding BTQBT derivatives **3b–f** in 16–82% yields. All of them have high melting points (mp >370 °C). BTQBT (**3a**) and derivatives **3b,c,f** could be purified by vacuum sublimation. Their solubility in several solvents is very low; the parent compound **3a** and derivatives **3b,e,f** have solubilities of less than 10^{-6} mol/L in solvents such as dichloromethane, benzene, tetrahydrofuran, acetonitrile, and ethanol. BTQBT (**3a**) was slightly soluble in nitrobenzene upon heating to give a single crystal. Tetraalkylthio derivatives **3c,d** have better solubilities, and the measurements of absorption spectra and cyclic voltammograms were possible. The color of the parent BTQBT solid is red-violet with absorption maxima at 542 (sh) and 470 nm in a KBr disk. The end absorption is beyond 700 nm. Tetraalkylthio derivative **3c** shows absorption maxima at 485 (sh) and 456 nm, respectively, in dichloromethane.

Redox potentials of BTQBT derivatives **3c,d** were measured by cyclic voltammetry in dichloromethane. They showed both oxidation potentials (E_{pa} = 0.81 V for **3c** and E_{pa} = 0.86 V for **3d**) and reduction potentials (E_{pc} = −0.84 V for **3c** and E_{pc} = −0.85 V for **3d**).[13] Since the introduction of tetramethylthio groups into a TTF skeleton makes the oxidation potential more positive by 0.13 V,[14] the oxidation potential of the parent BTQBT **3a** is assumed to be comparable to that of tetrakis(methylthio)-TTF (TMSTTF). Oxidation potentials reflect electron-donating properties of isolated molecules. In contrast, ionization potentials of solids reflect properties of molecular assemblies and do not parallel oxidation potentials. Compounds with stronger intermolecular interactions are known to have lower ionization potentials in the solid state. For example, oxidation potentials of TTF derivatives **1a,c** are almost the same, while the threshold ionization potentials of their solids are different (**1a**; 4.7 eV, **1c**; 5.1 eV).[4,15] The lower potential of **1a** is ascribed to the strong intermolecular interaction due to the long alkyl chains. BTQBT whose oxidation potential is comparable to TTF

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[13] V vs SCE. Measured at a Pt electrode in CH$_2$Cl$_2$ with 0.1 M Bu$_4$NBF$_4$ as a supporting electrolyte: scan rate 100 mV s^{-1}.

[14] The first oxidation potentials of TTF and TMSTTF in CH$_2$Cl$_2$ are 0.52 and 0.65 V vs SCE, respectively.

[15] Seki, K.; Tang, T. B.; Mori, T.; Wu, P.; Saito, G.; Inokuchi, H. *J. Chem. Soc., Faraday Trans. 2* **1986**, *82*, 1067.

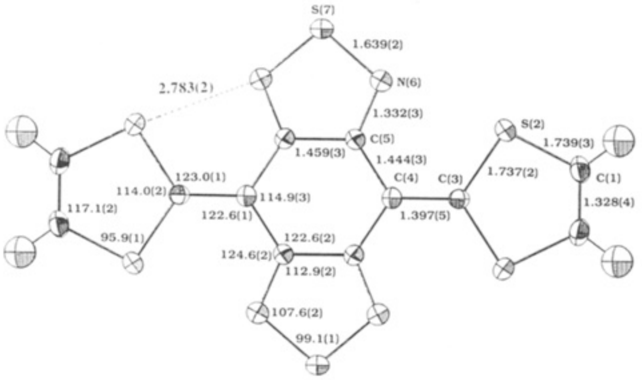

Figure 1. Molecular strucure of BTQBT (**3a**) with bond lengths (Å) and angles (deg) (ORTEP).

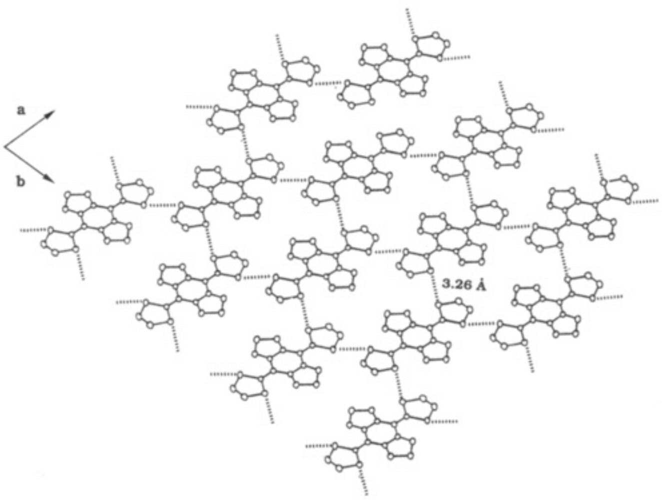

Figure 2. Sheetlike networks of **3a**. Broken lines; S- - -S interaction.

derivatives **1a,c** showed a lower threshold ionization potential in the solid state (4.57 eV).[16] This fact indicates that BTQBT has a stronger intermolecular interaction than **1a,c**.

In order to investigate the intermolecular interactions in BTQBT as well as the molecular structure, the X-ray structural analysis was carried out. The single crystal was obtained by recrystallization from nitrobenzene. The molecule is completely planar. The bond lengths and angles are shown in Figure 1. In the thiadiazole ring the S–N bond length (1.639 Å) is between those of an S–N single bond (1.73 Å) and an S–N double bond (1.53 Å). The C–N bond length (1.332 Å) is equal to those of conjugated N-heterocycles (avg 1.33 Å). The π-bond orders of the C(3)–C(4) and the C(4)–C(5) calculated from the bond lengths are 0.62 and 0.38, respectively.[17] These facts show some delocalization of the π-electrons in BTQBT. The distance between the S of the dithiole and the N of the thiadiazole (2.78 Å) is significantly shorter than the sum of the van der Waals distances (3.35 Å). Since the molecule is completely planar, the interaction between the heteroatoms is considered to be attractive. The delocalization of electrons through the S---N contact may be possible. Interestingly, the molecule forms a sheetlike network by interactions between the S atoms of the 1,3-dithiole rings as shown in Figure 2. The S---S contact distance of 3.26 Å is much shorter than the sum of their van der Waals radii (3.70 Å). The interactions between the heteroatoms in the thiadiazole rings, which are often seen in molecules containing thiadiazole rings,[8] are not observed in this network. Although the sheet is roughly planar, there is a little deviation of 0.90 Å between adjacent molecules. The molecules are uniformly stacked as shown in Figure 3. The distance between the molecular planes is 3.46 Å. The overlapping mode in the crystal is in accord with that of the most effective interaction between the HOMO and LUMO which are shown in Figure 4.[18] This fact suggests that an intermolecular charge-transfer interaction exists. The effect of the electron-withdrawing

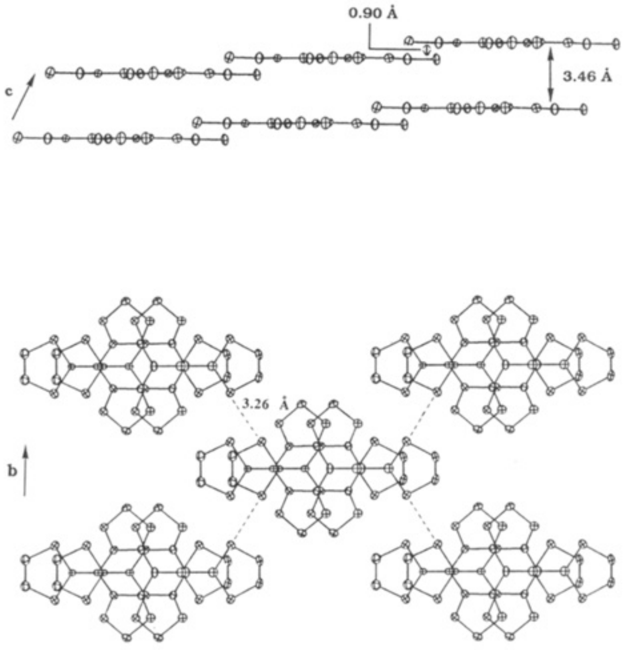

Figure 3. Overlap mode of **3a**.

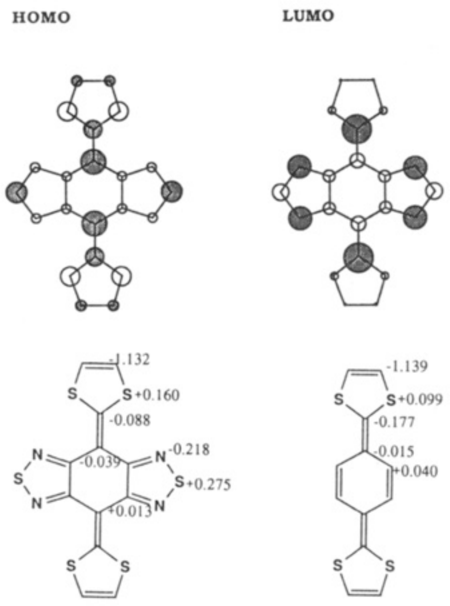

Figure 4. The HOMO, LUMO, and net atomic charges of **3a** calculated by the MNDO method.

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(16) The ionization potential was determined with the photoelectron spectroscopic method. The detail will be reported elsewhere. Fujimoto, H.; Tanaka, S.; Mori, T.; Yamashita, Y.; Inokuchi, H.; Seki, K. Submitted to *Chem. Phys*.

(17) The calculation was carried out according to an equation reported by Hafelinger. Hafelinger, G. *Chem. Ber.* **1970**, *103*, 2902.

(18) MNDO calculations (MOPAC program: Stewart, J. J. P. *QCPE Bull.* **1983**, *3*, 439) were performed by using the geometry determined from the X-ray analysis. These calculations were carried out at the Computer Center of the Institute for Molecular Science.

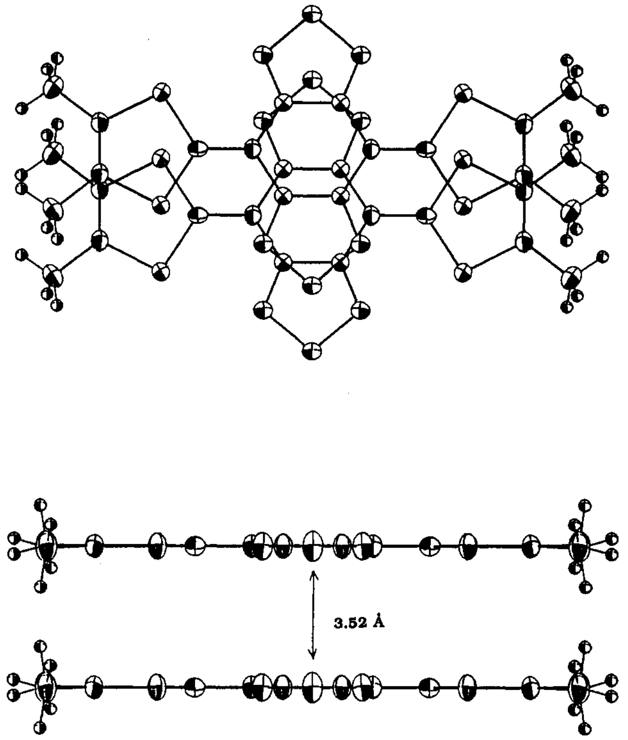

Figure 5. Crystal structure of tetramethylBTQBT (**3b**).

thiadiazole is seen in the atomic charges as shown in Figure 4. The molecule is polarized and the 1,3-dithioles are positively charged compared with those of *p*-quinobis(1,3-dithiole) (**4**). We suppose that the interaction between the positively-charged sulfur atoms attractively works to bring in the short S---S contacts. This idea is supported by the fact that the thiophene rings of thiopyran derivative **8** are twisted in the neutral state due to a repulsive interaction between the sulfur atoms, while the interaction in the cation radical becomes attractive, resulting in a planar geometry with very short S---S contacts (2.86 and 2.87 Å).[19]

Introduction of substituents is considered to change the crystal structure due to the steric effects of the substituents. In order to confirm this point, the X-ray analysis of tetramethyl derivative **3b** was carried out. The molecule is planar and has a short S---N contact of 2.78 Å similarly to the parent BTQBT. Although it is uniformly stacked according to the manner shown in Figure 5, the overlapping mode of molecules is completely different from that in BTQBT. In this case the molecule overlaps in the manner of avoiding the steric interactions of the methyl groups. The distance between molecular planes (3.52 Å) is a little longer than that of BTQBT (3.46 Å). Although the molecule arranges in almost the same plane, no special intermolecular interaction is found. It is impossible for **3b** to have short S---S contacts as found in the BTQBT crysal due to the presence of the substituents.

A single crystal of BTQBT obtained by recrystallization from nitrobenzene exhibited an unusually high electrical conductivity of 8.3×10^{-4} S cm^{-1} which was measured along the stacking direction.[20] The temperature dependence of conductivity showed a semiconductive behavior with E_a of 0.21 eV. On the other hand, the conductivity of a crystal obtained by sublimation fell to 3.7×10^{-6} S cm^{-1}, but is still high for a single component organic compound. The higher conductivity of the crystal prepared by recrystallization may be caused by a small amount of impurity such as nitrobenzene used as a recrystallization solvent. However, this point is still puzzling since a thin film (1000 Å) prepared by sublimation showed a high conductivity of 3.7×10^{-3} S cm^{-1}. The anisotropy in conductivity was measured using the crystal prepared by sublimation. The ratios of the conductivity along the stacking direction ($\sigma_{\parallel}$) to that along the intercolumn direction ($\sigma_{\perp}$) was ca. 2.[20] This small anisotropy shows that BTQBT is a two-dimensional semiconductor in which electrical conductivity is attained by the short S---S contacts besides by the overlapping of π-electrons.

Table I. Conductivities of BTQBT Derivatives[a]

compd	R,R	σ/S cm^{-1}
3a	H	5.3×10^{-6}
3b	CH_3	7.1×10^{-10}
3c	SCH_3	4.0×10^{-9}
3d	SCH_2CH_3	$<10^{-10}$
3e	$S(CH2)_9CH_3$	3.3×10^{-9}
3f	benzo	$<10^{-10}$

[a] Measured on compressed pellets by a two-probe technique at room temperature.

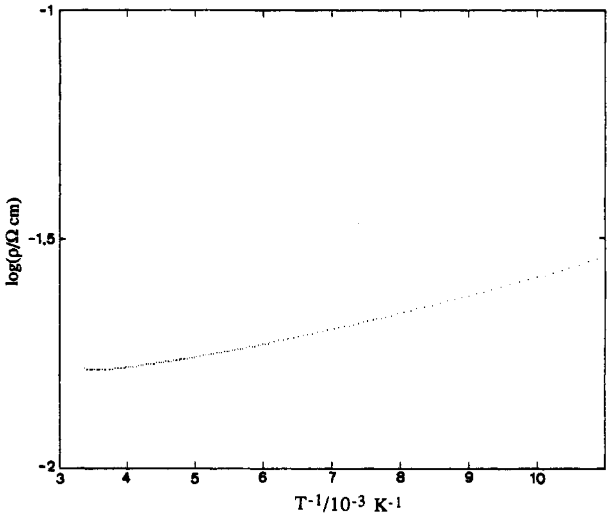

Figure 6. Temperature dependence of electrical resistivity of a ClO_4 salt of **3c**.

The conductivities of the substituents are summarized in Table I. The parent BTQBT showed the highest conductivity among them, indicating that the unique crystal structure of **3a** is needed for the good conductivity. The X-ray analysis of tetramethyl derivative **3b** supports this result since the crystal structure showed in Figure 5 is not suitable for ready electron movement between molecules. The conductivity of **3b** along the stacking direction in the single crystal was 2×10^{-9} S cm^{-1} and the activation energy (E_a) was 0.42 eV. Although those derivatives exhibit low conductivities as single components, high conductivities can be expected by doping. When dibenzo derivative **3f** was allowed to stand in an iodine vapor, the conductivity increased to 1.1×10^{-3} S cm^{-1} where the iodine content was 30%. Electrochemical oxidation of the tetrakis(methylthio) derivative **3c** in dichloromethane containing tetrabutylammonium perchlorate gave a perchlorate salt whose composition has not been determined definitely. The temperature dependence of the resistivity (Figure 6) shows that the salt is metallic around room temperature although it shows a semiconductive behavior with a small activation energy upon cooling. This result indicates that BTQBT derivatives are promising electron donors for affording organic metals.

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(19) The result will be reported soon elsewhere.

(20) Imaeda, K.; Yamashita, Y.; Li, Y.; Mori, T.; Inokuchi, H.; Sano, M. *J. Mat. Chem.* **1992**, *2*, 115.

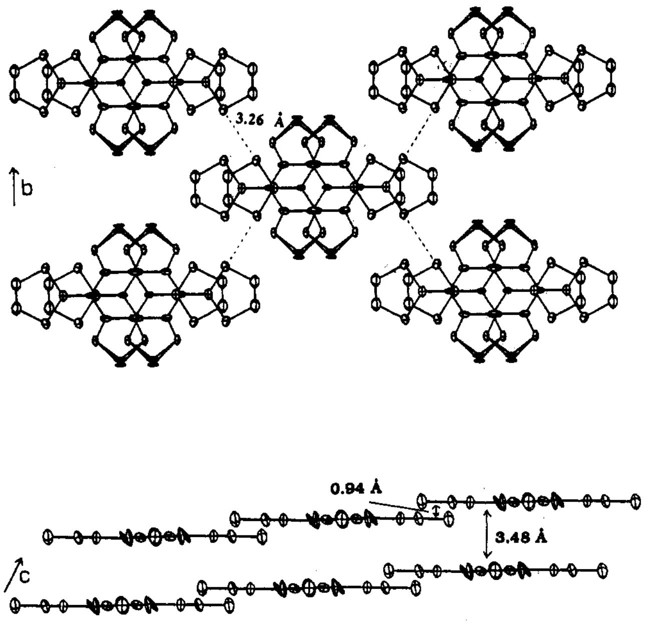
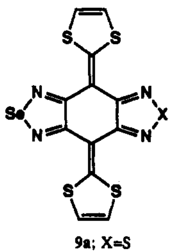
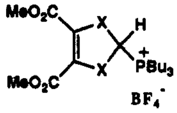


Figure 7. Crystal structure of TSQBT (**9a**).

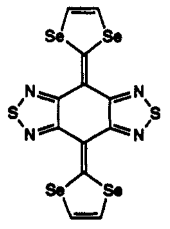
Next, we tried to replace the sulfur atoms in BTQBT with selenium atoms since the replacement is expected to strengthen intermolecular interactions due to the more polarized selenium atoms as found in the tetraselenafulvalene (TSF) series. TSQBT **9a** in which one thiadiazole of BTQBT is replaced by a selenadiazole ring was prepared by a Wittig–Horner reaction of **6a** with the corresponding dione **5b**[21] in 34% yield. BSQBT **9b** containing two fused-selenadiazole rings could not be obtained by the similar Wittig–Horner reaction with dione **5c**[11] probably due to the low solubility of **5c**. Finally, **9b** was prepared using a Wittig reaction of a ylide derived from phosphonium compound **10a**[22] with dione **5c** followed by decarboxylation with LiBr in 15% yield. The properties of **9a** and **9b** are similar to those of BTQBT. They have high melting points (>400 °C) and are sublimed at ca. 400 °C (0.1 Torr). They have very low solubility in several solvents. Their crystals are violet, and the absorption maxima were a little red-shifted compared with those of BTQBT. The conductivities of **9a** and **9b** as compressed pellets were 5.9×10^{-5} and 2.3×10^{-5} S cm^{-1}, respectively, which are a little higher than that of BTQBT (5.3×10^{-6} S cm^{-1}). The single crystal of **9a** was obtained by sublimation, although that of **9b** has not been obtained yet. The X-ray anlaysis of **9a** revealed that it crystallizes isomorphously with BTQBT as shown in Figure 7 where a sheetlike network is formed by short S---S contacts. The thiadiazole and selenadiazole rings are disordered. The conductivity along the stacking direction was measured to be 5.6×10^{-5} S cm^{-1}, which is 15 times bettern than that of BTQBT. The temperature dependence of the conductivity showed a semiconductive behavior with E_a of 0.17 eV. The higher conductivity can be attributed to the stronger intermolecular interactions due to the selenium atom, which was supported by the fact that the ionization potentials of **9a,b** in the solid state are lower than that of BTQBT. Bis[1,2,5]thiadiazolo-*p*-quinobis(1,3-diselenole) (BTQBS) (**11**) was also prepared by using a reaction of phosphonium compound **10b**[23] with dione **5a** followed by decarboxylation. Unfortunately, the sublimation temperature was so high that some decomposition occurred to eliminate selenium, and no single crystal has been prepared. The conductivity of BTQBS as a compressed pellet was 1.0×10^{-6} S cm^{-1}, which is similar to that of BTQBT.



9a; X=S
9b; X=Se



10a; X=S
10b; X=Se



11

Experimental Section

General. Melting points are uncorrected. IR spectra were taken in KBr disks. Mass data were obtained in the EI mode at 70 eV unless indicated otherwise.

4,8-Bis(1,3-dithiol-2-ylidene)-4*H*,8*H*-benzo[1,2-*c*:4,5-*c*′]bis[1,2,5]thiadiazole (BTQBT) (3a). To a stirred solution of 2-(dimethoxyphosphinyl)-1,3-dithiole (**6a**) (1.00 g, 4.46 mmol) in dry THF (25 mL) was added BuLi in hexane (1.6 M, 2.88 mL, 4.6 mmol) at −78 °C under argon. After the solution was stirred for 5 min at −78 °C, dione **5a** (385 mg, 1.71 mmol) was added. The mixture was further stirred for 5 min at −78 °C and allowed to warm to room temperature. Water (20 mL) and EtOH (20 mL) were added. The resulting solid was filtered and washed with water and ethanol to give a dark brown solid (467 mg) which was sublimed at 380 °C (0.1 Torr) to give **3a** as a red-violet solid (328 mg) in 48% yield: mp >400 °C; IR (ν/cm^{-1}) 3058, 1536, 1497, 1460, 1438, 1283, 801, 783, 683, 642, 491; UV (KBr; λ/nm) 542 (sh), 470; MS (*m*/*e* (relative intensity)) 396 (M$^+$, 100), 338 (20), 166 (13). Anal. Calcd for $C_{12}H_4N_4S_6$: C, 36.35; H, 1.02; N, 14.13. Found: C, 36.36; H, 0.99; N, 14.05.

When an equal amount of phosphonate ester **6a** was used in this reaction, 1,3-dithiole derivative **7** was obtained as a dark violet solid in 40% yield, which was purified by sublimation at 350 °C (0.1 Torr). **7**: mp >400 °C; IR (ν/cm^{-1}) 1645, 1494, 1459, 1303, 1077, 828, 798, 702, 501; MS (*m*/*e* (relative intensity)) 310 (M$^+$, 100), 252 (25), 166 (18). Anal. Calcd for $C_9H_2N_4S_4O$: C, 34.83; H, 0.65; N, 18.05. Found: C, 34.77; H, 0.71; N, 18.09.

Preparation of BTQBT Derivatives 3b–f. BTQBT derivatives **3b–f** were prepared by the Wittig–Horner reaction of phosphonate esters **6b–f** with dione **5a** similarly to **3a** in 16, 43, 82, 61, and 70% yields, respectively. Compounds **3b,c,f** were sublimed at 350–400 °C (0.1 Torr) for purification, and **3d,e** were repeatedly washed with acetone to give analytically pure samples. Physical data for those compounds are as follows.

3b: mp >400 °C; IR (ν/cm^{-1}) 2917, 1503, 1469, 1439, 1374, 1287, 800, 782, 500, 490; MS (*m*/*e* (relative intensity)) 452 (M$^+$, 100), 366 (6), 227 (3). Anal. Calcd for $C_{16}H_{12}N_4S_6$: C, 42.45; H, 2.67; N, 12.38. Found: C, 42.44; H, 2.63; N, 12.26.

3c: mp >377–380 °C; IR (ν/cm^{-1}) 1525, 1494, 1469, 1433, 1286, 806, 780, 493; UV (CH_2Cl_2; λ/nm (log ϵ)) 485 (sh, 4.04), 456 (4.32), 419 (s, 4.19), 396 (sh, 4.04), 281 (4.00); MS (*m*/*e* (relative intensity)) 580 (M$^+$, 100), 532 (38), 430 (48), 382 (21), 280 (23). Anal. Calcd for $C_{16}H_{12}N_4S_{10}$: C, 33.08; H, 2.08; N, 9.65. Found: C, 33.18; H, 1.99; N, 9.91.

3d: mp >400 °C; IR (ν/cm^{-1}) 2969, 2918, 1519, 1464, 1288, 1261, 805, 780, 495, 470; MS (*m*/*e* (relative intensity)) 636 (M$^+$, 100), 574 (54), 458 (21), 396 (42), 280 (43), 105 (22). Anal. Calcd for $C_{20}H_{20}N_4S_{10}$: C, 37.71; H, 3.16; N, 8.80. Found: C, 37.74; H, 3.10; N, 8.78.

3e: mp >400 °C; IR (ν/cm^{-1}) 1530, 1499, 1464, 1288, 1014, 800, 778, 495, 462. Anal. Calcd for $C_{16}H_8N_4S_{10}$: C, 33.31; H, 1.40; N, 9.71. Found: C, 33.28; H, 1.40; N, 9.97.

3f: mp >400 °C; IR (ν/cm^{-1}) 1567, 1501, 1474, 1433, 1283, 1260, 1139, 808, 782, 740, 680, 647, 490, 476; MS (*m*/*e* (relative intensity)) 496 (M$^+$, 100), 248 (12), 152 (14), 104 (71). Anal. Calcd for $C_{20}H_8N_4S_6$: C, 48.37; H, 1.62; N, 11.28. Found: C, 48.44; H, 1.62; N, 11.33.

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Preparation of 4,8-Bis(1,3-dithiol-2-ylidene)-4*H*,8*H*-[1,2,5]selenadiazolo[3,4-*f*]-2,1,3-benzothiadiazole (TSQBT) (9a). To a stirred solution of 2-(dimethoxyphosphinyl)-1,3-dithiole (**6a**) (330 mg, 1.56 mmol) in dry THF (15 mL) was added BuLi in hexane (1.6 M, 0.94 mL, 1.5 mmol) at −78 °C under argon. After the solution was stirred for 5 min at −78 °C, dione **5b** (145 mg, 0.54 mmol) was added. The mixture was stirred for 10 min at −78 °C and then warmed to room temperature. Addition of EtOH (30 mL) and filtration followed by washing with EtOH afforded a red-violet solid which was sublimed at 380 °C (0.1 Torr) to give **9a** as a violet solid: mp >400 °C; IR (ν/cm^{-1}) 1531, 1506, 1441, 1273, 805, 761, 684, 641, 491, 468; UV (KBr; λ/nm) 555 (sh), 485, 405; MS (*m/e* (relative intensity)) 444 (M$^+$, 100), 364 (53), 198 (46), 166 (40). Anal. Calcd for $C_{12}H_4N_4S_5Se$: C, 32.50; H, 0.91; N, 12.63. Found: C, 32.72; H, 0.91; N, 12.31.

Preparation of 4,8-Bis(1,3-dithiol-2-ylidene)-4*H*,8*H*-benzo[1,2-*c*:4,5-*c*′]bis[1,2,5]selenadiazole (BSQBT) (9b). To a stirred solution of dione **5c** (266 mg, 0.84 mmol) and phosphonium compound **10a** (1.71 g, 3.35 mmol) in dry THF (30 mL) was added BuLi in hexane (1.6 M, 2.10 mL, 3.35 mmol) at −78 °C under argon. After being stirred for 15 min at −78 °C, the mixture was allowed to warm to room temperature. Addition of EtOH (30 mL) gave a red precipitate which was filtered and washed with EtOH. The solid was used for the next reaction without further purification. A mixture of the solid and LiBr (1.17 g) in HMPA (19 mL) was heated for 1 h at 90 °C and then for 15 min at 150 °C. After EtOH (50 mL) was added, the resulting brown precipitate was filtered and washed with EtOH. Gradient sublimation at 400 °C (0.1 Torr) afforded **9b** (60 mg, 15%) and recovery of dione **5c** (110 mg, 41%). **9b**: mp >400 °C; IR (ν/cm^{-1}) 1435, 1387, 1063, 798, 738, 684, 490, 461; UV (KBr; λ/nm) 550 (sh), 480, 405; MS (*m/e* (relative intensity)) 492 (M$^+$, 28), 246 (25), 166 (100); high-resolution MS *m/e* calcd for 491.764 89, found 491.766 39.

Preparation of 4,8-Bis(1,3-diselenol-2-ylidene)-4*H*,8*H*-benzo[1,2-*c*:4,5-*c*′]bis[1,2,5]thiadiazole (BTQBS) (11). BuLi in hexane (1.6 M, 0.38 mL, 0.61 mmol) was added to a solution of dione **5a** (50 mg, 0.223 mmol) and phosphonium compound **10b** (377 mg, 0.62 mmol) in dry THF (20 mL) at −78 °C under argon. The mixture was stirred for 10 min at −78 °C and warmed to room temperature. After addition of EtOH (20 mL), the resulting brown precipitate was filtered and washed with EtOH. A mixture of the solid and LiBr (300 mg) in HMPA (5 mL) was heated for 1 h at 90 °C and then for 15 min at 150 °C. Addition of EtOH (30 mL), filtration, and washing with ethanol gave a violet solid (120 mg) which was sublimed at 400 °C (10^{-5} Torr) to give BTQBS (**11**) (15 mg, 11%): mp >400 °C; IR (KBr; ν/cm^{-1}) 1538, 1508, 1470, 1438, 1294, 794, 757, 662, 642, 475; UV (KBr; λ/nm) 620 (sh), 520 (sh), 440; MS (*m/e* (relative intensity)) 586 (M$^+$, 100), 480 (45), 292 (20), 240 (32), 160 (28); high-resolution MS *m/e* calcd for 585.654 54, found 585.656 05.

A Complex of DibenzoBTQBT (3f) with Iodine. Finely powdered **3f** (50 mg) was allowed to stand for 2 d in a sealed flask containing iodine (1.0 g). After the powder was dried under reduced pressure, a dark brown solid was obtained: mp >200 °C (elimination of iodine occurred above 200 °C). Anal. Calcd for $C_{20}H_8N_4S_6I_{0.6}$: C, 41.94; H, 1.40; N, 9.78; I, 13.29. Found: C, 42.29; H, 1.43; N, 10.19; I, 13.54.

ClO_4 Salt of BTQBT Derivative 3c. Electrochemical oxidation of a solution of **3c** (10 mg) and Bu_4NClO_4 (50 mg) in dichloromethane (50 mL) using a platinum electrode at 2 μA/cm^2 gave a ClO_4 salt as needles. The conductivity was measured by a four-probe technique.

X-ray Structural Analyses. All the data collections were performed on a Rigaku automated four-cycle diffractometer (AFC-5R) with a rotating anode. The structures were solved by the direct method with the aid of the MULTAN-78 program. The parameters of all the non-hydrogen atoms were refined by the block-diagonal least-squares method with the anisotropic factors. Crystal data are as follows.

BTQBT (**3a**): MF $C_{12}H_4N_4S_6$, MW 396.55, monoclinic, space group $C2/m$, $a = 16.226$ (4) Å, $b = 11.191$ (2) Å, $c = 3.833$ (1) Å, $\beta = 96.88$ (2)°, $V = 691.0$ (3) Å^3, $Z = 2$, $\rho_{calcd} = 1.91$ g cm^{-1}. A total of 1202 reflections was collected with Mo Kα radiation up to $2\theta = 60°$. The positions of hydrogen atoms were determined by a difference Fourier synthesis and refined at the final stage with isotropic temperature factors. The final R value is 0.0396 for 814 reflections with $|F_o|>3\sigma|F_o|$.

TetramethylBTQBT (**3b**): MF $C_{16}H_{12}N_4S_6$, MW 452.66, monoclinic, space group $C2/m$, $a = 12.166$ (6) Å, $b = 18.968$ (4) Å, $c = 3.915$ (4) Å, $\beta = 94.69$ (8)°, $V = 900.5$ (11) Å^3, $Z = 2$, $\rho_{calcd} = 1.67$ g cm^{-1}. A total of 1421 reflections was collected with Mo Kα radiation up to $2\theta = 60°$. The position of a hydrogen atom was determined by a difference Fourier synthesis, and others were calculated geometrically. The final R value is 0.0794 for 858 reflections with $|F_o|>3\sigma|F_o|$.

TSQBT (**9a**): MF $C_{12}H_4N_4S_5Se$, MW 443.45, monoclinic, space group $C2/m$, $a = 16.244$ (19) Å, $b = 11.169$ (19) Å, $c = 3.848$ (3) Å, $\beta = 96.75$ (9)°, $V = 693.3$ (15) Å^3, $Z = 2$, $\rho_{calcd} = 2.12$ g cm^{-1}. A total of 2427 reflections was collected with Mo Kα radiation up to $2\theta = 60°$. The positions of hydrogen atoms were calculated geometrically. The final R value is 0.1279 for 596 reflections with $|F_o|>3\sigma|F_o|$. The estimated standard deviations and R value are large because of the positional disorder of sulfur and selenium.

Acknowledgment. This work was supported by a Grant-in Aid of Scientific Research No. 03804039 from the Ministry of Education, Science and Culture, Japan.

Supplementary Material Available: Listings of atomic and thermal parameters and bond distances and angles for BTQBT **3a**, tetramethylBTQBT **3b**, and TSQBT **9a** (7 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.