SYNTHESIS AND STRUCTURE OF 1,3-DISELENOL-2-SELENONE

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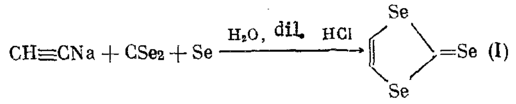
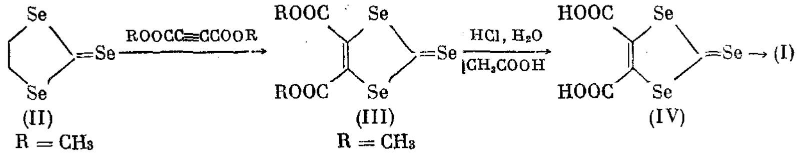
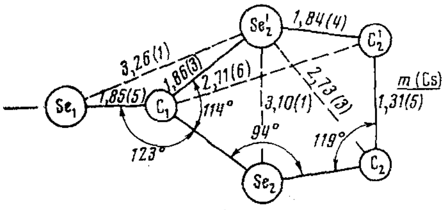
Ion-radical salts, which contain an Se compound as the donor component, represent considerable interest [1,2]. We developed a convenient method for the synthesis of 1,3-diselenol-2-selenone (I) and studied its structure. Compound (I) can be the donor in charge-transfer complexes, and an intermediate for obtaining organic conductors [2]. We synthesized (I) by the following scheme:



1,3-Diselenol-2-selenone (I) is obtained in only 10-15% yield by this route [3]. In contrast to this method, a second synthesis path, which is also used to obtain similar sulfur compounds [4], includes a greater number of steps:



However, here the yield in each step reaches 60-80%. The reddish-purple (I) crystals are shaped as thin plates and belong to the rhombic system. The principal crystallographic data are: $Se_3C_3H_2$; a = 9.273 (3), b = 8.525 (3), c = 7.483 (3)Å; M = 274.93; V = 591.55 Å^3; Z = 4; $\rho_{X\text{-ray}}$ + 3.105 g/cm^3; space group Pnma. The coordinates and individual heat factors are given in Table 1. The (I) molecule has a C_s symmetry, in which connection the crystallographic plane of symmetry is perpendicular to the plane of the molecule. We have drawn molecule (I) in Fig.1 and given the interatomic distances and valence angles. All of the lengths of the Se–C bonds are equal to 1.85 Å, which corresponds to a multiplicity of approximately 1.5. The length of the $C^2C^{2'}$ bond corresponds to that of a C–C double bond, similar to that found in the structure of 2,2-bis-1,3-dithiol $C_6H_4S_4$ (1.314 Å) [5]. The (I) molecule is flat, and the deviations of the atoms from the rays of the plane, 6.20x + 5.56y = 1.33, are: Se^1 – 0.06, Se^2 0.04, $Se^{2'}$ 0.04, C^1 0.05, C^2 – 0.04, $C^{2'}$ – 0.04 Å. The intermolecular contacts in the crystal do not exceed 3.64 Å.



EXPERIMENTAL METHOD

The IR spectra were taken on a UR-20 instrument, the absorption spectra were taken on a Specord UV-Vis instrument, and the NMR spectra were taken on a JNM-60 instrument. The x-ray structure

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TABLE 1

ATOM	x	y	z	B_j, Å^2
Se^1	0,0491(7)	1/4	0,3047(8)	5,2(1)
Se^2	0,2864(5)	0,0679(6)	0,5505(6)	4,7(1)
C^1	0,205(6)	1/4	0,459(7)	4,1(9)
C^2	0,407(4)	0,173(4)	0,705(4)	4,0(7)

analysis (159 independent nontrivial reflections) was run on a DAR-UM diffractometer [6] using Mo—K$_\alpha$ radiation. The structure was determined by the heavy atom method and refined by the method of least squares (MLS) as a full-matrix isotropic approximation to the R factor 0.115 [7].

1,3-Diselenol-2-selenone (I). To a solution of 2 g of Na in 130 ml of NH_3 at −70°C was added 100 ml of abs. ether, and then ethylene was passed in for 1 h. Then the cooling was removed and, with gradual removal of the NH_3, 5 g of powdered Se was added to the flask. The reaction mass turned green, and then a reddish brown color. The mixture was stirred at 10° for 1 h, and then were added 100 ml of CH_3CN and, in drops, 8 ml of CSe_2 in 40 ml of CH_3CN, after which the stirring was continued for another 2 h, 100 ml of dil. HCl solution was added, the mixture was stirred for 5 min, and the flask contents were poured into 1 liter of water. The organic layer was repeatedly extracted with ether, dried over $CaCl_2$, and the ether was distilled off completely. The solid residue was repeatedly extracted with boiling hexane. We obtained 2.1 g (10%) of (I) with mp 114-115° (from hexane). Found: C 12.88; H 0.82%. $C_3H_2Se_3$. Calculated: C 13.07; H 0.79%. Infrared spectrum (KBr, cm^{-1}): 1520, 1420, 1350, 1250, 1080, 920, 750, 740, 690. Ultraviolet spectrum (CH_3CN, nm): 236, 265, 298, 420. NMR spectrum ($CDCl_3$, TMS, δ): 7.90 ppm.

1,3-Diselenolane-2-selenone (II). Similar to [8], we obtained 2.5 g (40%) of product as reddish purple crystals, mp 95-96°. Found: C 12.89; H 1.53%. $C_3H_4Se_3$. Calculated: C 13.01; H 1.46%. Ultraviolet spectrum (CH_3CN): 565 nm.

Dimethyl Ester of 1,3-Diselenol-2-selenone-4,5-dicarboxylic Acid (III). To a solution of 2.4 g (0.0086 mole) of (II) was added 1.3 g (0.0086 mole) of dimethyl acetylenedicarboxylate and the mixture was heated at 70° for 6 h. Dark red crystals deposited on cooling. We obtained 3 g (87.5%) of (III), mp 125-126° (from toluene). Found: C 21.57; H 1.8; Se 60.3%. $C_7H_6Se_3O_4$. Calculated: C 21.7; H 1.54; Se 60.5%. Infrared spectrum (KBr, cm^{-1}): 1720, 1550, 1420, 1240, 1080, 1005, 980, 930, 895, 845, 790, 750, 650, 550. Ultraviolet spectrum (CH_3CN, nm): 222, 252, 272, 420. NMR spectrum ($CDCl_3$, TMS, δ): 3.93 ppm.

1,3-Diselenol-2-selenone-4,5-dicarboxylic Acid (IV). A mixture of 1.2 g (0.0031 mole) of (III), 10 ml of water, 6 ml of conc. HCl, and 8 ml of AcOH was heated in an argon atmosphere for 8 h at 80-90° (the product decomposes at higher temperatures with the liberation of elemental Se), filtered hot, and let stand overnight. The obtained lustrous purple-brown crystals of the product were dried in vacuo over P_2O_5. We obtained 0.62 g (60%) of (IV), mp 109° (decompn.). Found: C 16.03; H 0.90%. $C_5H_2O_4Se_3$. Calculated: C 16.6; H 0.60%. Infrared spectrum (KBr, cm^{-1}): 2930, 2370, 2350, 1710, 1670, 1580, 1528, 1445, 1287, 1060, 950, 920, 890, 733, 680, 420. Ultraviolet spectrum (CH_3CN, nm): 274, 334, 420. NMR spectrum (DMSO·d_6, TMS, δ): 4 ppm.

1,3-Diselenol-2-selenone (I). A mixture of 0.5 g (0.0014 mole) of (IV) and 10 ml of pyridine was heated in an argon atmosphere for 8 h at 80-95°. The pyridine was removed on a rotor evaporator at 40°. The residue was extracted thrice with boiling pentane. The pentane solution on cooling deposited 0.18 g (60%) of product as bright red-purple crystals, mp 114-115° (from pentane), which was completely identical with that described above.

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CONCLUSIONS

The reaction of 1,3-diselenolane-2-selenone with dimethyl acetylenedicarboxylate, and subsequent saponification and decarboxylation of the formed dimethyl ester of 1,3-diselenol-2-selenone-4,5-dicarboxylic acid, gave 1,3-diselenol-2-selenone, whose molecular structure was determined.

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