Synthesis, properties, and structure of 2-allylseleno-3,5-dicyano-6-hydroxy-4-phenylpyridine

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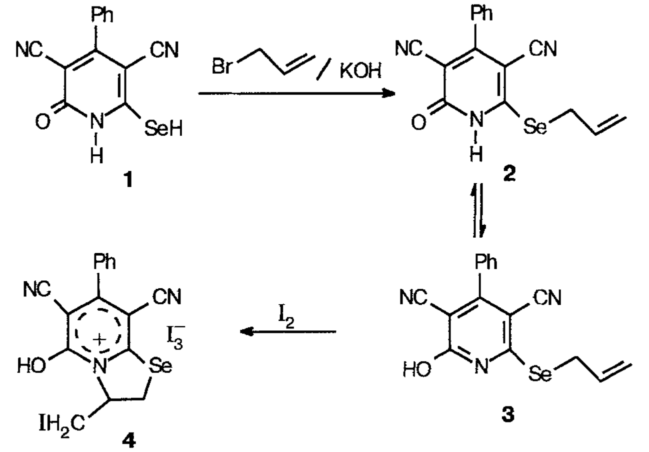
The synthesis of 2-allylseleno-3,5-dicyano-6-hydroxy-4-phenylpyridine has been carried out and its cyclization into 6,8-dicyano-5-hydroxy-3-iodomethyl-7-phenyl-2,3-dihydroselenazolo[3,2-a]pyridinium triiodide has been studied. X-ray investigation shows that allylselenopyridine in the crystalline state exists as hydroxy derivative and the allyl substituent is approximately perpendicular to the heterocyclic plane. In crystal the molecules are linked by hydrogen bonds forming dimers.

Key words: 3-cyano-6-hydroxy-2(1H)-pyridineselenone, allyl bromide, selenazolo[3,2-a]pyridinium salts, X-ray structural analysis, hydrogen bond.

The previously described substituted 3-cyano-6-hydroxy-2(1*H*)-pyridinechalcogenones are of considerable interest as intermediates in fine organic synthesis because of the presence of several reactive groups in their composition.[1,2] The respective substituted 6-oxo-2(1*H*)-pyridineselenones are alkylated by allyl bromide exlusively at the selenium atom. Thus 3,5-dicyano-6-oxo-4-phenyl-2-pyridineselenol (**1**) has been used to produce 2-allylseleno-3,5-dicyano-6-oxo-4-phenyl-1,2-dihydropyridine existing in solution as tautomeric forms **2** and **3**.



An X-ray study of 2-allylselenopyridine **3** has been made in order to establish unambiguously its structure and to confirm the mechanism of its cyclization into 2,3-dihydroselenazolo[3,2-*a*]pyridinium (**4**). It has been established that compound **3** is 2-allylseleno-3,5-dicyano-6-hydroxy-4-phenylpyridine. Figure 1 gives a general view of the molecule with bond lengths; the bond angles are listed in Table 1.

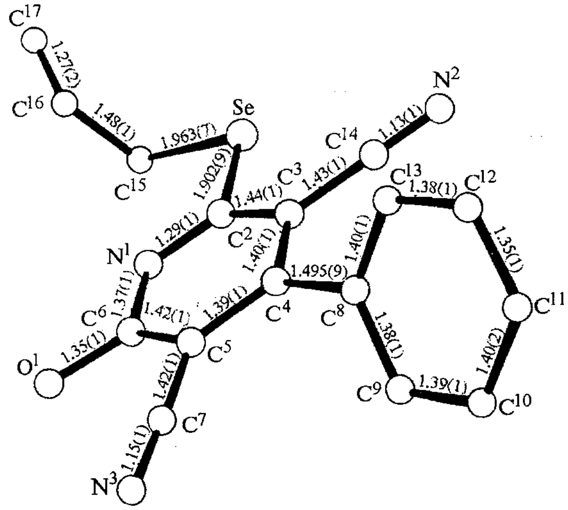


Fig. 1. A general view of molecule **3** and its bond lengths.

In molecule **3**, the intramolecular nonbond contacts (Table 2) account for turning of the phenyl substituent by 52.0° relative to the heterocycle plane. As in the previously studied molecule of 2-allylseleno-4,6-diamino-3-cyanopyridine (**5**),[3] in pyridine **3** the Se—C(15) bond is *cis*-oriented to the N(1)—C(2) bond of the cycle (torsion angle N(1)C(2)SeC(15) 1.6°; in compound **5**:

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Table 1. Bond angles ω (deg) in the molecule of compound **3**

Angle	ω	Angle	ω
C(2)SeC(15)	97.5(4)	N(1)C(6)C(5)	121.5(7)
C(2)N(1)C(6)	118.7(6)	O(1)C(6)C(5)	123.0(8)
SeC(2)N(1)	119.0(5)	N(3)C(7)C(5)	174.9(9)
SeC(2)C(3)	117.3(6)	C(4)C(8C(9)	121.2(7)
N(1)C(2)C(3)	123.6(8)	C(4)C(8)C(13)	119.4(7)
C(2)C(3)C(4)	118.5(7)	C(13)C(8)C(9)	119.4(7)
C(2)C(3)C(14)	118.5(8)	C(8)C(9)C(10)	120.7(9)
C(4)C(3)C(14)	122.8(6)	C(9)C(10)C(11)	118.6(9)
C(3)C(4)C(5)	117.7(6)	C(10)C(11)C(12)	120.3(8)
C(8)C(4)C(3)	121.2(7)	C(11)C(12)C(13)	121.7(10)
C(8)C(4)C(5)	121.1(7)	C(8)C(13)C(12)	119.3(8)
C(4)C(5)C(6)	119.8(8)	C(3)C(14)N(2)	178.2(10)
C(4)C(5)C(7)	123.4(7)	SeC(15)C(16)	11.7(7)
C(7)C(5)C(6)	116.9(7)	C(15)C(16)C(17)	128.8(13)
N(1)C(6)O(1)	115.2(6)		

Table 2. Shortened nonbond distances in the molecule of compound **3***

Distance	*d*/Å	Distance	*d*/Å
Se...C(14)	3.03(1)	C(7)...C(8)	2.95(1)
O(1)...C(7)	2.80(1)	C(7)...C(9)	3.05(1)
N(1)...C(15)	2.90(1)	C(8)...C(14)	2.95(1)
C(3)...C(13)	3.10(1)	C(13)...C(14)	3.05(1)
C(5)...C(9)	3.11(1)		

* Sums of van der Waals radii of Se and C are 3.61 Å, of O and C 3.00 Å, of N and C 3.21 Å; the doubled van der Waals radius of C atom is 3.42 Å[3,5].

−0.4(4) and −4.3(4)° in two independent molecules). An analogous *cis* orientation of the S—C bond of thiocyclohexenyl substituent relative to one of the N—C bonds of the pyridine cycle was observed by us previously[4] for the molecule of 3-cyano-2-(2-cyclohexen-1-yl)thio-5,6-ethano-5,6,7,8-tetrahydro-1,5-naphthyridine (**6**). The allyl substituent in the molecule of compound **3** is oriented approximately perpendicular to the heterocycle plane (torsion angles C(2)SeC(15)C(15) 85.6 and SeC(15)C(16)C(17) 101.9°; in pyridine **5**: −84(1) and 89(1), −110(2) and 114(1)°).

As in compound **5**, the investigated pyridine **3** shows a sharply shortened N(1)...C(15) 2.90(1) Å contact (the sum of van der Waals radii of N and C is 3.21 Å)[5] due to the observed mutual *cis* orientation of the selenoallyl substituent and the N(1)—C(2) bond of the pyridine cycle. If the conformation of molecule **3** in solution is retained, the *cis* conformation of the N(1)C(2)SeC(15) fragment favors the cyclization of such compounds in the selenazolo[3,2-*a*]pyridinium salts **4**. This assumption of the interrelation between the observed *cis* conformation of the molecule in the crystal and the direction of the reaction of intramolecular cyclization in solution was made by us earlier for compounds **5** and **6**. This was confirmed by a further study of their reactivity, *i.e.*, formation of selenazolo[3,2-a]pyridinium and thiazolo[3,2-*a*]1,5-naphthyridinium through the action of halogens on **5** and **6** in solution.[3,4]

The bond lengths and angles in molecules **3** and **5** coincide and are close to standard values.[6]

In the crystal there are two intermolecular contacts shortened as compared with the sums of van der Waals radii of the corresponding atoms: Se...Se 3.71(1) Å and Se...N(2) 3.37(1) Å (-x,1-y,1-z) (the sums of van der Waals radii of Se and Se are 3.80 Å, of Se and N 3.40 Å).[5,7]

In crystals of **3** the "active" hydrogen atom of the OH group has an intermolecular contact that can be considered a hydrogen bond: O(1)—H(1)...N(3) (2−*x*,-*y*,1−*z*) (O(1)...N(3) 3.10(1), O(1)—H(1) 0.95, H(1)...N(3) 2.20 Å, angle O(1)—H(1)...N(3) 159°). The hydrogen bonds link molecules **3** to form dimers in the crystal.

Therefore, the allylselenopyridines **3** exist in the crystalline state as hydroxy derivative, and the geometry of its molecule favors the cyclization in selenazolo[3,2-*a*]pyridines **4**.

Experimental

IR spectra of the synthesized compounds were recorded on an UR-20 spectrometer in vaseline oil. NMR spectra were recorded on a Bruker WP-100 SU spectrometer (100 MHz) in DMSO-d_6 solutions, with $SiMe_4$ as internal standard. The reaction course and the purity of prepared compounds was controlled by the TLC on Silifol-UV plates in the acetone-hexane (3:5) system.

Crystals of compound **3** are triclinic, at 20°C a = 6.607(1) Å, b = 10.173(2) Å, c = 12.470(2) Å, α = 110.05(3)°, β = 91.61(3)°, g = 100.23(3)°, V = 771.2(7) Å^3, d_c = 1.465 g cm^{-3}, Z = 2, space group $P1$. Cell dimensions and intensities of 2509 independent reflections were measured on a four-circle automatic Siemens P3/PC diffractometer (λ Mo-Kα, graphite monochromator, $\theta/2\theta$ scan technique, θ_{max} = 28°). An absorption correction was introduced. The structure was solved by the direct method using the SHELXTL program to identify all the nonhydrogen atoms and refined by the full-matrix least-squares method in the anisotropic approximation for nonhydrogen atoms using a total of 1755 reflections with $I > 4\sigma$. The hydrogen atoms were objectively identified with difference syntheses. However, due to the large thermal vibrations, they were included in the refinement with fixed positional and thermal parameters. The final R = 0.052 (R_w = 0.052). All the calculations were performed by using the SHELXL PLUS program (PC version). The atomic coordinates are given in Table 3 (isotropic equivalent thermal parameters of the nonhydrogen atoms can be obtained from the authors).

2-Allylseleno-6-hydroxy-4-phenyl-3,5-dicyanopyridine (3). A 10% solution of KOH in water (0.7 mL) and allyl bromide (0.1 mL, 1.3 mmol) were added while mixing to a suspension of pyridine **1** (1.3 mmol) in DMFA (8 mL). After 0.5 h the reaction mixture was diluted with water (5 mL): the precipitate was filtered off and washed with water. Compound **3** (0.37 g, 61 %) was obtained, m.p. 185—188 °C (from MeOH). IR spectrum, cm^{-1}: 2222 (ν CN). ^{1}H NMR spectrum, δ: 8.11 (s, 1 H, OH); 7.58 (m, 5 H, Ph); 6.00 (m, 1 H, CH); 5.07 (m, 2 H, CH_2); 3.98 (d, 2 H, CH_2Se). Found (%): C, 56.40; H, 3.34; N, 12.31; Se, 23.25. $C_{16}H_{11}N_3OSe$. Calculated (%): C, 56.48; H, 3.26; N, 12.35; Se, 23.21.

Table 3. Coordinates of the nonhydrogen atoms (×10^4) in molecule **3**

Atom	*x*	*y*	*z*
Se	1824(2)	3913(1)	4182(1)
O(1)	7335(12)	959(6)	3743(5)
N(1)	4841(11)	2319(6)	4085(4)
N(2)	1495(13)	4901(8)	7194(6)
N(3)	9055(13)	619(8)	6249(6)
C(2)	3721(14)	3069(7)	4774(5)
C(3)	3756(13)	3267(7)	5978(6)
C(4)	5148(13)	2667(7)	6437(5)
C(5)	6396(13)	1892(7)	5697(5)
C(6)	6256(13)	1759(7)	4522(6)
C(7)	7838(16)	1197(8)	6046(6)
C(8)	5310(12)	2870(7)	7684(5)
C(9)	7194(15)	3368(8)	8341(6)
C(10)	7326(19)	3557(9)	9503(7)
C(11)	5510(18)	3227(10)	9993(7)
C(12)	3679(17)	2723(9)	9343(7)
C(13)	3524(14)	2540(8)	8194(6)
C(14)	2493(15)	4171(8)	6669(6)
C(15)	2371(15)	3159(8)	2568(6)
C(16)	1119(24)	1716(12)	1965(8)
C(17)	−510(34)	1350(15)	1286(11)

6,8-Dicyano-5-hydroxy-3-iodomethyl-7-phenyl-2,3-dihydroselenazolo-[3,2-a]pyridinium triiodide (4). 2-Allylselenopyridine **3** (1 mmol) was dissolved in chloroform (15 mL), and a solution of of iodine (2 mmol) in chloroform (5 mL) was added to the resulting solution for 10 min while mixing. The reaction mixture was boiled and filtered hot. The filtrate was allowed to stand for 2 h at 25°C, the precipitate was separated and washed with chloroform. Product **4** (0.3 g, 72 %) was obtained, m.p. 136—138 °C (from chlorophorm). IR spectrum, cm^{-1}: 2248 (ν CN). NMR spectrum, δ_H: 9.84 (s, 1 H, OH); 7.6 (m, 5 H, Ph); 5.10 (m, 1 H, C(3)H); 4.05 (m, 2 H, CH_2I); 3.50 (m, 2 H, CH_2Se). Found (%): C, 41.14; H, 2,37; I, 27.17; N, 8.99; Se, 16.90. $C_{16}H_{11}I_4N_3OSe$. Calculated (%): C, 41.00; H, 2.41; I, 27.27; N, 8.88; Se, 16.89.

References

1. V. D. Dyachenko, Yu. A. Sharanin, V. P. Litvinov, and A. V. Turov, *Ukr. Khim. Zh.,* 1990, **56**, 408.
2. V. D. Dyachenko, Yu. A. Sharanin, A. M. Shestopalov, L. A. Rodinovskaya, A. V. Turov, V. P. Litvinov, and V. K. Promonenkov, *Zh. Obshch. Khim.*, 1990, **60**, 2384 [*J. Gen. Chem. USSR*, (Engl. Transl.)].
3. V. N. Nesterov, V. E. Shklover, Yu. T. Struchkov, Yu. A. Sharanin, and V. D. Dyachenko, *Izv. Akad. Nauk SSSR, Ser. khim.,* 1989, 2585 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1989 (Engl. Transl.)].
4. A. M. Shestopalov, V. N. Nesterov, Yu. A. Sharanin, V. P. Litvinov, V. Yu. Mortikov, V. E. Shklover, and Yu. T. Struchkov, *Khim. Geterotsikl. Soedin.*, 1989, 557 [*Chem. Heterocycl. Cpd.* (Engl. Transl.)].
5. Yu. V. Zefirov, *Zh. Obshch. Khim.,* 1976, **46**, 2636 [*J. Gen. Chem. USSR* (Engl. Transl.)].
6. F. H. Allen, O. Kennard, D. G. Watson, L. Brammer, A. G. Orpen, and R. Taylor, *J. Chem. Soc. Perkin Trans,* II, 1987, S1.
7. A. Bondi, *J. Phys. Chem.*, 1966, **70**, 3006.

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