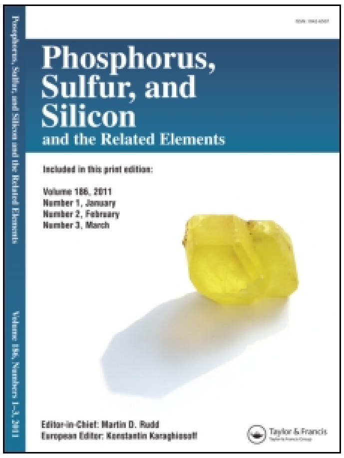

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TETRATHIO-DERIVATIVES OF *p*-QUINODIMETHANES FUSED WITH SELENADIAZOLE UNITS: A NOVEL TYPE OF ELECTRON DONORS

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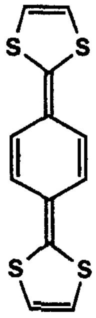
Abstract *The synthesis and properties of the novel electron* donors which are tetrathiafulvalene (TTF) analogues with a quinoid structure containing fused-selenadiazole rings are described.

INTRODUCTION

Recently much attention has been focused on development of new electron donors and acceptors which lead to organic conductors or superconductors.[1] *p*-Quinobis(1,3-dithiole) **1** is a tetrathiafulvalene analogue with a quinoid structure. Although **1** is a very strong electron donor, **1** is unstable and rapidly decomposed in solution.[2] In order to enhance the stability, we recently introduced 1,2,5-thiadiazole rings to give **2** (TQBT) and **3** (BTQBT).[3] It was found that **2** is a strong electron donor which affords highly conducting charge-transfer complexes, while **3** exhibits an unusual conductivity as a single component. In the continuation of this work, it is of interest to replace the thiadiazole rings to selenadiazole ones in **2** and **3** since the replacement may strengthen intermolecular interactions due



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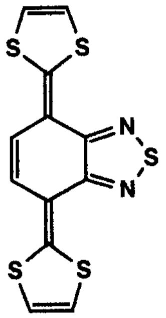
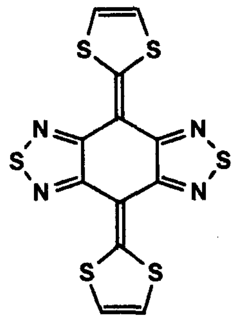
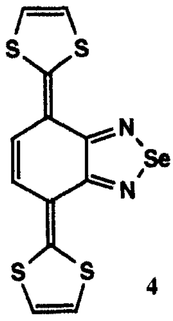


2 (TQBT)



3 (BTQBT)



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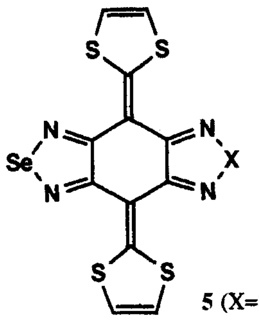
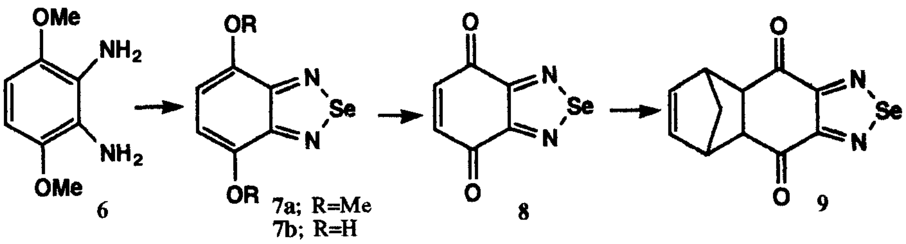


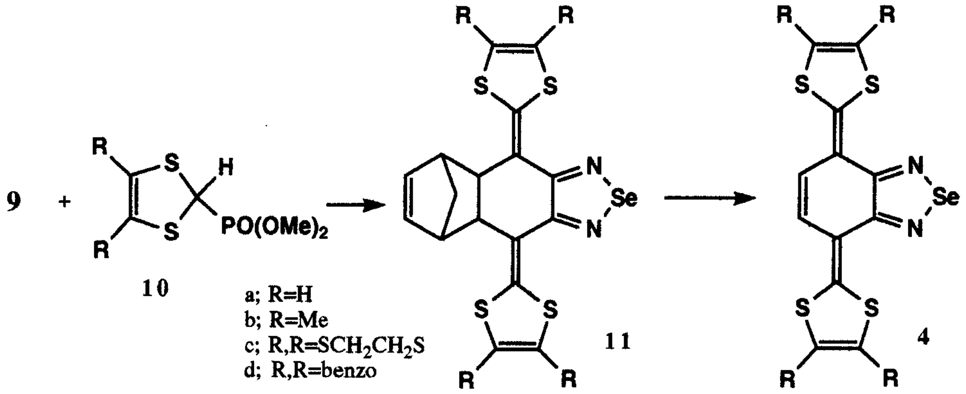
5 (X=S, Se)

to the more polarized selenium atoms. We report here the preparation and properties of [1,2,5]selenadiazole-fused derivatives **4** and **5**.

[1,2,5]Selenadiazolo-p-quinobis(1,3-dithiole) (4a) and its derivatives

The preparation of **4a** was started from 2,3-diamino-1,4-dimethoxybenzene **6** which can be obtained from *p*-dimethoxbenzene.[4] The reaction of **6** with selenium oxychloride in the presence of triethylamine resulted in the cyclization to give **7a** (mp 162-164 °C, 57%). Demethylation of **7a** with aluminium chloride in refluxing toluene gave **7b** (mp 182-184 °C, 91%), which was oxidized with silver oxide to give **8** (mp 194-196 °C, 70%). Before a Wittig-Horner reaction of **8** leading to **4**, the double bond of **8** was protected by cyclopentadiene using a Diels-Alder reaction of **8** with cyclopentadiene to give **9** (mp 164-166 °C, 89%). A Wittig-Horner reaction of dione **9** with 2-dimethoxyphosphinyl-1,3-dithioles **10a-d**[2,5] led to the formation of bis(1,3-dithiole)s **11a-d** in 10, 35, 50, 89 % yields, respectively. Thermolysis of **11a-d** at 180 °C under reduced pressure gave the desired donors **4a-d** in quantitative yields.[6] **4c** is an interesting donor as a derivative of bis(ethylenedithio)TTF which is the most important donor for organic superconductors.





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a; R=H
b; R=Me
c; R,R=SCH_2CH_2S
d; R,R=benzo

11

4

The absorption maxima in the electronic spectra of the bis(1,3-dithiole) donors **4** are shown in Table 1. Removal of the cyclopentadiene in **11** giving a quinoid structure makes the absorptions red-shift. The absorptions of **4** observed at longer wavelengths suggest that **4** are polarized by charge transfer from the 1,3-dithiole ring to the selenadiazole ring.

The cyclic voltammograms of the cyclopentadiene adducts **11** showed irreversible waves. A continuous scanning led to the appearance of new peaks, which are in accordance with those of **4**. This fact indicates that a retro-Diels-Alder reaction occurs during the CV measurement. Since the thermal reaction requires high temperatures, the reaction from the cationic species is considered to take place more easily than from the neutral species.

The oxidation potentials of **4** measured by cyclic voltammetry are shown in Table 1. The values for **4a-c** are lower than those for TTF, indicating that they are stronger donors than TTF in spite of the

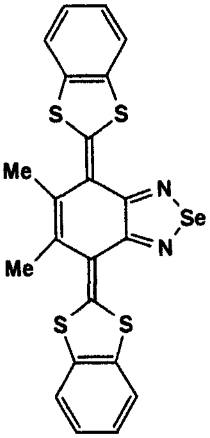
TABLE 1 Oxidation potentials[a] and absorption maxima of donors

Donor	E1	E2	ΔE	λmax/nm (log ε) in CH_2Cl_2
4a	+0.37	+0.55	0.18	497(4.09), 466(4.10)
4b	+0.31	+0.48	0.17	508(4.69), 478(4.65)
4c	+0.45	+0.62	0.17	511(4.28), 480(4.20)
4d	+0.55	+0.72	0.17	483(4.36), 454(4.32)
TTF	+0.46	+0.87	0.41	319(4.11), 309(4.12)

[a] 0.1 mol dm^{-3} Bu_4NClO_4 in C_6H_5CN, Pt electrode, scan rate 100 mV s^{-1}, V vs. SCE.

presence of the electron-withdrawing heterocycle. The high electron donating ability of **4** is attributed to the quinoid structure which can generate a new aromatic sextet upon oxidation. Another interesting feature is that the differences between the first and second oxidation potentials are smaller than that for TTF, indicating that the on-site Coulomb repulsion in **4** is decreased due to the extended π-conjugation.

For comparisons, dimethyl derivative **12** was prepared by the Wittig-Horner reaction of **10d** with the corresponding dione. The cyclic voltammogram showed a reversible two-electron oxidation wave at 0.48 V vs. SCE in benzonitrile different from two one-electron oxidation waves of **4**. This result is attributed to the nonplanarity of **12** caused by the methyl substituents, which affects the stability of the cation radical.



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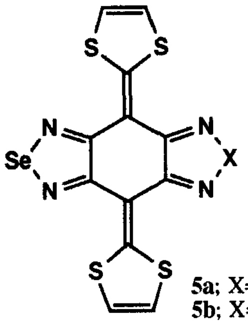
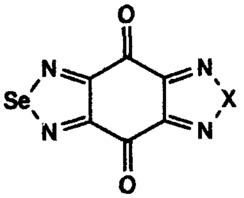
The donor **4b** gave a moderately conducting TCNQ complex [σ=5.9x10^{-2} S cm^{-1} as a compaction pellet, D:A=3:2]. In addition, a PF_6 salt of **4b** cation radical [σ=100 S cm-1 at room temperature as a single crystal, D:A=3:2], which was obtained by an electrochemical oxidation, showed metallic temperature dependence down to 100 K.[7]

Bis[1,2,5]selenadiazolo-p-quinobis(1,3-dithiole) (5)

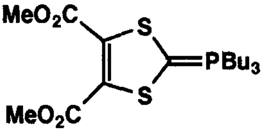
TSQBT **5a** in which one thiadiazole ring of BTQBT **3** is replaced by a selenadiazole was prepared by a Wittig-Horner reaction of **10a** with the corresponding dione **13a** in 34% yield. However, BSQBT **5b** containing two fused-selenadiazole rings could not be obtained by the similar reaction of **10a** with dione **13b** probably due to the low solubility of **13b**. Therefore, **5b** was prepared using a Wittig reaction of **14** with **13b** followed by decarboxylation with LiBr in 15% yield. Both **5a** and **5b** have a high melting point (>400 °C) and are sublimed around 400 °C /0.1 Torr. They are scarcely dissolved in any solvents. The colors of **5a,b** are violet in solid state and the absorption maxima were observed at 555sh, 485, and 405 nm for **5a**, and 550sh, 480sh, and 405 nm for **5b** in KBr disks.



5a; X=S (TSQBT)
5b; X=Se (BSQBT)



13a; X=S
13b; X=Se



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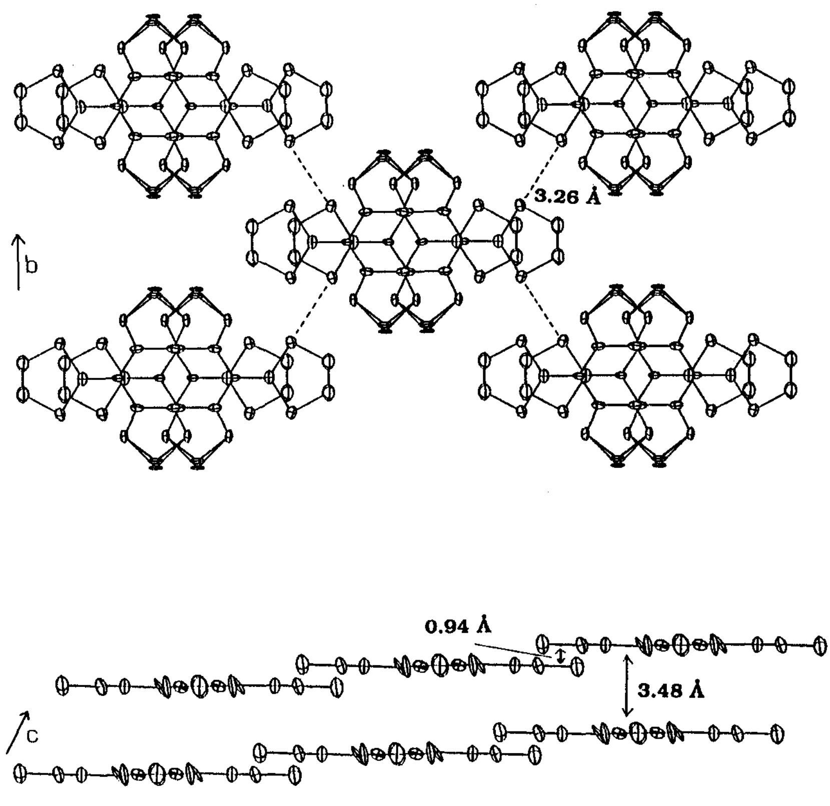

FIGURE 1 Crystal structure of **5a**.

Although usual organic compounds are insulators as single components, **5a,b** exhibited unusually high electrical conductivities. The conductivities of **5a,b** as compaction 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}). The single crystal of **5a** was obtained by sublimation,[8] although that of **5b** has not been successfully obtained yet. The conductivity of the single crystal was 5.6×10^{-5} S cm^{-1}, while that of BTQBT similarly obtained was 1.0×10^{-5} S cm^{-1}.

In order to investigate the effects of substitution of the selenium atom for the sulfur atom, the X-ray structural analysis for **5a** was carried out.[9] The crystal data show that **5a** crystallizes isomorphously with **3**, and the sulfur and selenium atoms in **5a** are disordered in the crystal. The molecule is planar and the intramolecular distance between the S of the dithiole and the N of the heterocycle (2.72 Å) is significantly shorter that the sum of the van der Waals distance (3.35 Å). The molecules form a sheet-like network by short S---S contacts (3.26 Å) as shown in Figure 1. The sheet is overlapped with the intermolecular distance of 3.48 Å according to the manner shown in Figure 1. The higher conductivity of **5a** than BTQBT **3** may be attributed to the larger polarizability of selenium atom, which can increase the intermolecular interaction along the stack.

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6. Decomposition points. **4a**; 280 °C, **4b**; 308-310 °C, **4c**, 288-290 °C, **4d**; 385-388 °C.
7. We thank Dr. Kenichi Imaeda for providing the measurement of the conductivity of the single crystal.
8. The single crystal was prepared by Prof. Mizuka Sano of International Christian University. We thank him for the preparation.
9. Crystal data for **5a**: $C_{12}H_4N_4S_5Se$, MW=443.45, monoclinic space group C2/m, a=16.244(19), b=11.169(19), c=3.848(3) Å, β=96.75(9), V=693.3(15), Z=2, D_{calcd}=2.12 g cm^{-3}. The final R value is 12.80% for 596 reflections with $|Fo|>3\sigma|Fo|$.