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1,5-Diselenacyclo-octane: Synthesis and the First Isolation of the Diselenide PF_6^- Salt $[R_2Se^+–Se^+R_2]$

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A new cyclic bis-selenide, 1,5-diselenacyclo-octane (1) has been prepared; two-electron oxidation of (1) with two equivalents of $NOPF_6$ gave a novel diselenide PF_6^- salt which acts as an oxidizing agent.

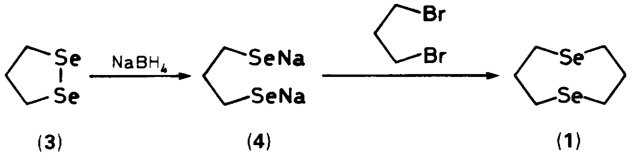
Dications consisting of two positively charged heteroatoms are little known, but their properties are of great interest.[1—3] No clear-cut example of transannular interactions between the two selenium atoms of medium-sized cyclic bis-selenides and formation of diselenide dications has been hitherto known. We report the synthesis of a new cyclic bis-selenide, 1,5-diselenacyclo-octane (**1**), the first isolation of its tetra-alkyl substituted diselenide PF_6^- salt (**2**), $[R_2Se^+–Se^+R_2]$, and the reactivity of (**2**).

The title compound (**1**) was synthesized as follows (Scheme 1). Sodium propane-1,3-diselenolate (**4**) was prepared by treatment of 1,2-diselenolane (**3**)[4] with $NaBH_4$. Compound (**4**) (5.02 g, 20.4 mmol) was treated with 1,3-dibromopropane (4.12 g, 20.4 mmol) in benzene–ethanol (500 ml, 1 : 1) using a high dilution technique at 40 °C under a N_2 atmosphere. The whole mixture was stirred at 40 °C for 18 h. After the usual work-up, the crude products were purified by silica-gel column chromatography (eluent, n-hexane/benzene) to give (**1**). Compound (**1**) was further purified by preparative liquid chromatography.†

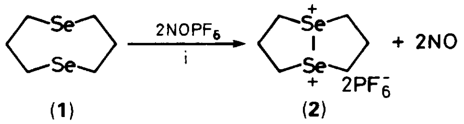
The diselenide PF_6^- salt (**2**) was prepared by a two-electron oxidation of the bis-selenide (**1**) with nitrosonium hexafluorophosphate, $NO^+PF_6^-$ (Scheme 2). Typically, a solution of $NOPF_6$ (749 mg, 4.28 mmol) in anhydrous dichloromethane–acetonitrile (10 ml) was added to (**1**) (518 mg, 2.14 mmol) in anhydrous dichloromethane (20 ml) at −78 °C, and after 1 h the solution was allowed to reach 0 °C and stirred for an additional 1 h. Evolution of NO gas was observed during the reaction. Filtration under rigorously anhydrous conditions and recrystallization from anhydrous acetonitrile–dichloromethane gave a white solid (**2**), m.p. 116—117 °C (decomp.).†

The ^{13}C NMR spectrum of the diselenide PF_6^- salt (**2**) in CD_3CN shows two peaks at δ 52.6 and 35.3, while the ^1H NMR spectrum shows multiplet peaks at δ 4.39—3.91 and 3.85—2.92 in a ratio of 2 : 1. Both the ^1H and ^{13}C NMR spectra indicate downfield shifts for the dication (**2**) compared to the bis-selenide.† Furthermore, (**2**) can be characterised by ^{77}Se NMR spectroscopy.[5] The ^{77}Se NMR spectrum of the bis-selenide (**1**) in MeCN at 0 °C shows a singlet peak at δ 141.3 (relative to Me_2Se), while (**2**) in MeCN shows a singlet at δ 806.5. This is a remarkable downfield shift, consistent with a dicationic structure for (**2**). The UV spectrum of (**2**) in MeCN exhibits λ_{max} at 248 nm with an extinction coefficient of 1.3×10^4.

The new diselenide PF_6^- salt (**2**) acted as an oxidizing agent as follows (Scheme 3). Treatment of 1,2-diphenylhydrazine (**5**) (1 equiv.) with (**2**) (1 equiv.) in the presence of 1,4-diazabicyclo[2.2.2]octane (DABCO) (1 equiv.) in MeCN under an Ar atmosphere at room temperature for 3 h gave azobenzene (**6**) as the oxidation product in 93% yield together with bis-selenide (**1**) as the reduction product. Similarly, benzenethiol (**7**) can be oxidized to diphenyl disulphide (**8**) in 92% yield on treatment with (**2**); during the reaction, solutions of (**2**) in $D_2O–CD_3CN$ were followed by NMR spectroscopy and no significant changes were observed over several hours.‡



Scheme 1



Scheme 2. *Reagents and conditions:* i, CH_2Cl_2–MeCN, −78 °C.

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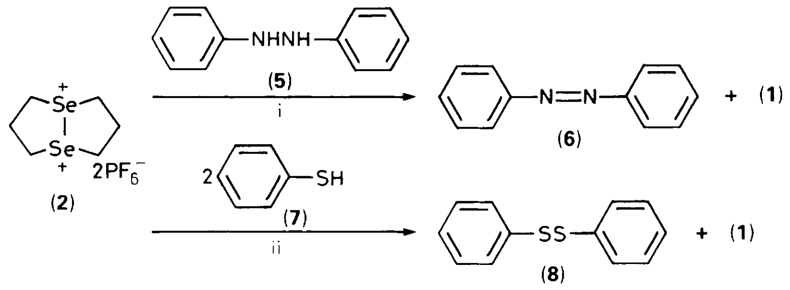
† *Spectroscopic data* for (**1**): ^1H n.m.r. ($CDCl_3$): δ 3.02—2.71 (m, 8H), 2.42—2.05 (m, 4H); ^{13}C n.m.r. ($CDCl_3$): δ 30.9, 23.4; *m/z* 244 (M^+), 242 (M^+ −2), 246 (M^+ +2). Satisfactory elemental analyses were obtained for (**1**) and (**2**).

‡ A similar result was found in the case of hydrazine dications.[1b]



Scheme 3. *Reagents and conditions:* i, DABCO, MeCN, room temp., 3 h, Ar; ii, MeCN, room temp., 3 h, Ar.

Compound (**2**) was recovered in a good yield after addition of H_2O, and could again act as an oxidant, *e.g.*, the reaction of hydrazine (**5**) with the dication afforded azobenzene (**6**) (90%) and the bis-selenide (**1**) (72%). In contrast, disulphide salts were easily hydrolysed to the corresponding *S*-oxides.[2,3]

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References

1 (a) R. W. Alder, A. G. Orpen, and J. M. White, *J. Chem. Soc., Chem. Commun.*, 1985, 949; (b) R. W. Alder, R. B. Sessions, J. O. Gmünder, and C. A. Grob, *J. Chem. Soc., Perkin Trans. 2*, 1984, 411.

2 W. K. Musker, *Acc. Chem. Res.*, 1980, **13**, 200.

3 H. Fujihara, R. Akaishi, and N. Furukawa, *J. Chem. Soc., Chem. Commun.*, 1989, 147; F. Iwasaki, N. Toyoda, R. Akaishi, H. Fujihara, and N. Furukawa, *Bull. Chem. Soc. Jpn.*, 1988, **61**, 2563.

4 G. T. Morgan and F. H. Burstall, *J. Chem. Soc.*, 1930, 1497.

5 ^{77}Se Chemical shifts of dialkyl-selenide, -diselenide, and -selenonium salt (relative to Me_2Se) are: δ 217 Et_2Se, 319 $(EtSe)_2$, and 325 p.p.m. $Et_2MeSe^+ I^-$. See: N. P. Luthra and J. D. Odom, in 'The Chemistry of Organic Selenium and Tellurium Compounds,' vol. 1, eds. S. Patai and Z. Rappoport, Wiley, New York, 1986, ch. 6.