

# Preparation and X-Ray Structure of 8,9,19,20-Tetrahydrodinaphtho[1',8'-jk; 1,8-bc][1,5,9,13]tetraselenacyclohexadecine, and its Novel Ring Contraction in Concentrated Sulfuric Acid

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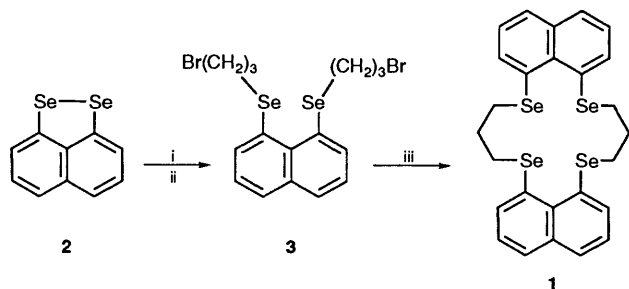
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The novel title compound **1** has been synthesized; upon hydrolysis in sulfuric acid it gave ring-contracted products naphtho[1,8-bc]-1,5-diselenocin and its selenoxide.

A number of macrocyclic polythioethers have been described but<sup>1,2</sup> very few polyselenoethers are known.<sup>3</sup> Recently, we reported that 1,8-bis(methylseleno)naphthalene gave a demethylated coupling product bearing a diselenide moiety upon treatment with concentrated sulfuric acid (conc. H<sub>2</sub>SO<sub>4</sub>).<sup>4</sup> Here we describe the synthesis and crystal structure of the new title compound **1** together with details of its electrochemical oxidation and novel ring-contraction in conc. H<sub>2</sub>SO<sub>4</sub>.

The cyclic tetraselenide **1** was prepared by the reaction of 1,8-bis(3-bromopropylseleno)naphthalene **3** with the disodium salt of naphtho[1,8-cd]-1,2-diselenole **2** (Scheme 1).



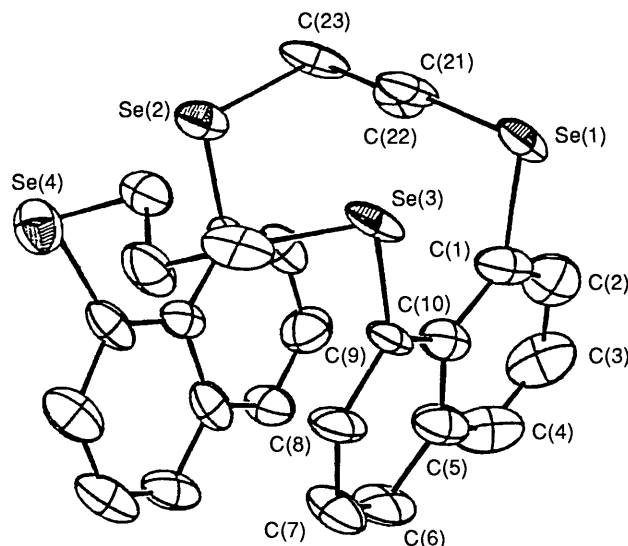
**Scheme 1** Reagents: i, NaBH<sub>4</sub>; ii, Br-(CH<sub>2</sub>)<sub>3</sub>-Br; iii, **2** and NaBH<sub>4</sub>.

An X-ray diffraction study of the tetraselenide **1** indicates the following characteristic properties (Fig. 1). The transannular Se...Se contacts are 3.19 Å for Se(1)-Se(3) and 3.17 Å for Se(2)-Se(4) which are remarkably shorter than the sum of the van der Waals radii (4.0 Å) of selenium. Further, in compound **1** there is intramolecular  $\pi$ - $\pi$  stacking of the naphthalene rings and its X-ray data suggest that it may have interesting chemical properties.

Compound **1** was subjected to electrochemical oxidation by cyclic voltammetry (CV), since little is known about the electrochemical behaviour of selenides. When the cyclic voltammogram of compound **1** was measured in Bu<sub>4</sub>NClO<sub>4</sub> (0.1 mol dm<sup>-3</sup> in CH<sub>2</sub>Cl<sub>2</sub>) with a glassy-carbon working electrode and Ag/AgNO<sub>3</sub> (0.01 mol dm<sup>-3</sup> in MeCN) as a reference electrode (scan rate; 300 mV s<sup>-1</sup>), one reversible oxidation peak appeared at the oxidation potential, +0.41 V. The latter is lower than that of 1-methylselenonaphthalene ( $E_p = +0.82$  V) which showed an irreversible oxidation wave. Normally selenides having alkyl and/or aryl groups show irreversible redox behaviour.

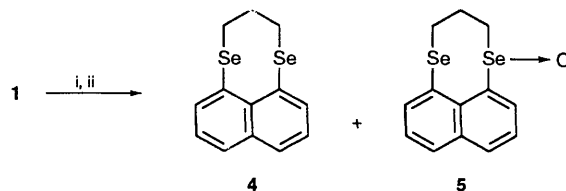
The tetraselenide **1** having been readily oxidized electrochemically, it was thus treated with conc. H<sub>2</sub>SO<sub>4</sub> as an oxidant.† Surprisingly, this afforded the ring-contraction products, naphtho[1,8-bc]-1,5-diselenocin **4** and its monoselenoxide **5** in

† Conc. H<sub>2</sub>SO<sub>4</sub> acts as both an oxidizing agent and a strong acid (ref. 5).



**Fig. 1** The X-ray crystal structure of **1**. For clarity, the hydrogen atoms are omitted.

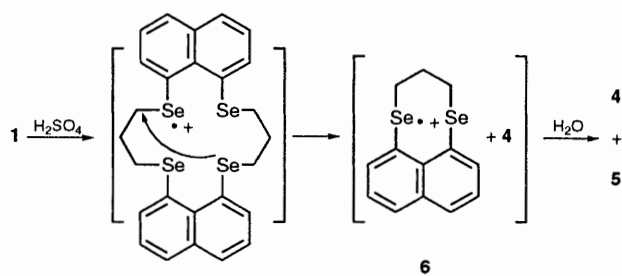
a 1 : 1 ratio (84%), i.e. the 16-membered ring of compound **1** has contracted to the 8-membered ring of compound **4** (Scheme 2). In order to explain this reaction, we propose the following radical mechanism based on the results of CV (*vide supra*) of compound **1** and an ESR signal ( $g = 2.0406$ ) of **1** in H<sub>2</sub>SO<sub>4</sub> (Scheme 3). The radical cation of **1** would be generated in H<sub>2</sub>SO<sub>4</sub> which, subsequently, could be converted into the radical cation **6** and the selenide **4** by an intramolecular reaction; i.e. the remote selenium atom could attack on the carbon atom adjacent to the selenide radical cation of **1**. The radical cation **6** could then react with water to give the selenoxide **5**. Mechanistic studies on this new type of ring contraction are in progress.



**Scheme 2** Reagents: i, H<sub>2</sub>SO<sub>4</sub>; ii, H<sub>2</sub>O

## Experimental

**Synthesis of the Tetraselenide 1.**—To a solution of naphtho[1,8-cd]-1,2-diselenole **2**<sup>4</sup> (497 mg, 1.75 mmol) and NaBH<sub>4</sub> (267 mg, 7.03 mmol) in anhydrous tetrahydrofuran



Scheme 3

(THF)–EtOH (25 cm<sup>3</sup> of each) was added a solution of 1,3-dibromopropane (5.6 cm<sup>3</sup>, 55 mmol) in anhydrous THF–EtOH (100 cm<sup>3</sup> of each). The mixture was stirred at room temp. for 2 h, after which it was worked up. The crude products were purified by silica-gel column chromatography (eluent CH<sub>2</sub>Cl<sub>2</sub>) to give the dibromide **3** (82%),  $\delta_{\text{H}}(\text{CDCl}_3)$  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);  $\delta_{\text{C}}(\text{CDCl}_3)$  30.4, 31.7, 33.3, 125.7, 128.6, 129.7, 133.5, 135.4 and 136.1;  $\delta_{\text{Se}}(\text{CDCl}_3)$  303.3 (relative to Me<sub>2</sub>Se); *m/z* 530 (M<sup>+</sup>, <sup>80</sup>Se). Solutions of the 1,8-diselenide **2** (167 mg, 0.59 mmol) in the presence of NaBH<sub>4</sub> (78 mg, 2.05 mmol) in anhydrous THF–EtOH (15 cm<sup>3</sup> of each) and dibromide **3** (440 mg, 0.83 mmol) in anhydrous THF–EtOH (15 cm<sup>3</sup> of each) were added separately and simultaneously over 70 min to a vigorously stirred solution of NaBH<sub>4</sub> (120 mg, 3.16 mmol) in anhydrous THF–EtOH (150 cm<sup>3</sup> of each). After work-up, the crude products were purified by silica-gel column chromatography (eluent CH<sub>2</sub>Cl<sub>2</sub>) to give the tetraselenide **1** (80%), m.p. 222.0–222.5 °C (from CHCl<sub>3</sub>–hexane);  $\delta_{\text{H}}(\text{CDCl}_3)$  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);  $\delta_{\text{C}}(\text{CDCl}_3)$  27.0, 33.0, 125.3, 128.8, 129.2, 135.6, 135.8 and 136.8;  $\delta_{\text{Se}}(\text{CDCl}_3)$  307.2; *m/z* 656 (M<sup>+</sup>, <sup>80</sup>Se) (Found: C, 47.8; H, 3.7. C<sub>26</sub>H<sub>24</sub>Se<sub>4</sub> requires C, 47.87; H, 3.71%).

*Crystal data for the Tetraselenide 1.*—C<sub>26</sub>H<sub>24</sub>Se<sub>4</sub>, monoclinic, space group P2<sub>1</sub>/n, *a* = 10.914(1), *b* = 13.172(2), *c* = 16.230(2) Å,  $\beta$  = 99.13(1)°, *V* = 2303.6(4) Å<sup>3</sup>, *Z* = 4, *D<sub>c</sub>* = 1.881 g cm<sup>-3</sup>, Cu-K $\alpha$  radiation ( $\lambda$  = 1.5418 Å), *F*(000) = 1264, a CAD4 diffractometer, 3418 reflections ( $4 \leq 2\theta \leq 120^\circ$ ), 2410 observed with *I*  $\geq 3.0\sigma(I)$ . The structure was solved by direct methods SIR and refined anisotropically by full-matrix least-squares using the MoIEN program package. The final *R* value was

\* *J* Values recorded in Hz.

† For full details of the deposition scheme, see *J. Chem. Soc., Perkin Trans. 1*, 1993, Issue 1, 'Instructions for Authors'.

0.077. Tables of fractional atomic coordinates, bond lengths and angles and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre.†

*Reaction of 1 with Concentrated H<sub>2</sub>SO<sub>4</sub>.*—The tetraselenide **1** was dissolved in conc. H<sub>2</sub>SO<sub>4</sub> (98%) at room temp. and the solution then poured into ice–water and neutralized with dilute aqueous sodium hydroxide. After work-up, the products were purified by silica-gel column chromatography to afford the selenide **4** and the selenoxide **5** in a 1 : 1 ratio (84%). Compound **4**: m.p. 92 °C;  $\delta_{\text{H}}(\text{CDCl}_3)$  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);  $\delta_{\text{C}}(\text{CDCl}_3)$  25.5, 30.1, 125.4, 128.1, 131.6, 135.4, 136.2 and 140.6;  $\delta_{\text{Se}}(\text{CDCl}_3)$  312.3; *m/z* 328 (M<sup>+</sup>, <sup>80</sup>Se) (Found: C, 47.9; H, 3.7. C<sub>13</sub>H<sub>12</sub>Se<sub>2</sub> requires C, 47.87; H, 3.71%).

Compound **5**: m.p. 149–151 °C;  $\nu_{\text{max}}(\text{KBr})/\text{cm}^{-1}$  824 (SeO);  $\delta_{\text{H}}(\text{CDCl}_3)$  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);  $\delta_{\text{C}}(\text{CDCl}_3)$  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;  $\delta_{\text{Se}}(\text{CDCl}_3)$  271.5 and 864.4; *m/z* 344 (M<sup>+</sup>, <sup>80</sup>Se) (Found: C, 45.3; H, 3.6. C<sub>13</sub>H<sub>12</sub>OSe<sub>2</sub> requires C, 45.63; H, 3.53%). Synthesis and conformational properties of compounds **4** and **5** will be reported elsewhere.

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