Polyfused nitrogen-containing heterocycles
23.* Methyl 4-hydroxy-3-phenyl-5-phenyl(alkyl)-2-phenyliminoselenazolidine-4-carboxylates and selenazolo[3,4-*a*]quinoxalin-4(5*H*)-one derivatives on their basis**

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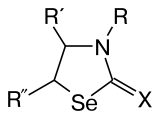
Condensation of methyl phenyl(alkyl)halopyrotartrates with *N*,*N*′-diphenylselenourea leads to the formation of methyl 4-hydroxy-3-phenyl-5-phenyl(alkyl)-2-phenyliminoselenazolidine-4-carboxylates, which undergo reaction with 1,2-phenylenediamines to give selenazolo-[3,4-*a*]quinoxalin-4(5*H*)-ones.

Key words: *N*,*N*′-diphenylselenourea, phenyl- and alkylhalopyruvates, methyl 4-hydroxy-3-phenyl-5-phenyl(alkyl)-2-phenyliminoselenazolidine-4-carboxylates, selenazolo[3,4-*a*]quinoxalin-4(5*H*)-ones, IR spectroscopy, NMR spectroscopy, X-ray diffraction.

During the last thirty years, organoselenium compounds are under intensive study in the field of synthetic organic chemistry and pharmacology, which is due to their high reactivity[2—8] and wide range of biological and pharmacological activity,[2,8—11] including antiviral,[2,9,10] antibacterial,[2,9,10] antifungus,[2,9] antioxidant,[9,10] anti-prolifiration,[12,13] and antitumor.[9,14—16] Derivatives of 1,3-selenazolidine **1** are of special interest among selenium-containing organic compounds,[16—19] the study of pharmaceutical potential of which showed a possibility to use these compounds as inhibitors of NO-synthase,[20,21] antimutagenes,[22] and cancer preventing agents.[23—26]

From the point of view of developing methods for the synthesis and study of pharmacological activity, the most prospective are selenazolidines corresponding to the structure **1**. For the most of them, a common feature is the presence of exocyclic double bond C=O, C=N, or C=C at the second position. The presence of other substituents in 1,3-selenazolidines **1** makes their synthesis and the search for new pharmacologically useful compounds more difficult.

Earlier, we have suggested (Scheme 1) a method for the synthesis of various thiazolo[3,4-*a*]quinoxalines **4** from 1,2-phenylenediamines **3** and structurally related to selenazolidines **1** methyl 4-hydroxy-3,5-diphenyl-

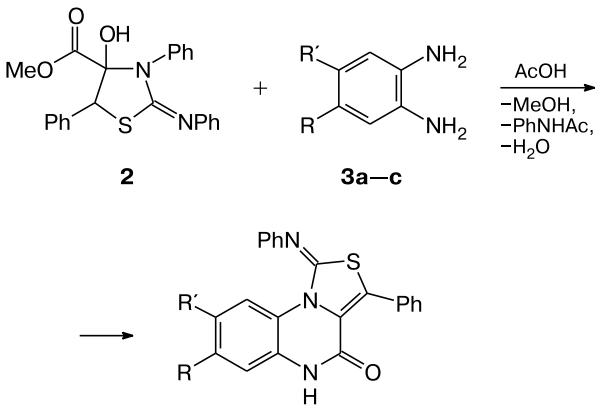


1

X = C(CN)CO_2Et, O, NH;
R = H, Alk, Ar;
R′ = H, Alk, CO_2H;
R″ = H, Alk

2-phenyliminothiazolidine-4-carboxylate (**2**),[27—30] as well as its aryl and hetaryl analogs.[29,31] However, synthetic possibilities of this reaction remain still little studied.[29—31]

Scheme 1



2 **3a—c** **4a—c**

R = R′ = H (**a**); R = H, R′ = Me (**b**); R = H, R′ = NO_2 (**c**)

* For Part 22, see Ref. 1

** Dedicated to Academician O. N. Chupakhin on the occasion of his 75th birthday.

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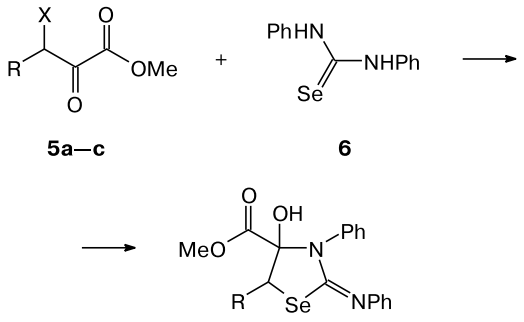
The present work is devoted to the synthesis (Scheme 2) and structural study of selenium analogs of methyl 4-hydroxythiazolidine-4-carboxylate **2**, *viz.*, 4-hydroxyselenazolidine-4-carboxylic esters **7**, as well as possibility of their use in the synthesis of selenazolo[3,4-*a*]quinoxalines according to Scheme 1.

Scheme 2



5, 7: R = Ph, X = Cl (**a**); R = $Ph(CH_2)_2$, X = Cl (**b**); R = C_6H_{13}, X = Br (**c**)

Condensation of methyl phenyl(chloro)- (**5a**), phenylethyl(chloro)- (**5b**), and *n*-hexyl(bromo)pyrotartrates (**5c**) with *N*,*N*′-diphenylselenourea (**6**)[32] proceeds with the formation of products, which in their elemental composition correspond to the expected isomeric methyl 4-hydroxyselenazolidine-4-carboxylates **7a—c** (see Scheme 2).

Similarly to the methyl ester **2** obtained by us earlier,[33] esters **7a—c** exist in solution (Scheme 3) in form of two cyclic diastereomers, α-**7a—c** and β-**7a—c**, the equilibrium between which, obviously, is established through the open-chain isothioureide structure **9a—c**.

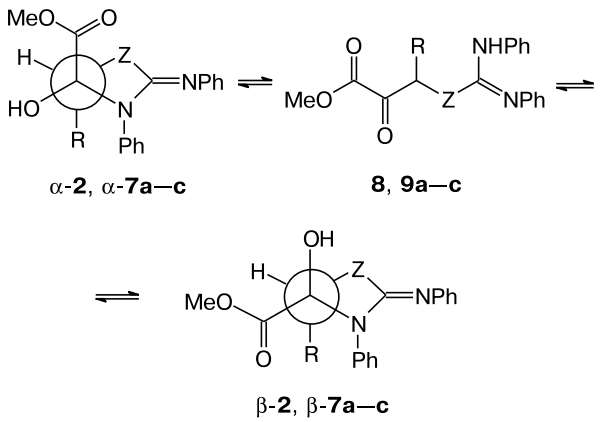
It should be noted that, as in the case of ester **2** studied by us earlier,[33] the ^{1}H NMR spectrum of ester **7a** in solution recorded right after dissolution exhibits only one pair of singlet signals for the methylene and methoxy groups (δ 5.58 and 3.57, respectively), whereas after one day, another pair of signals (δ 5.13 and 3.13) appears. In the ^{1}H NMR spectra of solutions of compounds **7b,c**, similar complication with time are also observed (Table 1). Going from ester **2** to its selenium analog **7a**, chemical shifts for the methoxy protons are displaced upfield, whereas for the methyne protons, downfield (see Table 1). In addition, in the ^{1}H NMR spectrum of selenazolidine **7a** solution preliminary heated for 10 min at ~100 °C, the third pair of singlet signals for the protons of the methylene and methoxy groups appears at δ 6.42 and 3.80, respectively, in contrast to the spectrum of the sample of thiazolidine **2** prepared similarly, in which the number of diastereomers remains equal to two. This is apparently due to the arising the open-chain tautomer **9a**. From the experimental data presented in Table 1, it is also seen that the signals for the methyne protons of esters **7b,c** are shifted upfield as compared to such signals of ester **7a**.

The IR spectra of esters **7** are characterized by the presence of broad absorption bands at 3514 (**7a**), 3485 (**7b**), and 3489 cm^{-1} (**7c**), which can be related to the vibrations ν_{O-H} of the bound hydroxy groups.

Condensation of 4-hydroxyselenazolidine-4-carboxylic esters **7a—c** with 1,2-phenylenediamine (**3a**) in boiling acetic acid gives the corresponding selenazolo[3,4-*a*]-quinoxalines **10a—c**, the yields of which, in contrast to the reaction of ester **2** with 1,2-phenylenediamine (**3a**) (~100%),[29] do not exceed 9, 54, and 30%, respectively (Scheme 4).

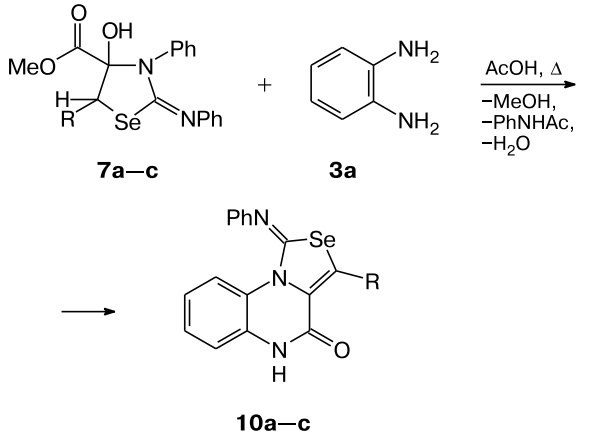
Characteristics of the IR and NMR spectra of selenazoloquinoxalines **10a—c** are virtually identical to the

Scheme 3



R = Ph, Z = S (**2**, **8**); R = Ph, Z = Se (**7a**, **9a**); R = $Ph(CH_2)_2$, Z = Se (**7b**, **9b**); R = C_6H_{13}, Z = Se (**7c**, **9c**)

Scheme 4



7, 10: R = Ph (**a**), $Ph(CH_2)_2$ (**b**), C_6H_{13} (**c**)

Table 1. The change in the ratio of isomers[a] of methyl 4-hydroxythiazolidine-4-carboxylate **2** and methyl 4-hydroxyselenazolidine-4-carboxylates **7a—c** in solution of DMSO-d_6 at room temperature depending on time (the ^{1}H NMR data)

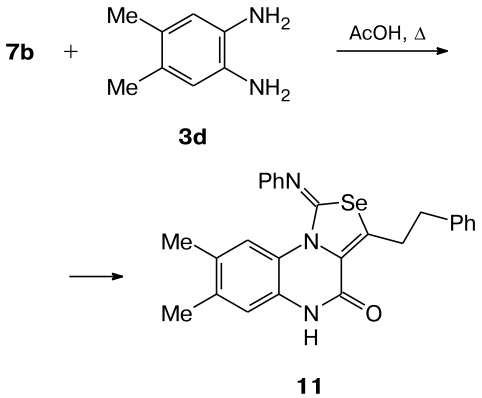
Object	Isomer	δ		I_{rel} (%)			
		OMe	C<u>H</u>(R)	3 min	2 h	24 h	10 min[b]
α-**2** + **8** + β-**2**[c]	*1*	3.16	5.05	0	19	33	—
	2	3.60	5.46	100	81	67	—
α-**7a** + **9a** + β-**7a**	*1*	3.13	5.13	0	8	18	14
	2	3.57	5.58	100	92	82	41
	3	3.80	6.42	—	—	—	45
α-**7b** + **9b** + β-**7b**	*1*	3.59	4.37—4.41	100	86	—	—
	2	3.85	4.22—4.25	0	14	—	—
α-**7c** + **9c** + β-**7c**	*1*	3.66	4.43—4.49	100	63	—	—
	2	3.89	4.33—4.37	0	37	—	—

[a] Calculated by averaging relative integral intensities of the methoxy and methyne protons.
[b] After heating the sample for 10 min at 100 °C.
[c] See Ref. 33.

corresponding characteristics of their thio analogs, excluding a small difference in chemical shifts of diagnostical signals for the proton H(9) and the proton of the carbamoyl group, which, in the case of selenium derivatives resonate more downfield (by 0.04—0.09 ppm).

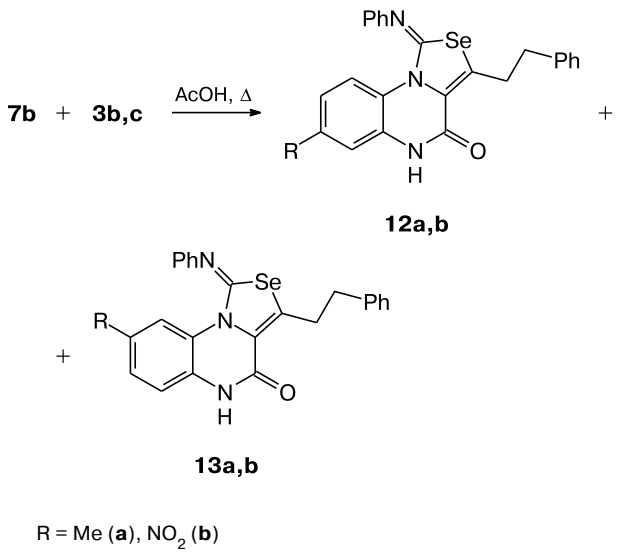
The reaction of 4-hydroxyselenazolidine-4-carboxylic ester **7b** with 4,5-dimethyl-1,2-phenylenediamine (**3d**) in boiling AcOH proceeds with the formation of expected tricyclic compound **11** (Scheme 5), and for the reaction to be completed, in this case it is necessary to reflux the reaction mixture for 1 h, in contrast to the reaction of ester **7b** with 1,2-phenylenediamine (**3a**) leading to tricycle **10b** over 1 min.

Scheme 5



The use of 4-substituted 1,2-phenylenediamines **3b,c** in the reaction with ester **7b** suggests a possibility to form two isomeric selenazolo[3,4-*a*]quinoxalines **12** and **13** differing in substituents at positions 7 and 8 (Scheme 6). In fact, during condensation of ester **7b** with 4-methyl-1,2-phenylenediamine (**3b**) a mixture of regioisomers **12a** and **13a** is formed (see Scheme 6), which is confirmed by the doubling of all the signals in the ^{1}H NMR spectrum of the crude product. The integral intensity of the diagnostical doublet signal for the proton H(9) (δ 9.17, J = 8.4 Hz) of compound **2a** is 2 times higher than the integral intensity of the singlet signal for the proton H(9) (δ 9.15) of compound **13a**.

Scheme 6



R = Me (**a**), NO_2 (**b**)

In contrast to 4-methyl-1,2-phenylenediamine (**3b**), the reaction of 4-nitro-1,2-phenylenediamine (**3c**) with ester **7b** proceeds regioselectively to form only one out of two possible isomeric selenazolo[3,4-*a*]quinoxalines, to which, with allowance for the predominant influence of *p*-amino group on the reactivity, the structure **13b** was

assigned (see Scheme 6). In fact, in the ^{1}H NMR spectrum of the crude reaction product, along with other signals, there is a diagnostical signal for the proton H(9) at δ 10.35 in the form of a doublet with J = 2.6 Hz. This fact indicates that the nitro group is on the atom C(8), rather than on C(7), since in this case the diagnostical signal for the proton H(9) would have resonate as a doublet of doublets with $J \approx 8.5$ and $J \approx 2.5$ Hz.[28,34] In contrast to the reactions given above, the condensation of ester **7b** with 4-nitro-1,2-phenylenediamine (**3c**) proceeds slower and to be completed requires reflux of the reaction mixture for 4 h, which is due to the strong electron-withdrawing power of the nitro group decreasing the reactivity of 1,2-phenylenediamine **3c**. The structure of selenazolo[3,4-*a*]quinoxaline **13b** formed was confirmed by X-ray diffraction analysis (Fig. 1). The molecule of **13b** crystallizes with the DMF molecule in the ratio 1 : 1.

The selenazolo[3,4-*a*]quinoxaline fragment of the molecule is planar within experimental error (0.095(1) Å) (the value corresponds to the maximum deviation of one of the atoms, in this case, of the selenium atom, from the mean-square plane of the tricycle), with the nitro group of the molecule being also in the plane of the tricyclic fragment. The dihedral angles between the planes of the phenyl substituents C(11)—C(16) and C(32)—C(37) and the plane of the tricyclic system are 64.3(1) and 70.3(1)°, respectively.

Similarly to the fact observed by us earlier[31,33,35,36] in the crystals of pyrrolo- and azoloquinoxalines, for the intermolecular interactions in the crystal of selenazolo[3,4-*a*]quinoxaline **13b** there is observed characteristic blockage by the present solvate DMF molecule of the formation of H-dimers of the molecules due to the intereactions involving the carbamoyl groups. In the crystal, the oxygen atom of the DMF molecule is involved into the hydrogen bond with the N—H group of the tricyclic fragment (parameters of the bond: d(H(5)...O(40)), 1.91(3) Å; d(N(5)...O(40)), 2.751(3) Å; the angle N(5)—H(5)...O(40), 171(3)°), whereas the carbonyl group of the molecule **13b** is involved into the hydrogen bond of the type C—H...O with the hydrogen atom of the methyl group of the neighboring DMF molecule (d(O(4)...H(42A′)), 2.36 Å; d(O(4)...C(42′)), 3.252(6) Å; the angle O(4)...H(42A′)—C(42′), 155° (the symmetry operation $1/2 - x$, $1/2 + y$, $1/2 - z$)).

From the intramolecular interactions having certain stabilizing influence on the conformation of the molecule, the hydrogen bonds involving the following atoms as acceptors should be mentioned: the oxygen atom of the carbonyl group (d(H(30A)...O(4)), 2.25 Å; d(C(30)...O(4)), 2.822(4) Å; the angle C(30)—H(30A)...O(4), 117°), the imine atom N(11) (d(H(9)...N(11)), 2.17 Å; d(C(9)...N(11)), 2.806(3) Å; the angle C(9)—H(9)...N(11), 125°), and the selenium atom (d(H(31B)...Se(2)), 2.87 Å; d(C(31)...Se(2)), 3.197(4) Å; the angle C(31)—H(31B)...Se(2), 101°). The interactions of the π—π type in the crystal have been analyzed using formal criteria of the presence of the π—π interaction.[37,38] In the crystal of compound **13b**, there is observed a stacking-effect: the electronic systems of the tricyclic fragments of the molecules, bound with the starting center of symmetry and translation along the 0b axis, interact with each other by the head-to-tail type so that

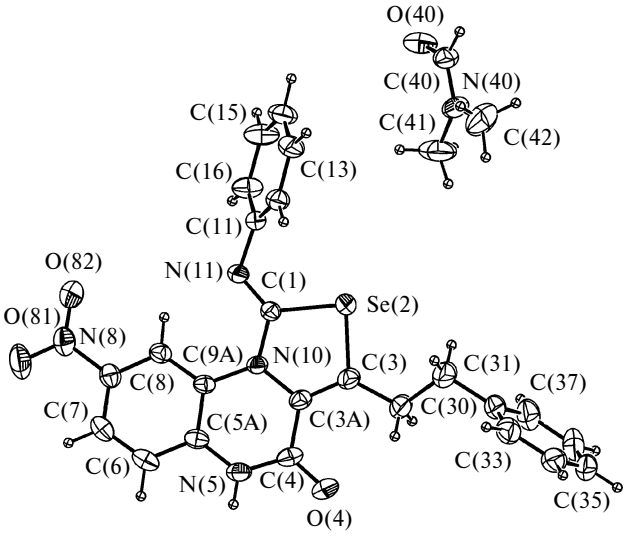


Fig. 1. Molecular geometry of **13b** in crystal. Nonhydrogen atoms are given as probability ellipsoids of thermal vibrations (p = 30%), hydrogen atoms as spheres of arbitrary radii. Some bond distances in the tricyclic fragment/Å: Se(2)—C(1), 1.914(2); Se(2)—C(3), 1.882(3); C(3)—C(3a), 1.333(4); C(3a)—C(4), 1.479(4); C(4)—N(5), 1.341(4); N(5)—C(5a), 1.366(4); C(3a)—N(10), 1.419(3); C(1)—N(10), 1.399(3); C(1)—N(11), 1.266(3); C(9a)—N(10), 1.423(3).

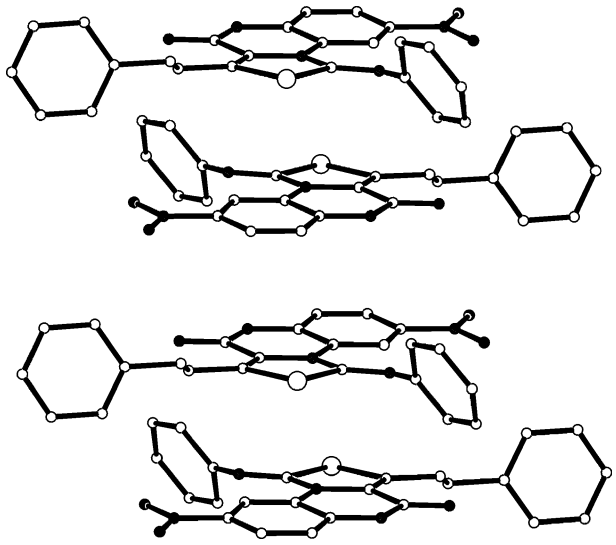


Fig. 2. A fragment of an inclined stack of selenazolo[3,4-*a*]-quinoxaline **13b** molecules in crystal. The DMF solvate molecules and hydrogen atoms are not shown.

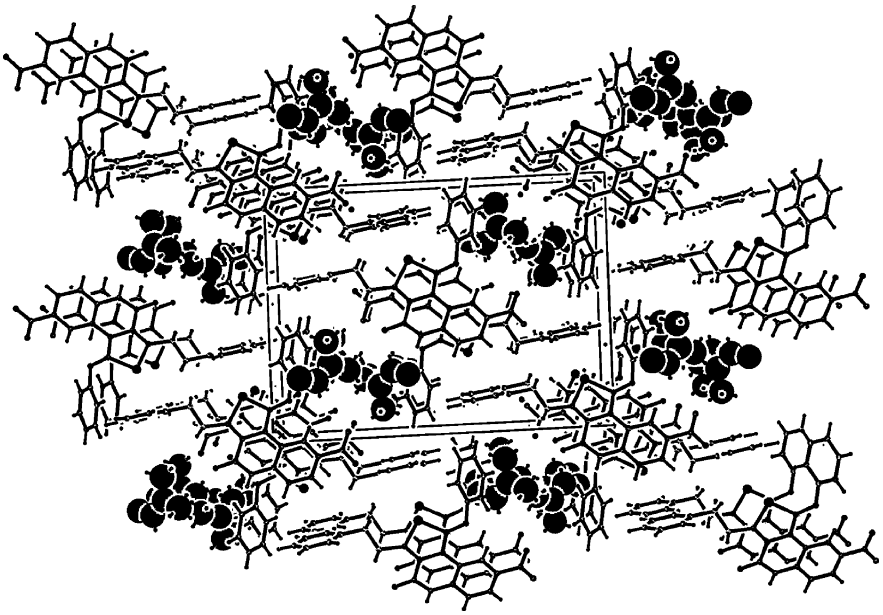
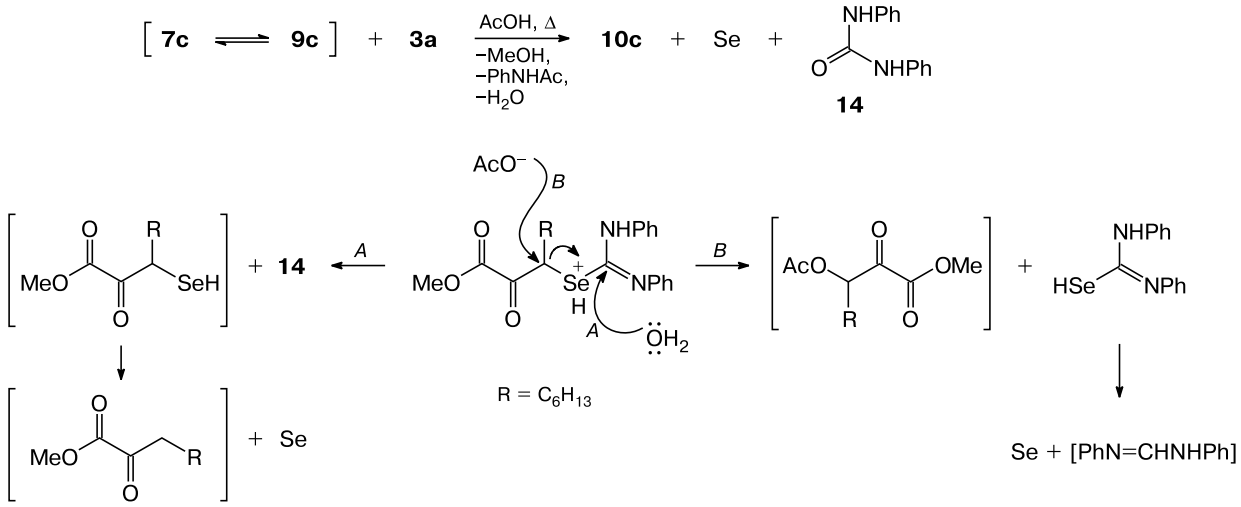


Fig. 3. Formation of pseudochannels with the DMF molecules in the crystal of compound **13b**. The view is along the 0*b* axis, the DMF molecules are shown as large spheres.

Scheme 7



the five-membered heterocycle of one of the molecule is flanked from both sides by the fused benzene fragments of the neighboring molecules (Fig. 2).

As a result, the inclined stacks of the molecules are formed along the 0*b* crystallographic axis with the two alternating distances between the mean-square planes of the molecules (3.47 and 3.70 Å) in the stacks, the dihedral angle between the planes is 0°. More close contact of the molecules, apparently, is prevented by position of the phenyl substituent on the imine nitrogen atom. The inconvenience of mutual packing of bulky substituents also explains the low value of calculated coefficient of molecule packing, 67.7%. The DMF molecules, being placed between the stacks of the selenazolo[3,4-*a*]quinoxaline molecules, are associated with each other by the van der Waals contacts, which leads to the formation of pseudochannels in the crystal filled with the solvate molecules (Fig. 3).

To understand the reasons for the low yields of selenazolo[3,4-*a*]quinoxalines, the composition of the reaction mixture from the reaction of ester **7c** with 1,2-phenylenediamine (**3a**) has been thoroughly analyzed. It was found that, in addition to the desired product, tricycle **10c**, selenium is formed (the mass spectrum is identical to the mass spectrum of the Se_8 allotrope of molecular selenium given in the NIST 98 library)[39] and *N*,*N*′-diphenylurea **14** (Scheme 7). This is evidence of gradual decomposition of selenazolidine **7c**, probably,

through the open-chain form under the action of water liberating during the reaction (pathway *A*) and acetic acid used as the solvent for the reaction (pathway *B*).

Experimental

^{1}H NMR spectra were recorded on a Bruker-AVANCE-600 spectrometer (600.00 MHz). Chemical shifts were measured experimentally relatively to DMSO-d_6 and given in δ scale. IR spectra were recorded on a VECTOR 22 spectrometer in KBr pellets. Melting points were determined on a Boetius heating stage. Methyl chlorophenylpyrotartrate (**5a**) (see Ref. 40) and methyl 3-chloro-2-oxo-5-phenylpentanoate (**5b**) (see Ref. 41) were obtained according to the known procedures. Mass spectra EI were obtained on a TRACE MS quadrupole mass spectrometer (ThermoQuest). The inflow of the sample was made by a direct injection with water cooling (DIP). In the mass spectra, the peaks of ions with relative intensity less than 5% are not given. The masses of polyisotopic (Se) molecular ions are given in bold.

Methyl 3-bromo-2-oxononanoate (5c). Potassium *tert*-butoxide (2.5 g, 22 mmol) was added in small portions to a solution of heptanal (2.5 g, 22 mmol) and methyl dichloroacetate (3.1 g, 22 mmol) in THF (150 mL) under argon at −10—−15 °C. The mixture was stirred for 1 h at this temperature and for 5 h at room temperature, poured into 20% aqueous NaCl. The organic layer was separated, the aqueous layer was extracted with AcOEt (2×20 mL). The organic layer and the extracts were combined, dried with $MgSO_4$, the solvent was evaporated, and the residue was dissolved in THF (150 mL). Magnesium bromide (3 g, 16 mmol) was added in small portions to the thus obtained solution under argon at 0—−5 °C. The reaction mixture was stirred for 2 h at room temperature, kept for ~14 h, and poured into 20% aq. NaBr. The organic layer was separated, the aqueous layer was extracted with ethyl acetate (2×20 mL). The organic layer and the extracts were combined, dried with $MgSO_4$, and the solvent was evaporated to obtain compound **5c** (4 g, 95%), orange oily liquid. IR, ν/cm^{-1}: 2957, 2930, 2859, 1737 (C=O), 1458, 1438. ^{1}H NMR ($CDCl_3$), δ: 0.88 (t, 3 H, C$\underline{H}_3$(CH$_2$)$_5$, J = 7.0 Hz); 1.22—2.22 (m, 10 H, CH$_3$(C$\underline{H}_2$)$_5$); 3.91 (s, 3 H, OCH$_3$); 4.90—4.95 (m, X-part of ABX-system, 1 H, CHBr, $J_{A,X} + J_{B,X}$ = 14.7 Hz).

***N*,*N*′-Diphenylselenourea (6)** was obtained similarly to *N*-*n*-butyl-*N*′-cyclohexylselenourea[42] using phenylisocyanide and aniline instead of cyclohexylisocyanide and *n*-butylamine, respectively. A powder of gray selenium (2.4 g, 30 mmol) and aniline (2.8 g, 30 mmol) was added to a solution of phenylisocyanide[43] (3.4 g, 33 mmol) in THF (40 mL). The reaction mixture was stirred for 2 h at 65 °C. A precipitate formed was filtered off and washed with THF to obtain compound **6** (6.1 g, 74%) (gray crystals), m.p. 188—190 °C (from EtOH) (*cf.* Ref. 32: m.p. 185—186 °C). The filtrate was concentrated, the residue was recrystallized from EtOH to additionally obtain compound **6** (1 g, 12%). Found (%): C, 56.72; H, 4.18; N, 9.66. $C_{13}H_{12}N_2Se$. Calculated (%): C, 56.74; H, 4.39; N, 10.18. IR, ν/cm^{-1}: 3169—2999, 1598, 1590, 1547, 1524, 1492. ^{1}H NMR, δ: 7.16 (dd, 2 H, 2 *p*-H$_{Ph}$, J = 7.6 Hz, J = 7.1 Hz); 7.33 (dd, 4 H, 4 *m*-H$_{Ph}$, J = 8.1 Hz, J = 7.6 Hz); 7.39 (d, 4 H, 4 *o*-H$_{Ph}$, J = 7.6 Hz); 10.11 (s, 2 H, 2 NH).

Methyl 4-hydroxy-3,5-diphenyl-2-phenyliminoselenazolidine-4-carboxylate (7a). Sodium acetate (3.7 g, 45.5 mmol) was poured to a suspension of *N*,*N*′-diphenylselenourea **6** (5 g, 18.2 mmol) in CH_2Cl_2 (150 mL), followed by a dropwise addition of a solution of methyl chlorophenylpyrotartrate (**5a**) (3.9 g, 18.2 mmol) in CH_2Cl_2 (40 mL). The reaction mixture was stirred for 9 h at room temperature, refluxed for 1 h, and cooled to room temperatures. A precipitate was filtered off and the filtrate was poured into water. The organic layer was separated, the aqueous layer was extracted with $CHCl_3$ (2×20 mL). The organic layer and the extracts were combined, dried with $MgSO_4$, the solvent was evaporated, and the residue was recrystallized from Pr^{i}OH to obtain compound **7a** (7 g, 72%), m.p. 143—148 °C. Found (%): C, 61.45; H, 4.02; N, 6.19. $C_{23}H_{20}N_2O_3Se$. Calculated (%): C, 61.20; H, 4.47; N, 6.21. IR, ν/cm^{-1}: 3514 (OH), 3065—2853, 1740 (C=O), 1648, 1589. ^{1}H NMR, δ: 3.13, 3.57 (both s, 3 H each, OCH$_3$); 5.13, 5.58 (both s, 1 H each, CH); 6.84—7.46 (m, 2S16 H, 2S3 C$_6$H$_5$ + 2 OH). MS, *m*/*z* (I_{rel} (%)): **454 (6)**, **453 (10)**, **452 (30)**, **451 (10)**, **450 (16)**, **449 (9)**, **448 (6)** ([M]$^{\bullet+}$), 393 (10), 391 (5), 274 (6), 273 (6), 211 (9), 210 (62), 196 (19), 195 (91), 194 (100), 182 (9), 180 (14), 179 (8), 171 (15), 170 (14), 169 (19), 168 (14), 167 (29), 166 (8), 165 (7), 149 (16), 147 (5), 137 (16), 136 (18), 135 (9), 132 (10), 123 (16), 122 (6), 121 (28), 120 (11), 119 (14), 118 (26), 117 (8), 109 (15), 107 (13), 105 (9), 104 (12), 103 (8), 95 (25), 94 (7), 93 (21), 92 (29), 91 (55), 90 (23), 89 (14), 82 (12), 81 (60), 79 (11), 78 (9), 77 (72).

Methyl 4-hydroxy-3-phenyl-5-(2-phenylethyl)-2-phenyliminoselenazolidine-4-carboxylate (7b) was obtained similarly to ester **7a** from methyl 3-chloro-2-oxo-5-phenylpentanoate (**5b**) (3.1 g, 12.9 mmol). The reaction mixture was poured into water. The organic layer was separated, the aqueous layer was extracted with $CHCl_3$ (2×20 mL). The organic layer and the extracts were combined, dried with $MgSO_4$. The solvent was evaporated *in vacuo* of a water-jet pump, the residue was triturated with Pr^{i}OH, the crystals were filtered off. The filtrate was concentrated to obtain compound **7b** (4.2 g, 75%) (orange oil). Found (%): C, 62.94; H, 5.02; N, 5.81. $C_{25}H_{24}N_2O_3Se$. Calculated (%): C, 62.63; H, 5.05; N, 5.84. IR, ν/cm^{-1}: 3485 (OH), 3176—2854, 1741 (C=O), 1632, 1588. ^{1}H NMR ($CDCl_3$), δ: 2.04—2.13, 2.26—2.36 (both m, 2 H each, 2 PhCH$_2$C$\underline{H}_2$); 2.51—2.58, 2.66—2.75 (both m, 2 H each, 2 PhC$\underline{H}_2$CH$_2$); 3.59, 3.85 (both s, 3 H each, OCH$_3$); 4.22—4.25 (m, X-part of ABX-system, 1 H, CH, $J_{A,X} + J_{B,X}$ = 14.4 Hz); 4.37—4.41 (m, X-part of ABX-system, 1 H, CH, $J_{A,X} + J_{B,X}$ = 14.7 Hz); 6.92—7.43 (m, 2×16 H, 2×3 C$_6$H$_5$ + 2 OH).

Methyl 5-hexyl-4-hydroxy-3-phenyl-2-phenyliminoselenazolidine-4-carboxylate (7c) was obtained similarly to ester **7b** from methyl 3-bromo-2-oxononanoate (**5c**) (3 g, 13.6 mmol). The yield of compound **7c** was 2 g (36%) (brown oil). Found (%): C, 60.43; H, 6.11; N, 6.07. $C_{23}H_{28}N_2O_3Se$. Calculated (%): C, 60.13; H, 6.14; N, 6.10. IR, ν/cm^{-1}: 3489 (OH), 3369—2854, 1730 (C=O), 1637, 1589. ^{1}H NMR ($CDCl_3$), δ: 0.86 (t, 3 H, C$\underline{H}_3$(CH$_2$)$_5$, J = 7.3 Hz); 0.89 (t, 3 H, C$\underline{H}_3$(CH$_2$)$_5$, J = 7.0 Hz); 1.18—1.99 (m, 2×10 H, 2 CH$_3$(C$\underline{H}_2$)$_5$); 3.66, 3.89 (both s, 3 H each, OCH$_3$); 4.33—4.37 (m, X-part of ABX-system, 1 H, CH, $J_{A,X} + J_{B,X}$ = 15.0 Hz); 4.43—4.49 (m, X-part of ABX-system, 1 H, CH, $J_{A,X} + J_{B,X}$ = 15.4 Hz); 6.88—7.55 (m, 2×11 H, 2×2 C$_6$H$_5$ + 2 OH). MS, *m*/*z* (I_{rel} (%)): **462 (10)**, **461 (18)**, **460 (41)**, **459 (19)**, **458 (22)**, **457 (14)**, **456 (9)** ([M]$^{\bullet+}$), 403 (7), 402 (9), 401 (37), 400 (5), 399 (20), 398 (8), 397 (7), 298 (7), 288 (6), 287 (14), 286 (6), 275 (7), 274 (7), 273 (9), 271 (5), 268 (8), 267 (10), 213 (6), 212 (13), 196 (51), 195 (99),

194 (100), 193 (21), 191 (10), 190 (6), 183 (8), 179 (9), 178 (5), 177 (29), 175 (14), 174 (6), 173 (8), 172 (5), 171 (11), 169 (6), 168 (11), 167 (12), 166 (6), 135 (8), 133 (5), 132 (6), 130 (7), 127 (13), 120 (23), 119 (16), 118 (17), 117 (16), 115 (6), 113 (6), 109 (5), 107 (5), 104 (16), 103 (18), 95 (7), 94 (24), 93 (80), 92 (53), 91 (49), 90 (6), 78 (10), 77 (77).

1-Phenylimino-3-phenylselenazolo[3,4-*a*]quinoxalin-4(5*H*)-one (10a). A solution of 1,2-phenylenediamine (**3a**) (0.2 g, 1.85 mmol) and ester **7a** (0.8 g, 1.85 mmol) in AcOH (10 mL) was refluxed for 2 h. Gray selenium (75 mg) was decanted from the hot reaction mixture. The crystals precipitated from the filtrate on cooling were filtered off to obtain analytically pure compound **10a** (72 mg, 9%) (bright yellow crystals), m.p. 290—293 °C. Found (%): C, 63.45; H, 3.60; N, 10.12. $C_{22}H_{15}N_3OSe$. Calculated (%): C, 63.47; H, 3.63; N, 10.09. IR, ν/cm^{-1}: 3182—2767 (NH), 1674 (C=O), 1619 (C=N), 1605, 1586. ^{1}H NMR, δ: 7.07—7.46 (m, 13 H, 2 C_6H_5 + H(6) + H(7) + H(8)); 9.29 (d, 1 H, H(9), J = 8.6 Hz); 11.09 (s, 1 H, NH). MS, m/z (I_{rel} (%)): **419 (6)**, **418 (7)**, **417 (30)**, **415 (15)**, **414 (6)**, **413 (6)** ([M]$^{\bullet+}$), 316 (9), 315 (8), 314 (50), 312 (25), 311 (7), 310 (9), 236 (7), 235 (40), 234 (100), 207 (8), 206 (31), 205 (33), 169 (25), 167 (14), 165 (5), 160 (10), 158 (6), 117 (10), 104 (7), 103 (7), 90 (5), 89 (15), 77 (19).

1-Phenylimino-3-(2-phenylethyl)selenazolo[3,4-*a*]quinoxalin-4(5*H*)-one (10b). A solution of 1,2-phenylenediamine (**3a**) (0.23 g, 2.09 mmol) and ester **7b** (1 g, 2.09 mmol) was refluxed for 1 min in AcOH (5 mL). A precipitate was filtered off, washed with AcOH, and dried in air to obtain compound **10b** (0.5 g, 54%) (grayish green crystals), m.p. 273—275 °C (from DMF). Found (%): C, 64.52; H, 4.47; N, 8.94. $C_{24}H_{19}N_3OSe$. Calculated (%): C, 64.87; H, 4.31; N, 9.46. IR, ν/cm^{-1}: 3187—2766 (NH), 1669 (C=O), 1621 (C=N), 1590. ^{1}H NMR, δ: 2.82—2.86 (m, 2 H, $PhC\underline{H}_2CH_2$); 3.52—3.54 (m, 2 H, $PhCH_2C\underline{H}_2$); 6.99—7.45 (m, 13 H, 2 C_6H_5 + H(6) + H(7) + H(8)); 9.29 (d, 1 H, H(9), J = 8.4 Hz); 11.06 (s, 1 H, NH).

3-Hexyl-1-phenyliminoselenazolo[3,4-*a*]quinoxalin-4(5*H*)-one (10c). A solution of 1,2-phenylenediamine (**3a**) (0.05 g, 0.44 mmol) and ester **7c** (0.2 g, 0.44 mmol) in AcOH (5 mL) was refluxed for 2 h. Gray selenium (5 mg) was decanted from the hot reaction mixture. The crystals precipitated from the filtrate on cooling were filtered off to obtain analytically pure compound **10c** (54 mg, 30%) (light green crystals), m.p. 199—200 °C. Found (%): C, 61.92; H, 5.39; N, 9.75. $C_{22}H_{23}N_3OSe$. Calculated (%): C, 62.26; H, 5.46; N, 9.90. IR, ν/cm^{-1}: 3182—2767 (NH), 1674 (C=O), 1619 (C=N), 1605, 1586. ^{1}H NMR, δ: 0.82 (t, 3 H, $CH_2CH_2(CH_2)_3C\underline{H}_3$, J = 6.8 Hz); 1.22—1.32 (m, 6 H, $CH_2CH_2(C\underline{H}_2)_3CH_3$); 1.51 (quint, 2 H, $CH_2C\underline{H}_2(CH_2)_3CH_3$, J = 7.7 Hz); 3.25 (t, 2 H, $C\underline{H}_2CH_2(CH_2)_3CH_3$, J = 7.7 Hz); 7.00—7.18 (m, 6 H, 2 o-H_{Ph} + p-H_{Ph} + H(6) + H(7) + H(8)); 7.41—7.45 (t, 2 H, 2 m-H_{Ph}, J = 7.9 Hz); 9.29 (d, 1 H, H(9), J = 7.3 Hz); 11.02 (s, 1 H, NH). MS, m/z (I_{rel} (%)): **427 (16)**, **426 (20)**, **425 (80)**, **424 (10)**, **423 (41)**, **422 (15)**, **421 (14)** ([M]$^{\bullet+}$), 324 (8), 323 (8), 322 (45), 321 (5), 320 (23), 319 (9), 318 (9), 267 (6), 266 (15), 265 (26), 264 (8), 263 (14), 262 (7), 261 (5), 254 (8), 253 (28), 252 (34), 251 (33), 250 (20), 249 (19), 248 (9), 242 (18), 241 (73), 240 (23), 239 (7), 213 (9), 212 (7), 211 (19), 199 (29), 198 (30), 197 (38), 187 (6), 186 (41), 185 (100), 184 (45), 183 (7), 181 (7), 174 (10), 173 (40), 172 (21), 171 (79), 169 (12), 167 (11), 161 (11), 160 (37), 156 (11), 155 (8), 147 (5), 144 (6), 143 (21), 142 (6), 132 (6), 131 (8), 118 (8), 117 (5), 116 (6), 104 (13), 103 (9), 102 (15), 92 (6), 90 (20), 77 (19). The filtrate was concentrated, the residue was worked up with water (5 mL), a precipitate was filtered off, dried in air, and recrystallized from Pr^{i}OH to obtain *N*,*N*′-diphenylurea **14** (0.12 g, 26%), m.p. 187—189 °C. IR, ν/cm^{-1}: 3327—2849, 1651, 1595, 1556, 1497. ^{1}H NMR, δ: 7.16 (dd, 2 H, 2 p-H_{Ph}, J = 7.6 Hz, J = 7.1 Hz); 7.33 (dd, 4 H, 4 m-H_{Ph}, J = 8.1 Hz, J = 7.6 Hz); 7.39 (d, 4 H, 4 o-H_{Ph}, J = 7.6 Hz); 10.11 (s, 2 H, 2 NH). The aqueous layer was extracted with ethyl acetate (3×20 mL). Ethyl acetate was evaporated, the residue was worked up with diethyl ether, and an orange precipitate was filtered off to obtain acetanylide (19 mg, 32%), m.p. 111—113 °C (*cf.* Ref. 44: m.p. 113 °C). IR, ν/cm^{-1}: 3292—2853 (NH), 1664 (C=O), 1619, 1599, 1556. ^{1}H NMR, δ: 2.03 (s, 3 H, $COCH_3$); 7.21 (dd, 1 H, p-H_{Ph}, J = 7.8 Hz, J = 7.3 Hz); 7.27 (dd, 2 H, 2 m-H_{Ph}, J = 7.8 Hz, J = 7.3 Hz); 7.56 (d, 2 H, 2 o-H_{Ph}, J = 7.8 Hz); 9.88 (s, 1 H, NH).

7,8-Dimethyl-1-phenylimino-3-(2-phenylethyl)selenazolo-[3,4-*a*]quinoxalin-4(5*H*)-one (11). A solution of 4,5-dimethyl-1,2-phenylenediamine (**3d**) (0.2 g, 1.46 mmol) and ester **7b** (0.7 g, 1.46 mmol) was refluxed for 1 h in AcOH (5 mL). A light green precipitate was filtered off, washed with AcOH, and dried in air to obtain compound **11** (0.18 g, 21%) (mustard crystals), m.p. >300 °C. Found (%): C, 65.85; H, 4.98; N, 8.57. $C_{26}H_{23}N_3OSe$. Calculated (%): C, 66.10; H, 4.91; N, 8.89. IR, ν/cm^{-1}: 3170—2874 (NH), 1668 (C=O), 1617 (C=N), 1589. ^{1}H NMR, δ: 2.16, 2.17 (both s, 3 H each, CH_3); 2.81—2.85 (m, 2 H, $PhC\underline{H}_2CH_2$); 3.51—3.55 (m, 2 H, $PhCH_2C\underline{H}_2$); 6.84 (s, 1 H, H(6)); 6.99—7.45 (m, 10 H, 2 C_6H_5); 9.11 (s, 1 H, H(9)); 10.93 (s, 1 H, NH).

7-Methyl-1-phenylimino-3-(2-phenylethyl)selenazolo-[3,4-*a*]quinoxalin-4(5*H*)-one (12a) and **8-methyl-1-phenylimino-3-(2-phenylethyl)selenazolo[3,4-*a*]quinoxalin-4(5*H*)-one (13a)** (a mixture of isomers **12a** + **13a** in the percentage ratio 65 : 35). A solution of 4-methyl-1,2-phenylenediamine (**3b**) (0.13 g, 1.0 mmol) and ester **7b** (0.5 g, 1.0 mmol) in AcOH (5 mL) was refluxed for 1 h. A yellow precipitate was filtered off, washed with AcOH, and dried in air to obtain a **12a** + **13a** mixture (0.11 g, 19%) (light green crystals), m.p. 268—270 °C (from DMF). Found (%): C, 65.83; H, 4.59; N, 9.12. $C_{25}H_{21}N_3OSe$. Calculated (%): C, 65.50; H, 4.62; N, 9.17. IR, ν/cm^{-1}: 3173—2890 (NH), 1671 (C=O), 1618 (C=N), 1589. ^{1}H NMR, δ: 2.25, 2.26 (both s, 3 H each, CH_3); 2.81—2.85 (m, 2×2 H, 2 $PhC\underline{H}_2CH_2$); 3.51—3.55 (m, 2×2 H, 2 $PhCH_2C\underline{H}_2$); 6.86—7.45 (m, 24 H, 4 C_6H_5 + 2 H(6) + H(7) + H(8)); 9.15 (s, 1 H, H(9)); 9.17 (d, 1 H, H(9), J = 8.4 Hz); 10.98, 11.01 (both s, 1 H each, NH).

8-Nitro-1-phenylimino-3-(2-phenylethyl)selenazolo[3,4-*a*]-quinoxalin-4(5*H*)-one (13b). A solution of 4-nitro-1,2-phenylenediamine (**3c**) (0.16 g, 1.04 mmol) and ester **7b** (0.5 g, 1.04 mmol) in AcOH (5 mL) was refluxed for 4.5 h. A precipitate was filtered off, washed with AcOH, and dried in air to obtain compound **13b** (0.1 g, 20%) (red crystals), m.p. >300 °C. Found (%): C, 58.90; H, 3.87; N, 10.93. $C_{24}H_{18}N_4O_3Se$. Calculated (%): C, 58.90; H, 3.71; N, 11.45. IR, ν/cm^{-1}: 3139—2919 (NH), 1697 (C=O), 1675, 1617 (C=N), 1592. ^{1}H NMR, δ: 2.83—2.87 (m, 2 H, $PhC\underline{H}_2CH_2$); 3.51—3.55 (m, 2 H, $PhCH_2C\underline{H}_2$); 7.03—7.56 (m, 11 H, 2 C_6H_5 + H(6)); 8.07 (dd, 1 H, H(7), J = 8.8 Hz, J = 2.6 Hz); 10.35 (d, 1 H, H(9), J = 2.6 Hz); 11.64 (s, 1 H, NH).

X-ray diffraction analysis. The study of a monocrystal of compound **13b** was performed in the Division of X-ray Structural

Studies of the Community Center on the basis of Laboratory of Diffraction Research Methods in the A. E. Arbuzov Institute of Organic and Physical Chemistry of the Kazan Research Center of the Russian Academy of Sciences. The experiments were performed on a Bruker AXS SMART APEX II automatic three-circle diffractometer equipped with a plane CCD detector. Crystals $C_{24}H_{18}N_4O_3Se \cdot C_3H_7NO$, M = 562.48, monoclinic; at 23 °C a = 15.3058(11) Å, b = 8.0597(6) Å, c = 20.6632(15) Å, β = 90.748(1)°, V = 2548.8(3) Å^3, Z = 4, d_{calc} = 1.466 g cm^{-3}, space group $P2_1/n$, μ(Mo-Kα) = 15.17 cm^{-1}, F(000) = 1152. Parameters of the unit cell and intensities of 18396 reflections (R_{int} = 0.0224), from which 3913 were observed reflection with $I \geq 2\sigma$, were measured at 23 °C on Mo-Kα irradiation (λ(Mo-Kα) = 0.71073 Å, a graphite monochromator, φ- and ω-scanning; the region of measurement: the range on the indices $-19 \leq h \leq 19$, $-10 \leq k \leq 10$, $-25 \leq l \leq 25$, θ_{min} = 2.66° and θ_{max} = 26.50°). The allowance for the absorption was made using the SADABS program.[45] The structure was decoded by the direct method and refined by the least squares method first in isotropic, then, in anisotropic approximation for all the nonhydrogen atoms. The coordinates of the hydrogen atoms of the amino group were found from the differential series of electron density and refined isotropically. The coordinates of other hydrogen atoms were calculated based on the stereochemical criteria and refined using the corresponding riding model. The final divergence factor values: R_1 = 0.0400, wR_2 = 0.1049 on 3913 independent reflections with $I \geq 2\sigma(I)$, R_1 = 0.0582, wR_2 = 0.1153 on all the data, GOOF 1.027, the number of parameters 281. The maximum and the minimum peaks are 0.879 and −0.503 e A^{-3}. The data collection and processing, as well as refinement of the unit cell parameters were performed using the APEX2 program.[46] All calculations on determining and refining the structures were performed using the SHELXTL[47] and WinGX[48] programs, the analysis of the intermolecular interactions and the figures of the molecules were made using the PLATON program.[37] The atom coordinates in the structure **13b** and their temperature parameters were deposited with the Cambridge Structural Database (http://www.ccdc.cam.ac.uk; the deposit number is CCDC 703890).

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