

**TRANSANNULAR INTERACTION BETWEEN SELENIUM AND SULFUR ATOMS  
IN 5H,7H-DIBENZO[*b,g*][1,5]SELENATHIOCIN:  
FORMATION OF A NEW HETEROATOM DICATION [ $>Se^{+}-^{+}S<$ ]**

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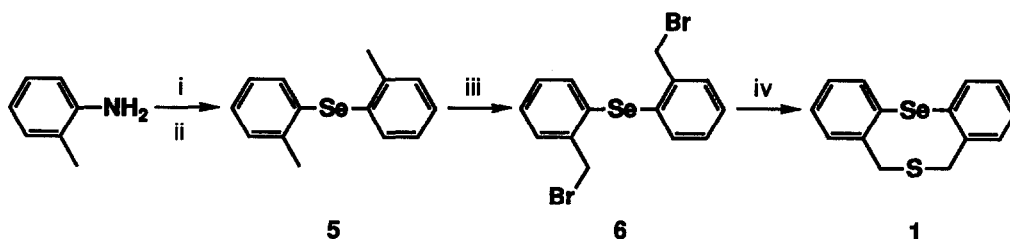
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**Abstract:** A new medium-sized heterocycles, 5H,7H-dibenzo[*b,g*][1,5]selenathiocin (**1**) has been prepared. The transannular interaction between selenium and sulfur atoms in **1** and the formation of dication were found in the reaction of **1**, and its oxides with concd  $H_2SO_4$ .

There has been of great interest on the transannular interaction or bond formation between heteroatoms in heterocyclic analogue of dibenzo[*a,d*]cyclooctane and related compounds.<sup>1,2</sup> On the other hand, the structure and reactivity of medium-sized cyclic compounds containing selenium atoms have received less attention. Recently, we reported the first crystal structure and the reactivity of dithia dication, 1,5-dithioniabicyclo[3.3.0]octane bis(trifluoromethanesulfonate).<sup>3</sup> However, the dications having two positive charges on the adjacent two different heteroatoms are not well explored. We now report herein the preparation and property of 5H,7H-dibenzo[*b,g*][1,5]selenathiocin (**1**) as a new medium-sized heterocyclic compound and its oxides, and the first observation of the transannular bond formation between selenium and sulfur atoms, *i.e.*, the formation of selenathia dication [ $>Se^{+}-^{+}S<$ ].

The title compound **1** was prepared as follows (Scheme 1). Bis(2-methylphenyl)-selenide (**5**) was obtained by reaction of the diazonium salt of 2-methyl aniline with potassium selenide.<sup>4</sup> The treatment of the selenide **5** with N-bromosuccinimide (NBS) in the presence of benzoyl peroxide in  $CCl_4$  at 80 °C gave the bis(2-bromomethylphenyl)selenide (**6**).<sup>5</sup> The compound **6** (1.7 g, 4.1 mmol) was treated with  $Na_2S \cdot 9H_2O$  (1.2 g, 4.9 mmol) in ethanol (300 mL) using a high dilution technique at room temperature. After usual work-up, the residue was recrystallized from benzene to give the compound **1** in 90% yield.<sup>6</sup>

The oxidation of **1** with *m*-chloroperbenzoic acid (MCPBA) gave a 2:1 mixture of the sulfoxide, 5H,7H-dibenzo[*b,g*][1,5]selenathiocin 6-oxide (**3**) and the selenoxide, 5H,7H-dibenzo[*b,g*][1,5]selenathiocin 12-oxide (**4**) which were separated readily by column chromatography (Scheme 2).<sup>7</sup> In contrast, only the benzylic sulfur atom of a cyclic bis-sulfide, 5H,7H-dibenzo[*b,g*][1,5]dithiocin (**7**) was oxidized to its 6-oxide upon treatment with MCPBA.<sup>1,2</sup>

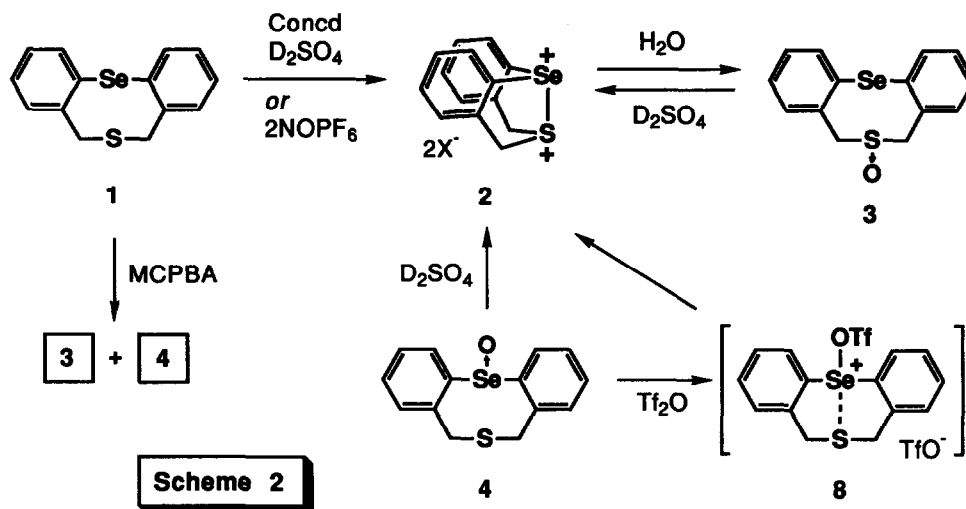


**Scheme 1.** Reagents: i, HCl, NaNO<sub>2</sub>; ii, K<sub>2</sub>Se; iii, NBS; iv, Na<sub>2</sub>S.

The conformational behaviors in **1** concerning eight-membered ring are of interest, because generally, two typically different conformers, *i.e.*, chair and boat-forms can exist.<sup>8</sup> The conformers can be assigned by the <sup>1</sup>H NMR spectral data for benzylic protons of the eight-membered ring.<sup>8</sup> The 500 MHz <sup>1</sup>H NMR spectrum of **1** in CDCl<sub>3</sub> at 25 °C shows the existence of two conformers in the ratio of 64 (chair) : 36 (boat). Namely, the major conformer gives one AB type absorption at δ 3.87 and 5.05 with *J*=14.5 Hz, and the minor form gives one broad singlet peak at δ 3.72. On the other hand, the 500 MHz <sup>1</sup>H NMR spectrum of sulfoxide **3** in CDCl<sub>3</sub> at 25 °C showing one AB system at δ 3.90 and 3.95 (*J*=13 Hz), and other AB system at δ 4.23 and 5.68 (*J*=12 Hz), is assigned to the boat-form (90%) for the former and the chair-form (10%) for the latter. The <sup>1</sup>H NMR spectrum of selenoxide **4** in CDCl<sub>3</sub> at 25 °C shows the two conformers.<sup>9</sup> While the 12-oxide of bis-sulfide **7** shows a single conformer.

The electrochemical oxidations of **1** and **7** were studied by cyclic voltammetry. Peak potentials of first oxidation peak determined at a glassy carbon electrode, 300 mV/s scan rate, in CH<sub>3</sub>CN-0.1M NaClO<sub>4</sub> vs. Ag/0.01M AgNO<sub>3</sub>. The oxidation potentials (E<sub>p</sub>) showed 0.75 V for **1** and 1.05 V for **7**, indicating that **1** can be oxidized more readily than **7**.

When the compound **1** was dissolved in concentrated sulfuric acid-*d*<sub>2</sub> (concd D<sub>2</sub>SO<sub>4</sub>) (98%) at room temperature, the solution became yellowish-red. The reaction was followed by both high-field <sup>1</sup>H (500 MHz) and <sup>13</sup>C (125 MHz) NMR spectroscopy. In the <sup>1</sup>H NMR spectrum, the methylene signals for **1** in CDCl<sub>3</sub> disappeared and new AB quartet peaks appeared at δ 4.96 and 5.31 (*J*=16 Hz) in concd D<sub>2</sub>SO<sub>4</sub>, which indicates the formation of the selenathia dication **2** (Scheme 2). While in the <sup>13</sup>C NMR spectrum of **1** in concd D<sub>2</sub>SO<sub>4</sub>, the signal of the methylene carbon atoms was shifted to downfield from δ 42.1 (**1** in CDCl<sub>3</sub>) to δ 50.5. Only a *single conformer*, boat-form, **2**, was detected in concd D<sub>2</sub>SO<sub>4</sub> solution of **1** as evidenced by NMR spectra [dication **2**: <sup>1</sup>H NMR (500 MHz) δ 4.96, 5.31 (ABq, *J*=16 Hz, 4H), 7.24 (d, *J*=8.5 Hz, 2H), 7.30-7.36 (m, 4H), and 7.57 (d, *J*=8 Hz, 2H); <sup>13</sup>C NMR (125 MHz) δ 50.5, 125.3, 126.7, 128.4, 130.5, 132.2, and 134.3]. These spectra did not change for several days at room temperature.



On treatment of the  $D_2SO_4$  solution of 1 with ice- $H_2O$ , the sulfoxide 3 was obtained in 91% isolated yield, and neither the selenoxide 4 nor 1 were obtained. On the other hand, two-electron oxidation of 1 with 2 equiv of  $NOPF_6$ , a one-electron-oxidizing agent, in  $CH_2Cl_2$ - $CH_3CN$  also gave the dication ( $PF_6$ )<sub>2</sub> salt, which on treatment with  $H_2O$  again resulted in the formation of sulfoxide 3 (Scheme 2). In contrast, the oxidation of 1 with MCPBA gives a mixture of sulfoxide 3 and selenoxide 4 (*vide supra*). The reaction of 1 in concd  $D_2SO_4$  may proceed through the initial formation of the monocationic species such as the cation radical  $[Se-S]^{\cdot+}$  by an electron-transfer, which is subsequently converted into the stable dication 2. This finding is quite different from that of the cyclic bis-sulfide 7 which was unstable in concd  $H_2SO_4$ , and the  $^1H$  and  $^{13}C$  NMR spectra of the  $D_2SO_4$  solution of 7 showed complex signals. Actually the complex mixtures were obtained after the hydrolysis of the  $D_2SO_4$  solution of 7. These results indicate that the cationic species from 1 are more stabilized by transannular Se-S interaction as compared with those of 7.

Dissolution of the selenoxide 4 in concd  $D_2SO_4$  also led to the formation of the dication 2 as determined by the  $^1H$  and  $^{13}C$  NMR spectroscopy. Hydrolysis of the  $D_2SO_4$  solution of 4 gave the sulfoxide 3 in 86% yield. Addition of a solution of trifluoromethanesulfonic anhydride [ $(CF_3SO_2)_2O$ ,  $Tf_2O$ ; 1 equiv] in anhydrous  $CH_2Cl_2$  to a stirred solution of selenoxide 4 (1 equiv) in anhydrous  $CH_2Cl_2$  under Ar at  $-20$  °C gave the salt 2a ( $X=CF_3SO_3^-$ ), mp  $115$  °C (decomp). The salt 2a was assigned as a dicationic structure by  $^1H$  NMR spectroscopy. The  $^1H$  NMR spectrum of 2a in  $CD_3CN$  showed peaks at  $\delta$  5.53 (br s, 4H), 7.58-7.82 (m, 6H), and 8.16-8.37 (m, 2H) which are remarkable downfield shifts compared to 4. This reaction should proceed *via* the intermediate 8. The hydrolysis of the dicationic salt afforded the sulfoxide 3, and none of the selenoxide 4 was obtained (Scheme 2).

The dication **2** was also formed upon treatment of the sulfoxide **3** with concd  $D_2SO_4$ , since the  $^1H$  and  $^{13}C$  NMR chemical shifts of **3** in concd  $D_2SO_4$  observed agreed well with those for **2** obtained from **1** and **4**. Treatment of the  $D_2SO_4$  solution of **3** with  $H_2O$  gave again the mono-sulfoxide **3** (87%) (Scheme 2).

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### References and Notes

- 1) (a) K. Ohkata, K. Okada, and K. Akiba, *Tetrahedron Lett.*, **26**, 4491 (1985).  
(b) K. Akiba, K. Takee, Y. Shimizu, and K. Ohkata, *J. Am. Chem. Soc.*, **108**, 6320 (1986)
- 2) (a) H. Fujihara, A. Kawada, and N. Furukawa, *J. Org. Chem.*, **52**, 4254 (1987).  
(b) H. Fujihara, J.-J. Chiu, and N. Furukawa, *J. Am. Chem. Soc.*, **110**, 1280 (1988).
- 3) (a) H. Fujihara, R. Akaishi, and N. Furukawa, *J. Chem. Soc. Chem. Commun.*, 930 (1987); (b) F. Iwasaki, N. Toyoda, R. Akaishi, H. Fujihara, and N. Furukawa, *Bull. Chem. Soc. Jpn.*, **61**, 2563 (1988); (c) H. Fujihara, R. Akaishi, and N. Furukawa, *J. Chem. Soc. Chem. Commun.*, 147 (1989).
- 4) Compound **5**: mp 60-61 °C;  $^1H$  NMR ( $CDCl_3$ )  $\delta$  2.39 (s, 6H,  $CH_3$ ), 7.03-7.06 (m, 2H, ArH), and 7.17-7.24 (m, 6H, ArH). Anal. Calcd for  $C_{14}H_{14}Se$ : C, 64.37; H, 5.40%. Found: C, 64.39; H, 5.37%.
- 5) Compound **6**: mp 68-69 °C;  $^1H$  NMR ( $CDCl_3$ )  $\delta$  4.70 (s, 4H,  $CH_2$ ) and 7.09-7.58 (m, 8H, ArH).
- 6) Compound **1**: mp 132-132.5 °C; MS ( $m/z$ ): 292 ( $M^+$ ), 290 ( $M^+-2$ ), 294 ( $M^++2$ );  $^1H$  NMR ( $CDCl_3$ )  $\delta$  3.72 (br s,  $CH_2$ ), 3.87, 5.05 (ABq,  $J=14.5$  Hz,  $CH_2$ ), and 7.05-7.91 (m, ArH)<sup>9</sup>. Anal. Calcd for  $C_{14}H_{12}SSe$ : C, 57.73; H, 4.15%. Found: C, 57.38; H, 4.25%.
- 7) Compound **3**: mp 195-196 °C; FT-IR (KBr) 1050  $cm^{-1}$  (SO);  $^1H$  NMR ( $CDCl_3$ )  $\delta$  3.90, 3.95 (ABq,  $J=13$  Hz,  $CH_2$ ), 4.23, 5.68 (ABq,  $J=12$  Hz,  $CH_2$ ) and 7.11-7.92 (m, ArH)<sup>9</sup>. Anal. Calcd for  $C_{14}H_{12}OSSe$ : C, 54.73; H, 3.94%. Found: C, 54.54; H, 3.88%.  
Compound **4**: mp 200-202 °C; FT-IR (KBr) 831  $cm^{-1}$  (SeO);  $^1H$  NMR ( $CDCl_3$ )  $\delta$  3.89, 4.19 (ABq,  $J=15.5$  Hz,  $CH_2$ ), 4.06, 4.44 (ABq,  $J=15.5$  Hz,  $CH_2$ ), 7.12-7.48 (m, ArH), and 8.06-8.29 (m, ArH)<sup>9</sup>.
- 8) (a) R. P. Gellatly, W. D. Ollis, and I. O. Sutherland, *J. Chem. Soc. Perkin Trans 1*, 913 (1976).  
(b) L. E. Bricaddy, B. S. Hurlbert, and N. B. Mehta, *J. Org. Chem.*, **46**, 1630 (1981).
- 9) The protons and carbons of the aromatic rings in the NMR spectra (500 MHz- $^1H$  and 125 MHz- $^{13}C$ ) of **1**, **3**, and **4**, except for dication **2**, showed two sets of signals due to the existence of two conformers; the detailed analysis of conformations will be reported in full text.