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Recyclization of 2,6-Diamino-4-aryl(cyclohexyl)-3,5-dicyano-4*H*-thio(seleno)pyrans

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Abstract — Recyclization of 2,6-diamino-4-aryl(cyclohexyl)-3,5-dicyano-4*H*-thio(seleno)pyrans in the presence of an equimolar amount of an α-bromo carbonyl compound, ethyl iodide, 1,2-dibromoethane, or 3-chlorophenyl isocyanate yields, respectively, 3-aryl(cyclohexyl)-2-[thiazol(selenazol)-2-yl]acrylonitriles, 6-amino-4-phenyl-2-ethylsulfanyl-1,4-dihydropyridine-3,5-dicarbonitrile, 5-amino-7-phenyl-2,3,4,7-tetrahydrothiazolo[3,2-*a*]pyridine-6,8-dicarbonitrile, or *N*,*N*'-bis(3-chlorophenyl)urea.

It was shown previously [1–3] that recyclization of 2,6-diamino-4-alkyl(aryl, heteryl)-3,5-dicyano-4*H*-thio(seleno)pyrans in refluxing ethanol in the presence of *N*-methylmorpholine yields *N*-methylmorpholinium 6-amino-4-alkyl(aryl, heteryl)-3,5-dicyano-2-thio(seleno)lates. With hydrazine or aniline used as the base in the reaction, 2,6-dihydrazino-4-phenyl-3,5-dicyanopyridine or 6-amino-2-phenylamino-4-phenyl-3,5-dicyanopyridine, respectively, is formed [4]. At the same time, with pyridinium ylides or aliphatic ketones used as CH acids in this recyclization, 3-(1-pyridinio)-5-cyano-3,4-*trans*-1,2,3,4-tetrahydro-6-pyridinethiolate [5] or 5,6-dialkyl-4-aryl-3-cyanopyridine-2(1*H*)-thiones [6], respectively, are formed as a result of interchange of the methylene components.

Here we report on the recyclization of 2,6-diamino-4-aryl(cyclohexyl)-3,5-dicyano-4*H*-thio(seleno)pyrans **Ia**–**Ii** in the presence of an equimolar amount of an α-bromo carbonyl compound **IIa**–**IIm**, ethyl iodide, 1,2-dibromoethane, or 3-chlorophenyl isocyanate. The reactions of **Ia**–**Ii** with α-bromo ketones **IIa**–**IIm** in refluxing ethanol yield substituted acrylonitriles **IIIa**–**IIIz** and **III**α. This reaction pathway involves opening of the thio(seleno)pyran ring with the formation of unstable thio(seleno)amides of aryl(cycloalkyl)methylenecyanoacetic acid **A** and malonodinitrile. This is followed by the Hantzsch reaction yielding 2-aryl(cyclohexyl)-2-[thiazol(selenazol)-2-yl]acrylonitriles **IIIa**–**IIIz** and **III**α, which are potentially bioactive compounds [7, 8]. Recyclization of thiopyran **Ih** with an equimolar amount of ethyl iodide yields 6-amino-4-phenyl-2-ethylsulfanyl-1,4-dihydropyridine-3,5-dicarbonitrile **IV**. The scheme of its formation apparently involves regioselective S-alkylation of **A** with ethyl iodide to the corresponding 1,4-dihydropyridine **IV**.

Replacement of ethyl iodide in this reaction by 1,2-dibromoethane led to the formation of 5-amino-7-phenyl-2,3,4,7-tetrahydrothiazolo[3,2-*a*]pyridine-6,8-dicarbonitrile **V**. Thus, in this case the reaction goes beyond formation of sulfide **D** and involves subsequent chemoselective intramolecular alkylation of the nitrogen atom of the dihydropyridine ring with the bromoethyl group, yielding heterocyclic system **V**.

The spectral characteristics confirm the structures of **III**–**V**. In particular, their IR spectra contain characteristic absorption bands of stretching vibrations of a conjugated cyano group (see Experimental, Tables 1, 2). The ^{1}H NMR spectra of dihydropyridines **IV** and **V** contain, along with the proton signals of the substituents in the expected regions, a singlet of the C^4H proton of the dihydropyridine ring at δ 4.24 and 4.27 ppm, respectively (see Experimental), in agreement with data from [9–11].

The reaction of thiopyran **Ia** with 3-chlorophenyl isocyanate in refluxing toluene yielded *N*,*N*'-bis(3-chlorophenyl)urea **VI**. Apparently, its formation became possible owing to the presence of 2-chloroaniline **E** in the reaction mixture. Compound **E**, in turn, could be formed by decomposition of hypothetical unstable 3-chlorophenylthiocarbamic acid **F** formed by the reaction of 3-chlorophenyl isocyanate with H_2S released in the course of transformation of **A** into arylmethylenemalonodinitrile **G**. Note that the addition of H_2S to the nitrile group is reversible [12].

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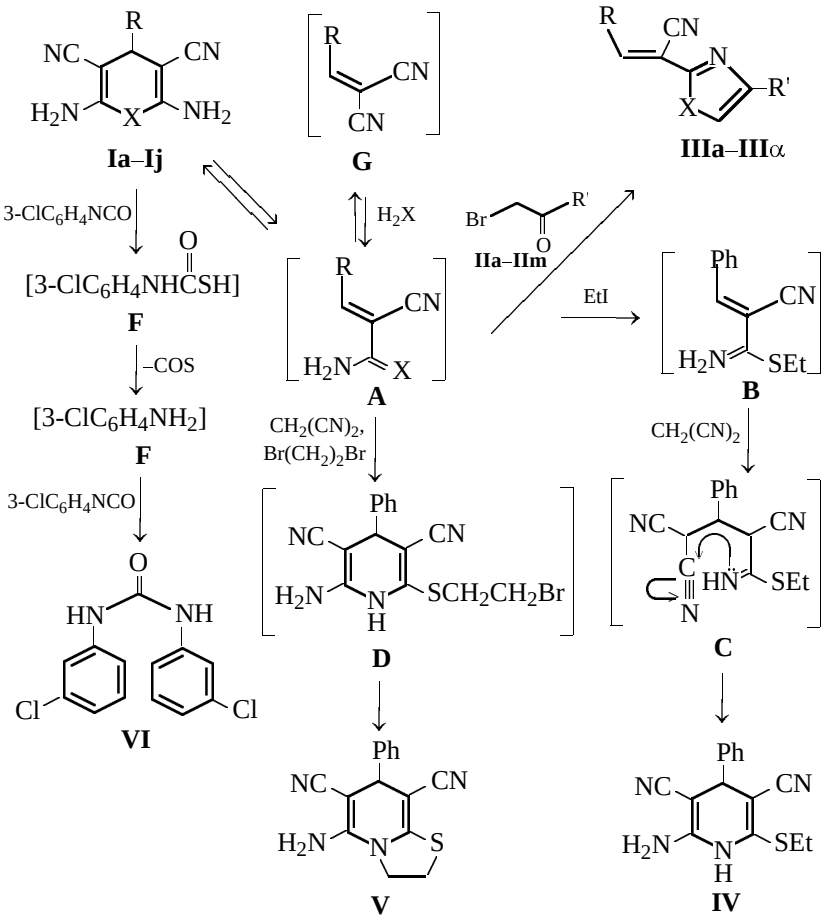

I, X = S (**a**–**f, h**–**j**), Se (**g**); R = 4-EtC$_6$H$_4$ (**a**), 3-PhOC$_6$H$_4$ (**b**), 4-NO-3-MeOC$_6$H$_3$ (**c**), 4-PhC$_6$H$_4$ (**d**), cyclohexyl (e), 1-naphthyl (**f**), Ph (**g, h**), 4-ClC$_6$H$_4$ (**i**), 2,4-(EtO)$_2$C$_6$H$_3$ (**k**). **II**, R' = 4-PhC$_6$H$_4$ (**a**), 3-coumarinyl (**b**), Ph (**c**), 4-FC$_6$H$_4$ (**d**), cyclopropyl (**e**), 4-BuC$_6$H$_4$ (**f**), 4-MeOC$_6$H$_4$ (**g**), 4-MeC$_6$H$_4$ (**h**), 4-ClC$_6$H$_4$ (**i**), 2-HOC$_6$H$_4$ (**j**), 8-bromocoumarin-3-yl (**k**), 6-methyl-3-cyano-2-ethylsulfanylpyridin-5-yl (**l**), 4-cyclohexylphenyl (**m**). **III**, X = S (**a**–**h, j**–**z,** α), Se (**i**); R = 4-EtC$_6$H$_4$ (**a**), 1-naphthyl (**b**–**e**), 2,4-(EtO)$_2$C$_6$H$_3$ (**f, g**), 3-PhOC$_6$H$_4$ (**h, q**–**u**), Ph (**i**–**l**), 4-NO-3-MeOC$_6$H$_3$ (**m**–**p**), 4-ClC$_6$H$_4$ (**v, x, y**), cyclohexyl (**w, z**), 4-PhC$_6$H$_4$ (α); R' = 3-coumarinyl (**a, p, s**), 4-PhC$_6$H$_4$ (**b, f, h, l, n**), Ph (**c, o, t**), 4-FC$_6$H$_4$ (**d**), cyclopropyl (**e**), 4-BuC$_6$H$_4$ (**g, m, x**), 4-MeOC$_6$H$_4$ (**i, k, u,** α), 4-MeC$_6$H$_4$ (**j**), 4-cyclohexylphenyl (**q**), 4-ClC$_6$H$_4$ (**r, z**), 6-methyl-2-ethylsulfanyl-3-cyanopyridin-5-yl (**v**), 8-bromocoumarin-3-yl (**w**), 2-HOC$_6$H$_4$ (**y**).

The structure of **VI** was unambiguously confirmed by single crystal X-ray diffraction. The general view of the molecule of **VI** and its main geometric parameters are shown in Fig. 1. The main bond lengths (Å) and bond angles (deg) are as follows: N^1–C^1 1.348(3), N^1–C^2 1.412(3), O^1–C^1 1.238(5), C^1–$N^{1'}$ 1.348(3), $C^1N^1C^2$ 123.9(2), $O^1C^1N^1$ 122.3(2), $O^1C^1N^{1'}$ 122.3(2), $N^1C^1N^{1'}$ 115.4(3). The central group $C^2N^1C^1O^1N^1C^{2'}$ is approximatley planar: The deviations of atoms from the least-squares plane do not exceed 0.054 Å, and the torsion angles $C^2N^1C^1O^1$ and $C^2N^1C^1N^{1'}$ are –6.8° and 173.2°, respectively. The benzene rings $C^{2–7}$ and $C^{2'–7'}$ are turned relative to this plane by 51.4°, forming with each other a dihedral angle of 85.6°. The N^1 atom has a trigonal planar configuration: the sum of the bond angles at this atom is 359.9°. The very efficient $n(N^1)\pi(C^1{=}O^1)$ conjugation causes shortening of the N^1–C^1 bond to 1.348(3) Å (typical N_{sp^2}–C_{sp^2} bond length is 1.43–1.45 Å [13, 14]). Note that the bond lengths and bond angles in **VI** are relatively close to those found in the previously studied diaryl derivatives of urea [15]. The molecules of **VI** in the crystal are linked in infinite chains (Fig. 2) through bifurcate hydrogen bonds N^1–$H^1\cdots O^1$ of medium strength [16] [$N^1\cdots O^1$ 2.856(3), $H^1\cdots O^1$ 2.12(4), N^1–H^1 0.80(4) Å, $\angle N^1H^1O^1$ 154(3)°].

Urea is one of a few presently known organic crystals with large birefringence and high nonlinear coefficients in combination with good transparence (down to 200 nm) and radiation resistance, which makes it

Table 1. Yields, constants, and elemental analyses of substituted acrylonitriles **IIIa**–**IIIz** and **III**α

Comp. no.	Yield, %	mp, °C	Found, %			Formula	Calculated, %		
			C	H	N		C	H	N
IIIa	85	170–172	71.75	4.12	7.06	$C_{23}H_{16}N_2O_2S$	71.86	4.20	7.29
IIIb	81	195–197	80.95	4.14	6.59	$C_{28}H_{18}N_2S$	81.13	4.38	6.76
IIIc	76	129–131	77.95	3.99	8.13	$C_{22}H_{14}N_2S$	78.08	4.17	8.28
IIId	79	143–145	73.97	3.50	7.71	$C_{22}H_{13}FN_2S$	74.14	3.68	7.86
IIIe	82	100–102	75.32	4.50	9.09	$C_{19}H_{14}N_2S$	75.47	4.67	9.26
IIIf	90	174–176	74.22	5.16	6.07	$C_{28}H_{24}N_2O_2S$	74.31	5.35	6.19
IIIg	72	94–95	72.02	6.44	6.31	$C_{26}H_{28}N_2O_2S$	72.19	6.52	6.48
IIIh	79	132–133	78.81	4.13	6.02	$C_{30}H_{20}N_2OS$	78.92	4.42	6.14
IIIi	77	120–121	64.30	3.71	7.52	$C_{19}H_{14}N_2OSe$	62.47	3.86	7.67
IIIj	72	144–145	75.29	4.58	9.14	$C_{19}H_{14}N_2S$	75.47	4.67	9.26
IIIk	88	122–123	71.52	4.35	8.68	$C_{19}H_{14}N_2OS$	71.68	4.43	8.80
IIIl	68	188–190	78.85	4.19	7.48	$C_{24}H_{16}N_2S$	79.09	4.43	7.69
IIIm	84	100–101	70.61	5.49	7.12	$C_{23}H_{22}N_2O_2S$	70.74	5.68	7.17
IIIn	70	185–186	72.95	4.30	6.77	$C_{25}H_{18}N_2O_2S$	73.15	4.42	6.82
IIIo	81	149–150	68.13	4.05	8.19	$C_{19}H_{14}N_2O_2S$	68.25	4.22	8.38
IIIp	92	178–180	65.48	3.39	7.15	$C_{22}H_{14}N_2O_4S$	65.66	3.51	6.96
IIIq	94	150–151	77.72	5.48	5.89	$C_{30}H_{26}N_2OS$	77.89	5.67	6.06
IIIr	84	157–158	69.22	3.49	6.60	$C_{24}H_{15}ClN_2OS$	69.48	3.64	6.75
IIIs	91	161–163	72.18	3.48	6.14	$C_{27}H_{16}N_2O_3S$	72.31	3.60	6.25
IIIt	75	108–109	75.60	4.12	7.23	$C_{24}H_{16}N_2OS$	75.77	4.24	7.36
IIIu	80	118–119	72.98	4.37	6.71	$C_{25}H_{18}N_2O_2S$	73.15	4.42	6.82
IIIv	84	200–202	59.51	3.42	13.09	$C_{21}H_{15}ClN_4S_2$	59.64	3.58	13.25
IIIw	70	193–195	57.99	3.75	6.21	$C_{21}H_{17}BrN_2O_2S$	57.15	3.88	6.35
IIIx	84	88–89	69.64	4.88	7.19	$C_{22}H_{19}ClN_2S$	69.74	5.05	7.39
IIIy	88	179–180	63.69	3.12	8.05	$C_{18}H_{11}ClN_2OS$	63.81	3.27	8.27
IIIz	80	98–100	65.60	5.02	8.43	$C_{18}H_{17}ClN_2S$	65.74	5.21	8.52
IIIα	77	160–162	75.94	4.49	6.97	$C_{25}H_{18}N_2OS$	76.12	4.60	7.10

[a] Fluorescence is observed under UV irradiation.

Table 2. IR and ^{1}H NMR spectra of substituted acrylonitriles **IIIa**–**IIIz** and **III**α

Comp. no.	IR spectrum,[a] cm^{-1},	^{1}H NMR spectrum, δ, ppm (*J*, Hz)	
		C^3H (s), C^5H (s) of thiazole	other signals
IIIa	2218, 1738 (C=O)	8.49, 8.31	1.32 t (3H, Me, *J* 6.24), 2.73 q (2H, CH_2), 7.39 m (4H, H arom.), 7.62 m (1H, H arom.), 7.78 d (1H, H arom., *J* 6.81), 7.97 d (2H, H arom., *J* 7.14), 8.88 s (1H, C^4H of coumarin)
IIIb	2217	9.05, 8.40	7.36–7.88 m (12H, H arom.), 8.01–8.29 m (4H, H arom.)
IIIc	2214	9.07, 8.39	7.41–7.82 m (7H, H arom.), 8.06–8.29 m (5H, H arom.)
IIId	2219	9.01, 8.30	7.19–7.40 m (2H, H arom.), 7.51–7.78 m (4H, H arom.), 7.99–8.23 m (5H, H arom.)
IIIe	2218	8.86, 7.52	7.61–7.80 m (3H, H arom.), 8.02–8.17 m (4H, H arom.), 0.82–1.13 m (4H, $2CH_2$), 2.10–2.33 m (1H, C^1H of cyclopropane)

Table 2. (Contd.)

Comp. no.	IR spectrum,[a] cm^{-1}	^1H NMR spectrum, δ, ppm (*J*, Hz)	
		C^3H (s), C^5H (s) of thiazole	other signals
IIIf	2215	8.45, 8.21	1.12–1.52 m (6H, 2Me), 4.02–4.35 m (4H, $2CH_2$), 6.67 d (2H, H arom., *J* 8.34), 7.46 m (3H, H arom.), 7.75 m (5H, H arom.), 8.11 d (2H, H arom., *J* 7.06)
IIIg	2205	8.40, 8.06	0.89 t (3H, Me, *J* 7.11), 1.12–1.73 m (10H, 2Me and $2CH_2$), 2.59 t (2H, CH_2, *J* 7.54), 4.14 m (4H, $2CH_2$), 6.63 s (1H, C_6H_3), 6.78 d (1H, C_6H_3, *J* 8.05), 7.26 d (2H, C_6H_4, *J* 8.79), 7.88 d (2H, C_6H_4), 8.13 d (1H, C_6H_3)
IIIh	2220	8.39, 8.31	7.02–7.28 m (5H, H arom.), 7.39–7.64 m (5H, H arom.), 7.72–7.89 m (6H, H arom.), 8.13 d (2H, H arom., *J* 8.41)
IIIi	2217	8.59, 8.33	3.81 s (3H, Me), 7.05 d and 7.50 d (2H each, C_6H_4, *J* 8.84), 7.58 m (3H, Ph), 8.07 m (2H, Ph)
IIIj	2219	8.32, 8.15	2.38 s (3H, Me), 7.30 d and 7.93 d (2H each, C_6H_4, *J* 7.72), 7.59 m (3H, Ph), 8.02 m (2H, Ph)
IIIk	2222	8.26, 7.98	3.83 s (3H, Me), 6.94 d and 7.92 d (2H each, C_6H_4, *J* 8.84), 7.52 m (3H, Ph), 7.99 m (2H, Ph)
IIIl	2214	8.31, 8.12	7.33–7.71 m (7H, H arom.), 8.01–8.08 m (7H, H arom.)
IIIm	2208, 3612 (OH)	8.16, 8.11	0.91 t (3H, Me, *J* 6.25), 1.14–1.78 m (4H, $2CH_2$), 2.61 t (2H, CH_2, *J* 6.18), 3.87 s (3H, MeO), 6.96 d and 7.62 d (1H each, C_6H_3, *J* 7.11), 7.29 d and 7.92 d (2H each, C_6H_4, *J* 7.05), 7.48 s (1H, C_6H_3), 10.22 br.s (1H, OH)
IIIn	2216, 3622 (OH)	8.25, 7.89	3.88 s (3H, Me), 6.98 d and 7.76 d (1H each, C_6H_3, *J* 7.07), 7.39–7.65 m (9H, H arom.), 8.11 s (1H, C_6H_3), 10.22 br.s (1H, OH)
IIIo	2214, 3610 (OH)	8.19, 8.08	3.86 s (3H, Me), 6.96 d (1H, C_6H_3, *J* 7.04), 7.35–7.81 m (5H, H arom.), 8.01 d (2H, Ph, *J* 7.13), 10.21 br.s (1H, OH)
IIIp	2220, 3598 (OH), 1718 (C=O)	8.45, 8.21	3.92 s (3H, Me), 6.94 d and 7.86 d (1H each, C_6H_3, *J* 7.12), 7.36–7.68 m (4H, H arom.), 6.74 s (1H, C_6H_3), 8.87 s (1H, C^4H of coumarin), 9.92 br.s (1H, OH)
IIIq	2215	8.25, 7.98	1.21–1.59 m (6H, $3CH_2$), 1.63–1.98 m (5H, CH_2CHCH_2), 7.07 t (2H, Ph, *J* 7.62), 7.11 m (2H, H arom.), 7.23 d and 7.88 d (2H each, C_6H_4, *J* 8.10), 7.36 m (2H, H arom.), 7.51 t (1H, Ph, *J* 7.98), 7.63 s (1H, H arom.), 7.76 d (1H, H arom., *J* 6.72)
IIIr	2219	8.27, 8.15	7.03–7.19 m (4H, H arom.), 7.35–7.48 m (4H, H arom.), 7.52 t (1H, H arom., *J* 7.90), 7.62 m (1H, H arom.), 7.76 d (1H, H arom., *J* 7.82), 8.02 d (2H, H arom., *J* 8.50)
IIIs	2218, 1720 (C=O)	8.52, 8.34	7.08 d (2H, H arom., *J* 7.15), 7.18 d (2H, H arom., *J* 6.94), 7.41 m (4H, H arom.), 7.58 m (2H, H arom.), 7.69 s (1H, C_6H_4), 7.83 t (2H Ph, *J* 7.45), 8.88 s (1H, C^4H of coumarin)
IIIt	2214	8.31, 8.25	7.02–7.84 m (12H, H arom.), 8.03 d (2H, H arom., *J* 7.02)
IIIu	2222	8.34, 8.12	3.81 s (3H, Me), 7.07 d and 7.97 d (2H each, C_6H_4, *J* 8.85), 7.12–7.82 m (9H, H arom.)
IIIv	2217, 2224	8.41, 8.35	1.39 t (3H, Me, *J* 7.23), 2.80 s (3H, Me), 3.29 q (2H, CH_2), 7.52 d and 8.01 d (2H each, C_6H_4), 8.07 s (1H, C^4H of pyridine)
IIIw	2212, 1728 (C=O)	8.04 d (*J* 2.24), 8.45	1.05–1.48 m (6H, $3CH_2$), 1.64–1.87 m (4H, $2CH_2$), 1.63 m (1H, C^1H of cyclohexane), 7.33 d (1H, C^7H of coumarin, *J* 2.18), 7.38 d (1H, C^5H of coumarin, *J* 3.62), 7.68 d. d (1H, C^6H of coumarin, *J* 8.64 and 2.23), 8.77 s (1H, C^4H of coumarin)
IIIx	2220	8.26, 7.93	0.94 t (3H, Me, *J* 7.02), 1.39 m (2H, CH_2), 1.62 m (2H, CH_2), 2.61 t (2H, CH_2, *J* 7.12), 7.20 d and 7.88 d (2H each, C_6H_4, *J* 7.62), 7.52 d and 8.01 d (2H each, 4-ClC_6H_4, *J* 7.26)

Table 2. (Contd.)

Comp. no.	IR spectrum,[a] cm^{-1}	^1H NMR spectrum, δ, ppm (*J*, Hz)	
		C^3H (s), C^5H (s) of thiazole	other signals
IIIy	2218, 3614 (OH)	8.27, 8.24	6.88 m (2H, H arom.), 7.10 m (1H, H arom.), 7.54 d (2H, 4-ClC_6H_4, *J* 8.50), 8.07 m (3H, H arom.), 10.31 br.s (1H, OH)
IIIz	2223	7.35 d, (*J* 2.19), 8.11	1.18–1.54 m (6H, $3CH_2$), 1.69–1.95 m (4H, $2CH_2$), 2.71 m (1H, C^1H of cyclohexane), 7.46 d and 7.99 d (2H each, C_6H_4, *J* 8.49)
IIIα	2219	8.35, 8.21	3.82 s (3H, Me), 7.05 d and 7.50 d (2H each, C_6H_4, *J* 8.39), 7.72–8.12 m (9H, H arom.)

[a] ν(C≡N) unless otherwise indicated.

a valuable material for nonlinear conversion of the laser radiation frequency from the IR to UV range [17]. Therefore, the known and newly synthesized urea derivatives are very interesting and promising from the viewpoint of manifestation of nonlinear optical properties (e.g., quadratic nonlinear susceptibility). Therefore, we measured for **VI** the intensity of the generation of the second harmonic in polycrystalline samples by the Kurtz–Perry method. We found that the intensity of the second harmonic generation for powders of **VI** is about 80% of that for unsubstituted urea.

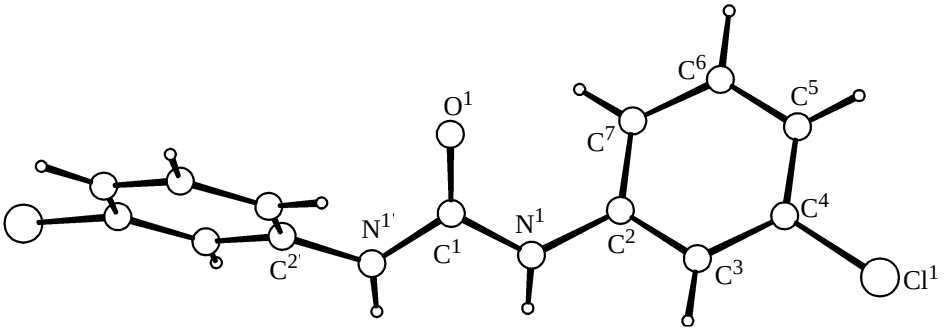

Fig. 1. General view of the molecule of *N*,*N*'-bis(3-chlorophenyl)urea **VI** with the atom numbering. Atoms symmetry-related (twofold axis) to the basis (symmetrically independent) atoms are marked with primes.

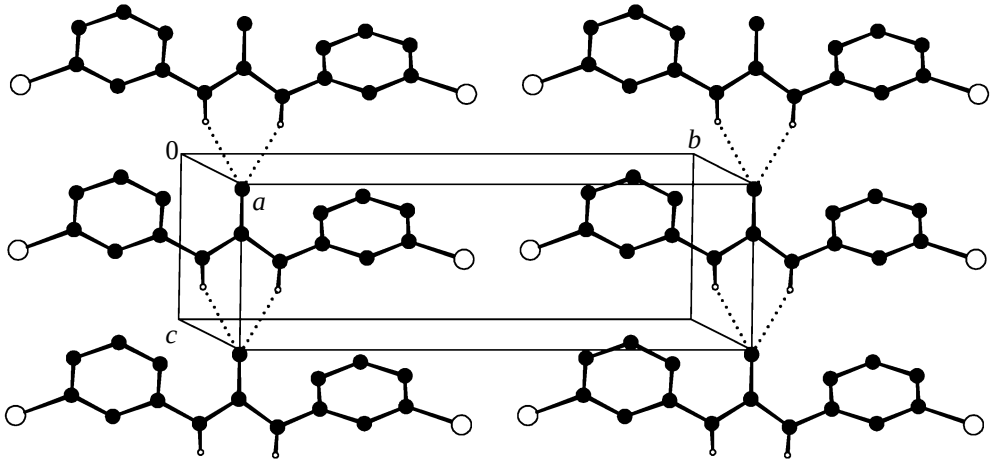

Fig. 2. Crystal packing of **VI**. Dotted lines denote intermolecular hydrogen bonds; *a*, *b*, and *c* are unit cell parameters.

EXPERIMENTAL

The IR spectra were recorded on an IKS-29 spectrometer (mulls in mineral oil). The ^{1}H NMR spectra were taken on Bruker WP-100SY (100 MHz) (**Ia, Ic–Ie, IIIb–IIIi, IIIm–IIIo, IIIt, IIIu, IIIα, VI**), Gemini-200 (199.975 MHz) (**IIIr, IIIw, IIIx**), Bruker AC-200 (200.13 MHz) (**IIIa, IIIp, IIIs**), Bruker WM-250 (250.13 MHz) (**IIIz**), Bruker AM-300 (300.13 MHz) (**Ib**), and Bruker DR-500 (500.13 MHz) (**IIIv, IIIy, IV, V**) spectrometers in DMSO-d_6, internal reference TMS. The mass spectra were measured on a Kratos MS-890 spectrometer (electron impact, 70 eV) with direct sample inlet.

The melting points were determined with a Koefler unit.

The reaction progress was monitored on Silufol UV-254 plates, eluent acetone–hexane, 3 : 5 by volume, development with iodine vapor.

The intensity of the second harmonic generation for **VI** was measured with a pulse YAG:Nd^{3+} laser (1064 nm) in the modulated *Q*-factor mode. The recording system consisted of a monochromator with a series of photoreceivers.

X-ray diffraction study of **VI** was performed with a $0.28 \times 0.30 \times 0.59$-mm single crystal at room temperature on an Enraf-Nonius CAD-4 automatic four-circle diffractometer (MoK_α radiation, λ 0.71069 A, scanning rate ratio $2\theta/\omega$ 1.2, θ_{max} 25°, sphere segment $0 \le h \le 11$, $0 \le k \le 17$, $0 \le l \le 5$, 696 reflections). Crystal data: rhombic system, *a* 9.707(1), *b* 14.358(2), *c* 4.577(2) Å; *V* 637.9(2) Å^3, *M* 281.1, *Z* 2, ρ_{calc} 1.46 g cm^{-3}, μ 4.96 cm^{-1}, *F*(000) 288, space group $P2_12_12$. The structure was solved by the direct method and refined by the least-squares method in the full-matrix anisotropic approximation using SHELXS and SHELXL-93 programs [18, 19]. In the refinement we used 627 reflections with $I > 2\sigma(I)$ (103 refined parameters, 6.1 reflections per parameter). All the hydrogen atoms were revealed from the differential electron density synthesis and were refined isotropically. In the refinement we used the weight scheme $\omega = 1/[\sigma^2(F_0^2) + (0.046P)^2 + 0.137]$, where $R = (F_0^2 + 2F_c^2)/3$. The final divergence factors are $R(F)$ 0.033 and $R_W(F^2)$ 0.041, *GOF* 1.054. The residual electron density from the differential Fourier series was 0.13 and –0.20 e/Å^3. We made the correction for anomalous absorption and did not make absorption corrections. The absolute configuration of **VI** was determined by Flack's method [20]: $p = 0.3(2)$.

4-Aryl-2,6-diamino-3,5-dicyano-4*H*-thiopyrans Ia–If and Ih–Ij were prepared according to [1]; selenopyran **Ig** was described in [21]. Compound **If** was characterized in [2]; **Ih** and **Ii**, in [1]; and **Ij**, in [3].

2,6-Diamino-3,5-dicyano-4-(4-ethylphenyl)-4*H*-thiopyran Ia: yield 88%, mp 181–183°C (from EtOH). IR spectrum, ν, cm^{-1}: 3445, 3341, 3198 (NH_2), 2194 sh (C≡N), 1645 [δ(NH_2)]. ^{1}H NMR spectrum, δ, ppm: 1.19 t (3H, Me, *J* 6.23 Hz), 2.58 q (2H, CH_2), 4.23 s (1H, C^{4}H), 6.90 br.s (4H, 2NH_2), 7.18 s (4H, C_6H_4). Found, %: C 63.70; H 4.84; N 19.72. $C_{15}H_{14}N_4S$. Calculated, %: C 63.81; H 5.00; N 19.84.

2,6-Diamino-4-(3-phenoxy)-3,5-dicyano-4*H*-thiopyran Ib: yield 80%, mp 196–198°C (from EtOH). IR spectrum, ν, cm^{-1}: 3455, 3333, 3202 (NH_2), 2185 sh (C≡N), 1648 [δ(NH_2)]. ^{1}H NMR spectrum, δ, ppm: 4.32 s (1H, C^{4}H), 6.99 br.s (4H, 2NH_2), 7.07 s (1H, H arom.), 7.12–7.58 m (8H, H arom.). Found, %: C 65.71; H 3.90; N 16.14. $C_{19}H_{14}N_4OS$. Calculated, %: C 65.88; H 4.07; N 16.17.

4-(4-Hydroxy-3-methoxyphenyl)-2,6-diamino-3,5-dicyano-4*H*-thiopyran Ic: yield 71%, mp 140–142°C (from EtOH). IR spectrum, ν, cm^{-1}: 3590 (OH), 3440, 3302, 3195 (NH_2), 2176 sh (C≡N), 1640 [δ(NH_2)]. ^{1}H NMR spectrum, δ, ppm: 3.73 s (3H, MeO), 4.16 s (1H, C^{4}H), 6.48–6.95 m (7H, C_6H_3 and 2NH_2), 8.92 br.s (1H, OH). Found, %: C 55.80; H 3.89; N 18.58. $C_{14}H_{12}N_4O_2S$. Calculated, %: C 55.99; H 4.03; N 18.65.

2,6-Diamino-4-(biphenyl-4-yl)-3,5-dicyano-4*H*-thiopyran Id: yield 72%, mp 218–220°C (from EtOH). IR spectrum, ν, cm^{-1}: 3450, 3312, 2197 (NH_2), 2179 sh (C≡N), 1640 [δ(NH_2)]. ^{1}H NMR spectrum, δ, ppm: 4.35 s (1H, C^{4}H), 6.47 br.s (4H, 2NH_2), 7.32–7.71 m (9H, H arom.). Found, %: C 68.92; H 4.11; N 16.78. $C_{19}H_{14}N_4S$. Calculated, %: C 69.07; H 4.27; N 16.96.

2,6-Diamino-3,5-dicyano-4-cyclohexyl-4*H*-thiopyran Ie was prepared according to [22]; yield 86%, mp 215–217°C (from EtOH). IR spectrum, ν, cm^{-1}: 3450, 3390, 3300 (NH_2), 2190 sh (C≡N), 1640 [δ(NH_2)]. ^{1}H NMR spectrum, δ, ppm: 1.10 m (5H, CH_2CHCH_2), 1.69 m (6H, 3CH_2), 2.71 d (1H, C^{4}H, *J* 3.18 Hz), 6.80 br.s (4H, 2NH_2). Found, %: C 59.78; H 6.04; N 21.52. $C_{13}H_{16}N_4S$. Calculated, %: C 59.97; H 6.19; N 21.52.

3-Aryl-2-[4-R′-thiazol(selenazol)-2-yl]acrylonitriles IIIa–IIIz and IIIα. A mixture of 10 mmol of thio(seleno)pyran **I** and 10 mmol of α-bromo ketone **II** in 40 ml of absolute ethanol was refluxed for 8 h. The precipitate that formed on cooling was filtered off and washed with ethanol and hexane. The resulting compounds **IIIa–IIIz** and **IIIα** were recrystallized from BuOH (Tables 1, 2). Mass spectrum of **IIIr**, *m/z*

(I_{rel}, %): 417 (11) $[M + 2]^+$, 416 (33) $[M + 1]^+$, 415 (58) $[M]^+$, 414 (98) $[M - 1]^+$, 413 (100) $[M - 2]^+$, 388 (22), 321 (13), 207 (24), 168 (85), 133 (79), 89 (52), 77 (49) $[Ph]^+$, 51 (24), 39 (6). Mass spectrum of **IIIv**, *m/z* (I_{rel}, %): 425 (4) $[M + 2]^+$, 424 (12) $[M + 1]^+$, 423 (45) $[M]^+$, 422 (100) $[M - 1]^+$, 421 (10) $[M - 2]^+$, 407 (29), 389 (71), 206 (25), 173 (28), 146 (21), 120 (32), 82 (10), 69 (17), 51 (8), 45 (23). Mass spectrum of **IIIw**, *m/z* (I_{rel}, %): 443 (25) $[M + 2]^+$, 442 (100) $[M + 1]^+$, 441 (92) $[M]^+$, 440 (9) $[M - 1]^+$, 361 (39), 223 (18), 174 (22), 145 (57), 113 (14), 101 (22), 87 (9), 67 (28), 55 (19), 41 (68). Mass spectrum of **IIIy**, *m/z* (I_{rel}, %): 341 (13) $[M + 2]^+$, 340 (38) $[M + 1]^+$, 339 (46) $[M]^+$, 338 (100) $[M - 1]^+$, 337 (65) $[M - 2]^+$, 206 (10), 150 (14), 121 (72), 89 (24), 78 (19), 63 (9), 51 (12), 39 (7).

6-Amino-4-phenyl-2-ethylsulfanyl-1,4-dihydropyridine-3,5-dicarbonitrile IV. A mixture of 2.5 g of thiopyran **Ih** and 0.8 ml of ethyl iodide in 20 ml of absolute ethanol was refluxed for 5 h and filtered while hot; the filtrate was allowed to stand for 2 days at room temperature. The resulting precipitate was separated and washed with ethanol and hexane. Yield 1.7 g (60%), mp 151–153°C (from EtOH). IR spectrum, ν, cm^{-1}: 3400, 3372, 3330 (NH_2), 2177 sh (C≡N), 1638 [δ(NH_2)]. ^1H NMR spectrum, δ, ppm: 1.26 t (3H, Me, *J* 6.23 Hz), 2.98 m (2H, CH_2), 4.24 s (1H, C^4H), 5.81 br.s (2H, $2NH_2$), 7.19–7.38 m (5H, Ph), 9.04 br.s (1H, NH). Found, %: C 63.75; H 4.82; N 19.71. $C_{15}H_{14}N_4S$. Calculated, %: C 63.81; H 5.00; N 19.84.

5-Amino-7-phenyl-2,3,4,7-tetrahydrothiazolo-[3,2-*a*]pyridine-6,8-dicarbonitrile V was prepared similarly to **IV**, with ethyl iodide replaced by 0.9 ml of 1,2-dibromoethane, yield 1.5 g (53%), mp 181–183°C (from EtOH). IR spectrum, ν, cm^{-1}: 4122, 3354, 3193 (NH_2), 2190 sh (C≡N), 1650 [δ(NH_2)]. ^1H NMR spectrum, δ, ppm: 3.43 t (2H, SCH_2, *J* 6.64 Hz), 4.14 t (2H, NCH_2), 4.27 s (1H, C^7H), 6.28 br.s (2H, NH_2), 7.19–7.38 m (5H, Ph). Mass spectrum, *m/z* (I_{rel}, %): 282 (4) $[M + 2]^+$, 281 (6) $[M + 1]^+$, 280 (29) $[M]^+$, 213 (16), 203 (100) $[M - Ph]^+$, 176 (10), 140 (13), 77 (12) $[Ph]^+$, 51 (9), 39 (5). Found, %: C 64.14; H 4.20; N 19.87. $C_{15}H_{12}N_4S$. Calculated, %: C 64.26; H 4.32; N 19.98.

***N*,*N*′-Bis(3-chlorophenyl)urea VI.** A mixture of 2.5 g of thiopyran **Ih** and 1.2 ml of 3-chlorophenyl isocyanate in 30 ml of absolute toluene was refluxed for 2 h with protection from atmospheric moisture, filtered while hot, and allowed to stand for 24 h at 20°C. The resulting precipitate was separated and washed with toluene and hexane. Yield 1.0 g (36%), mp 238–240°C (from *i*-PrOH). IR spectrum, ν, cm^{-1}: 1658 (CONH). ^1H NMR spectrum, δ, ppm: 7.05–7.72 m (6H, H arom.), 7.72 s (2H, H arom.), 8.97 br.s (2H, 2NH). Found, %: C 55.31; H 3.40; N 10.12. $C_{13}H_{10}Cl_2N_2O$. Calculated, %: C 55.54; H 3.59; N 9.96.

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