Structure and Electrochemical Property of Novel 1,4-Diselenins

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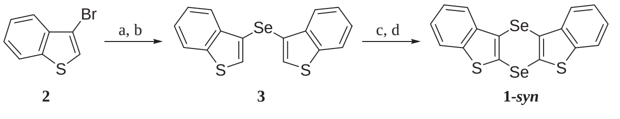
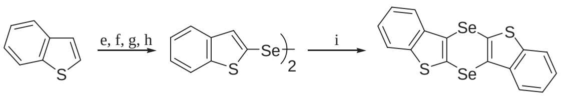
Novel isomeric 1,4-diselenins constituted of five rings showed well-defined intermolecular interactions, π–π and Ch–Ch contacts, in crystals. Investigation of electrochemical properties for 1,4-diselenins revealed unusual redox properties by CV measurements.

π-Conjugate organic hydrocarbons are the focus of much attention from the viewpoint of material science and technology.[1] In recent years, heteroatom-containing π-conjugate organic molecules also have been reported in the fields of organic synthesis, structure, property, and application. Recently, we reported the oxidation properties of isomeric 1,4-dithiins fused to two benzo[*b*]thiophenes which have five rings in a similar manner as pentacene analogues.[2] Although these 1,4-dithiins possessed well-defined reversibility and low oxidation potentials by CV measurements, they have less intermolecular interactions in the crystal lattice. Thus, we designed novel 1,4-diselenins expecting their low oxidation property and the enlargement of overlap integral compared with sulfur analogues. In this paper, we report the synthesis, structure, and oxidation property of novel 1,4-diselenins fused to two benzo[*b*]thiophenes which have five rings including four aromatics.

1,4-Diselenin **1-*syn*** was obtained according to a selective synthetic method from bis(3-benzo[*b*]thienyl) selenide (**3**). Selenide **3** was prepared from 3-bromobenzo[*b*]thiophene (**2**)[2,3] by halogen–metal exchange reaction and chalcogenation with $SeCl_4$.[4] Formation of the 1,4-diselenin ring was carried out by the reaction of selenide **3** with *t*-butyllithium and $SeOCl_2$ in Et_2O at −30 °C, to give the desired 1,4-diselenin **1-*syn*** in 9% yield as colorless needles (Scheme 1).[5] 1,4-Diselenin **1-*anti*** was prepared by recrystallization of a mixture of isomeric 1,4-diselenins, **1-*syn*** and **1-*anti*** obtained as follows. Bis(2-benzo[*b*]thienyl) diselenide (**5**) was synthesized in 50% yield from 2-lithiated benzo[*b*]thiophene with elemental selenium, followed by reduction using $LiAlH_4$, oxidation using O_2.[6] Surprisingly, treatment of **2** and **5** in the presence of CuI and KOH in DMF at 130 °C gave the mixture of 1,4-diselenins, **1-*syn*** and **1-*anti***. The reaction mechanisms may include deprotonation of benzo[*b*]thiophene at 3-position and Smiles rearrangement, however, those are not clear. 1,4-Diselenin **1-*anti*** was isolated from the mixture by recrystallization with CH_2Cl_2 in 3% yield as colorless needles (Scheme 2).[7]



Scheme 1. Reagents: a) BuLi, Et_2O, −40 °C, 1 h; b) $SeCl_4$, THF, rt, 1 h; c) ^{t}BuLi, Et_2O, −30 °C, 1 h; d) $SeOCl_2$, rt, 17 h.



Scheme 2. Reagents: e) BuLi, Et_2O, −30 °C, 3 h; f) Se, THF, rt, 18 h; g) $LiAlH_4$, THF, rt, 2 h; h) O_2, rt, 4 h; i) CuI, KOH, **2**, DMF, 130 °C, 38 h.

X-ray crystallographic analyses of 1,4-diselenins revealed the differences of intermolecular interactions on comparing with 1,4-dithiins, bis(benzo[*b*]thieno)[2,3-*b*:3′,2′-*e*][1,4]dithiin (**6-*syn***) and bis(benzo[*b*]thieno)[2,3-*b*:2′,3′-*e*][1,4]dithiin (**6-*anti***) in the crystal lattice. The structures of diselenins having benzo[*b*]thiophene moieties, **1-*syn*** and **1-*anti***, were determined by X-ray crystallographic analyses (Figure 1).[8] The 1,4-diselenin rings of **1-*syn*** and **1-*anti*** were nearly similar in terms of bond lengths and angles. The packing structures of diselenins showed the same arrangement for those of **6**, respectively. The C–Ch bond lengthened in the dichalcogenin ring and butterfly angles were narrowed with increase of intramolecular Se–Se distance (123.70(5)° for **1-*syn*** and 125.809(15)° for **1-*anti***, 128.808(52)° for **6-*syn*** and 129.574(9)° for **6-*anti***).

Crystal packing (Figure 2) showed Ch–Ch contacts in **1-*anti***, Se–S and Se–Se, in comparison with the case of **6-*anti***. Distances of Ch–Ch contacts were observed as 3.6270(5) Å for S–Se, 3.7016(4) Å for Se–Se; sum of van der Waals radii is 3.70 Å for S–Se and 3.80 Å for Se–Se. Intermolecular distances for π–π stacks were 3.443–3.574 Å for **1-*syn*** and 3.500–3.548 Å for **1-*anti*** (Figure 3). Minima of C–C intermolecular distances were 3.512(9) Å for **1-*syn*** and 3.570(3) Å for **1-*anti***, which were slightly longer than the sum of van der Waals radii of C–C (3.40 Å), but slightly shorter than those of pentacene C–C contacts (3.64 Å).[9] Distances between Se atoms of the stacked molecules were 4.0117(7) Å for **1-*syn*** and 3.9685(3) Å for **1-*anti***. These distances were elongated by the bent structure

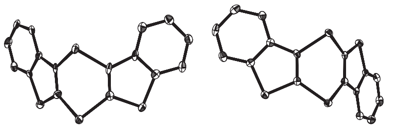


Figure 1. ORTEP drawings of **1-*syn*** and **1-*anti***.

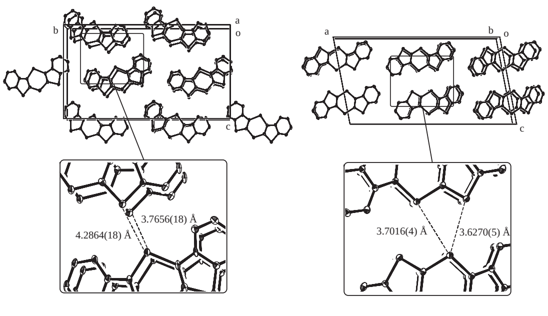


Figure 2. Packing structure of **1-*syn*** and **1-*anti***.

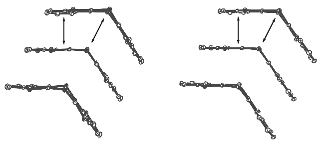


Figure 3. π–π distances of **1-*syn*** (left) and **1-*anti*** (right).

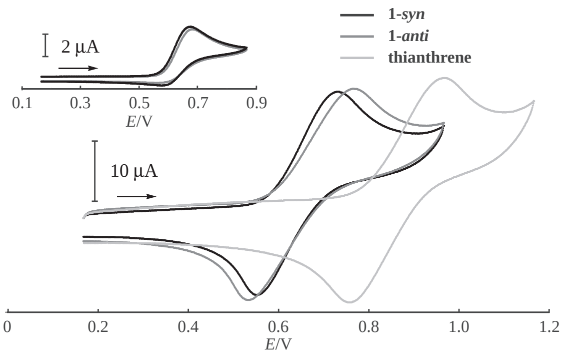


Figure 4. Cyclic voltammograms of **1-*syn***, **1-*anti***, and thianthrene. Scan rates were 5 and 0.1 (inset) V s^{-1}.

Table 1. Redox potentials [V] of diselenins and dithiins

	1-*syn*	**1-*anti***	Thianthrene	**6-*syn***	**6-*anti***
E_{pa}^{a}	0.73	0.77	0.97	0.69	0.69
E_{pc}^{a}	0.55	0.53	0.76	0.49	0.48
$E_{1/2}$^{a}	0.64	0.65	0.86	0.59	0.59
E_{pa}^{b}	0.69	0.69	0.90	0.66	0.65
E_{pc}^{b}	—	—	0.82	0.55	0.55
$E_{1/2}$^{b}	—	—	0.86	0.61	0.60

^{a}5 V s^{-1} as scan rate. ^{b}0.1 V s^{-1} as scan rate.

due probably in part to the greater repulsion between Se atoms than that of the usual π–π stack.

Redox properties of diselenins were measured using the cyclic voltammetry method; as a result, diselenins **1** showed irreversible waves with slow scan rates (Figure 4, inset). These findings indicate that diselenins **1** are less stable in their oxidation state as against the high reversibility of **6**. However, on measurement with 5 V s^{-1} scan rates, redox waves of **1** showed well-defined reversible peaks (Figure 4).

All peak potentials and redox half-wave potentials are summarized in Table 1.[10] The values of half-wave potentials of **1-*syn*** and **1-*anti*** were close similarly to those of dithiins **6-*syn*** and **6-*anti***. Interestingly, in comparison of half-wave potentials of **1** and **6**, in spite of the introduction of selenium atoms with low ionization potential, $E_{1/2}$ of diselenins **1** was slightly higher than those of dithiins **6**. These results suggest that the oxidation processes of 1,4-dichalcogenins fused to two benzo[*b*]thiophenes are involved in conjugation with chalcogen atoms in the 1,4-dichalcogenin ring and benzo[*b*]thiophene units.[11] Actually, HOMOs were spread on the whole of the molecule.[12]

In summary, we were able to show that 1,4-diselenins fused to two benzo[*b*]thiophenes possess two-dimensional intermolecular interaction in the single-crystal and unusual redox property.

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References and Notes

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4 **3**; bis(3-benzo[*b*]thienyl) selenide: Colorless crystal; mp 72.5–73.0 °C; ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.35 (dd, 2H, $J = 7.3$, 7.3 Hz, ArH), 7.39 (dd, 2H, $J = 7.5$, 7.5 Hz, ArH), 7.43 (s, 2H, ArH), 7.84 (dd, 2H, $J = 1.2$, 7.2 Hz, ArH), 7.92 (dd, 2H, $J = 1.2$, 7.1 Hz, ArH); ^{13}C NMR (101 MHz, CDCl$_3$) δ 119.3, 122.7, 123.5, 124.7, 124.8, 129.3, 139.5, 139.9; IR (KBr) ν 725, 754, 814, 1061, 1251, 1417 cm^{-1}; MS (70 eV) m/z 346 (M$^+$); Anal. Calcd for $C_{16}H_{10}S_2Se$: C, 55.65; H, 2.92%. Found: C, 55.46; H, 3.16%.

5 **1-*syn***; Bis(benzo[*b*]thieno)[2,3-*b*:3′,2′-*e*][1,4]diselenin: Colorless needles; mp 220.0–221.0 °C; ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.33 (dd, 2H, $J = 7.6$, 7.6 Hz, ArH), 7.41 (dd, 2H, $J = 7.3$, 7.3 Hz, ArH), 7.76 (d, 2H, $J = 7.8$ Hz, ArH), 7.81 (d, 2H, $J = 7.8$ Hz, ArH); ^{13}C NMR (101 MHz, CDCl$_3$) δ 122.26, 122.30, 124.9, 125.0, 125.9, 127.0, 138.4, 142.9; IR (KBr) ν 720, 743, 1247, 1419 cm^{-1}; HRMS Calcd for $C_{16}H_8S_2Se_2$ (M$^+$): 423.8399. Found (M$^+$): 423.8396.

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7 **1-*anti***; Bis(benzo[*b*]thieno)[2,3-*b*:2′,3′-*e*][1,4]diselenin: Colorless needles; mp 243.0–243.5 °C; ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.34 (dd, 2H, $J = 7.6$, 7.6 Hz, ArH), 7.41 (dd, 2H, $J = 7.5$, 7.5 Hz, ArH), 7.74 (d, 2H, $J = 8.0$ Hz, ArH), 7.77 (d, 2H, $J = 8.0$ Hz, ArH); ^{13}C NMR (101 MHz, CDCl$_3$) δ 122.0, 122.3, 124.8, 124.9, 125.6, 127.7, 138.3, 142.9; IR (KBr) ν 718, 740, 1247, 1416 cm^{-1}; HRMS Calcd for $C_{16}H_8S_2Se_2$ (M$^+$): 423.8399. Found (M$^+$): 423.8404.

8 Crystal data for **1-*syn***: $M = 422.26$, $C_{16}H_8S_2Se_2$, monoclinic, space group *Cc* (#9), $a = 4.0117(9)$ Å, $b = 24.806(9)$ Å, $c = 13.960(3)$ Å, $\beta = 95.560(12)°$, $V = 1382.7(7)$ Å^3, $Z = 4$, $D_{calcd} = 2.028$ g cm^{-3}. A colorless needle crystal of dimensions $0.60 \times 0.02 \times 0.02$ mm^3 was used for measurement at 123 K. The final cycle of full-matrix least-squares refinement was based on 2865 observed reflections and 181 variable parameters with $R_1 = 0.0407$, $wR_2 = 0.0720$ (all data) (CCDC-299107). Crystal data for **1-*anti***: $M = 211.14$, C_8H_4SSe, monoclinic, space group *C*2/*c* (#15), $a = 25.710(8)$ Å, $b = 3.9685(11)$ Å, $c = 13.698(4)$ Å, $\beta = 100.94(2)°$, $V = 1372.2(7)$ Å^3, $Z = 8$, $D_{calcd} = 2.044$ g cm^{-3}. A colorless needle crystal of dimensions $1.00 \times 0.06 \times 0.02$ mm^3 was used for measurement at 123 K. The final cycle of full-matrix least-squares refinement was based on 1571 observed reflections and 107 variable parameters with $R_1 = 0.0241$, $wR_2 = 0.0372$ (all data) (CCDC-299106). Copies of the data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge, CB2 1EZ, UK; Fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk).

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10 Cyclic voltammograms of dichalcogenins were measured in 2.0 mM concentration benzonitrile containing 0.1 M ^{n}Bu$_4$NClO$_4$ as a supporting electrolyte using a glassy-carbon working electrode, Pt counter electrode, and Ag/0.01 M AgNO$_3$ in the electrolyte solution as a reference electrode.

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12 Calculations were carried out with Gaussian 98 program using B3LYP/6-311+G(d,p)//B3LYP/6-31G(d).

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