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Synthesis and Characterization of Tetraethylethanediselenoamide

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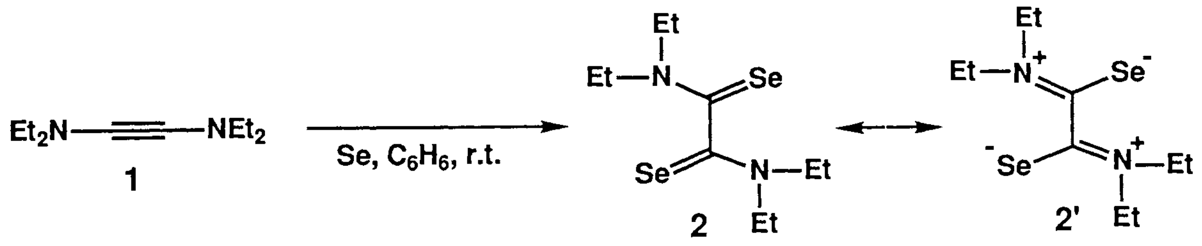
Tetraethylethanediselenoamide (**2**) was prepared in 81% yield by reaction of tetraethylethynediamine with elemental selenium. The X-ray single crystal structure analysis revealed that two $Et_2N(C{=}Se)$- units of **2** are perpendicular to each other. The oxidation of **2** with *m*-CPBA produced tetraethylmonoselenooxamide and the reaction with DMAD afforded dimethyl 4,5-bis(diethylamino)selenophene-2,3-dicarboxylate.

We have recently reported that tetraethylethynediamine (**1**) reacts with elemental sulfur to give tetraethylethanedithioamide in an excellent yield.[1)] We now report the synthesis of tetraethylethanediselenoamide (**2**) by reaction of **1** with elemental selenium and its X-ray single crystal structure analysis and some chemical properties. To our knowledge, no successfull isolation of 1,2-diselenoxo compounds has appeared.[2)] Thus, the compound **2** provides the first example of 1,2-diselenoxo compounds that is isolable at room temperature, even though **2** is not a true diselenoketone.

A mixture of **1**[3)] (1 mmol) and elemental selenium (4 mmol) in benzene (15 ml) was stirred at room temperature for 6 h under argon. The excess selenium was removed by filtration and the filtrate was evaporated under reduced pressure. The residue was chromatographed on a column of silica gel with dichloromethane as the eluent to give 264 mg (81%) of **2** as orange crystals.[4)] In the ^1H and ^{13}C NMR spectra, two ethyl groups of **2** attached to the nitrogen atom are nonequivalent because of the restricted rotation about the carbon(sp^2)-nitrogen bond, revealing that the carbon-nitrogen bond has considerable double-bond character by contribution of the canonical structure **2'**. Such restricted rotations were also observed with tetraalkylethanedithio-



amides and related compounds.$^{5-7)}$ Thus, compound **2** should be classified as the resonance-stabilized 1,2-diselenoxo compound. The selenocarbonyl carbon signal of **2** appeared at δ 197.69 ppm.

In the early stage of X-ray single crystal structure analysis of **2**,$^{8)}$ the crystallographically half part (indicated by asterisks in Fig. 1) of two molecules in an asymmetric unit was shown and ultimately the molecular structure given in Fig. 1 was determined. The relevant bond angles and bond distances are also summarized in Table 1. Interestingly, two C=Se bonds and two C(sp^2)-N bonds are twisted with a torsion angle of about 90°. This means that the planes of two Et_2N-C(=Se)- units are perpendicular to each other and hence no conjugation between them exists. The C=Se bond distance of **2** is as long as 1.82 Å and rather near to the mean value of the C=Se bond distance (1.76 Å) of selenoformaldehyde$^{9)}$ and the C-Se bond distance (1.94 Å) of dimethyl selenide$^{10)}$ which were determined by microwave spectroscopy.$^{11)}$ Meanwhile, the carbon(sp^2)-N bond distance is as short as about 1.31 Å and comparable with those of the common carbon-nitrogen double-bonded compounds (1.30 Å). In addition, the C(sp^2)-C(sp^2) bond distance is as long as 1.50-1.51 Å. These observations reveal that the canonical strucutre **2'** is the major contributor of the ground state of **2** in agreement with the conclusion reached by NMR.

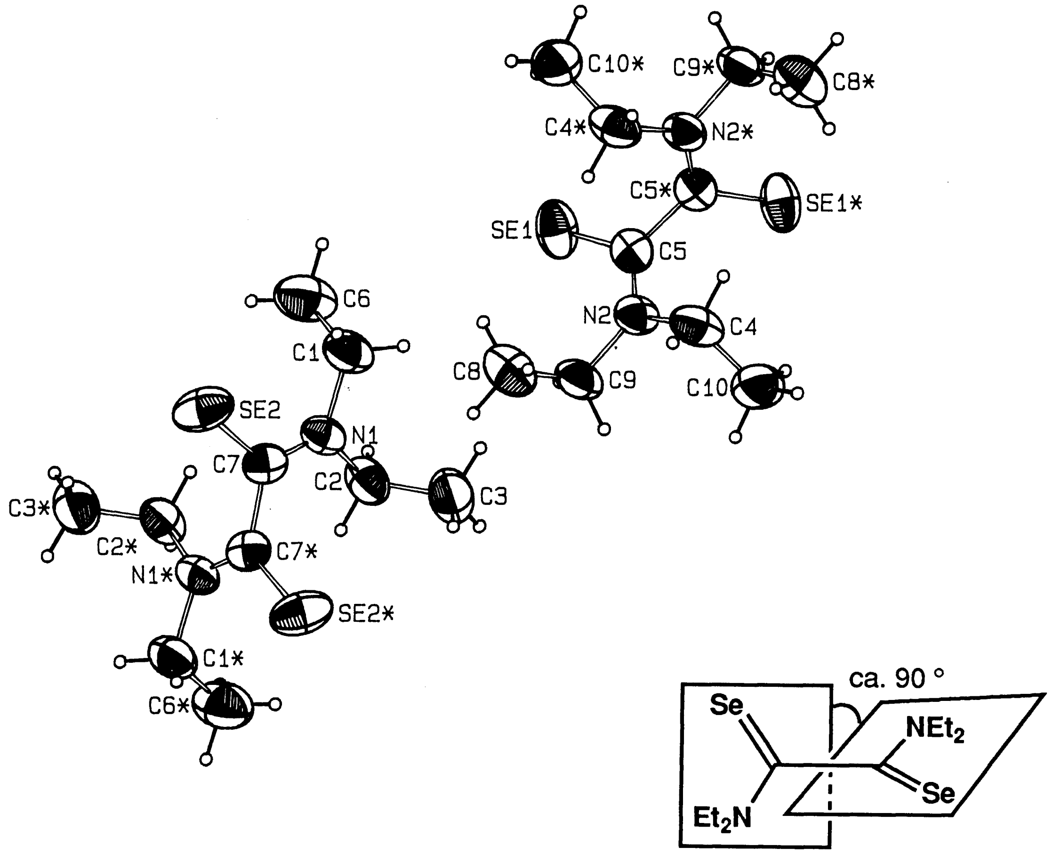


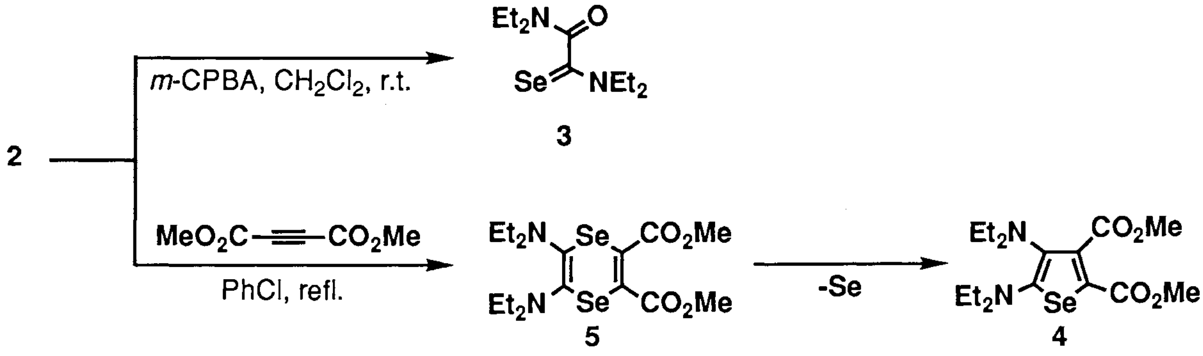
Fig. 1. Molecular structure of tetraethylethanediselenoamide (**2**).

Table 1. Relevant bond angles (°) and bond distances (Å) of **2**

Bond angles		Bond distances	
Se1-C5-C5*	115.5 (3)	N2-C5	1.309 (7)
Se1-C5-N2	126.3 (4)	N2*-C5*	1.309 (0)
N2-C5-C5*	118.2 (3)	N1-C7	1.307 (7)
Se1*-C5*-C5	115.5 (2)	N1*-C7*	1.307 (0)
Se1*-C5*-N2*	126 (0)	Se1*-C5*	1.819 (0)
N2*-C5*-C5	118.2 (2)	Se1-C5	1.820 (4)
Se2-C7-C7*	115.2 (3)	Se2-C7	1.823 (4)
Se2-C7-N1	126.3 (4)	Se2*-C7*	1.823 (0)
N1-C7-C7*	118.5 (3)	C5-C5*	1.506 (6)
Se2*-C7*-N1*	126 (0)	C7-C7*	1.501 (6)
Se2*-C7*-C7	115.2 (2)		
N1*-C7*-C7	118.5 (2)		

Numbers in parentheses are estimated standard deviations in the least significant digits.

Compound **2** was rather thermally stable and recovered in 57% yield even after heating in refluxing *o*-dichlorobenzene for 23 h. Oxidation of **2** with *m*-chloroperbenzoic acid (*m*-CPBA, 1 molar equiv.) afforded tetraethylmonoselenooxamide (**3**)[12] in 33% yield with 54% recovery of the starting material. In the ^{1}H and ^{13}C NMR, the both two ethyl groups in $Et_2N(C{=}O)$- and $Et_2N(C{=}Se)$- moieties appeared nonequivalent also in this compound. Heating **2** and dimethyl acetylenedicarboxylate (DMAD) in refluxing chlorobenzene for 23 h gave dimethyl 4,5-bis-(diethylamino)selenophene-2,3-dicarboxylate (**4**)[13] in 87% yield, which was probably produced by the initial cycloaddition of **2** with DMAD yielding the 1,4-diselenin **5** followed by thermal extrusion of selenium.



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4) **2**: Yellow needles, mp 104-105 °C (from hexane); ^{1}H NMR ($CDCl_3$) (90 MHz) δ=1.36 (6H, t, *J*=7.2 Hz), 1.38 (6H, t, *J*=7.2 Hz), 3.59 (4H, m), 4.08 (4H, m); ^{13}C NMR ($CDCl_3$) (22.5 MHz) δ=10.53 (q, CH_3), 11.58 (q, CH_3), 47.34 (t, CH_2), 48.23 (t, CH_2), 197.69 (s, C=Se); MS *m/z* 328 (M^+); λ_{max} (CH_2Cl_2) 292 (ε 11000), 321 nm (13100). Found: C, 36.77; H, 6.03; N, 8.54%. Calcd for $C_{10}H_{20}N_2Se_2$: C, 36.82; H, 6.18; N, 8.59%.

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8) Crystallographic data for **2**: $C_{10}H_{20}N_2Se_2$, FW=326.20, F(000)=648, crystal dimensions (0.40x0.30x0.30 mm), monoclinic, space group P2/n, a=16.745(6), b=6.145(1), c=16.928(5) Å, β=127.89(1)°, V=1374.8 Å^3, Z=4, ρ=1.57 g/cm^3, μ=52.8 cm^{-1}. The diffraction data were collected on a Enraf-Nonius CAD4 diffractometer at 23 °C in the ω-2θ mode using Mo-Kα radiation to a maximum 2θ value of 50° and corrected for Lorentz and polarization effects. The structure was solved by direct methods. The structure was refined in full-matrix least-squares where the function minimized was $\Sigma w(|F_o|-|F_c|)^2$ and the weight w is defined as 1.0 for all observed reflections. The final cycle of refinement included 127 variable parameters and converged with unweighted and weighted agreement factors of: $R_1=\Sigma|Fo-Fc|/\Sigma|Fo|=0.031$, $R_2=SQRT(\Sigma w(Fo-Fc)^2/\Sigma wFo^2)=0.032$.

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12) Mp 21-22 °C; ^{1}H NMR ($CDCl_3$) (400 MHz) δ=1.20 (3H, t, *J*=7.2Hz), 1.25 (3H, t, *J*=7.0 Hz), 1.32 (3H, t, *J*=7.2 Hz), 1.37 (3H, t, *J*=7.1Hz), 3,33 (3H, m), 3.53 (2H, q), 3.63 (1H, m), 3.89 (1H, m), 4.24 (1H, m); ^{13}C NMR ($CDCl_3$) (100.6 MHz) 10.89 (CH_3), 12.17 (CH_3), 12.80 (CH_3), 13.03 (CH_3), 38.42 (CH2), 42.55 (CH2), 47.52 (CH_2), 49.08 (CH_2), 167.00 (C=O), 196.37 (C=Se).

13) Viscous yellow oil: ^{1}H NMR ($CDCl_3$) (400 MHz) δ=1.00 (6H, t), 1.15 (6H, t), 2.95 (4H, q), 3.34 (4H, q), 3.76 (3H, s), 3.89 (3H, s); ^{13}C NMR ($CDCl_3$) (100.6 MHz) δ=12.45 (q), 13.88 (q), 47.05 (t), 49.47 (t), 51.89 (q), 52.41 (q), 114.85 (s), 132.95 (s), 144.53 (s), 162.58 (s), 163.41 (s), 168.20 (s).

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