Bis(ethylenedioxy)-1,4,5,8-tetraselenanaphthalene: The First Example of Tetraselenanaphthalene

Ryoji Watanabe, Yoshihiro Miyake, Yoshiyuki Kuwatani, and Masahiko Iyoda*

Department of Chemistry, Graduate School of Science, Tokyo Metropolitan University, Hachioji, Tokyo 192-0397

The titled tetraselenanaphthalene derivative (BEDO-TSeN) has been synthesized using the reaction of 1,4-dioxene-2,3-diselenolate with tetraiodo- or tetrabromoethylene. The structure of this tetraselenanaphthalene derivative was confirmed by X-ray analysis. The π-donor property of this molecule was determined by CV analysis.

There has been considerable current interest in tetrathianaphthalene **1**, because of its ability to act as an electron donor in pairs of the charge transfer complexes,[1] and because of its isomerization to tetrathiafulvalene by chemical or electrochemical oxidation[1c] or under basic conditions.[2] Although tetraselenanaphthalene **2** and tetratelluranaphthalene **3** can be constructed by changing the chalcogen from sulfur to selenium and tellurium atoms, a cyclopenta-fused derivative of **3** was the sole known counterpart.[3] Thus, **2** and its derivative were hitherto unknown compounds.

In the course of our study on π-donors fused by a 1,4-dioxene ring,[4] we investigated the synthesis of the title compound (BEDO-TSeN **4**) containing two fused 1,4-dioxene rings. Since the ethylenedioxy unit in a π-donor system is known to play a role by increasing either the donor property (inductive and mesomeric effects) or the stacking ability (CH···O hydrogen bond), TTFs and oligothiophenes having ethylenedioxy substituents have been employed for designing highly conducting materials.[5,6]
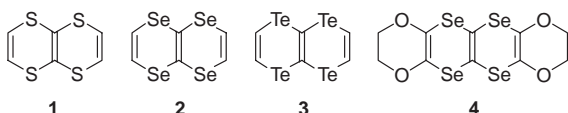
Before starting the synthesis of **4**, we planned to establish a new route to access the 2,3-dialkylseleno-1,4-dioxene system. As shown in Scheme 1, the reaction of 2,3-dibromodioxene **5**[7] with ^{t}BuLi (2 equiv.) at $-78\,^\circ$C, followed by treatment with selenium powder (1 equiv.) at $-20\,^\circ$C produced the monoselenolate **6**, which was reacted again with ^{t}BuLi (2 equiv.) at $-100\,^\circ$C, followed by treatment with Se powder (1 equiv.) at $-50\,^\circ$C to room temperature to form the diselenolate **7**. The reaction of **7** with MeI (excess) at $-78\,^\circ$C to room temperature afforded 2,3-dimethylseleno-1,4-dioxene **8** in 80% yield.[8] In a similar manner, the reaction of **7** with CH$_2$I$_2$ (1.2 equiv.) at $-78\,^\circ$C to room temperature for 3 days led to **9** in 22% yield. Since the reaction of **7** with thiophosgene (1.1 equiv.) produced **10**[9] in 45% yield, the low yield of **9** may be due to low CH$_2$I$_2$ reactivity. Taking into account the reactivity of **7** with alkyl halides, the reactions of **7** with tetrahalogenoethenes were carried out. The reaction of **7** with tetrachloroethene yielded no identified product, but a similar reaction of **7** with tetrabromoethene

afforded a trace amount of the desired **4**. Furthermore, treatment of **7** with tetraiodoethene resulted in the formation of **4** in 2% yield. Interestingly, the reaction of **7** with tetrabromoethene (0.4 equiv.) in the presence of LiCl (2 equiv.) produced **4** in 15% yield, although LiCl was not effective for the reactions of **7** with tetrachloro- and tetraiodoethylenes. It was reported that the reaction of dilithium 1,2-cyclopenteneditellurolate with tetrahalogenoethene in the presence of LiCl led to the production of a tetratellurafulvalene derivative.[10] However, a similar reaction of **7** with tetrahalogenoethene resulted in the formation of **4** selectively. The effect of LiCl might be explained by the enhanced reactivity of the monomeric **7** through the dissociation of aggregated species.
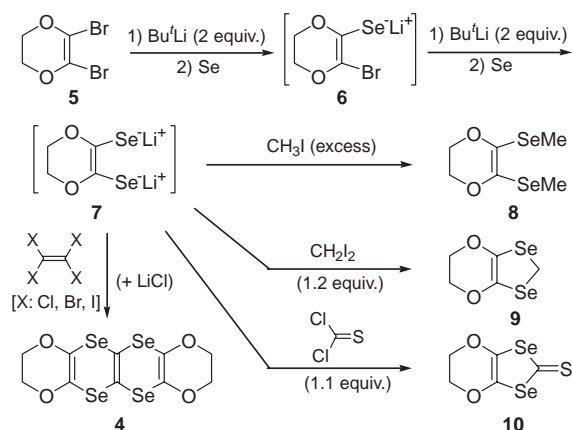
Scheme 1. Synthesis of **4** and **8–10** via **7**.

Recently, the synthesis and X-ray structural determination of bis(ethylenedioxy)tetraselenafulvalene (BEDO-TSeF) was reported.[11] Since BEDO-TSeF is a structural isomer of **4**, we confirmed the formation of **4** by X-ray analysis[12] and compared the structure with its sulfur and tellurium counterparts **1** and **3**. As shown in Figure 1a, **4** locates on a crystallographic center of symmetry, and the central Se$_2$C=CSe$_2$ unit is exactly planar. The neighboring OSeC=CSeO unit is also planar, and the maximum atomic deviation from the least-squares plane is 0.03 Å. However, the two 1,4-diselenin rings have a boat form, and the molecular structure of **4** adopts a non-planar, zigzag conformation. The dihedral angle between the Se$_2$C=CSe$_2$ and OSeC=CSeO units is 53° (Figure 1b). This structure is similar to those of **1** (dihedral angle, 49.7°)[1d] and **3** (dihedral angle of cyclopenta-fused derivative, 57.1°).[3a] The bond distances in the central 1,4,5,8-tetraselenanaphthalene and the outside 1,4-dioxene rings of **4** are normal. The molecule **4** stacks along the a-axis, and there are four intermolecular Se···Se contacts [Se(1)···Se(2) 3.6841(8) Å, Se(1)···Se(2)* 3.7598(7) Å, and
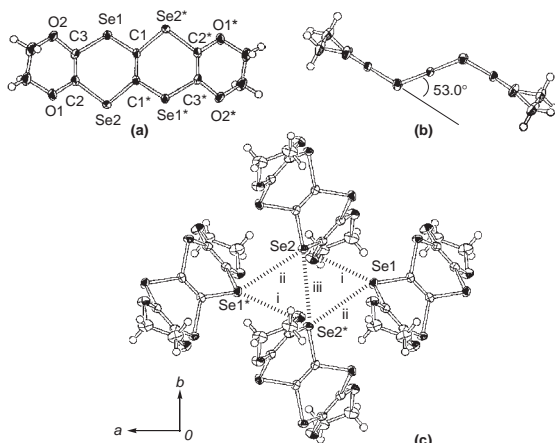
Figure 1. Crystal structure of **4**. (a) Top view. (b) Side view. (c) Crystal packing. Dotted lines indicate the three Se···Se short contacts (i, 3.6841(8), ii, 3.7598(7), and iii, 3.7583(8) Å. The Selected bond lengths (Å) and angles (°) are as follows: Se(1)–C(1) 1.901(4), Se(1)–C(3) 1.893(4), Se(2)–C(1)* 1.916(4), Se(2)–C(2) 1.902(4), O(1)–C(2) 1.373(5), O(2)–C(3) 1.380(5), C(1)–C(1)* 1.323(8), C(1)–Se(1)–C3 97.2(2), C(1)*–Se(2)–C(2) 98.1(2), Se(1)–C(1)–Se(2)* 113.7(2), Se(1)–C(1)–C(1)* 124.4(4).

Se(2)···Se(2)* 3.7583(8) Å], which are much shorter than the Se···Se van der Waals distance (4.00 Å) (Figure 1c).

As expected from the calculated HOMO level (-7.56 eV, HF/6-31G*), **4** exhibits oxidation potentials corresponding to the formation of its cation radical and dication. Thus, **4** shows two irreversible oxidation waves ($E_{pa}^1 = 0.62$ and $E_{pa}^2 = 0.95$ V vs Fc/Fc$^+$) in the cyclic voltammetric analysis (Figure 2). The oxidation potentials are comparable to **1** and the cyclopenta-fused derivative of **3** but seem to be higher than those of 1,4-dithiins,[13] presumably due to the non-planar, zigzag structure of **4** as shown in Figure 1b.
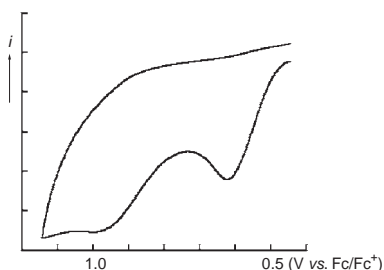

Figure 2. Cyclic voltammogram of **4** (0.1 M Bu$_4$NClO$_4$, PhCN, Pt working and counter electrodes, Ag/Ag$^+$ reference electrode, 50 mV·s^{-1}, rt). The potentials were measured against an Ag/Ag$^+$ electrode and converted to the values vs Fc/Fc$^+$.

Polyacenes and their hetero-analogues have recently received considerable attention,[14] because of their potential utility as organic field-effect transistor (OFET) materials. Studies on the properties and applications of tetraselenanaphthalenes are now under investigation.

References and Notes
1   a) M. Mizuno, M. P. Cava, and A. F. Garito, *J. Org. Chem.*, **41**, 1484 (1976). b) H. Bock, B. Roth, M. V. Lakshmikantham, and M. P. Cava, *Phosphorus Sulfur*, **21**, 67 (1984). c) T. Sugimoto, I. Sugimoto, A. Kawashima, Y. Yamamoto, Y. Misaki, and Z. Yoshida, *Heterocycles*, **25**, 83 (1987). d) K. S. Varma, N. Sasaki, R. A. Clark, and A. E. Underhill, *J. Heterocycl. Chem.*, **25**, 783 (1988). e) J. Garín, J. Orduna, J. M. Royo, A.-M. Le Quéré, and H. Müller, *Rapid Commun. Mass Spectrom.*, **17**, 547 (2003).
2   a) S. Nakatsuji, Y. Amano, H. Kawamura, and H. Anzai, *J. Chem. Soc., Chem. Commun.*, **1994**, 841. b) R. L. Meline and R. L. Elsenbaumer, *Synthesis*, **1997**, 617. c) R. Andreu, J. Garín, J. Orduna, and J. M. Royo, *Tetrahedron Lett.*, **41**, 5207 (2000). d) R. Andreu, J. Garín, J. Orduna, and J. M. Royo, *Tetrahedron Lett.*, **42**, 875 (2001).
3   a) N. Okada, G. Saito, and T. Mori, *Chem. Lett.*, **1986**, 311. b) N. Okada, G. Saito, and T. Mori, *Syhth. Met.*, **19**, 589 (1987).
4   a) M. Iyoda, Y. Kuwatani, E. Ogura, K. Hara, H. Suzuki, T. Takano, K. Takeda, J. Takano, K. Ugawa, M. Yoshida, H. Matsuyama, H. Nishikawa, I. Ikemoto, T. Kato, N. Yoneyama, J. Nishijo, A. Miyazaki, and T. Enoki, *Heterocycles*, **54**, 833 (2001). b) M. Iyoda in "TTF Chemistry," ed. by J. Yamada and T. Sugimoto, Kodansha-Springer, Tokyo (2004), Chap. 8, p 177.
5   a) T. Suzuki, H. Yamochi, G. Srdanov, K. Hinkelmann, and F. Wudl, *J. Am. Chem. Soc.*, **111**, 3108 (1989). b) D. L. Lichtenberger, R. L. Johnston, K. Hinkelmann, T. Suzuki, and F. Wudl, *J. Am. Chem. Soc.*, **112**, 3302 (1990). c) S. Aoyagi, K. Kato, A. Ota, H. Yamochi, G. Saito, H. Suematsu, M. Sakata, and M. Takata, *Angew. Chem., Int. Ed.*, **43**, 3670 (2004).
6   a) L. Groenendaal, F. Jonas, D. Freitag, H. Pielartzik, and J. R. Reynolds, *Adv. Mater.*, **12**, 481 (2000).
7   M. A. Pericas, A. Riera, O. Rossell, F. Serratosa, and M. Seco, *J. Chem. Soc., Chem. Commun.*, **1988**, 942.
8   Physical and spectroscopic data. **4**: yellow prisms, mp 229–231 °C (decomp.), EIMS *m/z* 512 (M$^+$ with an expected isotopic pattern); ^{1}H NMR (CS$_2$/CDCl$_3$ = 3/1) δ 4.13 (s, 8H); ^{13}C NMR (CS$_2$/CDCl$_3$ = 3/1) δ 130.51, 119.35, 65.33; UV–vis/CH$_2$Cl$_2$ (ε) 250 (9,640), 357 (926) nm; Anal. Found: C, 23.58; H, 1.63%. Calcd for C$_{10}$H$_8$O$_4$Se$_4$: C, 23.64; H,1.59%. **8**: light yellow oil, bp 76–78 °C/ 3 Torr, EIMS *m/z* 274 (M$^+$ with an expected isotopic pattern); ^{1}H NMR (CDCl$_3$) δ 4.20 (s, 4H), 2.19 (s, 6H); ^{13}C NMR (CDCl$_3$) δ 128.61, 66.00, 6.89; UV/CH$_2$Cl$_2$ (ε) 270 (2,470) nm. **9**: yellow cryst., mp 83–85 °C, EIMS *m/z* 258 (M$^+$ with an expected isotopic pattern); ^{1}H NMR (CDCl$_3$) δ 4.16 (s, 4H), 4.13 (s, 2H); ^{13}C NMR (CDCl$_3$) δ 124.68, 65.84, 7.95; UV/CH$_2$Cl$_2$ (ε) 294 (1,400) nm. **10**: orange yellow cryst., mp 144–146 °C, EIMS *m/z* 288 (M$^+$ with an expected isotopic pattern); ^{1}H NMR (CDCl$_3$) δ 4.40 (s, 4H); ^{13}C NMR (CDCl$_3$) δ 202.71, 134.59, 67.07; UV/CH$_2$Cl$_2$ (ε) 262 (4,730), 285 (5,710), 442 (8,040) nm.
9   M. Iyoda, R. Watanabe, and Y. Miyake, *Chem. Lett.*, **33**, 570 (2004).
10 D. E. Herr, M. D. May, R. D. McCullough, A. B. Bailey, and D. O. Cowan, *J. Org. Chem.*, **61**, 7006 (1996).
11 T. Imakubo, T. Shirahata, and M. Kibune, *Chem. Commun.*, **2004**, 1590.
12 X-ray data for **4**: C$_{10}$H$_8$O$_4$Se$_4$, M_r = 508.01, monoclinic, $P2_1/a$ (No. 14), Z = 2, a = 10.983(2) Å, b = 8.238(2) Å, c = 7.535(2) Å, β = 102.56(2)°, V = 665.4(3) Å^3, D_{calcd} = 2.535 g cm^{-3}, T = 173 K, μ(Mo Kα) = 110.30 cm^{-1}, Rigaku AFC7R, Mo Kα (λ = 0.71069 Å), 1725 reflections were collected, 1535 unique (R_{int} = 0.046), 1419 observed ($I > 3.00\sigma(I)$), 83 parameters, R = 0.061, wR_2 = 0.083, GOF = 1.99.
13 a) C. Martín, J. Irurre, A. Alvarez-Larena, J. F. Piniella, E. Brillas, L. Fajarí, C. Alemán, and L. Juliá, *J. Org. Chem.*, **59**, 6200 (1994). b) E. E. Bros and M. Harfenist, *J. Org. Chem.*, **63**, 10045 (1998). c) T. Yamamoto, S. Ogawa, and R. Sato, *Tetrahedron Lett.*, **45**, 7943 (2004).
14 For recent examples, see: a) K. Takimiya, Y. Kunugi, Y. Konda, N. Niihara, and T. Otsubo, *J. Am. Chem. Soc.*, **126**, 5084 (2004). b) S. Ando, J. Nishida, Y. Inoue, S. Tokito, and Y. Yamashita, *J. Mater. Chem.*, **14**, 1787 (2004).