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Cyclization of Nitriles: LIX.* Synthesis and Properties of 1-(2-Thienyl)-4-cyano-5,6,7,8-tetrahydro-3(2*H*)-isoquinolinethione Derivatives. Molecular and Crystal Structure of 3-Isobutylsulfanyl-1-(2-thienyl)-4-cyano-5,6,7,8-tetrahydroisoquinoline

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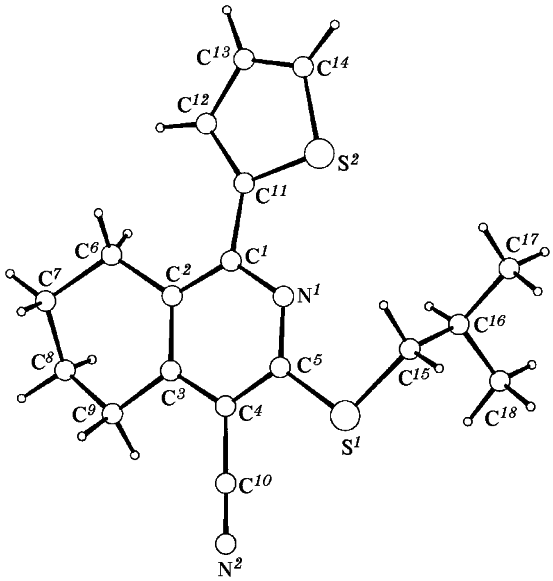
Abstract—By condensation of 2-(2-thenoyl)-1-cyclohexanone with cyanothioacetamide a new compound of a series of chalcogen-containing isoquinolines with a thiophene fragment in its structure was prepared. It was demonstrated that alkylation of the compound with haloalkanes and their derivatives, in particular with those having electron-withdrawing substituents furnished 3-alkylthio-4-cyano-5,6,7,8-tetrahydroisoquinolines. Some of the latter underwent cyclization into 3-amino-2-R-5-(2-thienyl)-6,7,8,9-tetrahydrothieno[2,3-*c*]-isoquinoline.

The structural fragment of isoquinoline and of its partially hydrogenated analogs are found in the molecules of many biologically active compounds, among them alkaloids and azoanalogs of steroids; some derivatives of this class show cardiotonic effect [2–4]. As show published sources, derivatives of cyanoacetic acids can serve convenient synthons for building up the isoquinoline skeleton [5, 6]. It was noted that the heterocyclyzation depends on a number of factors, for instance, on the structure of the original 1,3-diketone and of CH-acid component, on the nature of the catalyst and solvent [6, 7]. Thus the reaction of 2-acetylcyclohexanone with cyanoacetamide catalyzed with pyridine afforded a mixture of isoquinolines [8]. The condensation of cyanothioacetamide with 2-thenoylacetylacetone also provided a mixture of isomeric pyridines [9]. The cyclization of cyanothioacetamide with enamines of 2-acetylcyclohexane series proceeded regioselectively giving rise exclusively to a single isoquinoline isomer [10–12]. The reaction of heterocyclic cycloalkane derivatives with an exocyclic fragment of 1,3-dicarbonyl compound (in particular containing a thiophene moiety) with cyanothioacetamide was not investigated [6].

We showed that the condensation of 2-(2-thenoyl)-1-cyclohexanone (**I**) with cyanothioacetamide (**II**) in the presence of triethylamine resulted exclusively in 1-(2-thienyl)-4-cyano-5,6,7,8-tetrahydroisoquinoline-3-thione (**III**). The formation of isoquinoline **III** is caused apparently, firstly, by steric factor (axial position of carbonyl group in position *1* of the initial reagent **IA**), and secondly, the thiophene fragment introduced into compound **I** stabilizes the enol form of the carbonyl attached to the heterocycle and there-



General view of compound **Va** molecule. Main bond lengths (Å) and bond angles (deg): S^1–C^5 1.758(3), S^1–C^{15} 1.791(3), N^1–C^1, N^1–C^5 1.322(4), C^1–C^2 1.408(4), C^2–C^3 1.395(4), C^3–C^4 1.389(4), C^4–C^5 1.395(4), $C^5S^1C^{15}$ 104.18(14).

* For communication LVIII see [1].

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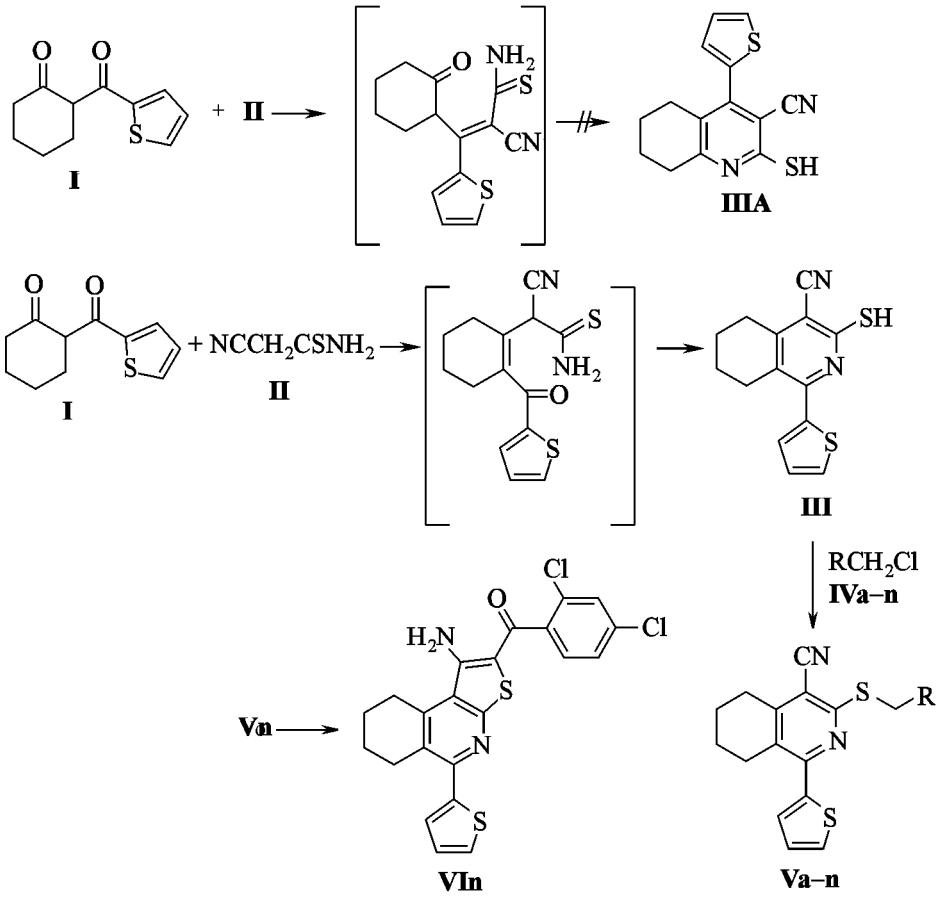
fore leads to elongation of the conjugation chain. We believe that the formation of isoquinoline **III** underlies a cascade reaction of nucleophilic addition of cyanothioacetamide to the carbonyl group of cyclohexanone; in the course of reaction the cyanothioacetamide plays the role of dinucleophile. The subsequent attack of the amino group from thioamide **II** on the second carbonyl linked to the heterocyclic fragment results in formation of the isoquinoline skeleton of compound **III**. Like the substituted 3-cyano-2(*H*)-pyridinethiones [5] and 3-cyano-2(1*H*)-quinolinethiones [7, 12] compound **III** easily undergoes alkylation with various haloalkanes and their derivatives **IVa–n** in dimethylformamide in the presence of KOH. Therewith were isolated and characterized derivatives of 3-alkylthio-4-cyano-5,6,7,8-tetrahydroisoquinoline **Va–n** (Tables 1, 2).

In the presence of excess alkali compound **Vn** undergoes cyclization giving in high yield a derivative of 1-aminothieno[2,3-*c*]isoquinoline **VIn**. The structure of compounds **Va–n**, **VIn** was confirmed by spectral data (Table 2). However the data of IR and ^{1}H NMR spectroscopy alone cannot ensure the choice of one of two alternative structures originating either from thione **III** or from **IIIA**.

To establish the structure of this class derivatives we carried out X-ray diffraction analysis on a single crystal of 3-isobutylthio-1-(2-thienyl)-4-cyano-5,6,7,8-tetrahydroisoquinoline (**Va**). The general view of molecule **Va** and its principal geometrical parameters are given on a figure. The central six-membered heterocycle N^1C^{1-5} is planar: the deviation of atoms from the root-mean-square plane does no exceed 0.019 Å. The five-membered ring S^1C^{11-14} is virtually coplanar with that plane (the corresponding dihedral angle is only 3.7°). The cyclohexene ring $C^{2,3,\ 6-9}$ has common for analogous systems [13] conformation of a distorted chair: the "twist angle" (pceudotorsional angle between the bonds C^2-C^3 and C^7-C^8) amounts to 31.5°,



IV, V, R = $CH(CH_3)_2$ (**a**), 3,4-$Cl_2C_6H_3$ (**b**), 4-ClC_6H_4 (**c**), C_6H_5 (**d**), 6-Cl-3,4-$CH_2OCH_2C_6H_2$ (**e**), 2,4-$Cl_2C_6H_3$ (**f**), 2-ClC_6H_4 (**g**), 4-ClC_6H_4CONH (**h**), $CH{=}CH_2$ (**i**), 2-$CH_3OC_6H_4CONH$ (**j**), 2-FC_6H_4CONH (**k**), 2-CH_3O-5-ClC_6H_3 (**l**), 4-ClC_6H_4CO (**m**), 2,4-$Cl_2C_6H_3CO$ (**n**).

Table 1. Characteristics of 3-methylsulfanyl-1-(2-thienyl)-4-cyano-5,6,7,8-tetrahydroisoquinolines **Va**–**n**

Compd. no.	Yield, %	mp, °C (solvent for crystallization)	Found, %				Formula	Calculated, %			
			C	H	N	S		C	H	N	S
Va	74	47–48 ($CHCl_3$)	65.28	6.10	8.60	19.30	$C_{18}H_{20}N_2S_2$	65.82	6.14	8.53	19.52
Vb	81	132–133 (CH_3CN)	58.12	3.90	6.60	14.54	$C_{21}H_{16}Cl_2N_2S_2$	58.47	3.74	6.49	14.86
Vc	76	120–121 (CH_3CN)	63.36	4.40	7.10	17.69	$C_{21}H_{17}ClN_2S_2$	63.54	4.32	7.06	16.15
Vd	79	89–90 (CH_3CN)	69.21	5.20	7.81	17.50	$C_{21}H_{18}N_2S_2$	69.58	5.00	7.73	17.69
Ve	92	76–77 (CH_3CN)	59.70	4.01	6.62	14.20	$C_{22}H_{17}ClN_2O_2S_2$	59.92	3.89	6.35	14.54
Vf	84	86–87 (CH_3CN)	58.64	3.88	6.61	14.71	$C_{21}H_{16}Cl_2N_2S_2$	58.47	3.74	6.49	14.86
Vg	90	97–98 (CH_3CN)	63.30	4.40	7.20	16.01	$C_{21}H_{17}ClN_2S_2$	63.54	4.32	7.06	16.15
Vh	95	187–188 (CH_3CN)	58.71	3.20	9.31	14.22	$C_{22}H_{18}ClN_3OS$	60.06	4.12	9.55	14.57
Vi	62	42–43 (C_6H_{14})	65.20	5.08	9.01	20.42	$C_{17}H_{16}N_2S_2$	65.35	5.16	8.97	20.52
Vj	93	175–176 (CH_3CN)	63.28	5.01	9.70	14.62	$C_{23}H_{21}N_3O_2S_2$	63.43	4.86	9.65	14.72
Vk	94	220–221 (CH_3CN)	62.24	4.40	9.71	15.03	$C_{22}H_{18}FN_3OS_2$	62.39	4.28	9.92	15.14
Vl	98	205–206 (CH_3CN)	58.56	4.34	9.10	13.52	$C_{23}H_{20}ClN_3O_2S_2$	58.78	4.29	8.94	13.64
Vm	81	198–199 (AcOH)	63.00	4.30	6.78	14.92	$C_{22}H_{17}ClN_2OS_2$	62.18	4.03	6.59	15.09
Vn	86	287–288 (AcOH)	60.30	4.01	6.22	13.80	$C_{22}H_{16}ClN_2OS_2$	57.52	3.51	6.10	13.96

Table 2. IR and ^{1}H NMR spectra of compounds **Va**–**n, VIn**

Compd. no.	IR spectrum, ν, cm^{-1}	^{1}H NMR spectrum, δ, ppm
Va	2220	1.22 s (6H, $2CH_3$), 1.86 s (4H, $2CH_2$), 2.11 q (1H, CH), 2.85 s (8H, $2CH_2$), 3.22 d (2H, CH_2), 7.22 d (1H, H thiophene), 7.68 t (2H, H thiophene)
Vb	2220	1.87 s (4H, $2CH_2$), 2.92 s (4H, $2CH_2$), 4.68 ©(2H, SCH_2), 7.09 d (1H, H thiophene), 7.16 d (1m, H thiophene), 7.39 d (1H, H thiophene), 7.56–7.69 d.d (3H, H arom)
Vc	2225	1.83 s (4H, $2CH_2$), 2.91 m (4H, $2CH_2$), 4.45 s (2H, SCH_2), 7.19 t (1H, H thiophene), 7.22 d (2H, H thiophene), 7.42 d (1H, H arom), 7.42 d (2H, H arom)
Vd	2221	1.85 m (4H, $2CH_2$); 2.93 s (4H, $2CH_2$); 4.58 s (2H, SCH_2), 7.17–7.58 m (8H, thiophene and arom)
Ve	2222	1.83 s (4H, $2CH_2$), 2.96 m (4H, $2CH_2$), 4.64 s (2H, SCH_2), 5.94 s (2H, O–CH_2–O), 6.92 s (1H, H arom), 7.03 s (1H, H arom), 7.19 t (1H, H thiophene), 7.62 d.d (2H, H thiophene)
Vf	2220	1.86 s (4H, $2CH_2$), 2.92 s (4H, $2CH_2$), 4.65 s (2H, SCH_2), 7.09 d (1H H thiophene), 7.16 d (1m, H thiophene), 7.39 d (1H, H thiophene), 7.51–7.58 d.d (3H, H arom)
Vg	2225	1.85 s (4H, $2CH_2$), 2.92 s (4H, $2CH_2$), 4.71 s (2H, SCH_2), 7.15 m (3H, H thiophene), 7.36–7.57 m (4m, H arom)
Vh	1670, 2224, 3440	1.88 s (4H, $2CH_2$), 2.92 s (4H, $2CH_2$), 3.99 s (2H, SCH_2), 7.01 d (2H, H arom), 7.16 t (1m, H thiophene), 7.26 t (2H, arom), 7.51 d (2H, H arom), 9.33 br.s. (1m, NH)
Vi	2222	1.89 s (4H, $2CH_2$), 2.95 s (4H, $2CH_2$), 3.92 d (2H, SCH_2), 5.09 d (1H, *cis*-CH_2=C), 5.33 d (1H *trans*-CH_2=C), 5.87 m 1H, CH=C), 7.25 t (1H, H thiophene), 7.85 d (1H, H thiophene), 8.15 d.d (1H, H thiophene)
Vj	1685, 3430, 2220	1.85 s (4H, $2CH_2$), 2.93 s (4H, $2CH_2$), 3.61 s (3H, OCH_3), 4.22 s (2H, SCH_2), 6.95 t (2H, H arom), 7.17 t (1H, H thiophene), 7.67 d (1H, H thiophene), 7.73 d (1H, H thiophene), 8.01 d (1H, H arom), 9.37 br.s (1m, NH)
Vk	1680, 3420, 2221	1.88 s (4H, $2CH_2$), 2.97 s (4H, $2CH_2$), 4.01 s (2H, SCH_2), 6.86 m (2H, H arom), 7.07 q (2H, arom), 7.26 q (1H, H thiophene), 7.56 d (1H, H thiophene), 7.63 d (1H, H thiophene), 9.14 br.s (1H, NH)
Vl	1660, 3435, 2220	1.83 s (4H, $2CH_2$), 2.91 s (4H, $2CH_2$), 3.69 s (3H, OCH_3) 4.20 s (2H, SCH_2), 6.95 d (2H, H arom), 7.14 t (1H, H thiophene), 7.67 q (2H, H thiophene), 8.10 d (1H, H arom), 9.37 br.s (1m, NH)
Vm	1640, 2227	1.81 s (4H, $2CH_2$), 2.91 s (4H, $2CH_2$), 4.91 s (2H, SCH_2), 7.17 t (1H, H thiophene), 7.55 d.d (4H, H thiophene, H arom), 8.04 d (2m, H arom)
Vn	1645, 2235	1.83 H (4H, $2CH_2$), 2.93 d (2H, $2CH_2$), 4.65 s (2H, SCH_2), 7.11 t (1H, H thiophene), 7.33–7.65 m (5H, H arom)
VIo	1650, 3320	1.90 H (4H, $2CH_2$), 2.98 d (2H, CH_2), 3.35 d (2H, CH_2), 7.19 t (1H, H thiophene), 7.40 br.s (2H, NH_2), 7.92 s (1H, H arom), 8.07 s (2H, H arom)

Table 3. Coordinates of atoms and equivalent isotropic thermal parameters U_{eq} (Å^2) in structure **Va**

Atom	*x*	*e*	*z*	U_{eq}
S^1	0.56048(17)	0.14100(9)	0.99535(9)	0.0865
S^2	0.89993(12)	0.61716(8)	1.24823(8)	0.0648
N^1	0.6945(30)	0.3786(2)	1.0273(2)	0.0490
N^2	0.3619(6)	–0.0362(3)	0.6420(3)	0.0944
C^1	0.7186(4)	0.4644(3)	0.9820(3)	0.0433
C^2	0.6441(4)	0.4276(3)	0.8459(3)	0.0458
C^3	0.5518(4)	0.2954(3)	0.7551(3)	0.0476
C^4	0.5316(4)	0.2087(3)	0.8035(3)	0.0512
C^5	0.6020(4)	0.2543(3)	0.9404(3)	0.0528
C^6	0.6597(5)	0.5264(3)	0.7986(3)	0.0599
C^7	0.5298(6)	0.4737(4)	0.6537(4)	0.0823
C^8	0.5452(6)	0.3410(4)	0.5665(4)	0.0802
C^9	0.4762(5)	0.2440(3)	0.6073(3)	0.0613
C^{10}	0.4372(5)	0.0717(3)	0.7134(3)	0.0650
C^{11}	0.8304(4)	0.5966(3)	1.0907(3)	0.0481
C^{12}	0.8996(4)	0.7183(3)	1.0933(3)	0.0609
C^{13}	1.0039(5)	0.8160(3)	1.2272(4)	0.0781
C^{14}	1.0130(50	0.7775(3)	1.3176(4)	0.0695
C^{15}	0.6917(5)	0.2314(3)	1.1713(3)	0.0624
C^{16}	0.9025(6)	0.2513(4)	1.2155(4)	0.0863
C^{17}	0.9845(9)	0.3302(8)	1.3672(6)	0.1468
C^{18}	0.966(1)	0.1314(7)	1.1699(8)	0.1622

torsional angles $C^2C^3C4^9C^8$, $C^3C^9C^8C^7$, $C^9C^8C^7C^6$, $C^8C^7C^6C^2$, $C^7C^6C^2C^3$ and $C^6C^2C^3C^9$ are equal to 11.9, –45.0, 62.5, –46.1, 12.9, 4.1°, modified Cramer-Pople parameters [14] S, φ and θ are 0.77, 29.0, and 38.7° respectively. The bond lengths and angles in the compound Va molecule are of common values [15, 16].

EXPERIMENTAL

IR spectra were measured on spectrophotometer UR-20 from KBr pellets, ^{1}H NMR spectra were registered on spectrometer Varian-VXR-300 (300 MHz) from solutions in DMSO with TMS as internal reference. Melting points were determined on Koeffler heating block. The reaction progress was monitored and the homogeneity of the compounds synthesized was checked by TLC on Silufol UV-254 plates, eluent acetone–hexane, 5:5, development under UV irradiation or with iodine vapor.

1-(2-Thienyl)-4-cyano-5,6,7,8-tetrahydro-3(2*H*)-isoquinolinethione (II). To a mixture of 30 mmol of 2-(2-thenoyl)-1-cyclohexanone (**I**) and 50 ml of methanol was added at stirring 30 mmol of cyanothioacetamide (**II**) and 25 ml of triethylamine. The stirring at 60°C was continued for 4–5 h, then the reaction mixture was maintained for 2 h at room temperature, and acidified with 10% solution of HCl. The precipitate was filtered off, washed with methanol, and recrystallized from AcOH to obtain 6.94 g (85%) of compound **III**, mp 257–258°C. IR spectrum, cm^{-1}: 2225 (CN), 3288 (NH). ^{1}H NMR spectrum, δ, ppm: 1.77– 1.85 m (4H, CH_2–CH_2), 2.77 d (2H, CH_2), 2.97 d (2H, CH_2), 7.24 t (1H, C^4 thiophene), 7.46 d (1H, C^5 thiophene), 7.65 d (1H, C^3 thiophene), 10.67 br.s (1H, NH). Found, % : C 61.22; H 4.47; N 10.31; S 23.19. $C_{14}H_{12}N_2S_2$. Calculated, %: C 61.73; H 4.44; N 10.70; S 23.54.

3-R-Methylsulfanyl-1-(2-thienyl)-4-cyano-5,6,7,8-tetrahydroisoquinolines (Va–n). General procedure. To a solution of 5 mmol of isoquinolinethione **III** in 15 ml of DMF was added at stirring in succession 2.8 ml of 10% KOH solution and 10 mmol of halide **IVa–n**. The mixture was stirred at room temperature for 1 h after the finish of reagents addition, and then it was diluted with 20 ml of water. The separated precipitate was filtered off, washed with aqueous methanol (2:1), and recrystallized from an appropriate solvent. The data on compounds **Va–n** are listed in Tables 1 and 2.

3-Amino-2-(2,4-dichlorobenzoyl)-5-(2-thienyl)-6,7,8,9-tetrahydrothieno[2,3-c]isoquinoline (VIn). To a solution of 10 mmol of compound Vn in 5 ml of DMF was added at stirring 3 ml of 10% water solution of KOH. The cyclization completed in 2 h (TLC monitoring). Then the mixture was diluted with 20 ml water. The precipitate was separated and recrystallized from AcOH to furnish 0.43 g (90%) of compound **VIn**, mp 261–262°C. IR spectrum, cm^{-1}: 1650 (C=O), 3288, 3440 (NH). ^{1}H NMR spectrum, δ, ppm: 1.90 m (4H, CH_2–CH_2), 2.98 d (2H, CH_2), 3.35 d (2H, CH_2), 7.14 t (1H, C^4 thiophene), 7.67 d (1H, C^5 thiophene), 7.62 d (1H, C^3 thiophene), 7.49 br.s (2H, NH_2) 7.43–7.98 m (3H, H arom). Found, %: C 57.40; H 3.02; Cl 15.30; N 15.33; S 13.19. $C_{22}H_{16}Cl_2N_2OS_2$. Calculated, %: C 57.52; H 3.51; Cl 15.43; N 6.10; S 13.96.

X-ray diffraction analysis of a single crystal of compound **Va**, crystal habit $0.34 \times 0.50 \times 0.56$ was carried out at room temperature on an automatic four-circle diffractometer Enraf-Nonius CAD-4 (CuK_α-radiation, ratio of scanning rates ω/2θ 1.2, θ_{max} 70°, spherical segment $0 \le h \le 9$, $-14 \le k \le 14$, $-14 \le l \le 14$). In total 3218 reflections was collected. The absorption in the crystal was accounted for by the method of azimuth scanning [17]. The crystals of

compound **Va** triclinic, *a* 7.448(1), *b* 11.757(3), *c* 11.953(1) Å, α 116.18(2), β 105.52(1), γ 96.25(2)°, *V* 873.3(4) Å^3, *M* 328.49, *Z* 2, d_{calc} 1.25 g cm^{-3}, μ 26.8 cm^{-1}, F(000) 350, space group P 1 (N^2). The structure was solved by the direct method and refined by the least-squares procedure in the full-matrix anisotropic approximation with the use of software package CRYSTALS [18]. In refining 2695 reflections were use with $I > 3(I)$ (199 parameters refined, number of reflections per parameter 13.5). All hydrogen atoms were revealed from the difference synthesis of electron density and included in calculations with fixed position and thermal parameters. We used in refining the weight scheme of Chebyshev [19] with four parameters: 0.65, –0.11, 0.20, and –0.34. The final values of divergence factors are *R* 0.066 and R_W 0.063, GOF 1.040. The residual electron density from the difference Fourier series amounts to 0.57 and –0.52 Å^3. Coordinates of nonhydrogen atoms are given in Table 1. The complete set of data on the X-ray analysis of compound **Va** was deposited into the Cambridge Structural Databank (no. 171738).

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