Synthesis, electrochemical and chemical oxidations, and *peri* selenium participation of macrocyclic polyselenides containing naphthalene rings

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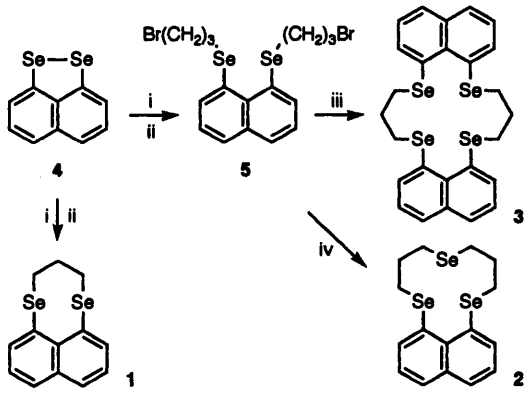
New macrocyclic polyselenides containing naphthalene rings 1–3 have been synthesized. The cyclic voltammograms of the selenides 1–3 show reversible oxidation peaks with remarkably low oxidation potentials. Hydrolysis of a solution of bis- and tris-selenides 1 and 2 in sulfuric acid gives the stable monoselenoxides 6 and 8. The *peri* interaction between the seleninyl and selanyl groups of 6 and 8 was identified by ^{77}Se NMR spectroscopy. In contrast to 1 and 2, the ring-contracted products are obtained from hydrolysis of a solution of 3 in sulfuric acid.

Transannular sulfur–sulfur interaction of cyclic bissulfides has been found in their electrochemical and chemical oxidations.[1,2] However, such interactions of selenium compounds have received less attention. We previously reported that a linear bisselenide, 1,8-bis(methylseleno)naphthalene, gave the demethylated coupling product bearing a diselenide moiety upon treatment with concentrated sulfuric acid (conc. H_2SO_4).[3] Recently, we have made new macrocyclic polyselenides (**1–3**) containing naphthalene rings which possess the possibility of the *peri* Se–Se interactions due to the alignment of selenium orbitals by the trimethylene bridge. Although a number of investigations have been reported on the synthesis, structure and property of macrocyclic polythioethers, very few examples of polyselenoethers are known.[4] This paper reports the facile electrochemical oxidations of **1–3** and the different reactivity in conc. H_2SO_4 of **1–3**, together with the first evidence for the *peri*-interaction between seleninyl and selanyl groups of monoselenoxides **6** and **8** by ^{77}Se NMR spectroscopy.[5]

Results and discussion

The synthesis of macrocyclic polyselenides **1–3** was performed as follows (Scheme 1). The cyclic bisselenide **1** was prepared by the reaction of naphtho[1,8-*cd*]-1,2-diselenole **4** with 1,3-dibromopropane (1 equiv.) using a high dilution method. However, when the diselenide **4** was treated with a large amount of 1,3-dibromopropane, the dibromide **5** was obtained instead of **1**. Dibromide **5** reacted with Na_2Se to give the cyclic trisselenide **2**, while the reaction of dibromide **5** with the disodium diselenolate of **4** afforded the cyclic tetraselenide **3**.

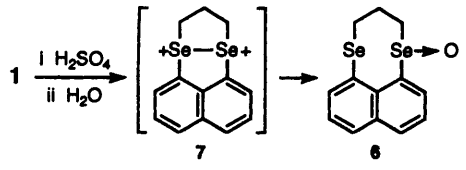
The electrochemical oxidation of selenides **1–3** was performed by cyclic voltammetry (CV), since little information on the electrochemical behaviour of selenides was available. When the cyclic voltammograms of **1–3** were measured in CH_3CN–0.1 M $NaClO_4$ for **1** and **2** or in CH_2Cl_2–0.1 M Bu_4NClO_4 for **3** with a glassy-carbon working electrode and Ag/0.01 M $AgNO_3$ in CH_3CN as a reference electrode (scan rate; 300 mV s^{-1}), the reversible oxidation peaks appeared at the oxidation potentials +0.15 V and +0.30 V for **1**, +0.40 V for **2** and +0.41 V for **3**. These oxidation potentials of **1–3** are remarkably lower than those of 1-methylselenonaphthalene (+0.82 V) and diphenylselenide (+0.97 V) which are irreversible oxidations. These findings indicate that **1–3** can be easily oxidized and **1–3** are good electron donors. Normally selenides having alkyl and/or aryl groups show irreversible redox behaviour. These facile oxidations of **1–3** and the unusual stability of cationic species of **1–3** are ascribed to the destabilization of **1–3** by transannular lone-pair–lone-pair repulsion and the stabilization of the oxidized products by *peri* selenium participation, that is, bond formation between the two selenium atoms. In contrast to **1**, naphtho[1,8-*bc*]-1,5-dithiocine as a sulfur analogue of **1** showed irreversible electrochemical oxidations.[6]



Scheme 1 *Reagents:* i, $NaBH_4$; ii, $Br(CH_2)_3Br$; iii, disodium diselenolate of **4**; iv, Na_2Se

Since bisselenide **1** was readily oxidized electrochemically **1** was therefore treated with conc. H_2SO_4 as an oxidant.[7] Hydrolysis of a solution of **1** in H_2SO_4 gave the selenoxide **6** (69%) and **1** (17%) (Scheme 2). The selenoxide **6** may be obtained from the hydrolysis of the dication **7** which is supported by ^{13}C and ^{77}Se NMR spectra: *i.e.* the signals of the methylene carbon atoms were shifted to δ_C 37.2 and δ_C 63.6 from δ_C 25.5 and δ_C 30.1 of **1** in $CDCl_3$; also the ^{77}Se NMR spectrum of **1** in conc. D_2SO_4 showed a downfield shift to 835.7 ppm from 312.3 ppm (relative to Me_2Se) of **1** in $CDCl_3$.[8] In contrast to **1**, open-chain 1,8-bis(alkylsubstituted-seleno)naphthalenes unlike **1** undergo dealkylation on treatment with conc. H_2SO_4.[3] This result suggests that the trimethylene bridge of **1** participates in the stabilization of the cationic species.

Although none of the selenoxide of the cyclic bisselenide 1,5-diselenacyclooctane (1,5-DSeCO) was obtained from either the hydrolysis of a solution of 1,5-DSeCO in H_2SO_4 or its oxidation with peracid, the selenoxide **6** was stable. Normally selenoxides having β-hydrogen atoms undergo elimination to give olefins.[4a]



Scheme 2

The interaction between the seleninyl and selanyl groups of **6** was found in the proton-decoupled ^{77}Se NMR spectrum (^{77}Se: spin 1/2, natural abundance 7.6%), *i.e.* two ^{77}Se peaks (δ 271.5 and δ 864.4) of **6** in $CHCl_3$ which revealed two clearly resolved satellite peaks due to ^{77}Se–^{77}Se coupling (large coupling constant of J_{Se-Se} 211 Hz) about each central peak.[4a] The intensity of the satellite relative to the central peak is 8%, which corresponds to the natural abundance. This is the first observation of ^{77}Se-satellites due to the interaction between the seleninyl and selanyl groups. This interaction may prevent also the decomposition of **6**.

Interestingly, similar treatment of trisselenide **2** with H_2SO_4 and H_2O led to the monoselenoxide **8** (50%) and **2** (25%), and none of the selenoxide **9** (Scheme 3). The *peri* seleninyl–selanyl interaction of **8** was confirmed by the observation of a large ^{77}Se–^{77}Se coupling (J_{Se-Se} 341 Hz).

In contrast to **1** and **2**, the hydrolysis of a H_2SO_4 solution of **3** afforded the ring contraction products bisselenide **1** and its monoselenoxide **6** in a 1:1 ratio (84%), *i.e.* the sixteen-membered ring of **3** was contracted to the eight-membered ring of **1** (Scheme 4). In order to explain this reaction, we propose the following radical mechanism based on the results of the CV (*vide supra*) of **3** and an EPR signal (*g* 2.0406) of **3** in H_2SO_4 (Scheme 4). The radical cation of **3** would be generated in H_2SO_4 which, subsequently, could be converted into the radical cation **10** and the selenide **1** by an intramolecular reaction, *i.e.* the remote selenium atom could attack the carbon atom adjacent to the selenide radical cation of **1**. Then the radical cation **10** could react with water to give the selenoxide **6**.

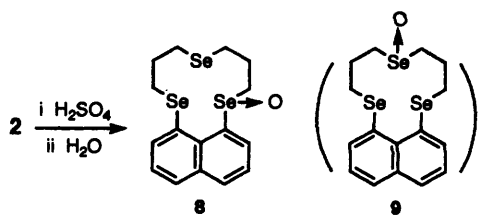
Experimental

General

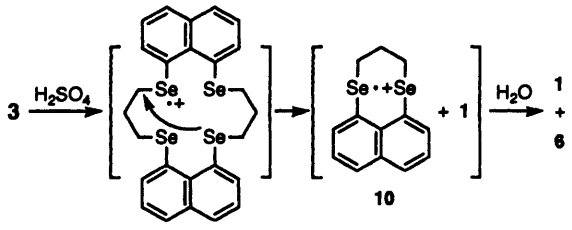
All NMR spectra were measured on a JEOL LMN-EX-270 or a BRUKER MSL-400 spectrometer. Chemical shifts for ^1H and ^{13}C NMR spectra were reported with respect to Me_4Si. *J* Values are given in Hz. IR spectra were obtained on a JASCO A-3 spectrometer. Mass spectra were taken with a Shimadzu QP-2000 and a JEOL JMX SX102 mass spectrometer. Elemental analyses were carried out by the Chemical Analysis Center at this university. For cyclic voltammetry measurements, Hokuto Denko Co. Model HB-104 electrochemical apparatus was used in conjunction with a Yokokawa Co. Model 3025A X-Y recorder. All reagents were obtained from Wako Pure Chemical Industries Ltd., Tokyo Kasei Co. Ltd., or Aldrich Chemical Co. The reagents used as reaction solvents were further purified by general methods.

Synthesis of 3,4-dihydro-2*H*-naphtho[1,8-*bc*]-1,5-diselenocine 1

Solutions of naphtho[1,8-*cd*]-1,2-diselenole **4**[3] (604 mg, 2.13 mmol) in the presence of $NaBH_4$ (290 mg, 6.9 mmol) in anhydrous THF (20 cm^3)–EtOH (20 cm^3) and 1,3-dibromopropane (275 μl, 2.6 mmol) in anhydrous THF (40 cm^3) were added separately and simultaneously over 70 min to a vigorously stirred solution of $NaBH_4$ (120 mg, 2.9 mmol) in anhydrous THF (200 cm^3)–EtOH (200 cm^3). After the usual work-up, the crude products were purified by silica-gel column chromatography (eluent CH_2Cl_2) to give the bisselenide **1** (55%), mp 92 °C; $\delta_H(CDCl_3)$ 1.88 (q, *J* 6, 2 H), 2.98 (t, *J* 6, 4 H), 7.19 (t, *J* 8, 2 H), 7.76 (d, *J* 8, 2 H) and 8.10 (d, *J* 8, 2 H); $\delta_C(CDCl_3)$ 25.5, 30.1, 125.4, 128.1, 131.6, 135.4, 136.2 and 140.6; $\delta_{Se}(CDCl_3)$ 312.3; *m/z* 328 (M^+, ^{80}Se) (Found: C, 47.88; H, 3.66. $C_{13}H_{12}Se_2$ requires C, 47.87; H, 3.71%).



Scheme 3



Scheme 4

Synthesis of 3,4,7,8-tetrahydro-2*H*,6*H*-naphtho[1,8-*bc*]-1,5,9-triselenacyclododecine 2

To a solution of diselenide **4** (497 mg, 1.75 mmol) and $NaBH_4$ (267 mg, 7.03 mmol) in anhydrous THF (25 cm^3)–EtOH (25 cm^3) was added a solution of 1,3-dibromopropane (5.6 cm^3, 55 mmol) in anhydrous THF (100 cm^3)–EtOH (100 cm^3). The whole mixture was stirred at room temperature for 2 h. After the usual work-up, the crude products were purified by silica-gel column chromatography (eluent CH_2Cl_2) to give 1,8-bis(3-bromopropylseleno)naphthalene **5** (82%), $\delta_H(CDCl_3)$ 1.96 (q, *J* 7, 4 H), 2.84 (t, *J* 7, 4 H), 3.30 (t, *J* 7, 4 H), 7.21 (t, *J* 8, 2 H), 7.58 (d, *J* 8, 2 H) and 7.65 (d, *J* 8, 2 H); $\delta_C(CDCl_3)$ 30.4, 31.7, 33.3, 125.7, 128.6, 129.7, 133.5, 135.4 and 136.1; $\delta_{Se}(CDCl_3)$ 303.3 (relative to Me_2Se); *m/z* 530 (M^+, ^{80}Se). Solutions of Na_2Se (123 mg, 0.99 mmol) in anhydrous EtOH (21 cm^3) and dibromide **5** (420 mg, 0.80 mmol) in anhydrous THF (20 cm^3) were added separately and simultaneously over 70 min to a vigorously stirred solution of $NaBH_4$ (200 mg, 4.8 mmol) in anhydrous THF (150 cm^3)–EtOH (100 cm^3). After the usual work-up, the crude products were purified by silica-gel column chromatography (eluent CH_2Cl_2) to give the trisselenide **2** (52%), mp 107.0–107.5 °C (from CH_2Cl_2–hexane); $\delta_H(CDCl_3)$ 2.06 (q, *J* 7, 4 H), 2.53 (t, *J* 7, 4 H), 3.05 (t, *J* 7, 4 H), 7.20 (t, *J* 8, 2 H), 7.63 (d, *J* 8, 2 H) and 7.85 (d, *J* 8, 2 H); $\delta_C(CDCl_3)$ 20.8, 30.0, 34.1, 125.5, 129.6, 130.0, 135.7 and 137.1; $\delta_{Se}(CDCl_3)$ 186.1, 309.2; *m/z* 450 (M^+, ^{80}Se) (Found: C, 42.98; H, 3.98. $C_{16}H_{18}Se_3$ requires C, 42.97; H, 4.06%).

Synthesis of 9,10,20,21-tetrahydro-8*H*,19*H*-dinaphtho[1′,8′-*jk*;1,8-*bc*][1,5,9,13]tetraselenacyclohexadecine 3

Solutions of diselenide **4** (167 mg, 0.59 mmol) in the presence of $NaBH_4$ (78 mg, 2.05 mmol) in anhydrous THF (15 cm^3)–EtOH (15 cm^3) and dibromide **5** (440 mg, 0.83 mmol) in anhydrous THF (15 cm^3)–EtOH (15 cm^3) were added separately and simultaneously over 70 min to a vigorously stirred solution of $NaBH_4$ (120 mg, 3.16 mmol) in anhydrous THF (150 cm^3)–EtOH (150 cm^3). After the usual work-up, the crude products were purified by silica-gel column chromatography (eluent CH_2Cl_2) to give the tetrakisselenide **3** (80%), mp 222.0–222.5 °C (from $CHCl_3$–hexane); $\delta_H(CDCl_3)$ 2.15 (q, *J* 7, 4 H), 3.24 (t, *J* 7, 8 H), 7.23 (t, *J* 8, 4 H), 7.64 (d, *J* 8, 4 H) and 7.73 (d, *J* 8, 4 H); $\delta_C(CDCl_3)$ 27.0, 33.0, 125.3, 128.8, 129.2, 135.6, 135.8 and 136.8; $\delta_{Se}(CDCl_3)$ 307.2; *m/z* 656 (M^+, ^{80}Se) (Found: C, 47.76; H, 3.72. $C_{26}H_{24}Se_4$ requires C, 47.87; H, 3.71%).

Reaction of 1–3 with concentrated H_2SO_4

Bisselenide **1** was dissolved in conc. H_2SO_4 (98%) at room temperature. The H_2SO_4 solution was then poured into ice-water, and the solution was neutralized with dilute sodium hydroxide solution. After the usual work-up, the products were purified by silica-gel column chromatography to afford the selenoxide **6** (69%) and the selenide **1** (17%).

1-Oxo-3,4-dihydro-2*H*-naphtho[1,8-*bc*]-1λ^4,5-diselenocine 6. Mp 149–151 °C; ν_{max}(KBr)/cm^{-1} 824 (SeO); δ_H($CDCl_3$) 1.49–1.58 (m, 1 H), 2.52–2.66 (m, 3 H), 3.01–3.09 (m, 1 H), 3.48–3.60 (m, 1 H), 7.35 (t, *J* 8, 1 H), 7.65 (t, *J* 8, 1 H), 7.86 (d, *J* 8, 1 H), 7.89 (d, *J* 8, 1 H), 7.92 (d, *J* 8, 1 H) and 8.73 (d, *J* 8, 1 H); δ_C($CDCl_3$) 26.6, 32.5, 60.1, 123.1, 126.2, 126.3, 127.3, 130.9, 131.5, 135.0, 137.3, 138.2 and 139.1; δ_{Se}($CDCl_3$) 271.5 and 864.4; *m/z* 344 (M^+, ^{80}Se) (Found: C, 45.31; H, 3.56. $C_{13}H_{12}OSe_2$ requires C, 45.63; H, 3.53%).

Analogous hydrolysis of **2** in conc. H_2SO_4 gave the mono-selenoxide **8** (50%) and **2** (25%).

1-Oxo-3,4,7,8-tetrahydro-2*H*,6*H*-naphtho[1,8-*bc*]-1λ^4,5,9-triselenacyclododecine 8. Mp 145–147 °C (decomp.); ν_{max}(KBr)/cm^{-1} 825 (SeO); δ_H($CDCl_3$) 1.94–2.06 (m, 1 H), 2.14–2.65 (m, 5 H), 2.73–2.82 (m, 1 H), 3.04–3.18 (m, 2 H), 3.21–3.29 (m, 1 H), 3.78–3.87 (m, 1 H), 4.29–4.38 (m, 1 H), 7.49 (t, *J* 8, 1 H), 7.73 (t, *J* 8, 1 H), 7.96 (d, *J* 8, 1 H), 7.99 (d, *J* 8, 1 H), 8.04 (d, *J* 8, 1 H) and 8.81 (d, *J* 8, 1 H); δ_C($CDCl_3$) 24.1, 25.2, 26.3, 27.9, 34.7, 56.0, 125.6, 126.2, 126.3, 126.5, 130.2, 132.4, 133.2, 135.9, 138.1 and 139.7; δ_{Se}($CDCl_3$) 54.5, 234.7 and 831.0; *m/z* 464 (M^+, ^{80}Se) (Found: C, 41.33; H, 3.93. $C_{16}H_{18}OSe_3$ requires C, 41.49; H, 3.92%).

Hydrolysis of **3** in conc. H_2SO_4 gave the selenide **1** and the selenoxide **6** in a 1:1 ratio (84%).

Acknowledgements

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