SYNTHESIS AND MOLECULAR STRUCTURE OF 3,4,13,14-TETRASELENATRICYCLO[14.4.0.0^{6,11}]ICOSA-1(16),6,8,10,17,19-HEXAENE

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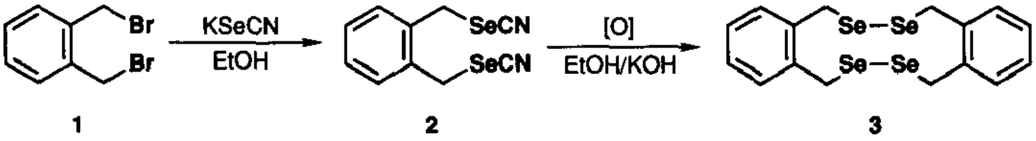
Abstract - A new selenium containing macrocyclic compound, 3,4,13,14-tetraselenatricyclo[14.4.0.0^{6,11}]icosa-1(16),6,8,10,17,19-hexaene (3), was prepared by oxidation of 1,2-bis(selenocyanatomethyl)benzene (2) in a moderate yield. The structure of compound (3) was determined by an X-ray crystallographic analysis and the activation parameters for the conformational changes of 3 in solution were calculated by DNMR experiments.

It has been well-known that 1,2-dithiane and 1,2-dithiin derivatives are generally stable liquid or solid compounds.[1] However, corresponding selenium analogues, 1,2-diselenanes and 1,2-diselenins, which have selenium-selenium bond in the six-membered ring, exist in their low molecular weight polymeric forms[2] except for a few examples.[3] Recently, we reported novel cycloaddition of 1,4-dihydro-2,3-benzodithiin[4] to alkenes in the presence of Lewis acid, $BF_3{\bullet}OEt$.[5] As one of the developments of our investigation on the preparations and reactions of cyclic polychalcogenides, these results prompted us to define whether 1,4-dihydro-2,3-benzodiselenin exists in the monomeric or oligomeric form. After several trials, we found that 1,4-dihydro-2,3-benzodiselenin could not be formed and 3,4,13,14-tetraselenatricyclo[14.4.0.0^{6,11}]icosa-1(16),6,8,10,17,19-hexaene (3) (a dimeric form of 1,4-dihydro-2,3-benzodiselenin) was obtained instead by oxidation of 1,2-bis(selenocyanatomethyl)benzene (2), which was stable both in a solid state and in solution. We present here the synthesis and X-ray crystallographic structural analysis of 3 together with the behavior of 3 in solution revealed by DNMR experiments.



Scheme 1

A typical synthetic procedure of **3** is as follows (Scheme 1). To a stirred solution of 1,2-bis(bromomethyl)benzene (**1**) (1.53 g, 5.80 mmol) in anhydrous ethanol (40 ml) was added 80% potassium selenocyanate (2.59 g, 14.4 mmol) at room temperature under N_2 atmosphere. After the mixture was stirred for 3 h under reflux conditions, the resulting inorganic precipitate was removed by filtration. The filtrate was evaporated and the residue was treated with water (20 ml). The mixture was extracted with dichloromethane (3 x 20 ml) and the combined organic layer was dried over anhydrous magnesium sulfate. After removal of the solvent, the residue was recrystallized from dichloromethane/hexane to give 1.46 g (80%) of 1,2-bis(selenocyanatomethyl)benzene (**2**).[6] To a stirred solution of **2** (320 mg, 1.02 mmol) in anhydrous ethanol (50 ml) was added 86% KOH (160 mg, 2.45 mmol) in anhydrous ethanol (15 ml). The mixture was stirred for 50 min at 40 °C under O_2 stream. After the solvent was removed under reduced pressure, the residue was treated with water (20 ml) and extracted with chloroform (3 x 20 ml). The extract was dried with anhydrous magnesium sulfate and the solvent was removed under reduced pressure. The residue was purified by column chromatography (silica gel; eluent, $CCl_4/CHCl_3$ = 5/1) followed by recrystallization from chloroform to give 110 mg (42%) of **3**.[7]

Although molecular mass of the crystalline compound was determined by vapor pressure osmometry to be 543, leading us to assign it to 3,4,13,14-tetraselenatricyclo$[14.4.0.0^{6,11}]$icosa-1(16),6,8,10,17,19-hexaene (2,3,12,13-tetraselena[4.4]orthocyclophane)[8] in solution, the final proof of the structure of **3** was obtained by an X-ray crystallographic analysis; the result is shown in Figure 1.[9] The Se-Se and Se-C bond lengths and Se-Se-C bond angle do not differ significantly from the averages of the corresponding ones of acyclic diselenides[10] and the dimer of *1H,4H*-naphtho[1,8-*d,e*][1,2]diselenepin.[11] Interestingly, the aromatic rings of **3** are approximately perpendicular to one another, which is in contrast to the corresponding tetrachalcogena[4.4]metacyclophanes previously reported.[12]

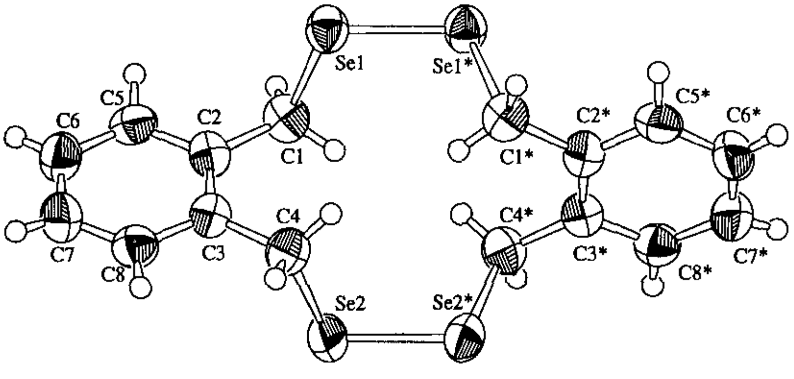


Figure 1. ORTEP Drawing of **3**, Selected Bond Distance (Å) and Angles (°), Se(1)-Se(1*) 2.308(2), Se(1)-C(1) 1.996(7), C(1)-C(2) 1.497(9), Se(1*)-Se(1)-C(1) 102.7(2), Se(1)-C(1)-C(2) 109.6(5), C(1)-C(2)-C(3) 121.6(6), Se(1*)-Se(1)-C(1)-C(2) 153.5(5), C(1*)-Se(1*)-Se(1)-C(1) -85.8(5), Se(1)-C(1)-C(2)-C(3) -83.1(8), C(1)-C(2)-C(3)-C(4) -2(1).

The variable-temperature ^1H nmr spectra of **3** were measured and the temperature-dependent spectra of benzyl protons have been interpretable in terms of conformational changes in solution (CD_2Cl_2 and toluene-d_8). The activation parameters of the conformational changes were evaluated from the simulation of the experimental spectra by analyzing the AB model.[13] The rate constant k was obtained for each temperature by comparing the experimental spectra with the simulated ones. The plot of log(k/T) against 1/T gave a good straight line and the activation enthalpy ($\Delta H^{\neq}$) and the activation entropy ($\Delta S^{\neq}$) were calculated by a least-square treatment using the Eyring model. Arrhenius plots were also linear and gave the values for activation energies (*Eact*). These results are summarized in Table 1, indicating that the activation free energies ($\Delta G^{\neq}$) of **3** are almost governed by the activation enthalpies ($\Delta H^{\neq}$) and the activation entropies ($\Delta S^{\neq}$) are negligible small. The activation free energies ($\Delta G^{\neq}$) for the conformational changes of **3** are 48.1 and 47.0 kJmol^{-1} in CD_2Cl_2 and toluene-d_8, respectively, and are not significantly different but slightly higher than that of the corresponding tetraselena[4.4]-metacyclophane.[14] These results suggest that the aromatic rings of **3** in solution must fold perpendicular by sequential rotations of aromatic-methylene carbon bonds and selenium-selenium bonds as well as those in a solid state.

Table 1. Activation Parameters for the Conformational Changes of **3**

Solvent	$\Delta\nu$	J_{AB}	T_2	Tc	$\Delta H^{\neq}$	$\Delta S^{\neq}$	$\Delta G^{\neq}$	*Eact*
	Hz	Hz	S^{-1}	K	kJmol^{-1}	Jmol^{-1}K^{-1}	kJmol^{-1}	kJmol^{-1}
CD_2Cl_2	191.0	10.1	0.16	250	49.6	5.1	48.1	51.6
Toluene-d_8	56.1	9.9	0.16	234	49.2	7.4	47.0	51.1

Consequently, the present studies on X-ray crystallographic analysis and variable-temperature nmr reveal the structure of large sized heterocyclic compound (**3**) containing four seleniums both in a solid state and in solution. Further studies on the stability and reactivity of tetraselenide (**3**) are under way.

ACKNOWLEDGEMENTS

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6. Compound **2**: Colorless needles; mp 112.0-113.0 °C; ^{1}H nmr (CDCl$_3$) δ 4.42 (s, 4H, CH$_2$), 7.40 (br s, 4H, ArH); ir (KBr) 3000, 2150, 1655, 1491, 1452, 1195, and 776 cm^{-1}; ms (m/z) 210 (M$^+$-SeCN); Anal. Calcd for $C_{10}H_8N_2Se_2$: C, 38.24; H, 2.57; N, 8.92. Found: C, 38.15; H, 2.49; N, 8.91.
7. Compound **3**: Yellow needles; mp 145.0-145.5 °C (decomp.); ^{1}H nmr (400 MHz, CDCl$_3$) δ 4.51 (br s, 8H, CH$_2$), 7.26 and 7.30 (A$_2$B$_2$m, 8H, ArH); ^{13}C{^{1}H} nmr (100 MHz, CDCl$_3$) δ 32.7, 128.3, 130.9, 136.9; ^{77}Se{^{1}H} nmr (76 MHz, CDCl$_3$) δ 357.0; ir (KBr) 2948, 1485, 1451, 1415, 1171, 1158, and 758 cm^{-1}; ms (m/z) 264 (M$^+$/2); molecular weight 543 (vapor pressure osmometry, benzene); Anal. Calcd for $C_{16}H_{16}Se_4$: C, 36.66; H, 3.08. Found: C, 36.52; H, 3.15.
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9. Crystallographic data for **3**: FW=524.14, orthorhombic, Pbcn(#60), a=18.821(4), b=9.614(3), c=9.353(3) Å, V=1692.3(7) Å^3, Z=4, Dc=2.057 g cm^{-3}, T=25 °C, R=0.040, Rw=0.043 for 982 reflections ($I>3.00\sigma(I)$) with Cu-Kα radiation.
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