Chemistry of Heterocyclic Compounds, Vol. 49, No. 3, June, 2013 (Russian Original Vol. 49, No. 3, March, 2013)

SYNTHESIS AND AMINOMETHYLATION OF 9-AZA-3-AZONIASPIRO[5,5]UNDECA-7,10-DIENE-8-SELENOLATES

K. A. Frolov[1]*, V. V. Dotsenko[1], S. G. Krivokolysko[1], R. I. Zubatyuk[2], and O. V. Shishkin[2]

10-Amino-7,11-dicyano-9-aza-3-azoniaspiro[5,5]undeca-7,10-diene-8-selenolates have been obtained by the interaction of N-alkylpiperidin-4-ones with 2 equiv. cyanoselenoacetamide or with malononitrile and cyanoselenoacetamide. Aminomethylation of the obtained compounds proceeded under mild conditions and led to the formation of 8'-selenoxo-3',5',7',11'-tetraazaspiro[piperidine-4,13'-tricyclo[7.3.1.0^{2,7}]tridec[2]ene]-1',9'-dicarbonitriles. The structure of 1-methyl-5',11'-di(4-methylphenyl)-8'-selenoxo-3',5',7',11'-tetraazaspiro[piperidine-4,13'-tricyclo[7.3.1.0^{2,7}]tridec[2]ene]-1',9'-dicarbonitrile was determined by X-ray structural analysis.

Keywords: *N*-alkylpiperidin-4-ones, cyanoselenoacetamide, malononitrile, Michael adducts, pyridine-2-selenolates, cyclocondensation, Mannich reaction, X-ray structural analysis.

Owing to unique reactivity and a wide range of useful properties, the heterocyclic compounds of selenium attract constant attention of investigators (see review articles [1-6]). Some of the most available structural blocks for obtaining Se- and N-containing heterocycles are the selenoamides [7-12]. In connection with our interest in the chemistry of cyanoselenoacetamide (**1**) [13-17], we decided to study its interaction with *N*-alkylpiperidin-4-ones, which offers a promising route to new selenium-containing pyridine derivatives.

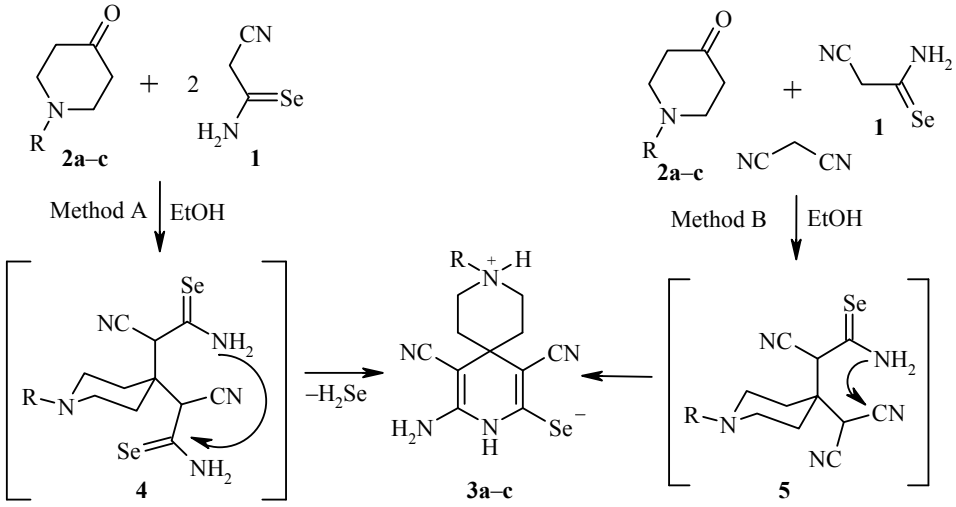
It was found that on interacting 2 equiv. cyanoselenoacetamide (**1**) with *N*-alkylpiperidin-4-ones **2a-c**, the previously unknown 10-amino-7,11-dicyano-9-aza-3-azoniaspiro[5,5]undeca-7,10-diene-8-selenolates **3a-c** were formed in 71-95% yields (method A).

The reaction had an autocatalytic character due to the basicity of the piperidinones **2** and probably proceeded through the formation of Michael adduct **4** with subsequent elimination of hydrogen selenide. Selenolates **3** were also formed when reactants **1** and **2** were used in a 1:1 ratio, but the yields did not exceed 50%, as expected. Selenolates **3** may also be obtained in 65-82% yields by the cyclocondensation of selenoamide **1**, piperidinones **2**, and malononitrile (method B). A probable intermediate of this process was the Michael adduct **5**. The yields, lower in this case in comparison with method A, may be explained by side

*To whom correspondence should be addressed, e-mail: victor_dotsenko@bigmir.net.

[1]"ChemEx" Laboratory, Vladimir Dal' East Ukrainian National University, 20-A Molodyozhny Kv., Lugansk 91034, Ukraine.
[2]Scientific-Technological Complex "Institute of Monocrystals", National Academy of Sciences of Ukraine, 60 Lenina Ave., Kharkiv 61001, Ukraine; e-mail: shishkin@xray.isc.kharkov.com.

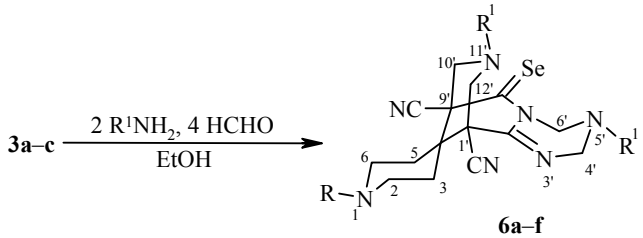
Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 3, pp. 507-513, March, 2013. Original article submitted October 12, 2012.



2–5 a R = Me, **b** R = Et, **c** R = CH_2Ph

processes of malononitrile condensation with piperidin-4-ones [18, 19]. In contrast to the previously reported [18, 20] reaction of piperidinones **2** with malononitrile and cyanothioacetamide, this condensation according to method B did not require the addition of base as catalyst. According to our observations, the yield of selenolates **3** and the reaction rate did not significantly depend on the presence of base (*N*-methylmorpholine) and its amount in the reaction mixture.

We have previously discovered and investigated the aminomethylation of 3-X-6-amino-5-cyano-1,4-dihydropyridine-2-thiolate derivatives (X = CN, CONHAr), leading to the formation of 3,5,7,11-tetraazatricyclo[7.3.1.$0^{2,7}$]tridec-2-ene derivatives [21-26]. It was established that selenolates **3a-c** also participated in the Mannich reaction under mild conditions with the formation of analogous products, the 8'-selenoxo-3',5',7',11'-tetraazaspiro[piperidine-4,13'-tricyclo[7.3.1.$0^{2,7}$]tridec[2]ene]-1',9'-dicarbonitriles **6a-f**.



6a–f

6 a R = Me, R^1 = 4-MeC_6H_4; **b** R = Et, R^1 = Me; **c** R = Et, R^1 = Ph; **d** R = Et, R^1 = 4-MeC_6H_4; **e** R = CH_2Ph, R^1 = Me; **f** R = CH_2Ph, R^1 = 4-MeC_6H_4

The structures of the obtained compounds **3a-c** and **6a-f** were confirmed by the results of spectral investigations and elemental analyses. In the IR spectra of pyridine-2-selenolates **3a-c** there were absorption bands corresponding to the stretching vibrations of the N–H bond (3290-3435 cm^{-1}), clearly expressed absorption bands of the conjugated cyano groups (2160-2195 cm^{-1}), and intense bands at 1635-1645 cm^{-1}, corresponding to the stretching vibrations of C=C bonds. The IR spectra of compounds **6a-f** lacked absorption bands corresponding to the stretching vibrations of N–H groups and conjugated cyano groups, instead there were low intensity absorption bands in the 2240-2250 cm^{-1} region, indicating the presence of unconjugated C≡N groups, and there were also intense absorption bands in the 1645-1665 cm^{-1} region (C=N).

The ^{1}H NMR spectra of compounds **3a-c** were characterized by signals of NH_2 and NH groups as broadened singlets at 5.54-5.90 and 8.56-9.27 ppm, respectively. Signals of NH^+ protons (for compound **3a** also the NH proton) were not found because of deuterium exchange. In the ^{1}H NMR spectra of compounds **6a-f** the

signals of the 4'- and 6'-CH_2 protons of the tetrahydro-1,3,5-triazine ring were resolved as pairs of doublets in the regions of 4.24-5.07 (^2J = 16.6-17.2 Hz) and of 4.96-5.82 ppm (^2J = 13.0-13.4 Hz), respectively. The 10'- and 1'-CH_2 protons resonated at 2.83-3.89 ppm and were displayed either as two pairs of doublets with coupling constant ^2J = 11.1-13.2 Hz or as multiplets caused by partial overlap of signals. A doubled set of signals for the R^1 fragment of the primary amine was also observed in the ^{1}H NMR spectra of compounds **6a-f**.

In order to establish unequivocally the structures of the synthesized compounds, the structure of 1-methyl-5',11'-di(4-methylphenyl)-8'-selenoxo-3',5',7',11'-tetraazaspiro[piperidine-4,13'-tricyclo[7.3.1.$0^{2,7}$]tridec[2]ene]- 1',9'-dicarbonitrile (**6a**) was studied by X-ray structural analysis (Fig. 1).

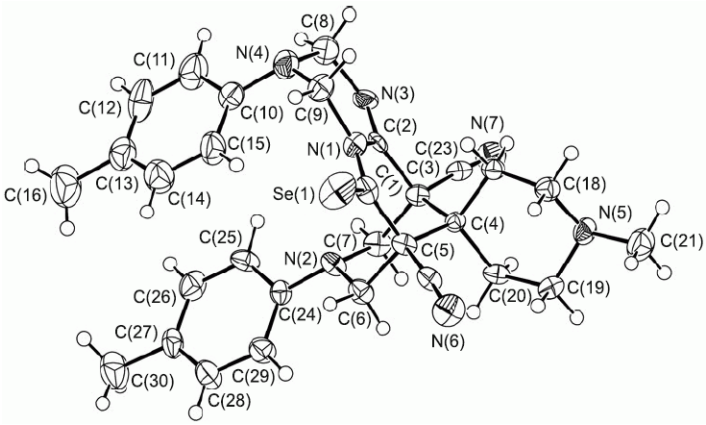


Fig. 1. Molecular structure of compound **6a** with atoms represented by thermal vibration ellipsoids of 50% probability.

The triazine ring and the pyridine ring containing the N(1) atom were in a "sofa" conformation with the N(4) and C(4) atoms deviating from the plane of the remaining atoms by -0.624(3) and 0.809(3) Å, respectively. The piperidine rings containing the N(2) and N(5) atoms were in a "chair" conformation with deviation of the N(2), C(4), and N(5), C(4) atoms from the plane of the remaining ring atoms by 0.658(3), -0.780(3), and 0.702(3), -0.495(3) Å, respectively. The N(2), N(4), and N(5) atoms had a trigonal-pyramidal configuration, the sum of the valence angles centered on the atoms were 346.1(6), 343.1(6), and 331.4(6)°, respectively. The methyl substituent at the N(5) atom had an equatorial orientation (C(21)–N(5)–C(18)–C(17) torsion angle was 173.2(2)°), The 4-methylphenyl substituent at the N(2) atom had an equatorial orientation, and an axial orientation at the N(4) atom (torsion angles C(24)–N(2)–C(6)–C(5) -162.53(19)° and C(10)–N(4)–C(8)–N(3) -84.7(3)°). In both substituents the aromatic ring was oriented somewhat away from perpendicular to the lone electron pair (LEP) of the nitrogen atom (torsion angles Lp(N2)–N(2)–C(24)–C(25) 54° and Lp(N4)–N(4)–C(10)–C(11) 61°, where Lp is the idealized position of the LEP). This was caused by the repulsion between the methylene groups linked to the nitrogen atoms and the *ortho*-hydrogen atoms in the substituent (shortened intramolecular contacts H(6b)···H(29) 2.23, H(7a)···H(25) 2.24, H(8a)···H(11) 2.17, and H(9a)···H(15) 2.13 Å with a sum of van der Waals radii of 2.32 Å [27]).

Shortened intramolecular contacts were also present in the molecule of compound **6a** involving nitrile groups H(17a)···C(23) 2.44 Å, H(18b)···C(22) 2.79 Å and H(19a)···C(22) 2.64 Å (sum of van der Waals radii 2.87 Å [27]). It may therefore be concluded that the presence of nitrile groups led to steric hindrance in the molecule.

Thus, a method has been developed for obtaining 10-amino-7,11-dicyano-9-aza-3-azoniaspiro[5,5]undeca-7,10-diene-8-selenolates by the reaction of *N*-alkylpiperidin-4-ones with cyanoselenoacetamide, or with malononitrile and cyanoselenoacetamide. The behavior of the obtained betaines was studied under Mannich reaction conditions. The structures of the synthesized compounds were confirmed by a set of analytical data, including X-ray structural analysis.

EXPERIMENTAL

The IR spectra were recorded on an IKS-29 spectrometer in nujol. The ^{1}H NMR spectra were recorded on a Bruker Avance II 400 instrument (400 MHz) in DMSO-d_6, internal standard was TMS. Elemental analysis was carried out on a Perkin-Elmer CHN analyzer. Purity of the obtained compounds was monitored by TLC on Silufol UV-254 plates, eluent was 1:1 acetone–hexane, visualization with iodine vapor, UV detector. Melting points were determined on a Kofler hot stage apparatus and were not corrected. All syntheses were carried out under an argon atmosphere. Cyanoselenoacetamide (**1**) was obtained by the known procedure [28]. *N*-Alkylpiperidin-4-ones **2** were purchased from Acros.

10-Amino-7,11-dicyano-9-aza-3-azoniaspiro[5,5]undeca-7,10-diene-8-selenolates 3a-c (General Method). A. A mixture of the corresponding *N*-alkylpiperidin-4-one **2a-c** (13.6 mmol) and freshly prepared cyanoselenoacetamide (**1**) (4.0 g, 27.2 mmol) in EtOH (30 ml) was stirred for 0.5 h until complete dissolution and then maintained for 24 h at ~20°C under an atmosphere of argon. The resulting solid was filtered off, washed with cold EtOH, acetone, and hexane.

B. Malononitrile (0.45 g, 6.8 mmol) and freshly prepared cyanoselenoacetamide (**1**) (1.0 g, 6.8 mmol) were added sequentially with vigorous stirring to a solution of the corresponding *N*-alkylpiperidin-4-one **2a-c** (6.8 mmol) in EtOH (30 ml). The mixture was stirred for 0.5 h and maintained for 24 h at ~20°C under an atmosphere of argon. The resulting solid was filtered off, washed with cold EtOH, acetone, and hexane.

10-Amino-7,11-dicyano-3-methyl-9-aza-3-azoniaspiro[5,5]undeca-7,10-diene-8-selenolate (3a). Yield 3.98 g (95%, method A), 1.69 g (81%, method B). Fine brick-colored crystals. Mp >160°C (decomp.). IR spectrum, ν, cm^{-1}: 3405, 3330 (N–H), 2175 (C≡N), 1645 (C=C). ^{1}H NMR spectrum, δ, ppm : 1.86 (3H, s, CH_3); 1.92-2.07 (2H, m), 2.23-2.36 (2H, m), 2.64-2.70 (2H, m) and 2.74-2.95 (2H, m, $(CH_2)_2N(CH_2)_2$); 5.90 (2H, s, NH_2). Found, %: C 46.62; H 4.95; N 22.59. $C_{12}H_{15}N_5Se$. Calculated, %: C 46.76; H 4.90; N 22.72.

10-Amino-7,11-dicyano-3-ethyl-9-aza-3-azoniaspiro[5,5]undeca-7,10-diene-8-selenolate (3b). Yield 3.90 g (89%, method A), 1.57 g (72%, method B). Mp 168-170°C (decomp.). IR spectrum, ν, cm^{-1}: 3435, 3330 (N–H), 2195 (sh), 2160 (C≡N), 1635 (C=C). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.20 (3H, t, ^3J = 7.1, $NCH_2C\underline{H}_3$); 1.84-1.88 (2H, m) and 1.95-1.98 (2H, m, $2CH_2$); 2.86 (2H, q, ^3J = 7.1, $NC\underline{H}_2CH_3$); 3.09-3.13 (4H, m, CH_2NCH_2); 5.54 (2H, s, NH_2); 8.56 (1H, br. s, NH). Found, %: C 48.29; H 5.39; N 21.57. $C_{13}H_{17}N_5Se$. Calculated, %: C 48.45; H 5.32; N 21.73.

10-Amino-3-benzyl-7,11-dicyano-9-aza-3-azoniaspiro[5,5]undeca-7,10-diene-8-selenolate (3c). Yield 3.71 g (71%, method A), 1.70 g (65%, method B). Mp 142-144°C (decomp.). IR spectrum, ν, cm^{-1}: 3330, 3290 (N–H), 2170 (C≡N), 1635 (C=C). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.80-1.85 (4H, m, $2CH_2$); 2.78-2.83 (2H, m, CH_2NCH_2); 3.44-3.63 (4H, m, CH_2NCH_2, NCH_2Ph); 5.71 (2H, s, NH_2); 7.20-7.35 (5H, m, H Ph); 9.27 (1H, br. s, NH). Found, %: C 56.06; H 5.09; N 18.04. $C_{18}H_{19}N_5Se$. Calculated, %: C 56.25; H 4.98; N 18.22.

8'-Selenoxo-3',5',7',11'-tetraazaspiro[piperidine-4,13'-tricyclo[7.3.1.0^{2,7}]tridec[2]ene]-1',9'-dicarbonitriles 6a-f (General Method). A mixture of selenolate **3a-c** (1.2 mmol), the corresponding primary amine (2.5 mmol), and 37% formalin (1.5 ml, 20 mmol) in EtOH (25 ml) was stirred for 5 min until complete dissolution of the starting materials. The mixture was boiled with vigorous stirring for 1-2 min, rapidly filtered through a paper filter under a stream of argon, and left for 24 h at room temperature. The resulting solid was filtered off, washed with EtOH, and with hexane. To obtain analytically pure samples the obtained products were recrystallized from DMF.

5',11'-Di(4-methylphenyl)-1-methyl-8'-selenoxo-3',5',7',11'-tetraazaspiro[piperidine-4,13'-tricyclo-[7.3.1.0^{2,7}]tridec[2]ene]-1',9'-dicarbonitrile (6a). Yield 151 mg (22%). Fine orange crystals. Mp 212-214°C. IR spectrum, ν, cm^{-1}: 2250, 2240 (2C≡N), 1655 (C=N). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.77-1.95 (2H, m), 2.31-2.36 (2H, m), 2.61-2.64 (2H, m), and 2.77-2.80 (2H, m, $(CH_2)_2N(CH_2)_2$); 2.10 (3H, s, NCH_3); 2.26 (3H, s, CH_3); 2.27 (3H, s, CH_3); 3.49-3.54 (2H, m) and 3.74-3.80 (2H, m, 10',12'-CH_2); 4.90 (1H, d, ^2J = 17.1) and 5.00 (1H, d, ^2J = 17.1, 4'-CH_2); 5.59 (1H, d, ^2J = 13.0) and 5.79 (1H, d, ^2J = 13.0, 6'-CH_2); 6.54 (2H, d, ^3J = 8.6,

H Ar); 6.92 (2H, d, ^3J = 8.6, H Ar); 6.64 (2H, d, ^3J = 8.3, H Ar); 6.67 (2H, d, ^3J = 8.3, H Ar). Found,%: C 62.99; H 5.89; N 17.04. $C_{30}H_{33}N_7Se$. Calculated, %: C 63.15, H 5.83; N 17.18.

1-Ethyl-5',11'-dimethyl-8'-selenoxo-3',5',7',11'-tetraazaspiro[piperidine-4,13'-tricyclo[7.3.1.0^{2,7}]-tridec[2]ene]-1',9'-dicarbonitrile (6b). Yield 156 mg (30%). Fine orange crystals. Mp 204-206°C. IR spectrum, ν, cm^{-1}: 2250 (2C≡N), 1645 (C=N). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.06 (3H, t, ^3J = 7.1, $NCH_2C\underline{H}_3$); 1.86-1.98 (2H, m) and 2.23-2.26 (2H, m, 3,5-CH_2); 2.34 (3H, s, CH_3); 2.49 (3H, s, CH_3); 2.46 (2H, q, ^3J = 7.1, $NC\underline{H}_2CH_3$); 2.70-2.73 (2H, m) and 2.80-2.85 (2H, m, 2,6-CH_2); 2.90 (1H, d, ^2J = 11.3), 2.98 (1H, d, ^2J = 11.2), 3.13 (1H, d, ^2J = 11.3), and 3.02 (1H, d, ^2J = 11.2, 10',12'-CH_2); 4.24 (1H, d, ^2J = 16.6) and 4.44 (1H, d, ^2J = 16.6, 4'-CH_2); 4.98 (1H, d, ^2J = 13.0) and 5.42 (1H, d, ^2J = 13.0, 6'-CH_2). Found, %: C 52.63; H 6.35; N 22.51. $C_{19}H_{27}N_7Se$. Calculated, %: C 52.77; H 6.29; N 22.67.

1-Ethyl-5',11'-diphenyl-8'-selenoxo-3',5',7',11'-tetraazaspiro[piperidine-4,13'-tricyclo[7.3.1.0^{2,7}]-tridec[2]ene]-1',9'-dicarbonitrile (6c). Yield 147 mg (22%). Fine orange crystals. Mp 222-224°C. IR spectrum, ν, cm^{-1}: 2250 (2C≡N), 1665 (C=N). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.06 (3H, t, ^3J = 7.2, $NCH_2C\underline{H}_3$); 1.77-1.93 (2H, m) and 2.24-2.38 (2H, m, 3,5-CH_2); 2.45 (2H, q, ^3J = 7.2, $NC\underline{H}_2CH_3$); 2.61-2.70 (2H, m) and 2.81-2.91 (2H, m, 2,6-CH_2); 3.59 (1H, d, ^2J = 12.5), 3.61 (1H, d, ^2J = 12.0), 3.82 (1H, d, ^2J = 12.5) and 3.89 (1H, d, ^2J = 12.0, 10',12'-CH_2); 4.94 (1H, d, ^2J = 17.1) and 5.07 (1H, d, ^2J = 17.1, 4'-CH_2); 5.71 (2H, br. s, 6'-CH_2); 6.70-7.17 (10H, m, H Ph). Found, %: C 62.46; H 5.65; N 17.50. $C_{29}H_{31}N_7Se$. Calculated, %: C 62.58; H 5.61; N 17.62.

1-Ethyl-5',11'-di(4-methylphenyl)-8'-selenoxo-3',5',7',11'-tetraazaspiro[piperidine-4,13'-tricyclo-[7.3.1.0^{2,7}]tridec[2]ene]-1',9'-dicarbonitrile (6d). Yield 232 mg (33%). Fine orange crystals. Mp 214-216°C. IR spectrum, ν, cm^{-1}: 2242 (2C≡N), 1656 (C=N). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.03 (3H, t, ^3J = 7.2, $NCH_2C\underline{H}_3$); 1.80-1.84 (2H, m) and 2.27-2.33 (2H, m, 3,5-CH_2); 2.08 (3H, s, CH_3); 2.24 (3H, s, CH_3); 2.43 (2H, q, ^3J = 7.2, $NC\underline{H}_2CH_3$); 2.62-2.66 (2H, m) and 2.78-2.83 (2H, m, 2,6-CH_2); 3.47 (1H, d, ^2J = 12.3, 3.56 (1H, d, ^2J = 12.0), 3.76 (1H, d, ^2J = 12.0), and 3.79 (1H, d, ^2J = 12.0, 10',12'-CH_2); 4.94 (1H, d, ^2J = 17.0) and 5.02 (1H, d, ^2J = 17.0, 4'-CH_2); 5.61 (1H, d, ^2J = 13.4) and 5.82 (1H, d, ^2J = 13.4, 6'-CH_2); 6.56 (2H, d, ^3J = 8.6, H Ar); 6.64 (2H, d, ^3J = 8.3, H Ar); 6.68 (2H, d, ^3J = 8.3, H Ar); 6.95 (2H, d, ^3J = 8.6, H Ar). Found, %: C 63.54; H 6.11; N 16.64. $C_{31}H_{35}N_7Se$. Calculated, %: C 63.69; H 6.03; N 16.77.

1-Benzyl-5',11'-dimethyl-8'-selenoxo-3',5',7',11'-tetraazaspiro[piperidine-4,13'-tricyclo[7.3.1.0^{2,7}]-tridec[2]ene]-1',9'-dicarbonitrile (6e). Yield 184 mg (31%). Fine orange crystals. Mp 205-207°C. IR spectrum, ν, cm^{-1}: 2244 (2C≡N), 1650 (C=N). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.87-1.94 (2H, m) and 2.25-2.28 (2H, m, 3,5-CH_2); 2.34 (3H, s, CH_3); 2.47 (3H, s, CH_3); 2.71-2.74 (2H, m), 2.83-2.92 (3H, m), 2.97 (1H, d, ^2J = 11.5), 3.03 (1H, d, ^2J = 11.5), and 3.13 (1H, d, ^2J = 11.1, 2,6,10',12'-CH_2); 3.56 (2H, br. s, CH_2Ph); 4.24 (1H, d, ^2J = 16.9) and 4.42 (1H, d, ^2J = 16.9, 4'-CH_2); 4.96 (1H, d, ^2J = 13.2) and 5.39 (1H, d, ^2J = 13.2, 6'-CH_2); 7.16-7.31 (5H, m, H Ph). Found, %: C 58.19; H 6.02; N 19.69. $C_{24}H_{29}N_7Se$. Calculated, %: C 58.29; H 5.91; N 19.83.

1-Benzyl-5',11'-di(4-methylphenyl)-8'-selenoxo-3',5',7',11'-tetraazaspiro[piperidine-4,13'-tricyclo-[7.3.1.0^{2,7}]tridec[2]ene]-1',9'-dicarbonitrile (6f). Yield 233 mg (30%). Fine beige crystals. Mp 181-183°C. IR spectrum, ν, cm^{-1}: 2248 (2C≡N), 1650 (C=N). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.87-1.93 (2H, m) and 2.26-2.31 (2H, m, 3,5-CH_2); 2.06 (3H, s, CH_3); 2.25 (3H, s, CH_3); 2.71-2.74 (2H, m) and 2.82-2.85 (2H, m, 2,6-CH_2); 3.50 (1H, d, ^2J = 12.1), 3.53 (1H, d, ^2J = 12.1), 3.74 (1H, d, ^2J = 13.2), and 3.79 (1H, d, ^2J = 13.2, 10',12'-CH_2); 3.55 (2H, br. s, CH_2Ph); 4.90 (1H, d, ^2J = 17.2) and 4.98 (1H, d, ^2J = 17.2, 4'-CH_2); 5.55 (1H, d, ^2J = 13.4) and 5.79 (1H, d, ^2J = 13.4, 6'-CH_2); 6.53 (2H, d, ^3J = 8.9, H Ar); 6.61 (2H, d, ^3J = 7.8, H Ar); 6.65 (2H, d, ^3J = 7.8, H Ar); 6.91 (2H, d, ^3J = 8.9, H Ar); 7.17-7.30 (5H, m, H Ph). Found, %: C 66.68; H 5.86; N 15.01. $C_{36}H_{37}N_7Se$. Calculated, %: C 66.86; H 5.77; N 15.16.

X-Ray Structural Investigation of Compound 6a. Crystals of compound **6a** were triclinic, $C_{30}H_{33}N_7Se$, at 298 K: *a* 8.6727(5), *b* 11.4177(5), *c* 13.8108(9) Å; α 89.674(5), β 83.235(5), γ 83.898(5)°; *V* 1350.34(13) Å^3; M_r 570.59; *Z* 2; space group $P\bar{1}$, d_{calc} 1.40 g/cm^3, μ(MoKα) 1.424 mm^{-1}, *F*(000) 592. The investigated crystal was a pseudomerohedric twin with two components turned by 180° along the *c** axis with

relative weights 0.605:0.305. The unit cell parameters and the intensities of 17887 reflections were measured on an Xcalibur 3 automatic four-circle diffractometer (MoKα, graphite monochromator, CCD detector, ω-scanning, $2\theta_{max}$ 55°). The structure was solved by the direct method with the SHELX-97 software package [29]. The positions of the hydrogen atoms were calculated geometrically and refined with the "rider" model with $U_{iso} = nU_{eq}$ for the supporting atom (n = 1.5 for methyl groups and n = 1.2 for the remaining hydrogen atoms). The structure was refined on F^2 by the full-matrix least-squares method with an anisotropic approximation for the non-hydrogen atoms to wR_2 0.116 at 17887 reflections (R_1 0.070 at 10195 reflections with $F > 4\sigma(F)$, S 1.02). A full set of crystallographic data has been deposited in the Cambridge Crystallographic Data Center (deposit CCDC 905390).

REFERENCES

1. V. P. Litvinov and V. D. Dyachenko, *Usp. Khim*., **66**, 1025 (1997).
2. D. R. Garud, M. Koketsu, and H. Ishihara, *Molecules*, **12**, 504 (2007).
3. J. Młochowski and M. Giurg, *Top. Heterocycl. Chem.*, **19**, 288 (2009).
4. J. Młochowski, K. Kloc, R. Lisiak, P. Potaczek, and H. Wójtowicz, *ARKIVOC*, vi, 14 (2007).
5. H. Heimgartner, Y. Zhou, P. K, Atanassov, and G. L. Sommen, *Phosphorus, Sulfur Silicon Relat. Elem.*, **183**, 840 (2008).
6. M. Ninomiya, D. R. Garud, and M. Koketsu, *Coord. Chem. Rev.*, **255**, 2968 (2011),
7. M. Ninomiya, D. R. Garud, and M. Koketsu, *Heterocycles*, **81**, 2027 (2010).
8. T. Murai, *Top. Curr. Chem.*, **251**, 247 (2005).
9. T. Murai and S. Kato, *Top. Curr. Chem.*, **208**, 177 (2000).
10. A. Ogawa, and N. Sonoda, in: E. Winterfeldt (editor), *Comprehensive Organic Synthesis*, Vol. 6, Pergamon, Oxford (1991), p. 461.
11. C. P. Dell, in: C. J. Moody (editor), *Comprehensive Organic Functional Group Transformations*, Vol. 5, Pergamon, Oxford (1995), p. 565.
12. A. J. Moore, in: R. Jones (editor), *Comprehensive Functional Group Transformations II*, Vol. 5, Pergamon, Oxford (2005), p. 519.
13. K. A. Frolov, V. V. Dotsenko, S. G. Krivokolysko, and V. P. Litvinov, *Khim. Geterotsikl. Soedin*., 471 (2012). [*Chem. Heterocycl. Compd.*, **48**, 442 (2012)].
14. K. A. Frolov, V. V. Dotsenko, and S. G. Krovokolysko, *Khim. Geterotsikl. Soedin*., 1083 (2012). [*Chem. Heterocycl. Compd.*, **48**, 1006 (2012)].
15. K. A. Frolov, S. G. Krivokolysko, V. V. Dotsenko, and V. P. Litvinov, *Khim. Geterotsikl. Soedin.*, 313 (2009). [*Chem. Heterocycl. Compd.*, **45**, 255 (2009).]
16. K. A. Frolov and S. G. Krivokolysko, *Khim. Geterotsikl. Soedin.*, 1104 (2011). [*Chem. Heterocycl. Compd.*, **47**, 909 (2011).]
17. K. A. Frolov, V. V. Dotsenko, and S. G. Krivokolysko, *Izv. Akad. Nauk*, *Ser. Khim.*, 364 (2012).
18. A. A. Shestopalov, *Diss. Cand. Chem. Sci.*, Moscow (2004).
19. A. M. Shestopalov, Yu. M. Emeliyanova, A. A. Shestopalov, L. A. Rodinovskaya, Z. I. Niazimbetova, and D. H. Evans, *Tetrahedron*, **59**, 7491 (2003).
20. A. M. Shestopalov, A. A. Shestopalov, L. A. Rodinovskaya, and A. V. Gromova, *Phosphorus, Sulfur Silicon Relat. Elem*., **184**, 1100 (2009).
21. V. V. Dotsenko, S. G. Krivokolysko, and V. P. Litvinov, *Izv. Akad. Nauk*, *Ser. Khim.*, 2605 (2005).
22. V. V. Dotsenko, S. G. Krivokolysko, A. N. Chernega, and V. P. Litvinov, *Izv. Akad. Nauk*, *Ser. Khim*., 1014 (2007).
23. V. V. Dotsenko, S. G. Krivokolysko, V. P. Litvinov, and E. B. Rusanov, *Dokl. Akad. Nauk*, **413**, 345 (2007).

24. V. V. Dotsenko, S. G. Krivokolysko, and V. P. Litvinov, *Khim. Geterotsikl. Soedin.*, 1709 (2007). [*Chem. Heterocycl. Compd.*, **43**, 1455 (2007)].
25. V. V. Dotsenko, S. G. Krivokolysko, A. N. Chernega, and V. P. Litvinov, *Monatsh. Chem.*, **138**, 35 (2007).
26. V. V. Dotsenko, S. G. Krivokolysko, and V. P. Litvinov, *Izv. Akad. Nauk*, *Ser. Khim.*, 134 (2012).
27. Yu. V. Zefirov and P. M. Zorkii, *Usp. Khim.*, **58**, 713 (1989).
28. V. P. Litvinov, V. Yu. Mortikov, Yu. A. Sharanin, and A. M. Shestopalov, *Synthesis*, 98 (1985).
29. G. Sheldrick, *Acta Cryst*., *Sect. A*, **64**, 112 (2008).