# A New Preparative Method and Reactivity of Diselenide Dication Salt from 5*H*,7*H*-Dibenzo[*b*,*g*][1,5]diselenocine

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A new medium-sized heterocycle, 5*H*,7*H*-dibenzo[*b*,*g*][1,5]diselenocine **1**, has been synthesized; the reaction of the selenoxide of **1** with two equivalents of $CF_3SO_3SiMe_3$ gave the stable diselenide dication salt, this is a new method for the preparation of the diselenide dication.

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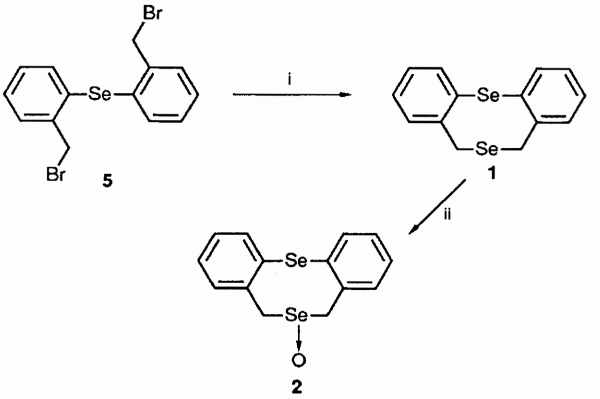
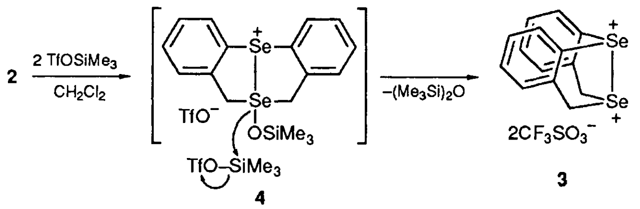
Transannular bond formation (*e.g.* dication) between heteroatoms in medium-sized heterocyclic compounds containing nitrogen and/or sulphur atoms has been extensively studied.[1–3] However, the properties of medium-sized selenium heterocycles have received less attention. Recently, we reported the first crystal structure and reactivity of a tetraalkyl substituted diselenide dication salt, 1,5-diselenoniabicyclo[3.3.0]octane bis(tetrafluoroborate), obtained by a two-electron oxidation of 1,5-diselenacyclooctane (1,5-DSeCO) with $NOBF_4$.[4] We have now found that the reaction of the selenoxide **2** of 5*H*,7*H*-dibenzo[*b*,*g*][1,5]diselenocine **1** with 2 equiv. of $CF_3SO_3SiMe_3$ afforded the corresponding diselenide dication salt **3** containing aromatic rings. This paper reports the conformational properties of **1** and **2**, and a new preparative method of the diselenide dication **3**, together with its reactivity.



**Scheme 1** *Reagents*: i, $Na_2Se$ in EtOH; ii, *m*-CPBA in $CHCl_3$



Tf = $CF_3SO_2$

**Scheme 2**

Compound **1** was synthesized as follows (Scheme 1). Bis(2-bromomethylphenyl)selenide **5**[5] (500 mg, 1.2 mmol) was treated with $Na_2Se$ (150 mg, 1.2 mmol) in ethanol (400 $cm^3$) using a high dilution technique at room temperature under an Ar atmosphere. The whole mixture was stirred at room temperature for 10 h. After usual work-up, the residue was recrystallized from benzene to give **1** in 71% yield.†‡ The oxidation of **1** with *m*-chloroperbenzoic acid (*m*-CPBA) gave exclusively 5*H*,7*H*-dibenzo[*b*,*g*][1,5]diselenocine 6-oxide **2** in 80% yield.†‡

With regard to the conformational properties of **1**, for eight-membered rings typically two different conformers, the chair and boat-forms can exist.[6]‡§ The $^{1}$H NMR (500 MHz) spectrum of **1** in $CDCl_3$ at 25 °C shows the benzylic methylene protons as a broad singlet at δ 3.70 and an AB type absorption at δ 3.91 and 5.20 (*J* 13 Hz); the former resonance is assigned to the boat form (28%), and the latter pair to the chair form (72%). These conformers can also be characterized by $^{77}$Se NMR spectroscopy;¶ the $^{77}$Se NMR spectrum of **1** in $CHCl_3$ at 25 °C shows four peaks at δ 352.5 (chair) and 381.9 (boat) for –SeAr, and δ 380.4 (chair) and 398.7 (boat) for $-SeCH_2Ar$, respectively, the ratio of the conformers being consistent with that obtained from the $^{1}$H NMR spectrum. The methylene protons in the $^{1}$H NMR (500 MHz) spectrum of selenoxide **2** in $CDCl_3$ at 25 °C showing one AB system at δ 3.79 and 4.14 (*J* 11.5 Hz), and another AB system at δ 4.18 and 5.81 (*J* 11.5 Hz), are assigned to the boat-form (64%) for the former and the chair-form (36%) for the latter. An analogous result was found from the $^{77}$Se NMR ($CHCl_3$) spectrum of **2** which shows four peaks at δ 368.2 (chair) and 387.6 (boat) for –SeAr, and δ 915.8 (boat) and 940.5 (chair) for $-Se(O)CH_2Ar$.¶||

The stable diselenide dication salt **3** was prepared by the reaction of selenoxide **2** with 2 equiv. of silylating reagent, trimethylsilyl trifluoromethanesulphonate ($CF_3SO_3SiMe_3$) as follows. A solution of $CF_3SO_3SiMe_3$ (125 mg, 0.56 mmol) in anhydrous $CH_2Cl_2$ (5 $cm^3$) was added to a stirred solution of **2** (100 mg, 0.28 mmol) in anhydrous $CH_2Cl_2$ (30 $cm^3$) under an Ar atmosphere at −78 °C, and after 1 h the solution was allowed to reach −20 °C and stirred for an additional 12 h, and a white precipitate was formed. Filtration under anhydrous conditions and recrystallization from anhydrous acetonitrile–diethyl ether gave a crystalline salt **3** in 97% yield, m.p. 140 °C (decomp.).** None of the silylated compound was obtained. This reaction may proceed *via* the initial formation of the *O*-silylated selenurane intermediate **4** which subsequently would be converted into the dication **3** (Scheme 2). This is a new method for the preparation of the diselenide dication, although the preparative methods of heteroatom dications from medium-sized heterocyclic compounds are little known.[1-3]

$$\mathbf{3} + 2\,\underset{\mathbf{6}}{\text{PhSH}} \xrightarrow{\text{i}} \mathbf{1} + \underset{\mathbf{7}}{\text{PhSSPh}}$$

**Scheme 3** *Conditions*: i, MeCN, Ar, room temp., 30 min

The dication salt **3** was identified by NMR spectroscopy and elemental analysis. The $^{1}$H and $^{13}$C NMR spectra of **3** in $CD_3CN$ are: $^{1}$H δ 5.57, 5.76 (ABq, *J* 14 Hz, 4 H, $CH_2$), 7.54–7.72 (m, 6 H, ArH) and 7.99–8.11 (m, 2 H, ArH); $^{13}$C δ 54.4, 129.2, 130.2, 131.1, 132.5, 133.0 and 139.7; while the $^{77}$Se NMR spectrum of **3** in MeCN shows only two peaks at δ 761.4 and 789.9.†† These spectral data indicate that the dication **3** exists as a single conformer, the boat-form. The $^{19}$F NMR spectrum of the $CF_3SO_3^-$ anion of **3** in MeCN shows a single peak at δ 85.2 (relative to $C_6F_6$), in the region of ionic $CF_3SO_3^-$. These results are consistent with a dicationic structure for **3**.

Hydrolysis of the salt **3** gave the selenoxide **2** in 85% yield. In contrast, a tetraalkyl substituted diselenide dication salt (1,5-DSeCO$^{2+}$, *vide supra*) was stable in $H_2O$.[4a] The difference in reactivity between **3** and 1,5-DSeCO$^{2+}$ was also observed, *i.e.* the dication **3** led to the selenide **1** (70%) on treatment with *N*,*N*-dimethylaniline (DMA, 2 equiv.), contrasting with the reaction of 1,5-DSeCO$^{2+}$ with DMA which gave the *para*-substituted product, selenonium salt.[4c] Thus, the dication **3** can be reduced by DMA, since the oxidation potential of DMA is lower than that of the dication precursor.

The redox reaction was found to proceed in the treatment of benzenethiol **6** (2 equiv.) with dication **3** (1 equiv.) in MeCN under argon which afforded diphenyl disulphide **7** as the oxidation product (86%) and selenide **1** as the reduction product (78%) (Scheme 3). This new dication **3** reacts as an oxidizing agent.

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† Compound **1**: m.p. 140 °C; MS, *m/z* 340 ($M^+$); $^{1}$H NMR (500 MHz, $CDCl_3$) δ 3.70 (br s, $CH_2$), 3.91, 5.20 (ABq, *J* 13 Hz, $CH_2$) and 7.02–7.93 (m, ArH).

Compound **2**: m.p. 119–120 °C; MS, *m/z* 356 ($M^+$); FTIR (KBr) 829 $cm^{-1}$ (Se=O); $^{1}$H NMR (500 MHz, $CDCl_3$) δ 3.79, 4.14 (ABq, *J* 11.5 Hz, $CH_2$), 4.18, 5.81 (ABq, *J* 11.5 Hz, $CH_2$) and 7.13–7.98 (m, ArH). Satisfactory elemental analyses were obtained for compounds **1** and **2**.

‡ The protons and carbons of the aromatic rings in the NMR spectra (500 MHz, $^{1}$H and 125 MHz, $^{13}$C) of **1** and **2**, except for dication **3**, show two sets of signals due to the existence of two conformers; the detailed analysis will be reported in elsewhere.

§ In each $^{13}$C NMR ($CDCl_3$) spectrum of **1** and **2**, two signals of the benzylic carbon atoms due to the two conformers appear at δ 25.5 and 32.1 for **1**, and δ 52.2 and 60.6 for **2**, respectively.

¶ The chemical shifts are relative to $Me_2Se$. The conformers were assigned by the integration of the selenium peaks. The peak of benzylic selenide of **1** was determined by off-resonance method.

|| $^{77}$Se chemical shifts for $Ph_2Se(O)$ and $(PhCH_2)_2Se(O)$ in $CHCl_3$ (relative to $Me_2Se$) are: δ 860.1 and 928.0, respectively.

** Satisfactory C and H analyses were obtained for dication salt **3**.

†† The $^{77}$Se chemical shift of 1,5-DSeCO dication salt is δ 806.5.[4a]