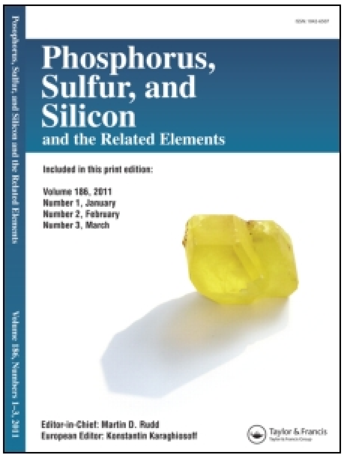

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# Electron Donors for Organic Conductors. Alkylenedithio Derivatives of 1,3-Bis(1,3-dithiol-2-ylidene)-1,3-dihydrobenzo[c]selenophene

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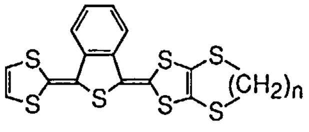
Methylene-, ethylene-, and propylenedithio derivatives of 1,3-bis(1,3-dithiol-2-ylidene)-1,3-dihydrobenzo[c]selenophene, MDT-, EDT-, and PDT-BDTBS have been synthesized. TCNQ complexes of MDT- and EDT-BDTBS showed fairly high conductivities and small activation energies even when measured on compressed pellets.

## INTRODUCTION

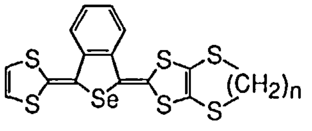
In order to develop new organic conductors based on novel heterocycle-extended donors, we have recently synthesized alkylenedithio derivatives of benzo[c]thienoquinoid-extended donors, **1**—**3**,[1] but single crystals of the donors and their complexes have not been obtained so far. The crystal growth and the intermolecular interaction in single crystals will be much improved by replacing the central sulfur atom embedded in the BDTBT derivatives with a selenium atom, since the diffused *p*-orbitals of the selenium atom may enhance the mutual intermolecular contacts. To this end, we have now synthesized new donors, MDT-BDTBS (**4**), EDT-BDTBS (**5**), and PDT-BDTBS (**6**), and investigated electric properties of their TCNQ complexes, and clarified the X-ray crystal structure of **7**, the diester derivative of **5**, which are reported herein.

## RESULT AND DISCUSSION

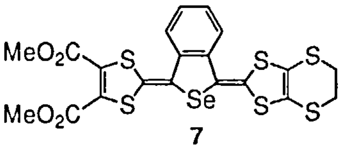
The new donors **4**—**6** were synthesized in good yields starting from selenophthalic anhydride and 1,3-dithiol-2-thione derivatives. The oxidation of **4**—**6** occurred in reversible two-step one-electron process in cyclic voltammetry. The $E_1^{ox}$ values of **4**—**6** (Table I) are higher by 0.06—0.03 V than those of the corresponding BDTBT derivatives **1**—**3**,[1] which can be ascribed to the fact that cation radicals of **4**—**6** acquire less stabilization energy than those of the cation radicals of **1**—**3**, since benzo[c]selenophene is less aromatic than benzo[c]thiophene. New donors **4**—**6** formed charge-transfer (CT) complexes with TCNQ, whose electric conductivities on compressed samples are fairly high (Table I). All the complexes possess a segregated stacking mode in a mixed valence



1 : MDT-BDTBT : n = 1
2 : EDT-BDTBT : n = 2
3 : PDT-BDTBT : n = 3



4 : MDT-BDTBS : n = 1
5 : EDT-BDTBS : n = 2
6 : PDT-BDTBS : n = 3



7

state, since they showed a very broad intra-stack CT absorption band at around 3000 cm$^{-1}$ in the solid state electronic spectra (Table I). Interestingly, the conductivity of the TCNQ complex of **6** is 7.6 times higher than that of the TCNQ complex of **3**,[1] suggesting that the intermolecular orbital overlap is enhanced by the diffused *p*-orbitals of the selenium atom of **6**. The temperature dependence of the conductivity shows that the powdered complexes of **4** and **5** are semiconductors, but with fairly low activation energies (Table I).

TABLE I
Physical properties of new donors and their TCNQ complexes

| Donor | Electrochemical property$^a$ | | | $\sigma_{RT}{}^b$, $E_a$,$^b$ and $\nu_{CT}$ of the complex | | | |
|---|---|---|---|---|---|---|---|
| | $E_1{}^{ox}$ | $E_2{}^{ox}$ | $\log K_{sem}$ | D : A | $\sigma_{RT}$ /Scm$^{-1}$ | $E_a$ | $\nu_{CT}$ /cm$^{-1}$ |
| **4** | +0.42 | +0.61 | 3.22 | 2 : 1 | 1.2 | 0.066 | 3000 (br) |
| **5** | +0.43 | +0.63 | 3.39 | 2 : 1 | 2.4 | 0.052 | 3000 (br) |
| **6** | +0.40 | +0.62 | 3.73 | 3 : 2 | 0.32 | — | 3000 (br) |
| **3** | +0.37 | +0.58 | 3.56 | 2 : 1 | $4.2 \times 10^{-2}$ | — | 3000 (br) |

a Potentials are given in V *vs*. SCE in PhCN with TBAP. b Four-probe method on a compaction pellet.

We have succeeded in preparing a single crystal of **7**, bismethoxycarbonyl derivative of **5**. The X-ray crystallographic analysis revealed that the diester **7** is an essentially planar molecule and stacks uniformly along the *b*-axis (Figure 1). The overlapping mode is so called ring-over-bond type (Figure 2) inducing a good intra-stack HOMO-HOMO interaction with an interplanar distance of 3.6 Å. These studies bring much expectation that cation radical salts of **4**—**6** might exhibit high conductivities on a single crystal.

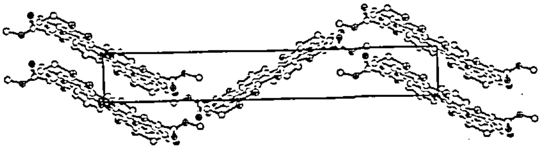


FIGURE 1 Crystal structure of **7**, viewed along the *a*-axis.

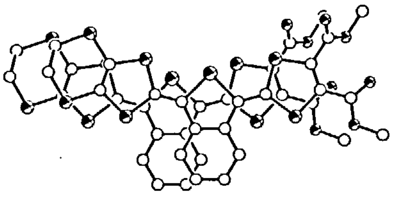


FIGURE 2 Overlapping mode of **7**.

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