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Fused Polycyclic Nitrogen-Containing Heterocycles: IX. Synthesis and Molecular Structure of Methyl 3-(2-R-5-phenylthiazol-4-yl)-7-phenyl-7*H*-[1,2,4]triazolo-[3,4-*b*][1,3,4]thiadiazine-6-carboxylates

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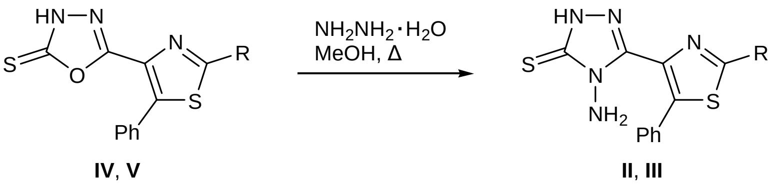
Abstract—4-Amino-3-(2-R-5-phenylthiazol-4-yl)-1,2,4-triazole-5-thiones react with methyl 3-chloro-2-oxo-3-phenylpropionate to give methyl 3-(2-R-5-phenylthiazol-4-yl)-7-phenyl-7*H*-[1,2,4]triazolo[3,4-*b*][1,3,4]thiadiazine-6-carboxylates. According to the X-ray diffraction data, the thiazole ring in the products is planar, while the thiadiazine ring has a distorted *unsymmetrical boat* conformation. Depending on the substituent in the thiazole ring, methyl 3-(2-R-5-phenylthiazol-4-yl)-7-phenyl-7*H*-[1,2,4]triazolo[3,4-*b*][1,3,4]thiadiazine-6-carboxylates in crystal give rise to different supramolecular structures, lamellar and cylindrical.

The most commonly used methods for the synthesis of 1,3,4-thiadiazines are based on transformations of compounds whose structural fragments can be converted into the S–C^2–N^3–N^4 and C^5–C^6 moieties of the target thiadiazine ring. Reactions of thiosemicarbazides with α-halo ketones have found wide application. Depending on the substituents in the α-halocarbonyl fragment and in the thiosemicarbazide, as well as on the reaction conditions, the products are thiadiazines [1–3], thiazoles [4, 5], dihydrothiazoles [6, 7], pyrazoles [3, 8], or other heterocyclic systems [7–9]. In some cases, the regioselectivity of the first reaction step can be controlled by variation of the above factors and pH of the medium. As a result, the process involves either alkylation of the sulfur atom with formation of isocarbothiohydrazides [10] or imination of the carbonyl group to afford α-halothiocarbazones according to the Schiff reaction pattern [11]. In order to eliminate various concurrent processes, 1,3,4-thiadiazines were also obtained from heterocyclic systems containing a carbothiohydrazide residue in which nitrogen atoms capable of being involved in side reactions are blocked in the ring [12–19]. In these reactions, the simplest α-halocarbonyl compounds, such as chloro- and bromoacetophenone [12, 13] and chloroacetone [19], were mainly studied.

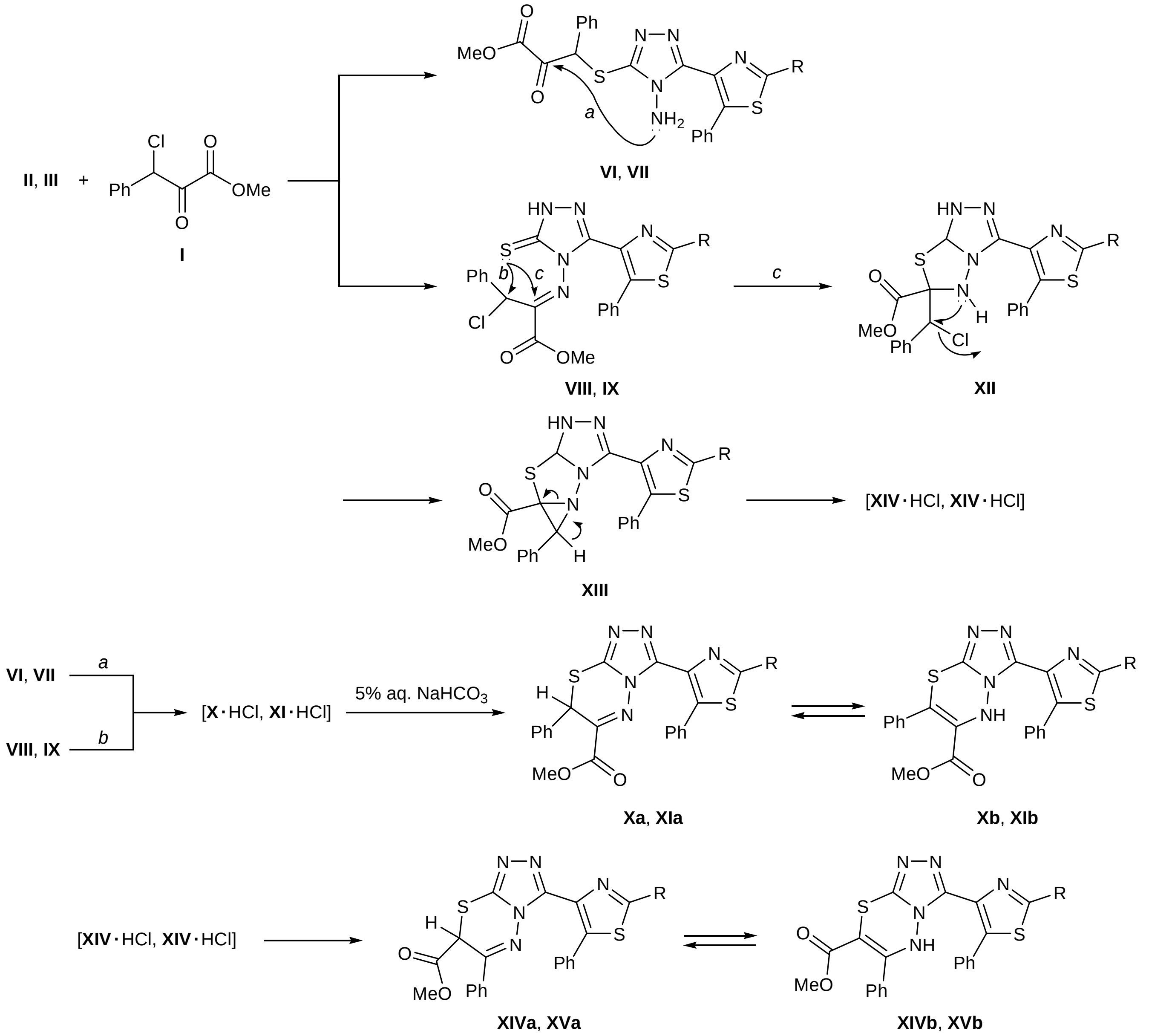
In the present work we used more complex functionally substituted compounds as α-halo ketone and carbothiohydrazide components, namely methyl 3-chloro-2-oxo-3-phenylpropionate (**I**) [20] and 4-amino-3-(2-R-5-phenylthiazol-4-yl)-1,2,4-triazole-5-thiones **II** and **III**. The latter were readily prepared

Scheme 1.



II, **IV**, R = Me; **III**, **V**, R = Ph.

Scheme 2.



VI, **VIII**, **X**, R = Me; **VII**, **IX**, **XI**, R =Ph.

with high yields (Table 1) by reaction of accessible 2-[2-methyl(or phenyl)-5-phenylthiazol-4-yl]-1,3,4-oxadiazol-5-ones **IV** and **V** with hydrazine hydrate [21] (Scheme 1).

The initial stage in the reaction of thiones **II** and **III** with α-chloro ketone **I** may lead to formation of both isothioureide derivative **VI** or **VII** and compound **VIII** or **IX**, respectively, as a result of S-alkylation and Schiff condensation [10, 11]. Intramolecular cyclization of intermediates **VI**, **VII** and **VIII**, **IX** according to pathways *a* and *b*, respectively, should give only methyl 7-phenyltriazolo[3,4-*b*][1,3,4]thiadiazine-6-carboxylates **Xa**, **Xb**, **XIa**, and **XIb**. We also cannot rule out an alternative cyclization of **VIII** and **IX** following pathway *c*, which should lead to triazolothiadiazines **XIVa**, **XIVb**, **XVa**, and **XVb** through intermediate condensation products **XII** and **XIII** (Scheme 2). Compounds **XIV** and **XV** are isomeric to **X** and **XI** with respect to the position of the ester and phenyl groups. Moreover, compounds **X**, **XI**, **XIV**, and **XV** can exist as amine and imine tautomers. The products were assigned the imine structure (**a**) on the basis of the

Table 1. Yields, melting points, and elemental analyses of compounds **II**, **III**, **Xa**, and **XIa**

Comp. no.	Yield, %	mp, °C (solvent)	Found, %				Formula	Calculated, %			
			C	H	N	S		C	H	N	S
II	81	214–216 (MeOH)	52.27	3.09	15.41	23.21	$C_{12}H_{11}N_5S_2$	52.35	3.27	15.26	23.30
III	87	236–238 (MeOH)	60.31	3.04	12.43	19.15	$C_{17}H_{13}N_5S_2$	60.54	3.26	12.45	19.02
Xa	91	165–167 (*i*-PrOH)	59.21	3.73	15.72	14.55	$C_{22}H_{17}N_5O_2S_2$	59.06	3.80	15.64	14.34
XIa	93	199–200 (*i*-PrOH)	63.47	3.71	13.91	12.47	$C_{27}H_{19}N_5O_2S_2$	63.65	3.73	13.74	12.59

Table 2. IR and ^{1}H NMR spectra of compounds **II**, **III**, **Xa**, and **XIa**

Comp. no.	IR spectrum, ν, cm^{-1}	^{1}H NMR spectrum, δ, ppm (solvent)
II	3340, 3300–3100, 2800–2600, 1630, 1470 br, 1380, 1350, 1190, 1010, 775	2.86 s (3H, CH_3), 5.7 s (2H, NH_2), 7.46 s (5H, C_6H_5) (DMSO-d_6)
III	3275, 3200–3000, 2800–2600, 1620, 1490, 1460, 1440, 1380, 1280, 1230, 1220, 1085, 1020, 1000, 960, 775, 700	5.6 s (2H, NH_2), 7.13–8.10 m (10H, $2C_6H_5$), 13.66 br.s (1H, NH) (DMSO-d_6)
Xa[a]	1740, 1450 br, 1380, 1330, 1260, 1190, 1110, 780	2.81 s (3H, CH_3), 3.83 s (3H, CH_3), 5.53 s (1H, CH), 7.01–7.32 m (10H, $2C_6H_5$) ($CDCl_3$)
XIa	1730, 1460 br,1380, 1335, 1250, 1215, 1110, 980, 770	3.64 s (3H, CH_3), 5.51 s (1H, CH), 7.07–8.10 m (15H, $3C_6H_5$) (acetone-d_6)

[a] ^{13}C–{^{1}H} NMR spectrum ($CDCl_3$––CCl_4, 1:1), $δ_C$, ppm: 19.96, 38.79, 53.99, 127.79, 129.06, 129.17, 129.70, 129.91, 130.09, 131.01, 134.87, 135.59, 140.41, 142.16, 146.29, 149.54, 162.74, 165.13.

^{1}H NMR spectra which contained singlets at δ 5.53 and 5.51 ppm. In keeping with published data [9] for structurally related systems, these signals correspond to the CH protons of the imine tautomer (Table 2). However, the ^{1}H NMR and IR spectra did not allow us to distinguish between isomeric structures **Xa** and **XIVa** and **XIa** and **XVa**. Unambiguous proofs for structures **Xa** and **XIa** were obtained by X-ray analysis.

Search for structurally related compounds in the Cambridge Structural Database [22] revealed the only publication [23] where five crystal structures were described. These structures included ionized [1,2,4]-triazolo[3,4-*b*][1,3,4]thiadiazine system crystallized with different solvate molecules: dioxane, methanol, ethanol, 2-propanol, and 2-methyl-2-propanol. The conformation of the bicyclic fragment changed from *sofa* to distorted *unsymmetrical boat*. The S^1 and N^5 atoms (according to the atom numbering accepted in the present work) are located in the thiadiazine ring plane whereas the C^7 and C^8 atoms deviate from that plane (in the two latter structures having an *unsymmetrical boat* conformation). The presence of a double bond in the thiadiazine ring of the compounds obtained in the present work gives rise to a different conformation of the bicyclic fragment.

Table 3. Parameters of intramolecular contacts in the crystal structure of methyl 3-(2,5-diphenylthiazol-4-yl)-7-phenyl-7*H*-[1,2,4]triazolo[3,4-*b*][1,3,4]thiadiazine-6-carboxylate (**XIa**)

Contact	d(H···A), Å	d(D···A), Å	∠(D–H···A), deg
C^8–H^8···O^{20}	2.39	2.85(1)	107.6(5)
C^{19}–H^{19}···N^6	2.62	3.26(1)	122.5(8)
C^{33}–H^{33}···S^9	2.69	3.13(1)	106.9(6)

Compounds **Xa** and **XIa** (Figs. 1, 2) differ by the substituent in the thiazole ring. Their crystal structures are characterized by the same space group, but they are not isostructural. The thiazole ring in both molecules is planar within 0.01 (**Xa**) and 0.005 Å (**XIa**). The endocyclic bond lengths are similar within experimental error. The N^5–N^6–C^7–C^8 fragments in the thiadiazine rings of **Xa** and **XIa** are planar within 0.01 Å, and the S^1 and C^{1a} atoms deviate from that plane, respectively, by 0.877(6) and 0.381(4) Å for **Xa** and 1.254(3) and 0.669(9) Å for **XIa**. This pattern corresponds to a distorted *unsymmetrical boat* conformation. The dihedral angles between the N^5–N^6–C^7–C^8 plane and the triazole ring plane are 28.5(7) and 15.8(6)° for compounds **Xa** and **XIa**, respectively. The phenyl substit-

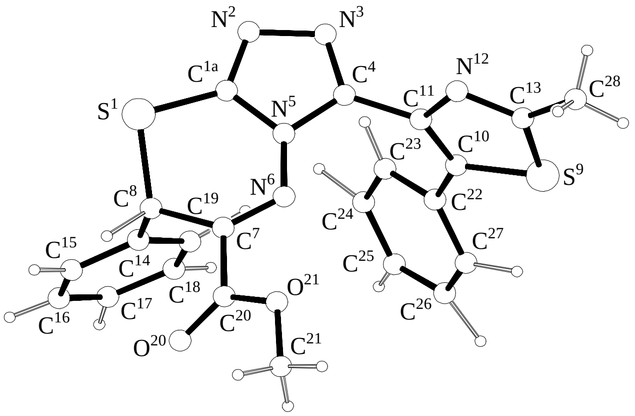


Fig. 1. Structure of the molecule of methyl 3-(2-methyl-5-phenylthiazol-4-yl)-7-phenyl-7*H*-[1,2,4]triazolo[3,4-*b*]-[1,3,4]thiadiazine-6-carboxylate (**Xa**) according to the X-ray diffraction data.

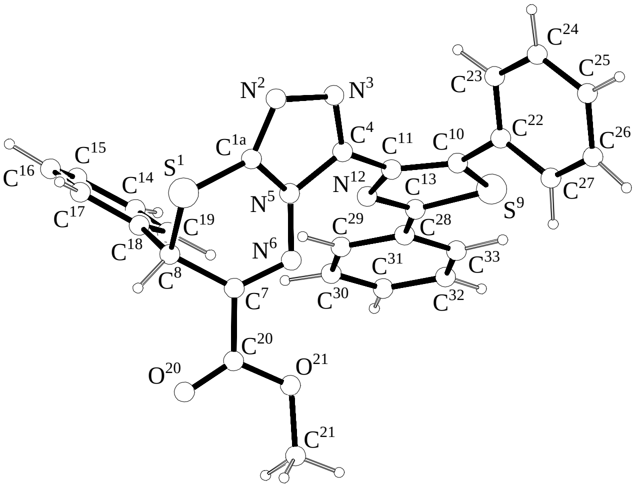


Fig. 2. Structure of the molecule of methyl 3-(2,5-diphenylthiazol-4-yl)-7-phenyl-7*H*-[1,2,4]triazolo[3,4-*b*][1,3,4]thiadiazine-6-carboxylate (**XIa**) according to the X-ray diffraction data.

uent (C^{14}–C^{19}) in the thiadiazine ring of both compounds occupies axial position. The triazole ring is planar, and its plane with the thiazole ring plane forms a dihedral angle of 74.4(3)° in **Xa** and 48.5(5)° in **XIa**. The phenyl ring on C^{10} (C^{22}–C^{27}) is turned through an angle of 57.9(5)° (**Xa**) or 28.2(3)° (**XIa**) with respect to the thiazole ring plane. The phenyl group on C^{13} in molecule **XIa** is almost coplanar to the thiazole ring: the dihedral angle between the corresponding planes is as small as 2.5(5)°.

Thus replacement of one phenyl substituent in the thiazole ring by methyl group leads to flattening of the [1,2,4]triazolo[3,4-*b*][1,3,4]thiadiazine system, its conformation remaining essentially unchanged. The substituent in the thiazole ring exerts a more appreciable effect on intra- and intermolecular interactions in crystal and the mode of crystal packing. It should be noted that the crystal structures of both compounds lack classical hydrogen bonds and that the observed contacts can be referred to as interactions like C–H···O(N, S). Molecules **XIa** in crystal give rise to intramolecular contacts involving protons of the thiadiazine ring and phenyl groups (H^8, H^{19}, H^{33}) and oxygen atom of the carbonyl group (O^{20}), nitrogen atom of the thiadiazine ring (N^6), and sulfur atom of the thiazole ring (S^9), respectively. The parameters of these contacts are given in Table 3. Only one intramolecular contact was detected in the crystal structure of compound **Xa**. It involves the H^{27} atom of the phenyl group in the thiazole ring and S^9: $d(H^{27}\cdots S^9)$ 2.48, $d(C^{27}\cdots S^9)$ 3.159(6) Å, $\angle(C^{27}\text{–}H^{27}\cdots S^9)$ 114.9°. The other interactions do not meet formal criteria for hydrogen bond formation accepted by PLATON [25]: $d(D\cdots A) < R(D) + R(A) + 0.50$, $d(H\cdots A) < R(H) + R(A) - 0.12$ Å, $\angle(D\text{–}H\cdots A) > 100.0°$.

Table 4 contains the parameters of intermolecular interactions revealed in the crystal structure of compounds **Xa** and **XIb**, which were determined using PLATON software. Each molecule **XIa** is involved in four intermolecular contacts (Fig. 3a); in two of these it acts as donor (H^{26}, H^{30}), and in the two other, as acceptor (N^2, O^{20}). As a result, infinite chains are formed via intermolecular hydrogen bonds. The mode of crystal packing can be regarded as a system of pseudolayers (Fig. 3b). It should be noted the thiazole and phenyl (C^{28}–C^{33}) rings of one molecule give rise to two π–π interactions with the corresponding thiazole and phenyl rings of the other molecule, the latter being related to the former through symmetry transformation. Both interactions are characterized by similar parameters: the distance between the centers of the rings is 3.76 Å, the dihedral angle is 2.5°, the shortest distance between the ring planes is 3.38 Å, and the angle between the vector connecting their centers and the normal to one of the rings is 23.4°.

Hydrogen bonds between the ester O^{21} atom and the H^{27} proton in the phenyl ring of the neighboring molecules of compound **Xa** give rise to dimers (Fig. 4a) which are packed in stacks (Fig. 4b). Both the position of the dimers in a stack and mutual arrangement of stacks in a unit cell are stabilized by intermolecular contacts. Although the above intermolecular interactions are considerably weaker than classical hydrogen bonds, the number of such interactions and their mutual influence are likely to determine supramolecular packing of molecules in crystal.

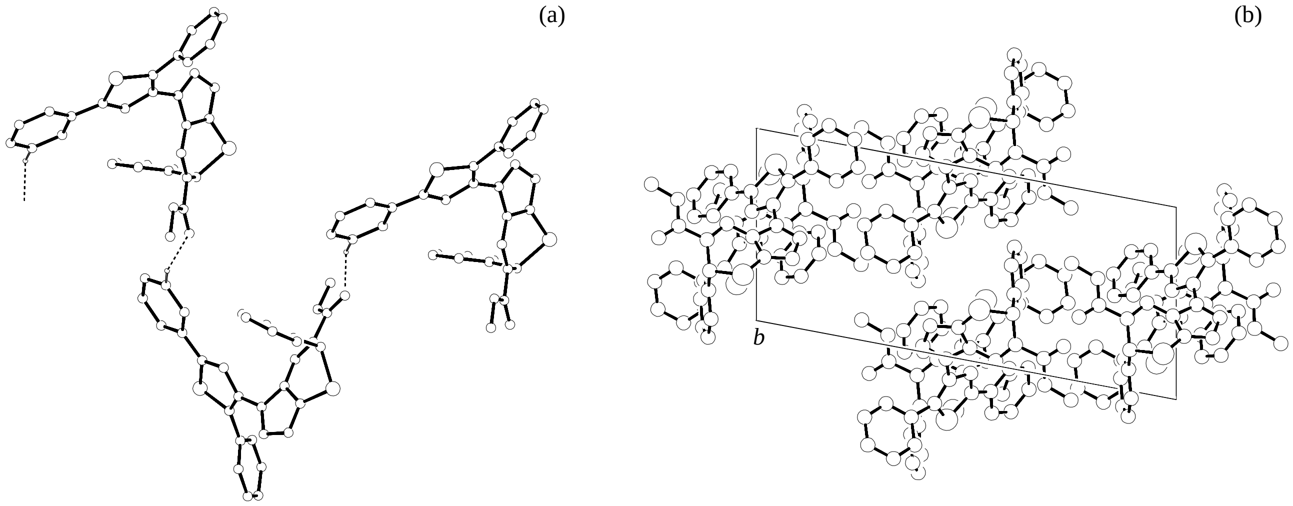


Fig. 3. Packing of molecules of methyl 3-(2,5-diphenylthiazol-4-yl)-7-phenyl-7*H*-[1,2,4]triazolo[3,4-*b*][1,3,4]thiadiazine-6-carboxylate (**XIa**) in crystal: (a) hydrogen bond system (shown by dashed lines) and (b) formation of pseudolayers (view along the 0*y* axis; hydrogen atoms are not shown).

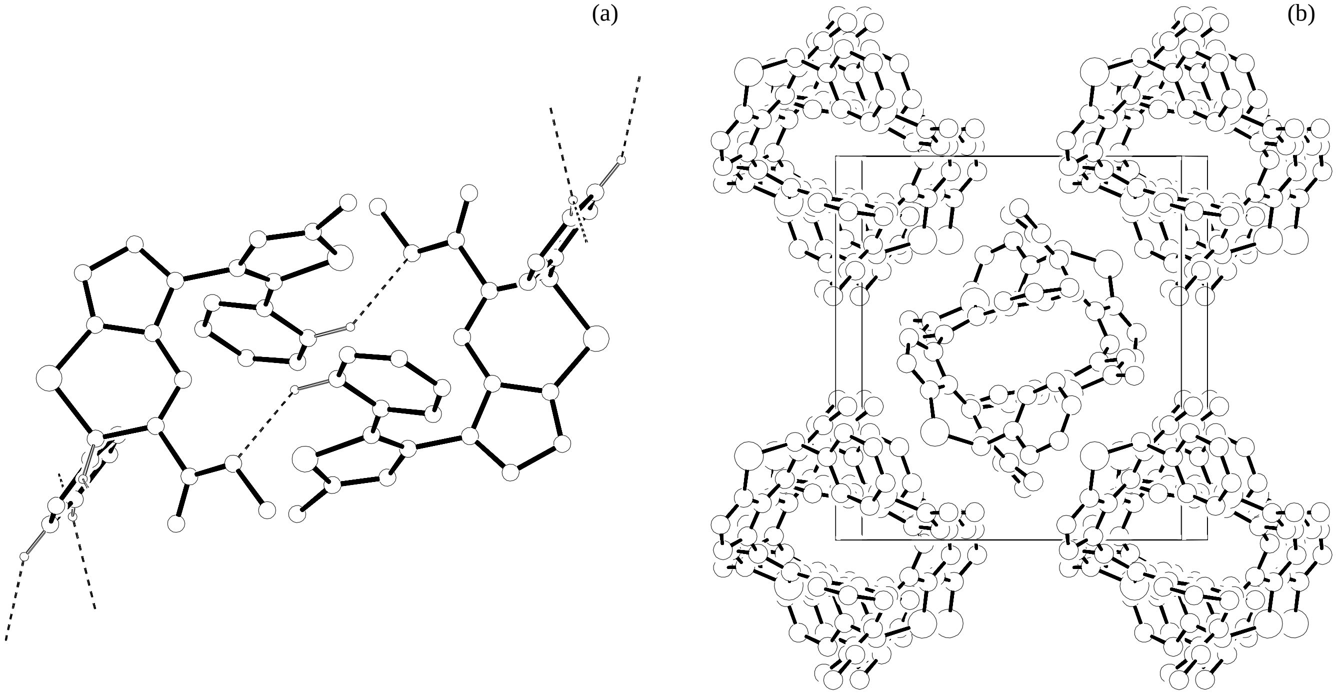


Fig. 4. Packing of molecules of methyl 3-(2-methyl-5-phenylthiazol-4-yl)-7-phenyl-7*H*-[1,2,4]triazolo[3,4-*b*][1,3,4]thiadiazine-6-carboxylate (**Xa**) in crystal: (a) formation of dimers through intermolecular hydrogen bonding (shown by dashed lines) and (b) formation of rods from the dimers (hydrogen atoms are not shown).

EXPERIMENTAL

The melting points were determined using a Boetius microscope. The IR spectra were recorded on a UR-20 spectrometer from samples dispersed in mineral oil. The ^{1}H NMR spectra were measured on a Bruker-250 instrument operating at 250.13 MHz, and the ^{13}C NMR spectrum of compound **XIa** was obtained on a Bruker MSL-400 spectrometer at 100.6 MHz. The X-ray diffraction data for single crystals of **Xa** and **XIa** were acquired at 20°C on an Enraf–Nonius CAD-4 automatic four-circle diffractometer ($\lambda \mathrm{Mo}K_{\alpha}$

Table 4. Parameters of intermolecular contacts in the crystal structure of methyl 3-(2-methyl-5-phenylthiazol-4-yl)-7-phenyl-7*H*-[1,2,4]triazolo[3,4-*b*][1,3,4]thiadiazine-6-carboxylate (**Xa**) and methyl 3-(2,5-diphenylthiazol-4-yl)-7-phenyl-7*H*-[1,2,4]triazolo[3,4-*b*][1,3,4]thiadiazine-6-carboxylate (**XIa**)

Comp. no.	Contact[a]	$d(H\cdots A)$, Å	$d(D\cdots A)$, Å	$\angle D–H\cdots A$, deg
Xa	$C^8–H^8\cdots N^3$ (*a*)	2.52	3.414(7)	129
Xa	$C^{16}–H^{16}\cdots N^6$ (*b*)	2.62	3.466(8)	144
Xa	$C^{17}–H^{17}\cdots N^2$ (*c*)	2.53	3.443(9)	133
Xa	$C^{17}–H^{17}\cdots O^{21}$ (*b*)	2.52	3.321(8)	123
Xa	$C^{27}–H^{27}\cdots O^{21}$ (*d*)	2.52	3.213(7)	116
XIa	$C^{26}–H^{26}\cdots N^{2*}$	2.44	3.34(1)	150
XIa	$C^{30}–H^{30}\cdots O^{20**}$	2.43	3.39(1)	159

[a] The atoms are related to the initial molecule via the following symmetry elements: (*) = 1 + *x*, *y*, *z*; (**) = –1/2 – *x*, 1/2 + *y*, 1/2 – *z*; (*a*) = 3/2 – *x*, 1/2 + *y*, 1/2 – *z*; (*b*) = –1/2 + *x*, 3/2 – *y*, –1/2 + *z*; (*c*) = 1 – *x*, 1 – *y*, –*z*; (*d*) = 1 – *x*, 1 – *y*, 1 – *z*.

irradiation, graphite monochromator, ω/2θ scanning to θ ≤ 23.3 deg). No drop in the intensity of three control reflections was observed during the data acquisition. The absorption was not taken into account, for the absorption coefficient of the crystals was small.

Compound **Xa**: monoclinic crystals with the following unit cell parameters: a = 12.205(5), b = 13.625(3), c = 13.112(7) Å; β = 94.05(5)°; V = 2175(1) Å^3; Z = 4; d_{calc} = 1.37 g/cm^3; space group $P2_1/n$. Total of 4617 reflection intensities were measured, 1323 of which were with $I \le 3\sigma$. The final divergence factors were R = 0.0517 and R_w = 0.0552 (from 1386 reflections).

Compound **XIa**: monoclinic crystals with the following unit cell parameters: a = 9.022(1), b = 13.996(1), c = 32.951(5) Å; β = 100.73(2)°; V = 3275.4(8) Å^3; Z = 4; d_{calc} = 1.37 g/cm^3; space group $P2_1/n$. Total of 4028 reflection intensities were measured, 1139 of which were with $I \le 3\sigma$. The final divergence factors were R = 0.0557 and R_w = 0.0769 (from 1367 independent reflections).

The structures were solved by the direct method using SIR program [22] and were refined first in isotropic and then in anisotropic approximation. All hydrogen atoms were visualized from the difference electron density series, and they were taken into account with fixed positional and temperature parameters in the final refinement steps. All calculations were performed on an Alpha Station 200 computer using MolEN software package [23]. The coordinates of non-hydrogen atoms and some bond lengths and

Table 5. Coordinates of non-hydrogen atoms and their equivalent isotropic temperature parameters B^a in the structure of methyl 3-(2-methyl-5-phenylthiazol-4-yl)-7-phenyl-7*H*-[1,2,4]triazolo[3,4-*b*][1,3,4]thiadiazine-6-carboxylate (**Xa**)

Atom	*x*	*y*	*z*	*B*	Atom	*x*	*y*	*z*	*B*
S^1	0.2787(1)	0.2815(1)	0.8868(1)	5.94(4)	C^{14}	0.5053(5)	0.2837(4)	0.8970(4)	4.9(2)
S^9	0.3600(2)	0.6193(1)	0.4450(1)	6.03(5)	C^{15}	0.5589(5)	0.2215(5)	0.9671(5)	6.8(2)
O^{20}	0.5493(4)	0.1524(3)	0.7047(3)	7.0(1)	C^{16}	0.6477(6)	0.2583(6)	1.0260(5)	9.5(2)
O^{21}	0.4484(3)	0.2012(3)	0.5662(3)	5.1(1)	C^{17}	0.6837(6)	0.3511(6)	1.0200(5)	8.4(2)
N^2	0.1929(4)	0.4604(3)	0.8396(3)	5.1(1)	C^{18}	0.6324(6)	0.4110(6)	0.9491(6)	8.9(2)
N^3	0.1937(4)	0.5260(3)	0.7572(3)	5.3(1)	C^{19}	0.5451(6)	0.3776(5)	0.8873(5)	7.4(2)
N^5	0.3044(3)	0.4043(3)	0.7291(3)	3.4(1)	C^{20}	0.4766(5)	0.2012(4)	0.6641(4)	4.6(2)
N^6	0.3662(3)	0.3412(3)	0.6747(3)	3.5(1)	C^{21}	0.5073(7)	0.1352(5)	0.5022(7)	8.9(2)
N^{12}	0.1991(4)	0.5273(3)	0.5157(3)	5.5(1)	C^{22}	0.4733(5)	0.6081(4)	0.6375(4)	4.2(1)
C^{1a}	0.2585(4)	0.3902(4)	0.8206(4)	4.1(1)	C^{23}	0.4661(5)	0.6219(4)	0.7418(4)	4.9(2)
C^4	0.2594(4)	0.4905(4)	0.6924(4)	3.7(1)	C^{24}	0.5592(5)	0.6441(5)	0.8041(5)	6.2(2)
C^7	0.4093(4)	0.2692(4)	0.7243(4)	3.6(1)	C^{25}	0.6580(5)	0.6570(5)	0.7623(5)	6.7(2)
C^8	0.4079(5)	0.2444(4)	0.8353(4)	4.6(2)	C^{26}	0.6636(5)	0.6459(4)	0.6598(5)	6.4(2)
C^{10}	0.3761(5)	0.5831(4)	0.5722(4)	4.2(1)	C^{27}	0.5741(5)	0.6214(4)	0.5953(4)	5.1(2)
C^{11}	0.2827(5)	0.5357(4)	0.5926(4)	4.2(1)	C^{28}	0.1618(7)	0.5722(5)	0.3355(5)	9.3(2)
C^{13}	0.2328(6)	0.5702(5)	0.4334(4)	5.7(2)					

[a] $B = 4/3 \sum_{i=1}^{3}\sum_{j=1}^{3}(a_i a_j)B(i,j)$, Å^2.

Table 6. Coordinates of non-hydrogen atoms and their equivalent isotropic temperature parameters B^a in the structure of methyl 3-(2,5-diphenylthiazol-4-yl)-7-phenyl-7*H*-[1,2,4]triazolo[3,4-*b*][1,3,4]thiadiazine-6-carboxylate (**XIa**)

Atom	*x*	*y*	*z*	*B*	Atom	*x*	*y*	*z*	*B*
S^1	0.7255(3)	–0.0050(2)	0.4685(1)	5.12(8)	C^{16}	0.366(1)	0.217(1)	0.3854(6)	8.1(4)
S^9	1.3295(3)	0.3779(2)	0.5464(1)	4.77(8)	C^{17}	0.412(1)	0.305(1)	0.3722(7)	8.5(4)
O^{20}	0.8342(9)	0.0380(6)	0.2685(3)	7.6(3)	C^{18}	0.558(1)	0.318(1)	0.3675(8)	10.7(5)
O^{21}	1.0525(7)	0.1047(5)	0.3130(3)	5.4(2)	C^{19}	0.659(1)	0.2405(9)	0.3758(7)	9.2(4)
N^2	0.8575(9)	0.0866(5)	0.5861(4)	4.5(2)	C^{20}	0.916(1)	0.0752(7)	0.3154(5)	4.5(3)
N^3	0.9696(9)	0.1562(6)	0.6036(4)	4.2(2)	C^{21}	1.106(1)	0.091(1)	0.2507(5)	7.7(4)
N^5	0.9322(8)	0.1368(5)	0.4917(4)	3.5(2)	C^{22}	1.351(1)	0.2184(7)	0.6311(4)	3.8(3)
N^6	0.9743(8)	0.1283(5)	0.4300(3)	3.5(2)	C^{23}	1.305(1)	0.2003(7)	0.6912(5)	4.6(3)
N^{12}	1.0648(8)	0.3274(5)	0.4897(4)	3.7(2)	C^{24}	1.397(1)	0.1508(8)	0.7422(5)	6.0(3)
C^{1a}	0.838(1)	0.0766(7)	0.5185(4)	3.9(3)	C^{25}	1.538(1)	0.1214(8)	0.7344(5)	5.4(3)
C^4	1.014(1)	0.1853(7)	0.5483(5)	3.9(3)	C^{26}	1.584(1)	0.1355(7)	0.6733(5)	4.8(3)
C^7	0.872(1)	0.0907(7)	0.3829(4)	3.6(3)	C^{27}	1.493(1)	0.1854(8)	0.6230(5)	4.3(3)
C^8	0.713(1)	0.0657(7)	0.3894(4)	3.7(3)	C^{28}	1.140(1)	0.4756(7)	0.4418(4)	3.4(3)
C^{10}	1.258(1)	0.2749(7)	0.5755(4)	3.8(3)	C^{29}	1.003(1)	0.4863(7)	0.3978(5)	4.7(3)
C^{11}	1.117(1)	0.2606(7)	0.5403(4)	3.4(3)	C^{30}	0.981(1)	0.5624(8)	0.3527(5)	5.1(3)
C^{13}	1.165(1)	0.3954(7)	0.4873(5)	4.1(3)	C^{31}	1.091(1)	0.6280(7)	0.3506(5)	5.2(3)
C^{14}	0.611(1)	0.1499(7)	0.3864(5)	4.5(3)	C^{32}	1.226(1)	0.6184(8)	0.3935(6)	6.6(3)
C^{15}	0.463(1)	0.1383(8)	0.3922(6)	6.1(3)	C^{33}	1.251(1)	0.5420(8)	0.4389(5)	5.7(3)

[a] $B = 4/3 \sum_{i=1}^{3}\sum_{j=1}^{3}(a_i a_j)B(i, j)$, Å^2.

Table 7. Bond angles (φ, deg) in the molecules of triazolothiadiazines **Xa** and **XIa**

Angle	**Xa**	**XIa**	Angle	**Xa**	**XIa**
$C^{1a}S^1C^8$	98.5(3)	94.3(4)	$N^6C^7C^{20}$	115.5(5)	116.0(9)
$C^{10}S^9C^{13}$	90.8(3)	91.1(5)	$C^8C^7C^{20}$	114.6(4)	117.5(7)
$C^{20}O^{21}C^{21}$	117.4(5)	117.4(8)	$S^1C^8C^7$	111.4(4)	107.0(6)
$N^3N^2C^{1a}$	106.7(4)	106.3(8)	$S^1C^8C^{14}$	112.0(4)	113.2(7)
$N^2N^3C^4$	107.7(4)	109.0(7)	$C^7C^8C^{14}$	112.6(5)	113.9(8)
$N^6N^5C^{1a}$	129.6(4)	126.6(7)	$S^9C^{10}C^{11}$	106.6(4)	109.0(7)
$N^6N^5C^4$	125.1(4)	125.3(7)	$S^9C^{10}C^{22}$	122.1(4)	120.0(7)
$C^{1a}N^5C^4$	104.4(4)	104.7(7)	$C^{11}C^{10}C^{22}$	131.3(5)	131.1(9)
$N^5N^6C^7$	116.1(4)	114.1(8)	$N^{12}C^{11}C^4$	115.3(5)	115.8(8)
$C^{11}N^{12}C^{13}$	107.6(5)	111.6(7)	$N^{12}C^{11}C^{10}$	118.9(5)	116.0(9)
$S^1C^{1a}N^2$	127.7(4)	127.7(8)	$C^4C^{11}C^{10}$	125.8(5)	128.3(8)
$S^1C^{1a}N^5$	120.5(4)	121.5(7)	$S^9C^{13}N^{12}$	116.1(4)	112.3(7)
$N^2C^{1a}N^5$	111.3(5)	110.6(8)	$S^9C^{13}C^{28}$	122.9(5)	123.9(7)
$N^3C^4N^5$	109.9(4)	109.4(8)	$N^{12}C^{13}C^{28}$	121.0(6)	123.8(8)
$N^3C^4C^{11}$	125.7(5)	129.1(8)	$O^{20}C^{20}O^{21}$	124.8(5)	123.7(9)
$N^5C^4C^{11}$	124.4(5)	121.3(8)	$O^{20}C^{20}C^7$	121.5(5)	123(1)
$N^6C^7C^8$	129.9(5)	126.4(8)	$O^{21}C^{20}C^7$	113.7(5)	113.5(8)

Table 8. Some bond lengths (*d*, Å) in the molecules of triazolothiadiazines **Xa** and **XIa**

Bond	**Xa**	**XIa**	Bond	**Xa**	**XIa**
S^{1}–C^{1a}	1.725(6)	1.716(9)	N^{5}–C^{4}	1.370(6)	1.40(1)
S^{1}–C^{8}	1.830(6)	1.85(1)	N^{6}–C^{7}	1.270(6)	1.30(1)
S^{9}–C^{10}	1.738(5)	1.73(1)	N^{12}–C^{11}	1.388(7)	1.39(1)
S^{9}–C^{13}	1.688(7)	1.731(9)	N^{12}–C^{13}	1.318(7)	1.32(1)
O^{20}–C^{20}	1.203(7)	1.20(1)	C^{4}–C^{11}	1.492(7)	1.43(1)
O^{21}–C^{20}	1.305(7)	1.31(1)	C^{7}–C^{8}	1.495(8)	1.50(1)
O^{21}–C^{21}	1.455(9)	1.43(1)	C^{7}–C^{20}	1.500(8)	1.49(1)
N^{2}–N^{3}	1.403(6)	1.40(1)	C^{8}–C^{14}	1.490(8)	1.49(1)
N^{2}–C^{1a}	1.283(7)	1.33(1)	C^{10}–C^{11}	1.353(8)	1.35(1)
N^{3}–C^{4}	1.302(7)	1.31(1)	C^{10}–C^{22}	1.453(8)	1.49(1)
N^{5}–N^{6}	1.375(6)	1.36(1)	C^{13}–C^{28}	1.497(9)	1.43(1)
N^{5}–C^{1a}	1.373(7)	1.38(1)			

Table 9. Some dihedral angles (ω, deg) in the molecules of triazolothiadiazines **Xa** and **XIa**

Angle	**Xa**	**XIa**	Angle	**Xa**	**XIa**
$C^{8}S^{1}C^{1a}N^{2}$	–164.2(5)	158.9(9)	$C^{11}N^{12}C^{13}S^{9}$	0.1(6)	1.1(9)
$C^{8}S^{1}C^{1a}N^{5}$	24.7(4)	–27.2(8)	$C^{11}N^{12}C^{13}C^{28}$	178.8(5)	–177.5(8)
$C^{1a}S^{1}C^{8}C^{7}$	–37.8(4)	51.4(7)	$N^{3}C^{4}C^{11}N^{12}$	–74.2(6)	–128(1)
$C^{1a}S^{1}C^{8}C^{14}$	89.3(4)	–74.9(7)	$N^{3}C^{4}C^{11}C^{10}$	105.4(6)	52(1)
$C^{13}S^{9}C^{10}C^{11}$	0.8(4)	–0.6(7)	$N^{5}C^{4}C^{11}N^{12}$	105.5(5)	45(1)
$C^{13}S^{9}C^{10}C^{22}$	–176.3(4)	179.2(7)	$N^{5}C^{4}C^{11}C^{10}$	–74.8(7)	–135(1)
$C^{10}S^{9}C^{13}N^{12}$	–0.5(5)	–0.2(7)	$N^{6}C^{7}C^{8}S^{1}$	33.6(7)	–50(1)
$C^{10}S^{9}C^{13}C^{28}$	–179.3(6)	178.3(8)	$N^{6}C^{7}C^{8}C^{14}$	–93.2(6)	76(1)
$C^{21}O^{21}C^{20}O^{20}$	1.8(8)	–0(1)	$C^{20}C^{7}C^{8}S^{1}$	–149.8(3)	132.7(7)
$C^{21}O^{21}C^{20}C^{7}$	–178.3(5)	178.4(8)	$C^{20}C^{7}C^{8}C^{14}$	83.3(5)	–101.3(9)
$C^{1a}N^{2}N^{3}C^{4}$	0.7(5)	0(1)	$N^{6}C^{7}C^{20}O^{20}$	154.5(5)	177.1(9)
$N^{3}N^{2}C^{1a}S^{1}$	–171.7(4)	174.4(7)	$N^{6}C^{7}C^{20}O^{21}$	–25.3(6)	–2(1)
$N^{3}N^{2}C^{1a}N^{5}$	–0.0(7)	0(1)	$C^{8}C^{7}C^{20}O^{20}$	–22.5(7)	–5(1)
$N^{2}N^{3}C^{4}N^{5}$	–1.1(5)	1(1)	$C^{8}C^{7}C^{20}O^{21}$	157.5(4)	175.8(8)
$N^{2}N^{3}C^{4}C^{11}$	178.6(4)	175(1)	$S^{1}C^{8}C^{14}C^{15}$	99.1(5)	–57(1)
$C^{1a}N^{5}N^{6}C^{7}$	–18.5(7)	32(1)	$S^{1}C^{8}C^{14}C^{19}$	–81.5(6)	125(1)
$C^{4}N^{5}N^{6}C^{7}$	173.9(4)	–171.6(8)	$C^{7}C^{8}C^{14}C^{15}$	–134.3(5)	–179.5(8)
$N^{6}N^{5}C^{1a}S^{1}$	2.2(7)	–15(1)	$C^{7}C^{8}C^{14}C^{19}$	44.9(7)	3(1)
$N^{6}N^{5}C^{1a}N^{2}$	–170.2(5)	160.1(7)	$S^{9}C^{10}C^{11}N^{12}$	–1.0(6)	2(1)
$C^{4}N^{5}C^{1a}S^{1}$	171.7(3)	–174.5(7)	$S^{9}C^{10}C^{11}C^{4}$	179.3(4)	–178.4(8)
$C^{4}N^{5}C^{1a}N^{2}$	–0.6(5)	0(1)	$C^{22}C^{10}C^{11}N^{12}$	175.8(5)	–178.4(8)
$N^{6}N^{5}C^{4}N^{3}$	171.2(4)	–160.7(8)	$C^{22}C^{10}C^{11}C^{4}$	–3.7(9)	2(1)
$N^{6}N^{5}C^{4}C^{11}$	–8.5(7)	25(1)	$S^{9}C^{10}C^{22}C^{23}$	149.1(4)	121.1(9)
$C^{1a}N^{5}C^{4}N^{3}$	1.1(5)	0(1)	$S^{9}C^{10}C^{22}C^{27}$	–28.9(7)	–57(1)
$C^{1a}N^{5}C^{4}C^{11}$	–178.6(4)	–175.0(8)	$C^{11}C^{10}C^{22}C^{27}$	154.5(5)	124(1)
$N^{5}N^{6}C^{7}C^{8}$	–3.2(7)	6(1)	$C^{8}C^{14}C^{15}C^{16}$	–178.6(5)	–176.3(9)
$N^{5}N^{6}C^{7}C^{20}$	–179.8(4)	–176.8(7)	$C^{10}C^{22}C^{27}C^{26}$	179.4(5)	178.2(9)
$C^{13}N^{12}C^{11}C^{4}$	–179.6(4)	178.1(8)	$S^{9}C^{13}C^{28}C^{33}$	–	5(1)
$C^{13}N^{12}C^{11}C^{10}$	0.6(6)	–2(1)	$N^{12}C^{13}C^{28}C^{33}$	–	–176.7(9)

bond and dihedral angles in the structure of compounds **Xa** and **XIa** are listed in Tables 5–9.

4-Amino-3-(2-methyl-5-phenylthiazol-4-yl)-1*H*-1,2,4-triazole-5-thione (II). To a solution of 3.3 g (12 mmol) of thiazolyloxadiazole **IV** [21] in 10 ml of methanol we added 5 g (60 mmol) of 60% hydrazine hydrate. The mixture was stirred for several minutes, heated for 6 h under reflux, cooled, diluted with water, and acidified with 20% hydrochloric acid. The crystals were filtered off, washed with water, dried, and recrystallized from methanol.

4-Amino-3-(2,5-diphenylthiazol-4-yl)-1*H*-1,2,4-triazole-5-thione (III) was synthesized in a similar way using oxadiazole **V** [21] as initial compound.

Methyl 3-(2-methyl-5-phenylthiazol-4-yl)-7-phenyl-7*H*-[1,2,4]triazolo[3,4-*b*][1,3,4]thiadiazine-6-carboxylate (Xa). A mixture of equimolar amounts of ester **I** and thione **II** in anhydrous methanol was heated for ~5 h under reflux. The mixture was cooled to room temperature, the solvent was removed under reduced pressure, the semicrystalline residue was treated with 5% aqueous $NaHCO_3$, and the precipitate was filtered off, washed with water, dried, and recrystallized from 2-propanol.

Methyl 3-(2,5-diphenylthiazol-4-yl)-7-phenyl-7*H*-[1,2,4]triazolo[3,4-*b*][1,3,4]thiadiazine-6-carboxylate (XIa) was synthesized in a similar way using thione **III** as initial compound.

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