Selenium-Containing Heterocycles from Isoselenocyanates: Synthesis of 5-Amino-2,4-dihydro-3*H*-1,2,4-triazole-3-selones

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The reaction of *S*-methylisothiosemicarbazide hydroiodide (= *S*-methyl hydrazinecarboximidothioate hydroiodide; **1**), prepared from thiosemicarbazide by treatment with MeI in EtOH, and aryl isoselenocyanates **5** in CH_2Cl_2 affords 3*H*-1,2,4-triazole-3-selone derivatives **7** in good yield (*Scheme 2*, *Table 1*). During attempted crystallization, these products undergo an oxidative dimerization to give the corresponding bis(4*H*-1,2,4-triazol-3-yl) diselenides **11** (*Scheme 3*). The structure of **11a** was established by X-ray crystallography.

1. Introduction. – The biochemistry and pharmacology of selenium is of current interest, particularly with regard to public health. Selenium has long been recognized as a dietary antioxidant and is now known to be an essential component to the active sites of several enzymes, including glutathione peroxidase [1] and thioredoxine reductase, which catalyze reactions essential for the protection of cellular components against oxidative and radical damage [2]. A too low concentration of selenium in the plasma has been identified as a risk factor for several diseases, including cancer [3], cardiovascular disease [4], and osteoarthritis or AIDS [5]. Therefore, consumption of Se-rich plants or yeast-based nutritional supplements is reported to reduce the risk of cancer. It has also been suggested that plants are able to convert inorganic Se in the soil or growth medium into organoselenium compounds, such as selenoamino acids [6], by following a route similar to the sulfur assimilatory pathway [7].

In recent years, the interest in organoselenium chemistry increased remarkably. There is no doubt that Se-containing organic molecules have played and continue to play an important role in biology and medicine, and a large number of them are now accepted as useful antioxidants [8], anticancer [9] and melanin-synthesis-regulating agents [10], superoxide-anion scavengers [11], anti-inflammatory agents [12], and compounds with antihypertensive [13], antinociceptive [14], antibiotic [15], and antiviral activity [16], *i.e.*, organoselenium compounds are nowadays an important class of biologically active products [17] with pharmaceutical applications [18].

The interest in Se-compounds may also be attributed to their specific chemical properties, which fit well into the requirements of modern organic synthesis, and many of them are well adapted to chemo-, regio-, and stereoselective reactions [19][20].

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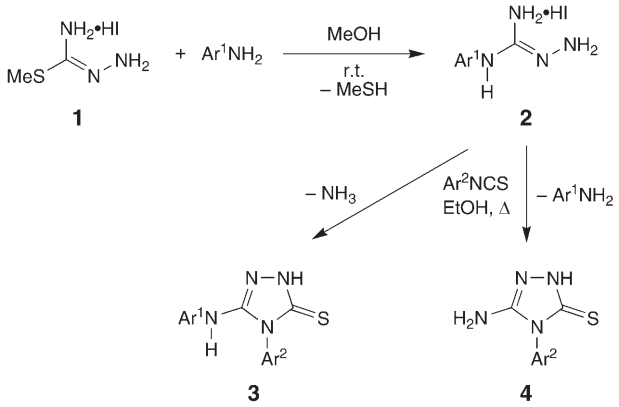
For all of these reasons, isoselenocyanates became a focus of interest in our research group as building blocks in the synthesis of Se-containing heterocycles. Their special chemical properties [21] make them very useful starting materials in heterocyclic chemistry [22], as they are easy to prepare and safe to store [23]. Nevertheless, under mild conditions, they undergo reactions, which are compatible with the presence of a variety of unsaturated as well as multi-functional structural units. Therefore, they are useful reagents in the preparation of natural products [24].

Within the family of triazoles, the corresponding thiones have gained special importance. Several examples were described to be of pharmaceutical interest, *e.g.*, as agents with antibacterial activity [25]. A series of 1,2,4-triazolethiones have been prepared by using isothiocyanates [25–27] (and refs. cited therein). For example, 2,4-dihydro-3*H*-1,2,4-triazole-3-thione derivatives were synthesized by the reaction of isothiocyanates with amidrazone hydrochlorides (=carboximidic acid hydrazide hydrochlorides) [26]. Correspondingly, 5-amino derivatives were obtained when *S*-methylisothiosemicarbazide hydroiodide (= *S*-methyl hydrazinecarboximidothioate hydroiodide; **1**) [28] was reacted with primary aryl- or benzylamines, and the resulting carbonohydrazonic diamide hydroiodide **2** was subsequently treated with aryl isothiocyanates in EtOH [25b] (*Scheme 1*). Depending on the reaction temperature, a 5-(arylamino)- (**3**) or 5-amino-2,4-dihydro-3*H*-1,2,4-triazole-3-thione (**4**) was isolated.

Scheme 1



As for the reaction of isoselenocyanates with nucleophiles, it is known that N-, O-, S-, and Se-nucleophiles add to the central C-atom [21a], whereas P-nucleophiles attack either the central C-atom or the Se-atom [21b][29]. However, only a few examples have been reported for the reaction of hydrazine derivatives with isoselenocyanates [30], and nothing is known on the reaction with carbonohydrazonic diamide compounds. Very recently, we have published the synthesis of 1,3,4-selenadiazine derivatives from hydrazine, α-bromoacetophenones, and isoselenocyanates [31].

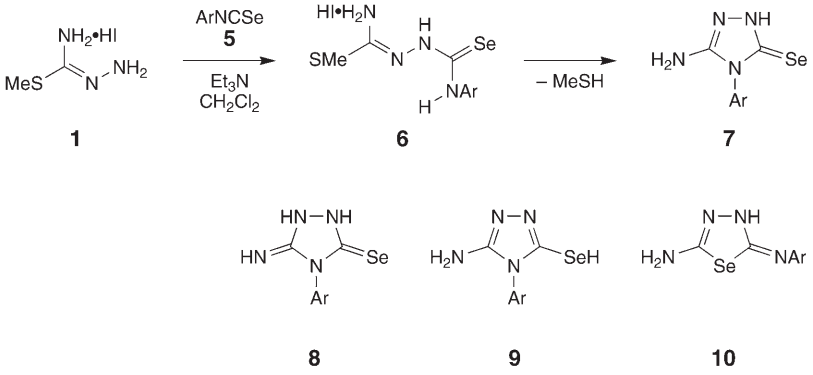
As a continuation of the previously published studies on the synthesis of Se-containing heterocycles based on isoselenocyanate chemistry [32], we have recently reported on the synthesis of 5-selenoxo-1,2,4-triazole-1-carboxylates by using a

Mitsunobu strategy [33]. Following a similar strategy, *Koketsu et al.* have published the preparation of 3-selenoxo-1,2,4-triazole derivatives by the reaction of acyl isoselenocyanates with phenylhydrazine [30]. Furthermore, reactions of isoselenocyanates **5** with mercapto acids led to 2-selenoxo-1,3-thiazolidin-4-ones and 2-selenoxo-1,3-thiazinan-4-ones in good yields [34].

In the present paper, the results of the investigations aimed at extending this methodology to the synthesis of 5-amino-3*H*-1,2,4-triazole-3-selone derivatives are reported.

2. Results and Discussion. – In the synthesis of the 1,3,4-selenadiazine derivatives [31], hydrazine was used as a bis-nucleophilic reagent, which combined first with the aryl isoselenocyanate **5** and, in a later reaction step, underwent the cyclization with the acetophenone residue of the intermediate. In this case, cyclization occurred *via* a condensation reaction. We report here the use of *S*-methylisothiosemicarbazide hydroiodide (**1**) bearing a methylthio group, which will be the leaving group in the cyclization step of the preparation of 5-amino-4-aryl-3*H*-1,2,4-triazole-3-selones **7** according to *Scheme 2*. After stirring for 12 h, the products were separated by filtration; they were obtained in good yields and were pure enough to give unambiguous spectroscopic data and elemental analyses (*Table 1*).

Scheme 2



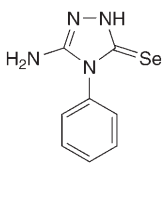
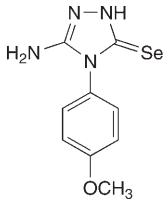
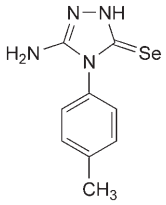
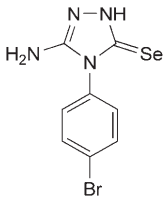
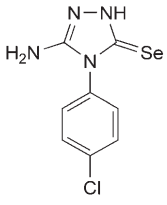
1 **6** **7**

8 **9** **10**

The structures of compounds **7** were established on the basis of their spectroscopic data, which correspond reasonably well with those of the previously described 5-selenoxo-1,2,4-triazole-1-carboxylates [33]. In the IR spectra (KBr), the triazoleselones **7** show weak absorptions for NH at 3380–3150 cm^{-1} and a strong C=N absorption at *ca.* 1640 cm^{-1}. The ^{1}H-NMR signals for the NH and NH_2 groups in $CDCl_3$ appear at δ(H) 13.6–12.9 and 6.5–5.3, respectively. Characteristic signals in the ^{13}C-NMR spectra are observed for the triazole C-atoms (C(5) and C(3)) at δ(C) 152–159). Furthermore, the ESI-MS show the $[M + Na]^+$ signal as the characteristic ensemble of the peaks for the Se-isotopes.

A reaction mechanism for the formation of **7** is proposed in *Scheme 2*. After deprotonation of the hydroiodide **1**, nucleophilic addition of *S*-methylisothiosemicar-

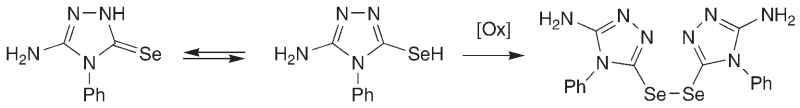
Table 1. *Preparation of 5-Amino-2,4-dihydro-3*H*-1,2,4-triazole-3-selones* **7** *from Isoselenocyanates* **5**

	a	**b**	**c**	**d**	**e**
7					
Yield [%]	78	72	80	82	75

bazide onto **5** leads to an intermediate **6**, which undergoes a cyclization *via* elimination of MeSH.

Although all analytical data are in accordance with structure **7**, we cannot exclude the tautomeric structures **8** and **9** with certainty. Even structure **10**, which could be the result of the alternative cyclization of **6** *via* the Se-atom, is compatible with the data. Therefore, we decided to establish the structure by X-ray crystallography. However, the triazoles **7**, which were obtained directly from the reaction mixture after filtration, were always amorphous, and the crystallization of these products proved to be a difficult task. An explanation for this behavior could be the presence of NH groups with the possibility of the formation of different tautomeric structures (*i.e.*, **7**–**9**). The recrystallization needed rather polar solvents, and the formation of metallic Se and decomposition of the product was observed even at low temperature. After several attempts, crystallization of **7a** from MeOH/CH_2Cl_2 gave orange crystals with a m.p. 206–208° and a molecular mass of 478 (ESI-MS). Therefore, the structure of the recrystallized product was proposed to be the diselenide **11a**, which could be formed from the tautomeric triazoleselenol **9a** by oxidative dimerization (*Scheme 3*). This assumption was established by an X-ray crystal-structure determination (*Fig. 1*).

Scheme 3



7a **9a** **11a**

The asymmetric unit in the crystal structure contains one molecule of **11a**, one MeOH molecule, and two molecules of H_2O (*Fig. 2*). The five-membered heterocyclic rings are planar, with the adjacent atoms N(3), Se(1) and N(14), C(17), respectively, also being in the corresponding plane, while C(6) and Se(2) deviate by 0.213(2) and 0.114(1) Å, respectively, from these planes. The torsion angle C(1)–Se(1)–Se(2)–C(12) is −96.08(9)°, as usually observed for oligosulfides and di- and triselenides (see, *e.g.*, [36][37]). The planes of the Ph groups at N(2) and N(13)

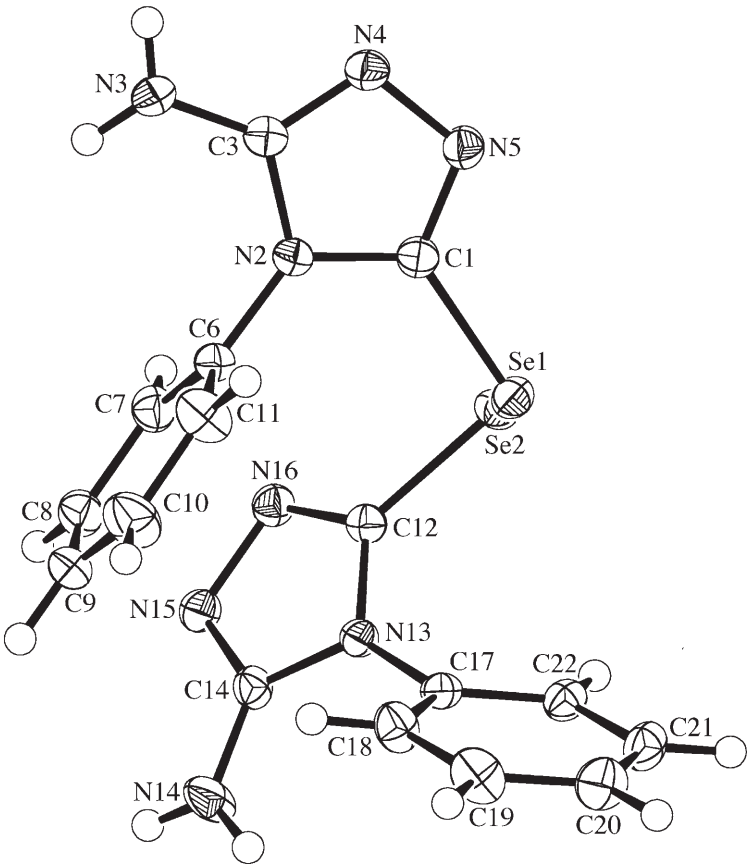


Fig. 1. *ORTEP Plot* [35] *of the molecular structure of* **11a** (arbitrary atom numbering; 50% probability ellipsoids)

are significantly twisted out of the planes of their parent heterocyclic rings with the dihedral angles between the planes being 87.95(11) and 55.67(11)°, respectively.

Intermolecular H-bonds link the molecules of **11a**, MeOH, and H_2O into a three-dimensional framework. Each molecule of **11a** donates H-bonds to one neighboring molecule of **11a**, as well as to three different H_2O molecules. One of the two symmetry-independent H_2O molecules donates H-bonds to two different molecules of **11a**. The other H_2O molecule donates one H-bond to a molecule of **11a** and a second H-bond to the O-atom of a MeOH molecule. The MeOH molecule donates a H-bond to one of the H_2O molecules. The H-bond acceptor atoms in **11a** are the unsubstituted N-atoms in the five-membered rings.

In conclusion, we have shown that isoselenocyanates **5** react with isothiosemicarbazide hydroiodide **1** in basic media to give an intermediate, which undergoes a ring formation to give 4-aryl-2,4-dihydro-3*H*-1,2,4-triazole-3-selones **7** in good yields. These products are easily oxidized to give bis(4*H*-triazol-3-yl) diselenides **11**.

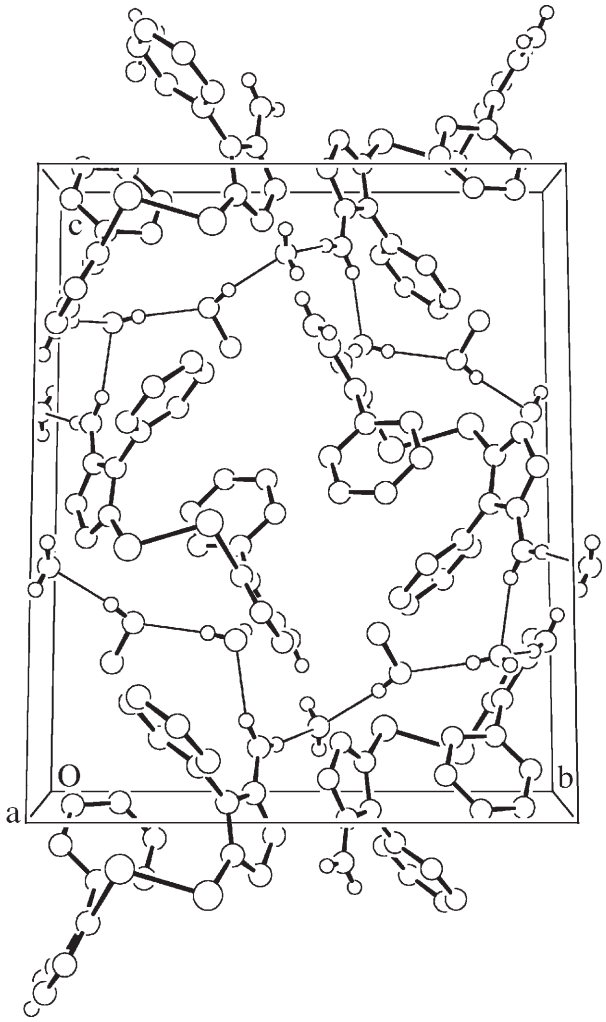


Fig. 2. *Molecular packing of* **11a** *projected down the* a-*axis showing the H-bonding scheme* (equivalent isotropic spheres for atoms; uninvolved H-atoms are omitted for clarity)

We thank the analytical units of our institute for spectra and analyses. Financial support of this work by the *Dr. Helmut Legerlotz-Foundation* and *F. Hoffmann–La Roche AG*, Basel, is gratefully acknowledged.

Experimental Part

1. *General*. See [32e][32f]. TLC: silica gel *60* F_{254} plates (0.25 mm; *Merck*). Column chromatography (CC): silica gel *60* (0.040–0.063 mesh; *Merck*). M.p.: *Büchi B-540* apparatus, in capillaries; uncorrected. ^{1}H- (300 MHz) and ^{13}C-NMR (75.5 MHz) Spectra: *Bruker ARX-300* instrument; in (D_6)DMSO, unless otherwise specified; chemical shifts in ppm. ESI-MS: *Finnigan MAT-TSQ-700* instrument; in *m*/*z* (rel. %).

2. *Starting Materials.* Isoselenocyanates were prepared according to *Barton*'s procedure starting from formamides [23]. Formanilide (= *N*-phenylformamide) is commercially available (*Fluka*), *N*-(4-bromophenyl)-, *N*-(4-chlorophenyl)-, *N*-(4-methylphenyl)-, and *N*-(4-methoxyphenyl)formamide were prepared from the respective commercial anilines and 95% HCOOH [38]. The soln. was heated to reflux for 30 min and concentrated. The residue was dissolved in Et_2O and washed with 5% AcOH soln., H_2O, and 5% aq. $NaHCO_3$ soln. The aq. phase was extracted with Et_2O, the combined org. extract dried ($MgSO_4$), and concentrated, and the crude products purified by recrystallization in H_2O.

S-Methylisothiosemicarbazide hydroiodide (**1**) was prepared by treatment of thiosemicarbazide (= hydrazinecarbothioamide; 9.10 g, 0.10 mol) with MeI (14.20 g, 0.10 mol) in refluxing abs. EtOH for 2 h. The mixture was allowed to cool, and filtration and purification by recrystallization in abs. EtOH yielded 18.71 g (80%) of **1**. M.p. 137–139° ([39]: 138°). ^{1}H-NMR: 2.69 (*s*, Me). ^{13}C-NMR: 12.7 (Me); 170.2 (C=N). ESI-MS: 234 (2, $[M+1]^+$), 106 (100, $C_2H_8N_3S^+$), 92 (53). Anal. calc. for $C_2H_8IN_3S$ (233.07): C 10.31, H 3.46, N 18.03, S 13.76; found: C 10.30, H 3.44, N 18.24, S 13.59.

*3. 3*H-*1,2,4-Triazole-3-selones* **7**: *General Procedure.* To a soln. of **1** (233 mg, 1.0 mmol) and isoselenocyanate **5** (1.0 mmol) in CH_2Cl_2 (20 ml), Et_3N (0.28 ml, 2.0 mmol) was added, whereby the suspension became instantaneously colorless and then rapidly yellow. The evolution of a gas (methanethiol) was detected. The mixture was stirred overnight, then, the white precipitate was filtered and washed with cold CH_2Cl_2 to give anal. pure **7**.

*5-Amino-2,4-dihydro-4-phenyl-3*H-*1,2,4-triazole-3-selone* (**7a**). From phenyl isoselenocyanate (**5a**): 187 mg (78%) of **7a**. White crystals. M.p. 191–193° (CH_2Cl_2). IR (KBr): 3363*w*, 3287*w*, 3249*w*, 3158*m* (br.), 2970*w*, 2936*w*, 2785*w*, 1640*s*, 1593*m*, 1496*s*, 1450*m*, 1336*m*, 1237*m*, 1139*w*, 1071*w*, 1011*w*, 991*w*, 784*w*, 749*m*, 690*s*, 567*m*. ^{1}H-NMR: 5.94 (br. *s*, NH_2); 7.25 (*d*, $J = 8.1$, 2 arom. H); 7.42–7.49 (*m*, 3 arom. H); 13.57 (br. *s*, NH). ^{13}C-NMR: 128.4 (2 arom. CH); 129.2 (3 arom. CH); 133.3 (1 arom. C); 153.1 (C(5)); 155.8 (C=Se). ESI-MS: 265 (12), 264 (10), 263 (100, $[M + Na]^+$), 262 (5), 261 (47), 260 (14), 259 (13). Anal. calc. for $C_8H_8N_4Se$ (239.14): C 40.18, H 3.37, N 23.43; found: C 39.93, H 3.49, N 23.20.

*5-Amino-2,4-dihydro-4-(4-methoxyphenyl)-3*H-*1,2,4-triazole-3-selone* (**7b**). From 4-methoxyphenyl isoselenocyanate (**5b**): 194 mg (72%) of **7b**. White crystals. M.p. 177–179° (CH_2Cl_2). IR (KBr): 3373*w*, 3307*w*, 3261*w*, 3200*w*, 3158*w*, 2999*w*, 2935*w*, 2808*w*, 1646*s*, 1604*w*, 1583*w*, 1513*s*, 1459*m*, 1442*m*, 1338*m*, 1302*m*, 1259*s*, 1240*m*, 1184*w*, 1170*m*, 1130*m*, 1103*w*, 1048*w*, 1021*w*, 1007*w*, 989*w*, 833*m*, 803*w*, 768*w*, 728*w*, 665*w*, 629*w*, 619*w*, 573*w*. ^{1}H-NMR: 4.06 (*s*, MeO); 6.25 (br. *s*, NH_2); 7.31, 7.49 (*AA′BB′*, $J = 8.1$, 4 arom. H); 13.52 (br. *s*, NH). ^{13}C-NMR: 55.3 (MeO); 114.4 (2 arom. CH); 125.8 (1 arom. C); 129.7 (2 arom. CH); 153.3 (1 arom. C); 156.1 (C(5)); 159.5 (C=Se). ESI-MS: 295 (12), 294 (11), 293 (100, $[M + Na]^+$), 292 (9), 291 (45), 290 (16), 289 (18). Anal. calc. for $C_9H_{10}N_4OSe$ (269.17): C 40.16, H 3.74, N 20.82; found: C 40.31, H 3.40, N 21.06.

*5-Amino-2,4-dihydro-4-(4-methylphenyl)-3*H-*1,2,4-triazole-3-selone* (**7c**). From 4-methylphenyl isoselenocyanate (**5c**): 203 mg (80%) of **7c**. White crystals. M.p. 182–184° (CH_2Cl_2). IR (KBr): 3367*w*, 3298*w*, 3255*w*, 3159*w*, 2999*w*, 2942*w*, 2798*w*, 1645*s*, 1599*w*, 1578*w*, 1500*s*, 1465*m*, 1443*m*, 1332*m*, 1295*m*, 1245*m*, 1240*m*, 1178*w*, 1165*m*, 1128*m*, 1105*w*, 1055*w*, 1018*w*, 1000*w*, 978*w*, 835*w*, 798*w*, 777*w*, 725*w*, 656*w*. ^{1}H-NMR: 2.42 (*s*, Me); 5.28 (br. *s*, NH_2); 7.26, 7.30 (*AA′BB′*, $J = 8.1$, 4 arom. H); 12.91 (br. *s*, NH). ^{13}C-NMR: 20.6 (Me); 127.1 (2 arom. CH); 129.7 (1 arom. C); 129.8 (2 arom. CH); 139.3 (1 arom. C); 156.1 (C(5), C=Se). ESI-MS: 279 (12), 278 (12), 277 (100, $[M + Na]^+$), 276 (7), 275 (55), 274 (12), 273 (17). Anal. calc. for $C_9H_{10}N_4Se$ (253.17): C 42.70, H 3.98, N 22.13; found: C 42.56, H 4.12, N 22.23.

*5-Amino-4-(4-bromophenyl)-2,4-dihydro-3*H-*1,2,4-triazole-3-selone* (**7d**). From 4-bromophenyl isoselenocyanate (**5d**): 261 mg (82%) of **7d**. White crystals. M.p. 192–194° (CH_2Cl_2). IR (KBr): 3383*w*, 3294*w*, 3080*m* (br.), 2927*w*, 2774*w*, 1633*s*, 1586*m*, 1573*m*, 1489*m*, 1450*m*, 1403*w*, 1330*m*, 1226*m*, 1103*w*, 1069*w*, 1005*m*, 985*w*, 835*m*, 820*w*, 771*w*, 741*w*, 715*w*, 570*m*. ^{1}H-NMR: 6.46 (br. *s*, NH_2); 7.63, 8.05 (*AA′BB′*, $J = 8.1$, 4 arom. H); 13.42 (br. *s*, NH). ^{13}C-NMR: 122.5 (1 arom. C); 130.8 (2 arom. CH); 132.2 (2 arom. CH); 139.4 (1 arom. C); 152.9 (C(5)); 155.8 (C=Se). ESI-MS: 345 (13), 344 (8), 343 (78), 342 (11), 341 (100, $[M + Na]^+$), 340 (16), 339 (48), 338 (15), 337 (12). Anal. calc. for $C_8H_7BrN_4Se$ (318.04): C 30.21, H 2.22, N 17.62; found: C 30.36, H 2.55, N 17.63.

*5-Amino-4-(4-chlorophenyl)-2,4-dihydro-3*H-*1,2,4-triazole-3-selone* (**7e**). From 4-chlorophenyl isoselenocyanate (**5e**): 205 mg (75%) of **7e**. White crystals. M.p. 185–187° (CH_2Cl_2). IR (KBr): 3379*w*, 3294*w*, 3084*m* (br.), 2958*m*, 2931*m*, 2778*w*, 1634*s*, 1587*m*, 1574*m*, 1493*s*, 1453*m*, 1409*w*, 1331*m*, 1230*m*,

1106*w*, 1091*w*, 1007*m*, 986*w*, 840*m*, 822*w*, 774*w*, 734*w*, 717*w*, 574*m*. ^{1}H-NMR: 6.33 (br. *s*, NH_2); 7.58, 7.79 (*AA′BB′*, *J* = 8.7, 4 arom. H); 13.47 (br. *s*, NH). ^{13}C-NMR: 129.3 (2 arom. CH); 130.5 (2 arom. CH); 132.2 (1 arom. C); 133.9 (1 arom. C); 153.0 (C(5)); 155.8 (C=Se). CI-MS (NH_3): 277 (3), 275 (7, $[M+1]^+$), 273 (4), 197 (34), 196 (12), 195 (100), 194 (6). Anal. calc. for $C_8H_7ClN_4Se$ (273.59): C 35.12, H 2.58, N 20.48; found: C 34.90, H 2.80, N 20.34.

*Bis(5-amino-4-phenyl-4*H*-1,2,4-triazol-3-yl) Diselenide* (*=5,5′-Diselenobis[4-phenyl-4*H*-1,2,4-triazol-3-amine]*; **11a**). Repeated attempts to crystallize **7a** from CH_2Cl_2 gave orange crystals of **11a**. M.p. 206.0–208.3° (color change). ^{1}H-NMR: 6.05 (br. *s*, 2 NH_2); 6.97 (*d*-like, 4 arom. H); 7.42–7.50 (*m*, 6 arom. H). ESI-MS: 504 (9), 503 (29), 502 (20), 501 (100, $[M+Na]^+$), 500 (21), 499 (77), 498 (31), 497 (43), 496 (13), 495 (17), 479 (19, $[M+1]^+$), 477 (17).

X-Ray Crystal-Structure Determination of **11a** (see *Fig. 1* and *Table 2*)[2]). All measurements were made on a *Nonius-KappaCCD* diffractometer [40] by using graphite-monochromated MoK_α radiation (λ 0.71073 Å) and an *Oxford-Cryosystems-Cryostream-700* cooler. Data reduction was performed with HKL Denzo and Scalepack [41]. The intensities were corrected for *Lorentz* and polarization effects, and an absorption correction based on the multi-scan method [42] was applied. Equivalent reflections were merged. Data collection and refinement parameters are given in *Table 2*, and a view of the molecule is shown in *Fig. 1*. The structure was solved by direct methods with SHELXS97 [43], which revealed the positions of all non-H-atoms. The asymmetric unit contains one molecule of the Se-compound, one MeOH molecule and two molecules of H_2O. The non-H-atoms were refined anisotropically. The NH_2, H_2O, and hydroxy H-atoms were placed in the positions indicated by a difference electron density map, and their positions were allowed to refine together with individual isotropic displacement parameters. All remaining H-atoms were placed in geometrically calculated positions and refined by using a riding model where each H-atom was assigned a fixed isotropic displacement parameter with a value equal to 1.2 U_{eq} of its parent C-atom (1.5 U_{eq} for the Me group of the MeOH molecule). Refinement of the structure was carried out on F^2 by full-matrix least-squares procedures, which minimized the function $\Sigma w(F_o^2 - F_c^2)^2$. A

Table 2. *Crystallographic Data of Compound* **11a**

Crystallized from		CH_2Cl_2/MeOH	D_x [g cm^{-3}]	1.667
Empirical formula		$C_{17}H_{22}N_8O_3Se_2$	μ(MoK_α) [mm^{-1}]	3.447
M_r		544.33	Scan type	ϕ and ω
Crystal color, habit		orange, tablet	$2\theta_{(max)}$ [°]	60
Crystal dimensions [mm]		0.10 × 0.22 × 0.28	Transmission factors (min; max)	0.492; 0.717
Temperature [K]		160(1)	Total reflections measured	55961
Crystal system		monoclinic	Symmetry-independent reflections	6352
Space group		$P2_1/n$	Reflections with $I > 2\sigma(I)$	5010
Z		4	Reflections used in refinement	6348
Reflections for cell determination		65007	Parameters refined	309
2θ Range for cell determination [°]		4–60	Final $R(F)$ ($I > 2\sigma(I)$ reflections)	0.0340
Unit cell parameters	a [Å]	8.6743(1)	$wR(F^2)$ (all data)[a])	0.0841
	b [Å]	14.3351(1)	Goodness of fit	1.034
	c [Å]	17.8878(2)	Secondary extinction coefficient	0.0010(3)
	β [°]	102.8824(6)	Final Δ_{max}/σ	0.001
	V [Å^3]	2168.31(4)	$\Delta\rho$ (max; min) [e Å^{-3}]	0.62; −0.91

[a]) Weights: $w = [\sigma^2(F_o^2) + (0.0433P)^2 + 0.7378P]^{-1}$, where $P = (F_o^2 + 2F_c^2)/3$

[2]) CCDC-631597 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the *Cambridge Crystallographic Data Centre via* www.ccdc.cam.ac.uk/data_request/cif.

correction for secondary extinction was applied. Four reflections, whose intensities were considered to be extreme outliers, were omitted from the final refinement. Neutral-atom scattering factors for non-H-atoms were taken from [44], and the scattering factors for H-atoms were taken from [45]. Anomalous dispersion effects were included in F_c [46]; the values for f' and f'' were those of [47]. The values of the mass attenuation coefficients are those of [48]. All calculations were performed with the SHELXL97 [49] program.

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