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Selective synthesis, structure and oxidation properties of isomeric 1,4-dithiins fused to two benzo[*b*]thiophenes

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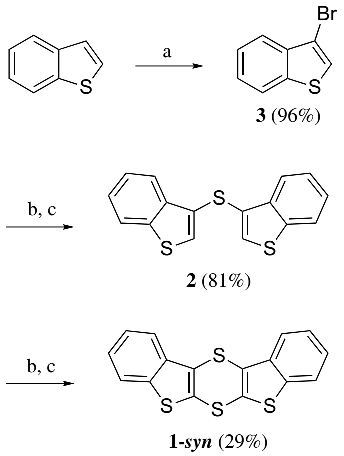
Abstract—Two novel isomers of 1,4-dithiins fused to two benzo[*b*]thiophenes on both sides were obtained by selective synthetic methods via the corresponding sulfides. The crystal structures of two dithiins were determined by X-ray crystallographic analyses. Examination of oxidation properties of the dithiins showed interesting results by CV measurement. The ESR spectra of chemically oxidized dithiins indicated formation of stable radical cations.

Organic field-effect transistors (OFETs) are the focus of much attention from the viewpoints of material science and technology.[1] It is well known that polyacene analogs, especially pentacene, have great mobility as carriers.[2] Although some polyaromatic compounds such as pentacene, tetracene, and anthracene have been currently studied, the importance of the criterion factor is not clear, therefore, ultimate success for manufacture of OFETs will require establishment of a new building block.[3] In this paper, we report the syntheses, characterization, and oxidation properties of two novel 1,4-dithiins, **1-*syn*** and **1-*anti*** as pentacene analogs[4], which consisted of the parent 1,4-dithiin with two benzo[*b*]thiophenes on both sides (Schemes 1 and 2). These structures were determined by X-ray crystallography. The oxidized compounds, radical cation, and dication, as well as neutral sulfur-rich pseudo-heteropentacene **1-*syn*** and **1-*anti*** are interesting from the standpoint of organic semiconductors. The dithiins were characterized by cyclic voltammetry and measurement of electron spin resonance.



Scheme 1. Reagents: (a) Br_2, CH_2Cl_2; (b) ^{n}BuLi, Et_2O; (c) SCl_2, Et_2O.

The syntheses of two isomers of 1,4-dithiins, **1-*syn*** and **1-*anti***, were established according to selective synthetic methods. Typical synthetic procedure of the symmetrical sulfide **2** is as follows (Scheme 1). After bromination of benzo[*b*]thiophene with bromine, the resulting 3-bromobenzo[*b*]thiophene (**3**) was converted to the corresponding sulfide **2** by halogen–metal exchange reaction and treatment of SCl_2. Formation of the 1,4-dithiin ring was carried out by the reaction of sulfide **2** with butyllithium following SCl_2 in Et_2O at −30 °C, to give the desired 1,4-dithiin **1-*syn*** in 29% yield as colorless needles.[5] Asymmetrical sulfide, 2,3′-bis(benzo[*b*]thienyl)sulfide (**4**)[6,7] was obtained by treating 2-mercaptobenzo[*b*]thiophene (**5**) with 3-bromobenzo[*b*]thiophene (**3**) in the presence of potassium hydroxide and cuprous iodide in dimethylformamide in 84% yield (Scheme 2). The desired 1,4-dithiin **1-*anti*** was obtained by lithiation of sulfide **4** with *tert*-butyllithium following thiolation using

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Keywords: 1,4-Dithiin; Benzo[*b*]thiophene; Cyclic voltammetry; Radical cation; ESR spectrum.

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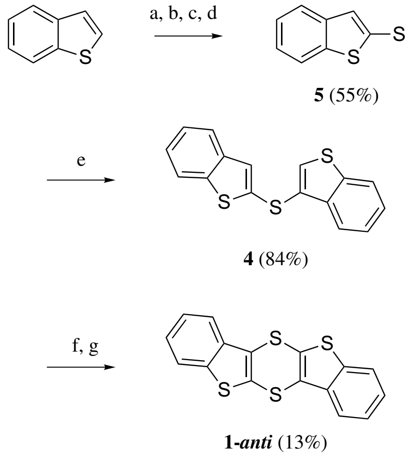

Scheme 2. Reagents: (a) ^{n}BuLi, Et$_2$O; (b) S$_8$; (c) NaBH$_4$, THF; (d) H$_3$O$^+$; (e) **3**, CuI, KOH, DMF; (f) ^{t}BuLi, Et$_2$O; (g) (PhSO$_2$)$_2$S, THF.

bis(phenylsulfonyl)sulfide in 13% yield as colorless crystal.[8]

The structures of the new type of two dithiins having benzothiophene moieties, **1-*syn***[9] (Fig. 1) and **1-*anti***[10] (Fig. 2), were determined by X-ray crystallographic analyses. The space groups of the two isomers, **1-*syn*** and **1-*anti***, were *Cc* and *C*2/*c*, respectively. Accordingly, two benzothiophene rings in **1-*syn*** have a distorted structure bending to the dithiin S–S axis. On the other hand, two benzothiophenes of **1-*anti*** did not show a distorted structure. The bond lengths and angles in the 1,4-dithiin rings were nearly similar to those of the known compounds.[11] We observed a little difference in the packing structures of **1-*syn*** (Fig. 3) and **1-*anti*** (Fig. 4). There were no intermolecular contacts, sulfur–sulfur and π–π interaction since interatomic sulfur–sulfur distances in the stacking of **1-*syn*** and **1-*anti*** were 3.90 and 3.88 Å, respectively.

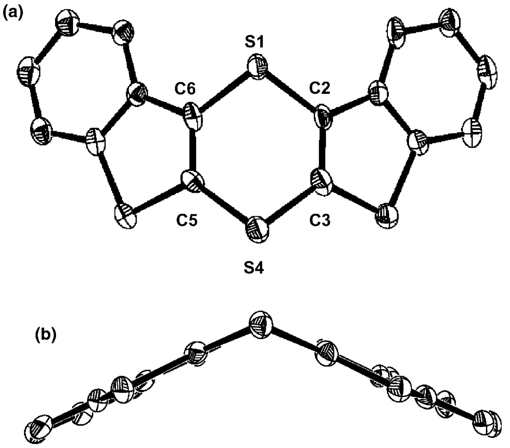

Figure 1. (a) ORTEP drawing of **1-*syn***. All hydrogens are omitted. Selected bond lengths (Å) and bond angles (°): S1–C2 1.782 (6), C2–C3 1.354 (9), C3–S4 1.759 (6), S4–C5 1.754 (6), C5–C6 1.350 (8), C6–S1 1.768 (6), S1–C2–C3 122.7 (4), C2–C3–S4 125.3 (5), C3–S4–C5 97.4 (3), S4–C5–C6 126.1 (4), C5–C6–S1 122.4 (5), C6–S1–C2 97.9 (3). (b) Side view of **1-*syn***. All hydrogens are omitted.

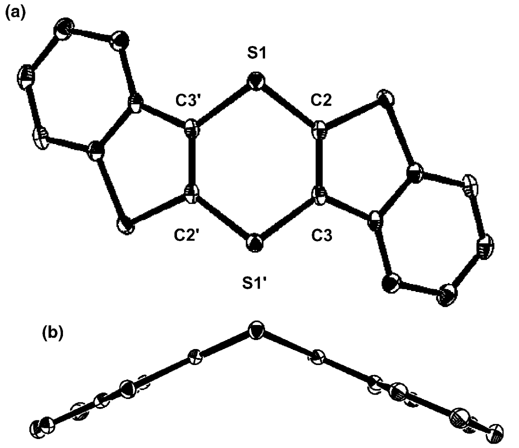

Figure 2. (a) ORTEP drawing of **1-*anti***. All hydrogens are omitted. Selected bond lengths (Å) and bond angles (°): S1–C2 1.753 (1), C2–C3 1.360 (2), C3–S1′ 1.763 (1), S1–C2–C3 125.5 (1), C2–C3–S1′ 123.1 (1), C3–S1′–C2′ 97.82 (5). (b) Side view of **1-*anti***. All hydrogens are omitted.

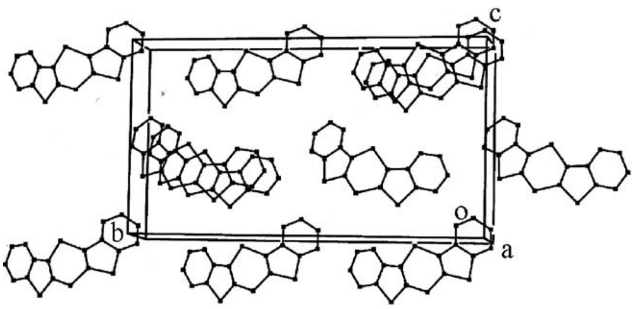

Figure 3. Packing structure of **1-*syn***. All hydrogens are omitted.

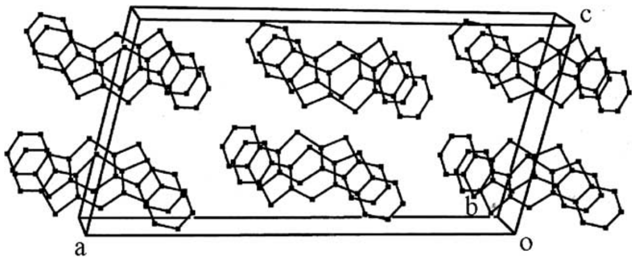

Figure 4. Packing structure of **1-*anti***. All hydrogens are omitted.

Cyclic voltammograms of **1-*syn*** and **1-*anti*** as shown in Figure 5 indicated four similar oxidation peaks in the range of 0–1.6 V, E_{pa} = ca. 0.65, 1.12, 1.28, 1.55 V (potentials were summarized in Table 1), in benzonitrile versus Ag/0.01 mol dm^{-3} AgNO$_3$.[12] The first peaks of both in **1-*syn*** and **1-*anti*** were found to show a couplet with reduction peaks. Interestingly, the first peaks showed well-defined reversible redox couples in the

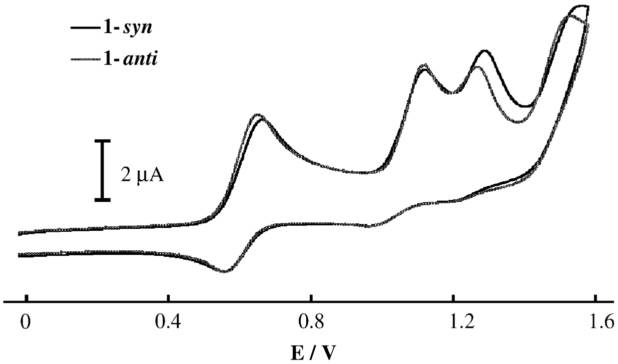

Figure 5. Cyclic voltammograms of **1-*syn*** and **1-*anti***.

Table 1. E_{pa}, E_{pc} values [V] of **1-*syn*** and **1-*anti***

	1-*syn*	**1-*anti***
E^1_{pa}	0.66	0.65
E^1_{pc}	0.56	0.56
E^2_{pa}	1.12	1.12
E^2_{pc}	—	—
E^3_{pa}	1.29	1.27
E^3_{pc}	—	—
E^4_{pa}	1.58	1.53
E^4_{pc}	—	—

range of 0–0.9 V as shown in Figure 6 and low half-wave potentials (Table 2; 0.61 V for **1-*syn*** and 0.60 V for **1-*anti***) compared with that of thianthrene (0.86 V).

The ESR spectra of chemically oxidized 1,4-dithiins were measured for clarification of the generated oxidation species in the first peaks. When **1-*syn*** or **1-*anti*** was treated with 1 equivalent of $NOPF_6$ in THF at −78 °C, the color of the reaction solution changed into deep blue. After evaporation of the solvents the residues were dissolved in CH_3CN. The ESR spectra of the dithiins in CH_3CN showed broad singlet peaks ($g = 2.0073$ for **1-*syn***, $g = 2.0072$ for **1-*anti***).[13] These results suggest that the first oxidation couplets of 1,4-dithiins in electrochemical oxidation correspond to the generation of stable radical cations.

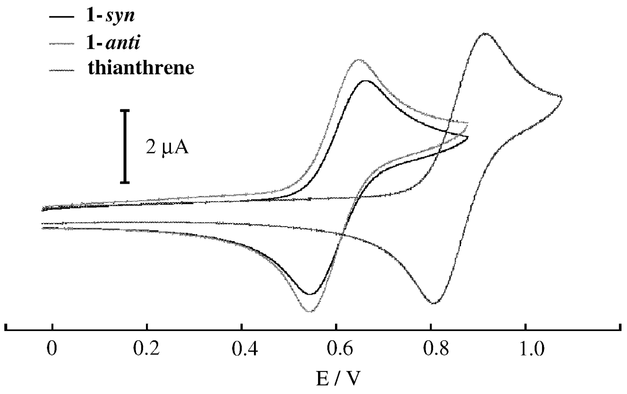

Figure 6. Cyclic voltammograms of **1-*syn***, **1-*anti*** and thianthrene.

Table 2. Redox potentials [V] of **1-*syn***, **1-*anti***, and thianthrene

	1-*syn*	**1-*anti***	Thianthrene
E_{pa}	0.66	0.65	0.92
E_{pc}	0.55	0.55	0.81
$E_{1/2}$	0.61	0.60	0.86

In summary, we have succeeded in the synthesis, structural characterization, and examination of redox properties of 1,4-dithiins fused to two benzo[*b*]thiophenes, **1-*syn*** and **1-*anti***. The molecules showed interesting redox properties, reversible peaks, and low first oxidation potential by CV measurement. Further studies on the properties of **1-*syn*** and **1-*anti*** are in progress in our laboratory.

Acknowledgements

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5. Selected data for **1-*syn***: colorless crystals; mp 195.0–196.0 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (t, 2H, $J = 7.8$ Hz, ArH), 7.41 (t, 2H, $J = 7.8$ Hz, ArH), 7.71 (d, 2H, $J = 7.8$ Hz, ArH), 7.76 (d, 2H, $J = 7.8$ Hz, ArH); ^{13}C NMR (101 MHz, $CDCl_3$) δ 120.9, 122.5, 125.0, 125.1, 126.4, 129.9, 136.5, 141.0; IR (KBr) ν 1423, 1314, 1250, 744, 720 cm^{-1}; MS (70 eV) *m*/*z* 328 (M$^+$); Anal. Calcd for $C_{16}H_8S_4$: C, 58.50; H, 2.45. Found: C, 58.18; H, 2.78.
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8. Selected data for **1-*anti***: colorless crystals; mp 207.0–208.3 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (t, 2H, $J = 7.4$ Hz, ArH), 7.41 (t, 2H, $J = 7.4$ Hz, ArH), 7.69 (d, 2H, $J = 7.9$ Hz, ArH), 7.73 (d, 2H, $J = 8.0$ Hz, ArH); ^{13}C NMR (101 MHz, $CDCl_3$) δ 120.6, 122.5, 124.9, 125.0, 125.7, 131.3,136.3, 140.9; IR (KBr) ν 1478, 1454, 1419, 1251, 1018, 910, 741, 718 cm^{-1}; MS (70 eV) *m*/*z* 328 (M$^+$); Anal. Calcd for $C_{16}H_8S_4$: C, 58.50; H, 2.45. Found: C, 58.48; H, 2.57.

9. Crystal data for **1-*syn***: $M = 328.48$, $C_{16}H_8S_4$, monoclinic, space group *Cc* (#9), $a = 3.904(2)$ Å, $b = 24.83(1)$ Å, $c = 13.931(7)$ Å, $\beta = 94.65(4)$ Å, $V = 1345(1)$ Å^3, $Z = 4$, $D_{\text{calc}} = 1.621\,\text{g cm}^{-3}$. A colorless plate crystal of dimensions 0.40 × 0.20 × 0.04 mm was used for measurement at 123 K on Rigaku R-AXIS RAPID diffractometer employing Mo Kα ($\lambda = 0.71075$ Å) radiation. The structure was solved by direct methods (SIR97) and expanded using Fourier technique (DIRDIF-99). All calculations were performed using the CrystalStructure 3.5.1 crystal structure analysis package of Rigaku and Rigaku/MSC. The final cycle of full-matrix least-squares refinement was based on 2174 observed reflections ($I > 2.00\sigma(I)$) and 215 variable parameters with $R_1 = 0.046$, $wR_2 = 0.115$ (all data) (CCDC 242426). SIR97; Altomare, A.; Burla, M.; Camalli, M.; Cascarano, G.; Giacovazzo, C.; Guagliardi, A.; Moliterni, A.; Polidori, G.; Spagna, R. *J. Appl. Crystallogr.* **1999**, *32*, 115–119. DIRDIF-99 Beurskens, P. T.; Admiraal, G.; Beurskens, G.; Bosman, W. P.; de Gelder, R.; Israel, R.; Smits, J. M. M. The DIRDIF-99 program system, Technical Report of the Crystallography Laboratory, University of Nijmegen, The Netherlands, 1999.
10. Crystal data for **1-*anti***: $M = 328.48$, $C_{16}H_8S_4$, monoclinic, space group *C2/c* (#15), $a = 25.862(2)$ Å, $b = 3.8788(3)$ Å, $c = 13.481(1)$ Å, $\beta = 101.261(5)$ Å, $V = 1326.3(2)$ Å^3, $Z = 4$, $D_{\text{calc}} = 1.645\,\text{g cm}^{-3}$. A colorless needle crystal of dimensions 0.20 × 0.15 × 0.40 mm was used for measurement at 123 K. The structure was solved by the same methods of **1-*syn***. The final cycle of full-matrix least-squares refinement was based on 1503 observed reflections ($I > 2.00\sigma(I)$) and 107 variable parameters with $R_1 = 0.022$, $wR_2 = 0.071$ (all data) (CCDC 242427).
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12. Cyclic voltammograms of **1-*syn***, **1-*anti***, and thianthrene were measured in $2.0\,\text{mmol dm}^{-3}$ concentration benzonitrile at rt containing $0.1\,\text{mol dm}^{-3}$ $^n\text{Bu}_4\text{NClO}_4$ as a supporting electrolyte using a grassy-carbon working electrode and Ag/$0.01\,\text{mol dm}^{-3}\text{AgNO}_3$ in the electrolyte solution as a reference electrode; scan rate was $100\,\text{mV s}^{-1}$.
13. The ESR data were taken in a JEOL RE 2XG spectrometer working in the X-band as CH_3CN solution with Mn^{2+} on MgO as field markers.