Fused polycyclic nitrogen-containing heterocycles

20.* Thiazolo[3,4-*a*]quinoxalines from 4-hydroxy-2-phenyliminothiazolidines and *C*-substituted 1,2-phenylenediamines**

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The condensation of 4-hydroxy-3,5-diphenyl-2-phenyliminothiazolidine with 4,5-dimethyl-1,2-phenylenediamine affords 7,8-dimethyl-3-phenyl-1-phenyliminothiazolo[3,4-*a*]quinoxalin-4(5*H*)-one; the condensation with 1,2-phenylenediamines containing different substituents at positions 4 and 5 gives both theoretically possible isomeric thiazolo[3,4-*a*]quinoxalines, which differ in the distribution of these substituents between positions 7 and 8 in the benzene ring of the quinoxaline system. 3a-Hydroxy-7,8-dimethyl-3-phenyl-1-phenylimino-3,3a-dihydrothiazolo[3,4-*a*]quinoxalin-4(5*H*)-one was isolated and characterized as the intermediate of the reaction giving rise to thiazolo[3,4-*a*]quinoxaline from 4,5-dimethyl-1,2-phenylenediamine. This intermediate is a covalent hydrate of the final product.

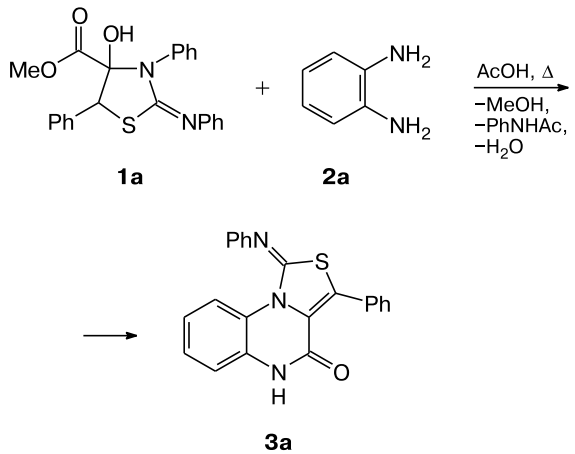
Key words: Hantzsch reaction, 4-hydroxythiazolidines, thiazolo[3,4-*a*]quinoxalines, IR spectroscopy, NMR spectroscopy, X-ray diffraction study.

Quinoxaline derivatives exhibit a broad spectrum of biological activities, including antibacterial, antitumor, and antiviral activities (in particular, anti-HIV activity).[2—4] The quinoxaline system and its azolo- and azino-fused derivatives are components of various biologically important compounds and medicines. The synthesis of these compounds is often carried out with the use of functionalized quinoxalines and their fused derivatives as key compounds. For example, quinoxalines and their derivatives were used as template agents in the synthesis of GABA/diazepine receptor agonists and antagonists,[5] cAMP- and cGMP phosphodiesterase inhibitors,[6] A_1 and A_{2a} adenosine agonists,[7] and many other pharmacologically active substances.[8—11] The discovery of nalidixic acid,[12] which is an efficient antibacterial synthetic medication[13] and is a derivative of the quinoxaline isomer, *viz.*, pyrido[2,3-*b*]pyridine, gave a strong impetus to the development of methods of synthesis and chemistry of quinoxalines.

The main approaches to the synthesis of fused pyrazines and quinoxalines have been described previously.[14,15] Among cyclization reactions giving rise to fused azaheterocyclic compounds, the reactions of compounds containing two nucleophilic groups with bifunctional electrophilic reagents are of special interest. The condensation of dicarbonyl compounds with 1,2-diaminoazines[16] can be referred to as examples of these reactions.

Earlier,[17—20] we have shown that the reaction of the stable intermediate of the Hantzsch reaction, *viz.*, 4-hydroxy-4-methoxycarbonyl-3,5-diphenyl-2-phenyliminothiazolidine (**1a**), with 1,2-phenylenediamine (**2a**) in boiling acetic acid readily leads to the condensation accompanied by elimination of methanol, acetanilide,

Scheme 1



1a **2a** **3a**

* For Part 19, see Ref. 1.

** Dedicated to Academician A. I. Konovalov on his 75th birthday.

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 1, pp. 190—200, January, 2009.

1066-5285/09/5801-0191

and water to form 3-phenyl-1-phenylimino-4,5-dihydrothiazolo[3,4-*a*]quinoxalin-4-one (**3a**) (Scheme 1).

With the aim of extending the scope of the method for the synthesis of thiazolo[3,4-*a*]quinoxalines, we investigated the pathways of the reactions of 4-hydroxy-2-phenyl- (**1a**) and 2-thiazol-2-yliminothiazolidine (**1b**) with several 1,2-phenylenediamines containing the mono- or disubstituted benzene ring.

In particular, the condensation of hydroxythiazolidine **1b** should afford 1-thiazolyliminothiazolo[3,4-*a*]quinoxalines containing an additional weakly basic thiazole nitrogen atom compared to the condensation products of hydroxythiazolidine **1a**. This holds promise for the design of biologically active thiazolo[3,4-*a*]quinoxalines.

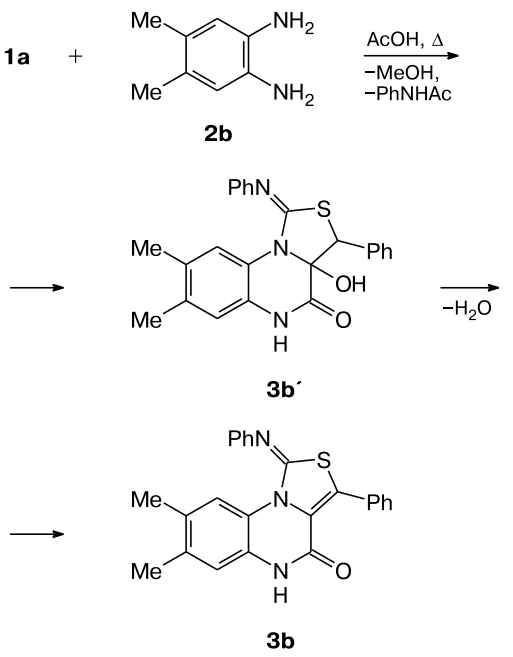
Unlike hydroxythiazolidine **1a** containing two phenyl substituents at the nitrogen atoms (hereinafter, this compound is referred to as structurally "symmetrical"), which has been characterized previously,[17—20] hydroxythiazolidine **1b** containing the phenyl and thiazol-2-yl substituents at the nitrogen atoms is "unsymmetrical." Hence, the condensation of **1b** with 1,2-phenylenediamines can afford a larger number of regioisomers of the final tricyclic compound. Analogously, unlike "symmetrical" diamines (unsubstituted 1,2-phenylenediamine (**2a**)[17—20] and 4,5-difluoro-1,2-phenylenediamine[19] used earlier and 4,5-dimethyl-1,2-phenylenediamine (**2b**) under study), which can give only one final product **3**, monosubstituted structurally "unsymmetrical" 4-methyl-1,2-phenylenediamine (**2c**) and 4-nitro-1,2-phenylenediamine (**2d**) can give two isomeric final products, which differ in the position of the substituent in the benzene fragment of the quinoxaline system.[19,20] In the present study, we investigated the isomeric composition of thiazolo[3,4-*a*]quinoxalines produced by the reactions of hydroxythiazolidines **1** with 1,2-phenylenediamines **2b—d** substituted at the benzene ring and considered the mechanisms of their formation.

Results and Discussion

Reactions of "symmetrical" 4-hydroxythiazolidine 1a with substituted 1,2-phenylenediamines. The reaction of 4-hydroxythiazolidine **1a** with 1,2-diamino-4,5-dimethylbenzene (**2b**) under standard conditions (in boiling acetic acid), like the reactions with 1,2-diaminobenzene (**2a**) and 1,2-diamino-4,5-difluorobenzene,[19] affords the expected tricyclic compound **3b** as the only final product (Scheme 2).

The structure of compound **3b** was confirmed by ^{1}H NMR spectroscopy. The NMR spectrum of thiazolo[3,4-*a*]quinoxaline **3b** shows three singlets for the protons H(6), H(9), and NH and the characteristic proton signals of two phenyl substituents occupying different positions. The signals for the protons H(6) and H(9) are shifted upfield by 0.2 ppm compared to the corresponding signals

Scheme 2



of benzene-unsubstituted thiazolo[3,4-*a*]quinoxaline **3a**.[20] The introduction of methyl groups at positions 7 and 8 of the thiazolo[3,4-*a*]quinoxaline system not only enhances the stability of intermediate covalent hydrate **3b´** but also causes an increase in the melting point of thiazolo[3,4-*a*]quinoxaline **3b**. The melting points of compound **3b** and its benzene-unsubstituted analog **3a** are 352—355 °C and 301—301.5 °C, respectively.

The structure of thiazolo[3,4-*a*]quinoxaline **3b** was confirmed also by X-ray diffraction (Fig. 1). Compound

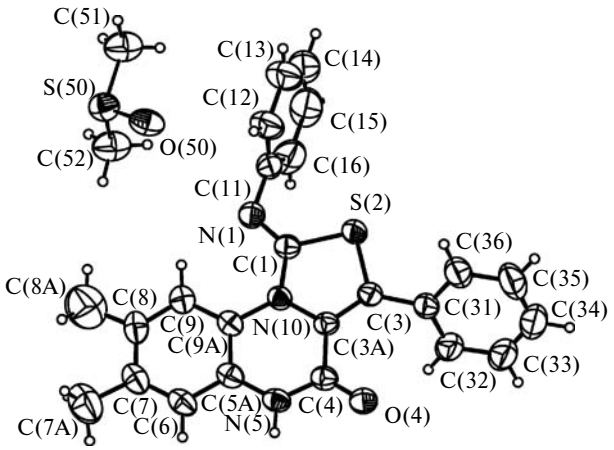


Fig. 1. Molecular structure of compound **3b** in the crystal. Nonhydrogen atoms are represented by displacement ellipsoids at the 50% probability level; the H atoms are represented by spheres with an arbitrary radius. The DMSO molecule is shown in the site with a higher occupancy.

3b crystallizes with the involvement of DMSO molecules in a ratio of 1 : 1. In the crystal structure, the solvent molecule being disordered over two positions with an occupancy ratio of 0.87 : 0.13.

The thiazolo[3,4-*a*]quinoxaline moiety in the molecule is planar within 0.045(2) Å. The dihedral angle between the plane of the thiazole ring and the planes of the phenyl substituents C(11)—C(16) and C(31)—C(36) are 82.4 and 52.9°, respectively.

The presence of the solvent molecules hinders the formation of hydrogen-bonded dimers with the involvement of the carbamoyl group, which is typical of intermolecular interactions in crystals of pyrrolo- and azoloquinoxalines.[21—24]

In the crystal structure of compound **3b**, the DMSO molecule forms a hydrogen bond with the NH group of the tricyclic fragment (H(5)...O(50), 2.01 Å; N(5)...O(50), 2.87(1) Å; N(5)—H(5)...O(50), 173°). Based on the formal criteria[25] for the presence of π—π interactions (the distances between the centers of aromatic rings (or aromatic systems) shorter than 6.0 Å and the angle between the normal to the plane of one of the rings and the vector between the centers of the rings smaller than 60°) and taking into account the published data,[26] we found that thiazoloquinoxaline molecules **3b** in the crystal structure form centrosymmetric dimers through π—π interactions between the aromatic systems of the tricyclic fragments of the molecules (the distances between the arbitrary centers of the tricyclic systems of the molecules is 4.10 Å, the dihedral angle between their mean planes is 0°, and the shortest distance between these planes is 3.49 Å). It should be noted that these π dimers are arranged in the crystal structure in a herringbone fashion so that pairs of DMSO solvent molecules are located in the cavities formed by eight thiazoloquinoxaline molecules **3b** (Fig. 2). The disorder of the DMSO molecules indicates that these molecules are not closely packed. This is also evidenced by the low packing coefficient (68.0%).

Unlike the reaction with unsubstituted 1,2-phenylenediamine (**2a**), which is completed within 3—5 min to give the final thiazolo[3,4-*a*]quinoxaline **3a** in quantitative yield (see Scheme 1), refluxing of the reaction mixture for 1 h is required for the reaction under consideration to proceed. Otherwise, the reaction affords a mixture of the final thiazolo[3,4-*a*]quinoxaline **3b** and its covalent hydrate **3b´** (see Scheme 2 and Table 1). This is evidenced by 1) the molecular ion peaks at *m/z* 397 and 415 assigned to compounds **3b** and **3b´** in the mass spectra of the crude products obtained after refluxing the reaction mixture for 0.1, 5, and 20 min; 2) the presence of a double set of all signals and the singlets for the protons at the C(3) atom and the hydroxy group at δ 5.45 and 7.20, respectively, in the ^{1}H NMR spectra; 3) the presence, along with other bands, an OH absorption band (3440 cm^{-1}) in the IR spectrum. In spite of the fact that two methyl groups in the compounds under consideration are nonequivalent, the proton signals of these groups appear in the ^{1}H NMR spectra as one singlet, whose integral intensity corresponds to six protons (δ 2.21 and 2.18 for compounds **3b** and **3b´**, respectively).

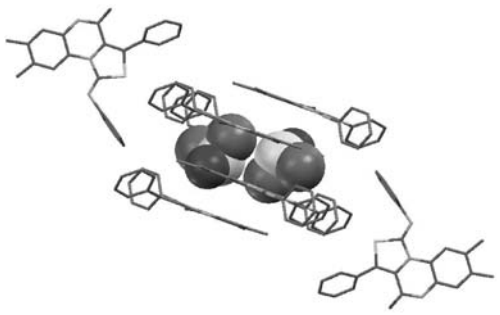


Fig. 2. Encapsulation of two DMSO molecules by eight molecules **3b** in the crystal structure. The DMSO molecules are represented in van-der-Waals radii in the sites with a higher occupancy. The H atoms are omitted.

Table 1. Ratios* of the final compound thiazolo[3,4-*a*]quinoxaline **3b** to the intermediate (covalent hydrate) **3b´** in the reaction mixture depending on the time of the reaction **1a** + **2b** (*t*)

t/min	**3b**/**3b´**	Yield of **3b** + **3b´** (%)
0.1	62/38	76
5	69/31	78
20	75/25	79
60	100/0	84

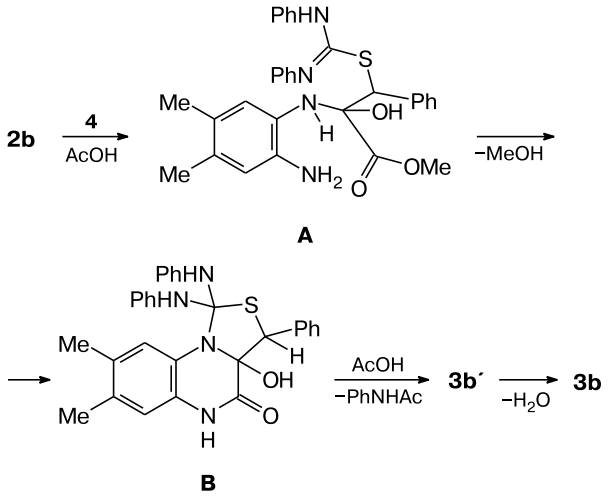
* The values were calculated from the integral intensities of the signals for the protons H(9) and the methyl groups in the ^{1}H NMR spectra of the crude reaction products.

The reaction performed at 80±5 °C for 50 min gives rise to pure crystals of compound **3b´**, as evidenced by elemental analysis data and spectroscopic characteristics.

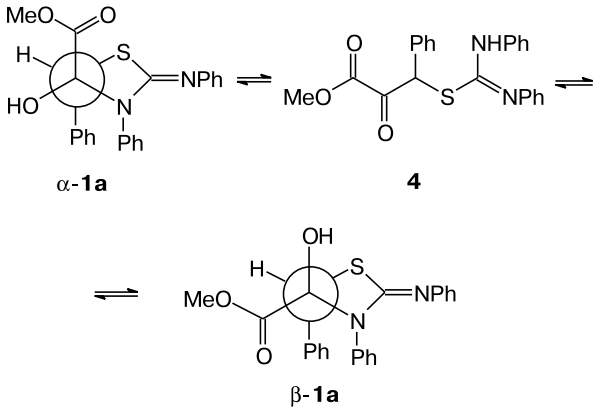
Since compound **3b´** contains two asymmetric centers, it would be expected that this compound will be obtained as a diastereomeric mixture. However, the signals for the protons at the C(3), C(6), and C(9) atoms and for the protons of the methyl groups in the ^{1}H NMR spectra of compound **3b´** are identical to the signals for the corresponding protons in samples produced in different syntheses. Hence, the highly stereoselective formation of covalent hydrate **3b´** is highly probable.

Under reflux in AcOH, *i.e.*, under the conditions of the synthesis of thiazolo[3,4-*a*]quinoxaline **3b**, compound **3b´** is quantitatively dehydrated to give **3b** (see Scheme 2). This confirms the fact that covalent hydrate **3b´** is the intermediate in the synthesis of thiazoloquinoxaline **3b**. The most probable route to the final product **3b** from the starting compounds through intermediate **3b´** is presented in Scheme 3. It is most probable that open-chain isomer **4** (see Refs 17—20 and 24) rather than cyclic isomers α-**1a** or β-**1a** are involved in the formation of intermediate **3b´** (Scheme 4).

Scheme 3



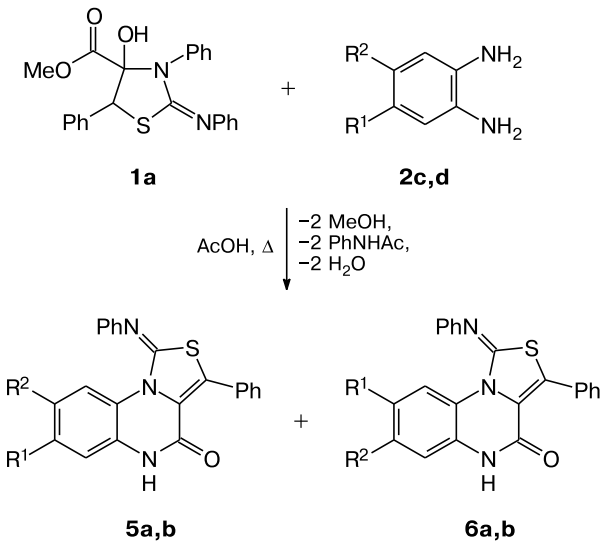
Scheme 4



Previously,[19,20] when studying the reactions of 4-hydroxythiazolidine **1a** with "unsymmetrical" 4-methyl-1,2-phenylenediamine (**2c**) and 4-nitro-1,2-phenylenediamine (**2d**), we have detected only one reaction product, *viz.*, 7-methyl derivative **5a** and 8-nitro derivative **6b**, respectively. However, the more thorough study of the reaction mixtures by ^{1}H NMR spectroscopy showed that both reactions afford two compounds (Scheme 5), which can be separated by column chromatography.

In particular, this is evidenced by the presence of a double set of all signals in the ^{1}H NMR spectrum of the crude product obtained in the reaction of 4-hydroxythiazolidine **1a** with diamine **2c**. The integral intensity of the diagnostic signal for the proton H(9), which is split into a doublet by the vicinal proton H(9) (δ 9.29, ^3J = 8.9 Hz) of the major isomer, *viz.*, 7-methylthiazolo[3,4-*a*]quinoxaline **5a**, is 1.5 times higher than the integral intensity of the singlet for the same proton (δ 9.28) in its 8-methyl isomer **6a** (the integral intensity ratio is the same). An analogous ^{1}H NMR spectral pattern is observed for the

Scheme 5



R^1 = Me, R^2 = H (**2c**, **5a**, **6a**); R^1 = NO_2, R^2 = H (**2d**, **5b**, **6b**)

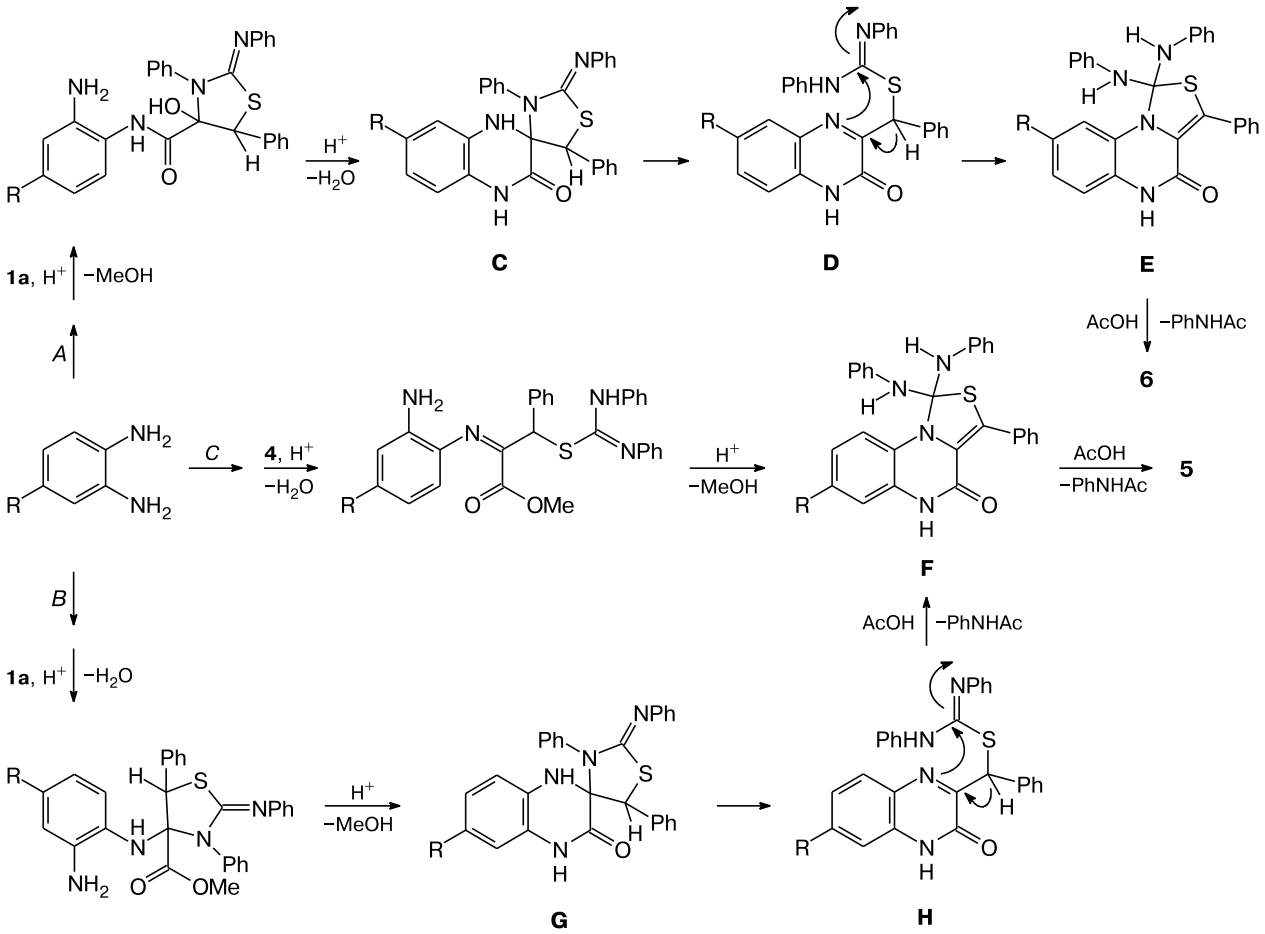
crude product obtained in the reaction of hydroxythiazolidine **1a** with 4-nitro-1,2-phenylenediamine (**2d**). However, the diagnostic signal for the proton H(9) (δ 10.42) of the major product **6b**, whose integral intensity is 9 times higher than the intensity of the signal of the minor product **5b**, appears as a singlet, whereas the diagnostic signal for the proton H(9) (δ 9.62) of the minor product **5b** appears as a doublet with the vicinal constant ^3J = 8.9 Hz. Individual compound **6b** was isolated by recrystallization of the mixture of the isomers. Earlier, we have established the structure of compound **6b** by X-ray diffraction.[19]

In the mechanism of formation of the thiazolo[3,4-*a*]-quinoxaline system, which we have suggested previously,[19,20] the linear (**4**) and cyclic tautomers of the starting 4-hydroxy-3,5-diphenyl-2-phenyliminothiazolidine **1a** are involved in the first step of the reaction (see Scheme 4).

Therefore, the reactions of 4-substituted "unsymmetrical" 1,2-phenylenediamines can afford two isomeric products **5** or **6** depending on which nitrogen atom is subjected to the primary attack (Schemes 6 and 7). This is consistent with the above-considered experimental results.

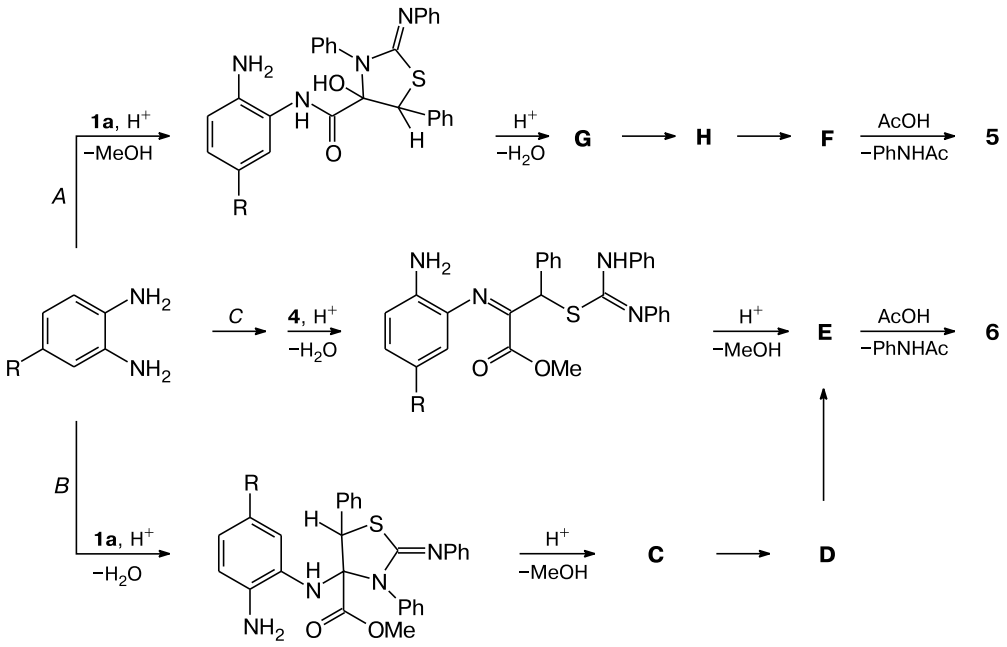
In each possible reaction pathways, *viz.*, amidation (*A*), amination (*B*), and imination (*C*), the first step involves different electrophilic substitution modes at the N atom of the amino group of 4-substituted 1,2-phenylenediamines. In the case of electron-donating substituents (in our case, the methyl group), which activate the amino group in the *para* position to the electrophilic attack, the pathways *B* or *C* should afford compounds containing the substituent at position 7 as the major products; in the case of electron-withdrawing substituents (in our case, the nitro group), which deactivate the amino

Scheme 6



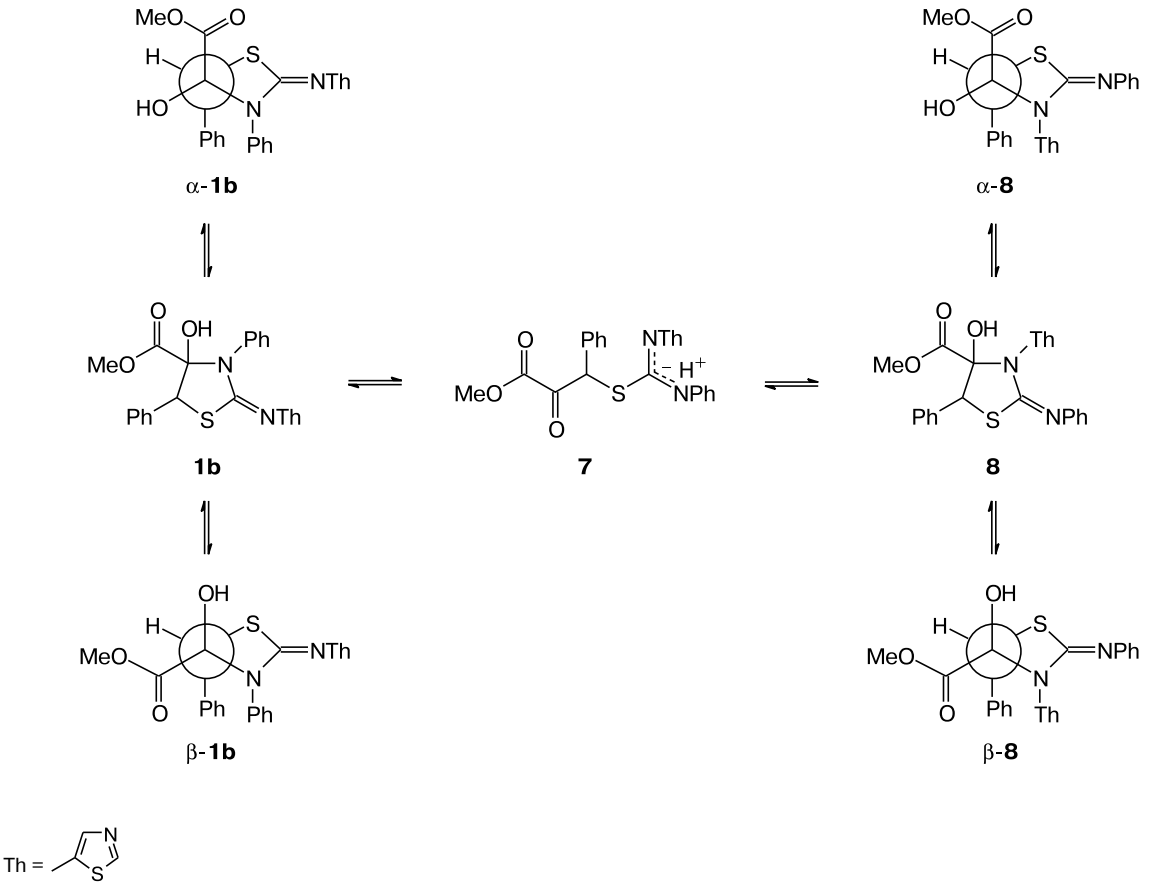
R is an electron-donating substituent

Scheme 7



R is an electron-withdrawing substituent

Scheme 8



group, these pathways should give rise to products containing the substituent at position 8. We experimentally observed this distribution of isomers.

If the pathway *A* would play an essential role, the regioselectivity would be opposite to that observed experimentally; consequently, the contribution of this reaction pathway to the final result is small.

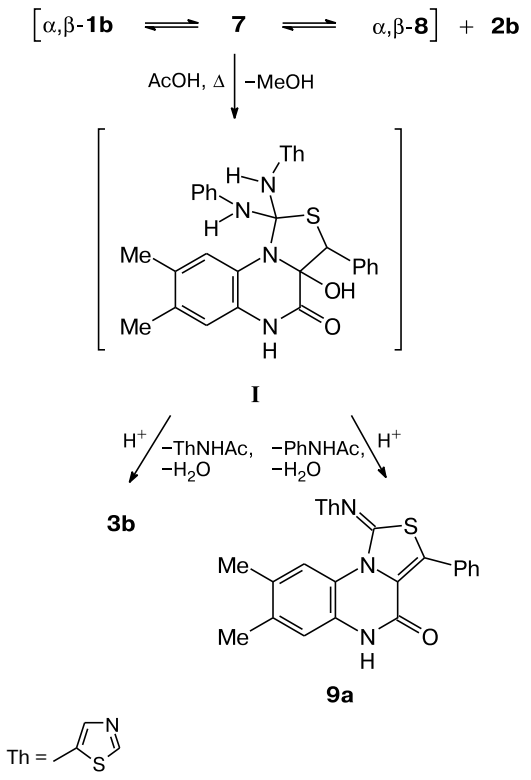
Reactions of "unsymmetrical" 4-hydroxythiazolidine 1b with substituted 1,2-phenylenediamines. 4-Hydroxythiazolidine **1b**, like its "symmetrical" analog **1a**, which we have considered earlier,[24] exists as a tautomeric mixture consisting of the open-chain and diastereomeric cyclic forms. However, unlike analog **1a**, 4-hydroxythiazolidine **1b** has two isomeric cyclic forms, resulting in a more complex tautomeric equilibrium (Scheme 8).

Based on the ^{1}H NMR and IR spectra of 4-hydroxythiazolidine **1b**, the ratio of the components in these mixtures strongly depends on the conditions under which the spectra are recorded, the nature of the substituents, and the conditions of isolation and purification of the products. The detailed consideration of the regio- and diastereomeric composition is beyond the scope of the present study. However, let us note that the ^{1}H NMR spectra of the sample prepared from a solution after its storage for one day show three groups of signals consisting of six singlets for the methoxy protons (δ 3.32, 3.41, 3.49, 3.72, 3.73, and 3.86), four singlets for the methine protons (δ 5.23, 5.30, 5.43, and 5.46), first of which is broadened and corresponds to three protons, and multiplets for aromatic protons (δ 6.89—7.65). For a solution of the product under study, the total integral intensity ratio for the signals of these tautomeric groups is still equal to 1 : 3 : 12 (at least for one day), and the chemical shifts remain unchanged. The percentage of the tautomers in the solution estimated from the integral intensities of the signals for the methoxy and methine protons is approximately 28, 3, 8, 12, 26, and 23%.

The origin of tautomerism resulting in the complication of the ^{1}H NMR spectra is apparently the same as that of the above-mentioned tautomerism of compound **1a**.[15,18—20,24] Some equilibria are presented in Scheme 8.

It should be noted that only one thiazolylimine isomer was isolated in the reaction of 4-hydroxythiazolidine **1b** with unsubstituted 1,2-phenylenediamine (**2a**),[19] whereas both expected thiazolo[3,4-*a*]quinoxalines **3b** and **9a** were isolated in a ratio of 1 : 1.4 in the reaction with 4,5-dimethyl-1,2-diaminobenzene (**2b**) (Scheme 9). The ratio of the yields of these thiazoloquinoxalines depends

Scheme 9

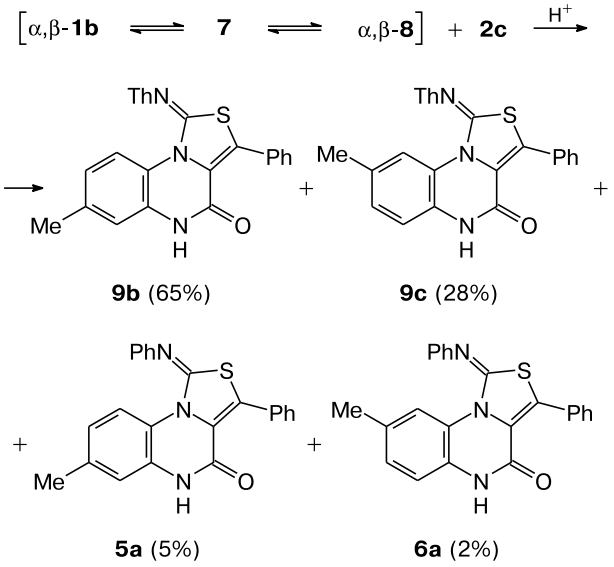


on the competition between the elimination of the nucleofuges PhNHAc or ThNHAc from the same intermediate **I** in an acidic medium.

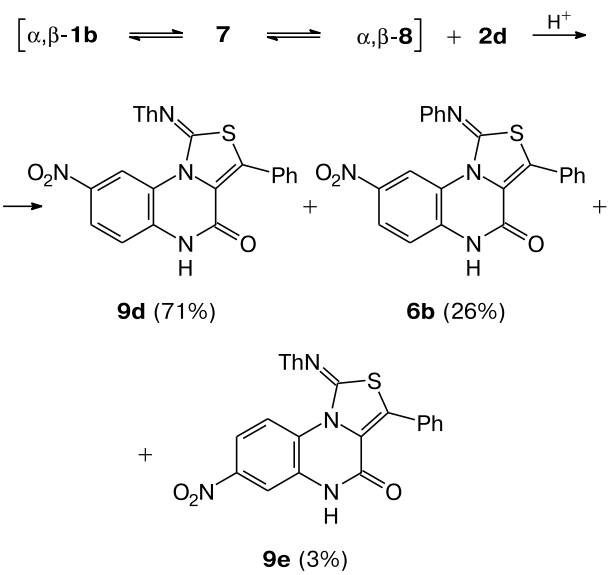
The use of "unsymmetrical" 4-monosubstituted 1,2-phenylenediamines in the reaction with thiazolidine **1b** can lead to the formation of four isomers (two pairs) of tricyclic products, which differ in the nature of substituents in the imine fragment and the benzene ring. Actually, the ^{1}H NMR spectrum of the crude product obtained in the reaction of 4-hydroxythiazolidine **1b** with 4-methyl-1,2-phenylenediamine (**2c**) (Scheme 10) shows four signals for the diagnostic proton H(9). Two of these signals appear as singlets at δ 9.27 and 9.52 (compounds **6a** and **9c** containing the 8-Me group), and two other signals appear as doublets at δ 9.29 (^3J = 8.9 Hz) and 9.55 (^3J = 8.4 Hz) (compounds **5a** and **9b** containing the 7-Me group). The formation of four compounds (two pairs of isomers) is evidenced also by the fact that the ^{1}H NMR spectrum contains, along with other signals, two groups of signals consisting of four singlets each, which correspond to methyl and carbamoyl protons. The ratio of the major thiazolylimine products (**9b,c**) to the minor phenylimine products (**5a** and **6a**) is 93 : 7. Compound **9b** that was formed in the highest yield was isolated preparatively.

The condensation of 4-hydroxythiazolidine **1b** with 4-nitro-1,2-phenylenediamine (**2d**) (Scheme 11) affords a mixture of three out of four possible products, as indicated by the fact that the ^{1}H NMR spectrum of the crude product shows three doublets for the proton H(9) at δ 10.69, 10.39, and 9.84 in the region diagnostic for thiazolo[3,4-*a*]quinoxalines. Compound **9d** that was formed in the highest yield and is characterized by the chemical shift of the diagnostic proton at δ 10.69 was isolated preparatively. The structure of compound **9d** was established by X-ray diffraction (Fig. 3). Small spin-spin coupling constants (J = 2.5 Hz) for the doublets of the proton H(9) at δ 10.69 and 10.39 indicate that these signals belong to 8-nitro-substituted thiazolo[3,4-*a*]-quinoxalines **9d** and **6b**, respectively; consequently, the

Scheme 10



Scheme 11



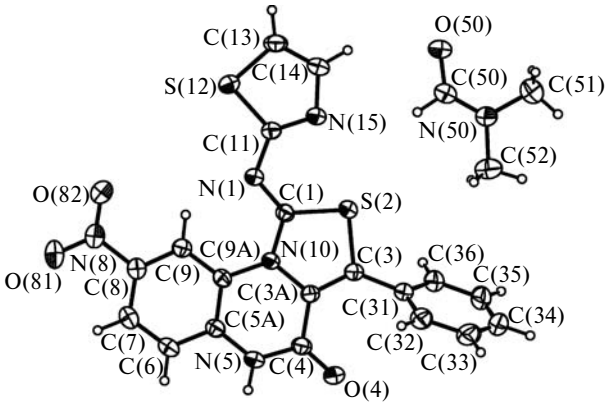


Fig. 3. Molecular structure of compound **9d** in the crystal.

chemical shift of the diagnostic proton at δ 10.39 is assigned to the latter compound. The doublet of the product with the chemical shift of the diagnostic proton at δ 9.84 and the characteristic vicinal constant (^3J = 9.4 Hz) belongs to either 7-nitro-substituted thiazolo[3,4-*a*]-quinoxaline **9e** or compound **5b**. The ratio of products **9d**, **6b**, and **9e** in the crude mixture, which was calculated from the integral intensities of the diagnostic signals for the proton H(9) in the ^{1}H NMR spectrum, is 71 : 26 : 3. The singlets for the protons of the NH groups are characterized by the same integral intensity ratio.

Returning to the above-considered products prepared by the reactions of 4-hydroxythiazolidine **1b** with 4-methyl-1,2-phenylenediamine (**2c**) and 4-nitro-1,2-phenylenediamine (**2d**), it should be noted that a comparison of the positions, multiplicities, and integral intensities of the protons of the thiazolyl and benzene rings in the tricyclic system allowed us to assign the signals to the corresponding thiazolo[3,4-*a*]quinoxaline derivatives.

Compound **9d** also crystallizes with DMF solvent molecules in a ratio of 1 : 1. Molecule **9d** is planar within experimental error (0.02(2) Å), the nitro group and the thiazole substituents also lying in the plane of the tricyclic fragment. Moreover, the planar DMF molecule also lies virtually in the plane of molecule **9d**. The dihedral angle between the plane of the DMF molecule and the mean plane of the tricyclic moiety of molecule **9d** is 2.8°. The distances from different atoms of the tricyclic moiety to the plane of the DMF molecule are in the range of 0.44—0.58 Å. The phenyl substituent C(31)—C(36) is the only fragment of the molecule, which deviates from the plane of the tricyclic moiety and is nearly perpendicular to the latter (the dihedral angle is 63.5°). As in the crystal structure of compound **3b**, the DMF solvent molecule hinders the formation of hydrogen-bonded dimers of molecules **9d** in the crystal structure through classical hydrogen bonds. The solvent molecule is involved in hydrogen bonding; this hydrogen bond is formed between the carbonyl group of the DMF molecule and the hydrogen atom of the amino group (H(5)...O(50), 2.00 Å; N(5)...O(50), 2.834(3) Å; N(5)—H(5)...O(50), 162°). The stacking effect is observed in the crystal structure of compound **9d**. Thus, the electronic systems of the tricyclic and thiazole moieties of the molecule interact with the thiazole ring and the tricyclic moiety, respectively (in a head-to-tail fashion) of the molecules related to the reference molecule by the translation ±1 along the 0*x* axis. The distance between the arbitrary center of the tricyclic moiety and the center of the thiazole ring of the adjacent molecule is 3.57 Å. The dihedral angle between their mean planes is 0°. The shortest distance between the planes of the molecules is 3.37 Å. The tetragonal packing of the molecular stacks gives rise to pseudochannels, which are occupied by the solvent molecules (Fig. 4). However, the packing coefficient is low (the calculated coefficient is 68.8%).

The factors determining the position of the methyl and nitro groups in the reaction products of 4-hydroxythiazolidine **1b** with "unsymmetrical" diamines **2c,d** and the ratio of isomeric products are the same as those observed in the reactions of "symmetrical" hydroxythiazolidine **1a**. The explanation of the predominant formation of 1-thiazolylimino derivatives of thiazolo[3,4-*a*]quinoxalines in the reactions of hydroxythiazolidine **1b** with both "unsymmetrical" diamines under study is problematic. Since the reaction is performed in acetic acid, the higher basicity of the thiazolyl group compared to that of the phenylamino group (pK_a of 2-aminothiazole is 5.39,[27] pK_a of aniline is 4.6 (see Ref. 28)) should lead to the predominant protonation of the thiazole fragment and elimination of aminothiazole **K** as a result of cyclization of intermediate **J** (Scheme 12) to form 1-phenylimino derivatives of thiazoloquinoxaline **5** and **6**. However, this is not observed; instead, the phenylamino group is eliminated and the reaction affords 1-thiazolylimino deriva-

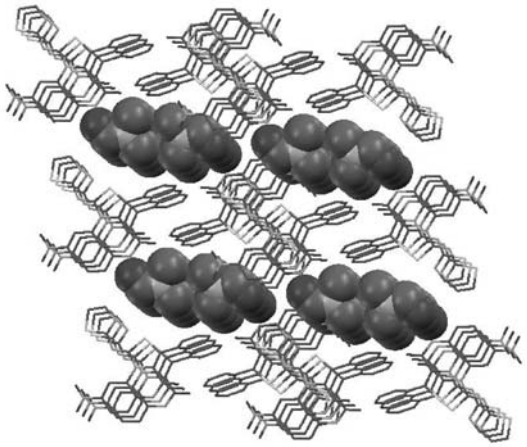
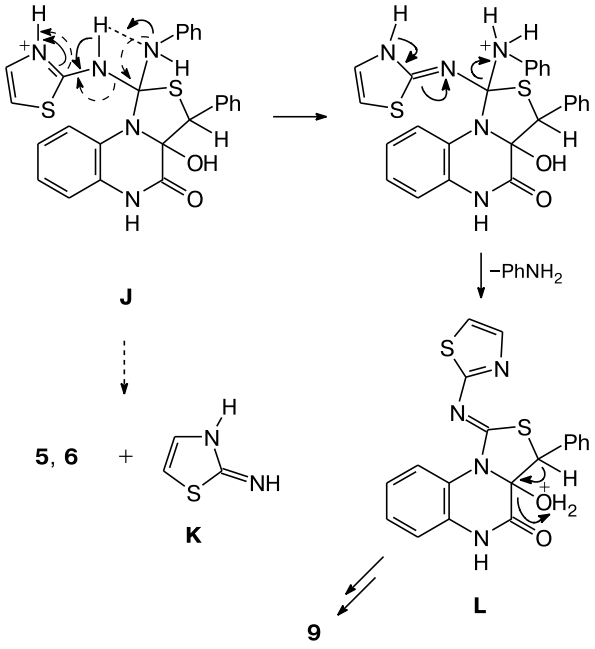


Fig. 4. Formation of pseudochannels filled by DMF molecules in the crystal structure of compound **9d**. The projection approximately along the 0*a* axis. The DMF molecules are represented in van-der-Waals radii. The H atoms are omitted.

tives **9** through the intermediate **L**. Like in the reactions of unsubstituted 1,2-phenylenediamine (**2a**) with "unsymmetrical" 4-hydroxy-3(5)-pyrid-2-yl- and 5(3)-phenyl-2-enyliminothiazolidines and their picolyl homologs, which we have described previously,[23] this fact can be attributed to the intramolecular transfer of the proton or the acetyl group from the thiazole nitrogen atom to the phenylamino nitrogen atom.

Scheme 12



Experimental

The ^{1}H NMR spectra were recorded on a Bruker-AVANCE-600 spectrometer operating at 600.00 MHz. The chemical shifts are given on the δ scale (experimentally measured with respect to DMSO-d_6). The IR spectra were measured on a Vector-22 Fourier-transform IR spectrometer (Bruker) in KBr pellets. The melting points were determined on a Boetius hot-stage apparatus. The electron-impact mass spectra were obtained on a TRACE MS quadrupole mass spectrometer (ThermoQuest/Finnigan) using a direct inlet system with water cooling. 4-Hydroxy-4-methoxycarbonyl-3,5-diphenyl-2-phenyliminothiazolidine (**1a**) was synthesized by the reaction of methyl 3-chloro-2-hydroxo-3-phenylpropionate with *N*,*N*′-diphenylthiourea according to a known procedure.[24]

4-Hydroxy-4-methoxycarbonyl-2-(thiazol-2-yl)imino-3,5-diphenylthiazolidine (1b). Sodium acetate (4.08 g, 0.05 mol) was added to a solution of *N*-phenyl-*N*′-thiazol-2-ylthiourea (4.7 g, 0.02 mol) in CH_2Cl_2 (150 mL). The reaction mixture was cooled to −15—−20 °C, and then a solution of methyl chlorophenylpyruvate (4.15 g, 0.02 mol) in CH_2Cl_2 (20 mL) was added dropwise. The reaction mixture was stirred at ~20 °C for 5 h and poured into water. The organic layer was separated, and the aqueous layer was extracted with CH_2Cl_2 (2×20 mL). The organic layer and the extract were combined and dried with $MgSO_4$. The solvent was evaporated. The residue was treated with diethyl ether. Compound **1b** was obtained in a yield of 4.3 g (52%), m.p. 150—155 °C (Pr^iOH). Found (%): C, 58.42; H, 4.26; N, 9.98; S, 15.47. $C_{20}H_{17}N_3O_3S_2$. Calculated (%): C, 58.38; H, 4.16; N, 10.21; S, 15.58. IR (Nujol), ν/cm^{-1}: 3500 (OH), 3189—3088, 1763 (C=O), 1737, 1630 (C=N), 1597, 1664, 1492. ^{1}H NMR ($CDCl_3$), δ: 3.32, 3.41, 3.49, 3.72, 3.73, and 3.86 (all s, 3 H each, OMe); 5.23 (br.s, 3 H, 3 CH); 5.30, 5.43, and 5.46 (all s, 3 H each, 3 CH); 6.89—7.65 (m, 6×14 H, 6×2 Ph, 6 H(4) and 6 H(5) thiazole, 6 OH). The percentage of tautomers in the solution was ~28, 3, 8, 12, 26, and 23%. The total integral intensity ratio of the methine, methoxy, and aromatic protons is 1 : 3 : 12.

3a-Hydroxy-7,8-dimethyl-3-phenyl-1-phenylimino-3,3a-dihydrothiazolo[3,4-*a*]quinoxalin-4(5*H*)-one (3b′). A solution of 1,2-diamino-4,5-dimethylbenzene (**2b**) (0.05 g, 0.37 mmol) and 4-hydroxythiazolidine **1a** (0.14 g, 0.37 mmol) in AcOH (5 mL) was heated at 80±5 °C for 50 min. The yellow precipitate that formed after cooling was filtered off. Compound **3b′** was obtained in a yield of 0.12 g (80%), m.p. 346—351 °C. Found (%): C, 69.09; H, 5.06; N, 9.09; S, 8.01. $C_{24}H_{21}N_3O_2S$. Calculated (%): C, 69.38; H, 5.09; N, 10.11; S, 7.72. IR, ν/cm^{-1}: 3370 (OH), 3181—2857 (NH), 1665 (C=O), 1638, 1617, 1593. ^{1}H NMR, δ: 2.18 (s, 6 H, 2 Me); 5.45 (s, 1 H, CH); 6.81 (s, 1 H, H(6)); 6.94 (d, 2 H, 2 *o*-H phenylimine, J = 7.6 Hz); 7.06 (dd, 1 H, *p*-H phenylimine, J = 7.3 Hz, J = 7.3 Hz); 7.20 (s, 1 H, OH); 7.27 (dd, 1 H, *p*-H_{Ph}, J = 7.1 Hz, J = 6.5 Hz); 7.31 (dd, 2 H, 2 *m*-H phenylimine, J = 7.8 Hz, J = 7.6 Hz); 7.31 (dd, 2 H, 2 *m*-H_{Ph}, J = 7.8 Hz, J = 7.6 Hz); 7.64 (d, 2 H, 2 *o*-H_{Ph}, J = 7.1 Hz); 8.27 (s, 1 H, H(9)); 10.78 (s, 1 H, NH).

7,8-Dimethyl-3-phenyl-1-phenyliminothiazolo[3,4-*a*]quinoxalin-4(5*H*)-one (3b). ***A***. A solution of 1,2-diamino-4,5-dimethylbenzene (**2b**) (0.5 g, 3.67 mmol) and 4-hydroxythiazolidine **1a** (1.42 g, 3.67 mmol) in AcOH (30 mL) was refluxed for 1 h. The yellow crystals that precipitated were filtered off. Compound **3b** was obtained in a yield of 1.21 g (84%), m.p. 352—355 °C. Found (%): C, 75.20; H, 4.65; N, 10.22; S, 8.02. $C_{24}H_{19}N_3OS$. Calculated (%): C, 72.52; H, 4.82; N, 10.57; S, 8.07. IR, ν/cm^{-1}: 3140—2880 (NH), 1684 (C=O), 1612 (C=N), 1575, 1515. ^{1}H NMR, δ: 2.21 (s, 6 H, 2 Me); 6.92 (s, 1 H, H(6)); 7.07 (d, 2 H, 2 *o*-H phenylimine, J = 7.8 Hz); 7.13 (dd, 1 H, *p*-H phenylimine, J = 7.8 Hz, J = 6.7 Hz); 7.34—7.36 (m, 3 H, 2 *o*-H_{Ph} + *p*-H_{Ph}); 7.41 (dd, 2 H, 2 *m*-H phenylimine, J = 7.8 Hz, J = 6.7 Hz); 7.45—7.48 (m, 2 H, 2 *m*-H_{Ph}); 9.21 (s, 1 H, H(9)); 11.09 (s, 1 H, NH).

B. A solution of compound **3b′** (100 mg) in AcOH (3 mL) was refluxed for 45 min. The precipitate was filtered off. Compound **3b** was obtained in a yield of 91 mg (95%). The characteristics of this compound are identical to those of the compound prepared according to the method ***A***.

7,8-Dimethyl-3-phenyl-1-phenyliminothiazolo[3,4-*a*]quinoxalin-4(5*H*)-one (3b) and 7,8-dimethyl-1-(thiazol-2-yl)imino-3-phenylthiazolo[3,4-*a*]quinoxalin-4(5*H*)-one (9a) (a mixture of isomers **3b** + **9a** in a percentage ratio of 41 : 59). A solution of 1,2-diamino-4,5-dimethylbenzene (**2b**) (1.17 g, 1.2 mmol) and 4-hydroxythiazolidine **1b** (0.5 g, 1.2 mmol) in AcOH (30 mL) was refluxed for 1.5 h. The reaction mixture was cooled. The yellow crystals that precipitated were filtered off. A mixture **3b** + **9a** was obtained in a yield of 0.37 g (77%). The mixture was

recrystallized from DMF. Compound **9a** was obtained in a yield of 0.18 g (38%), m.p. >350 °C. Found (%): C, 62.26; H, 4.28; N, 14.16; S, 15.65. $C_{21}H_{16}N_4OS_2$. Calculated (%): C, 62.36; H, 3.99; N, 13.85; S, 15.85. IR, ν/cm^{-1}: 3044—2853 (NH), 1688 (C=O), 1630, 1607, 1588, 1584, 1546. ^{1}H NMR, δ: 2.24 and 2.30 (both s, 3 H each, Me); 6.97 (s, 1 H, H(6)); 7.32 (d, 1 H, H(5) or H(4) thiazole, J = 3.5 Hz); 7.42—7.44 (m, 3 H, 2 o-H_{Ph} + p-H_{Ph}); 7.56—7.58 (m, 2 H, 2 m-H_{Ph}); 7.61 (d, 1 H, H(5) or H(4) thiazole, J = 3.5 Hz); 9.49 (s, 1 H, H(9)); 11.26 (s, 1 H, NH). Water (5 mL) was added to the filtrate in DMF. The crystals that precipitated were filtered off, washed with water (2×5 mL), and dried in air. Compound **3b** was obtained in a yield of 0.13 g (27%); m.p. and the spectroscopic characteristics of this compound are identical to those of the product prepared by the reaction of "symmetrical" 4-hydroxythiazolidine **1a** with 1,2-diamino-4,5-dimethylbenzene (**2b**).

7-Methyl-3-phenyl-1-phenyliminothiazolo[3,4-*a*]quinoxalin-4(5*H*)-one (5a) and 8-methyl-3-phenyl-1-phenyliminothiazolo-[3,4-*a*]quinoxalin-4(5*H*)-one (6a) (a mixture of isomers **5a** + **6a** in a percentage ratio of 61 : 39). A solution of 4-hydroxythiazolidine **1a** (1 g, 2.6 mmol) and 1,2-diamino-4-methylbenzene (**2c**) (0.31 g, 2.6 mmol) in AcOH (15 mL) was refluxed for 3 h. The yellow crystals that precipitated were filtered off. A mixture **5a** + **6a** was obtained in a yield of 0.85 g (85%), m.p. 269—273 °C. IR, ν/cm^{-1}: 3336—3028 (NH), 1671 (C=O), 1617 (C=N), 1514. ^{1}H NMR, δ: 2.31 and 2.32 (both s, 3 H each, Me); 6.96—7.48 (m, 24 H, 4 Ph, 2 H(6), H(7), H(8)); 9.28 (s, 1 H, H(9)); 9.29 (d, 1 H, H(9), J = 8.9 Hz); 11.15 and 11.18 (both s, 1 H each, NH). The isomers were separated by column chromatography on silica gel Kieselgel (chloroform—hexane, 2 : 1, as the eluent); R_f are given for a stationary layer of silica gel Silufol using a 1 : 3 : 2 chloroform—hexane—methanol system. The yield of compound **5a** was 0.41 g (48%), yellow crystals, R_f 0.68, m.p. 280—283 °C. Found (%): C, 72.06; H, 4.44; N, 10.97; S, 8.36. $C_{23}H_{17}N_3OS$. Calculated (%): C, 71.86; H, 4.14; N, 10.58; S, 8.29. IR, ν/cm^{-1}: 3195—2871 (NH), 1674 (C=O), 1614 (C=N), 1587, 1575, 1520, 1485. ^{1}H NMR, δ: 2.30 (s, 3 H, Me); 6.93—6.95 (m, 2 H, H(6), H(8)); 7.06 (d, 2 H, 2 o-H phenylimine, J = 7.6 Hz); 7.13 (dd, 1 H, p-H phenylimine, J = 7.6 Hz, J = 7.1 Hz); 7.35—7.37 (m, 3 H, 2 o-H_{Ph} + p-H_{Ph}); 7.40 (dd, 2 H, 2 m-H phenylimine, J = 7.3 Hz, J = 7.3 Hz); 7.45—7.47 (m, 2 H, 2 m-H_{Ph}); 9.27 (d, 1 H, H(9), J = 8.9 Hz); 11.15 (s, 1 H, NH). The yield of compound **6a** was 0.26 g (31%), yellow crystals, R_f 0.56, m.p. 317—320 °C. Found (%): C, 72.00; H, 4.42; N, 10.93; S, 8.34. $C_{23}H_{17}N_3OS$. Calculated (%): C, 71.86; H, 4.14; N, 10.58; S, 8.29. IR, ν/cm^{-1}: 3180—2854 (NH), 1671 (C=O), 1614 (C=N), 1587, 1513, 1488. ^{1}H NMR, δ: 2.31 (s, 3 H, Me); 7.02—7.04 (m, 2 H, H(6), H(8)); 7.07 (d, 2 H, 2 o-H phenylimine, J = 7.1 Hz); 7.14 (dd, 1 H, p-H phenylimine, J = 7.1 Hz, J = 7.1 Hz); 7.33—7.35 (m, 3 H, 2 o-H_{Ph} + p-H_{Ph}); 7.42 (dd, 2 H, 2 m-H phenylimine, J = 7.8 Hz, J = 7.1 Hz); 7.43—7.47 (m, 2 H, 2 m-H_{Ph}); 9.25 (s, 1 H, H(9)); 11.14 (s, 1 H, NH).

7-Nitro-3-phenyl-1-phenyliminothiazolo[3,4-*a*]quinoxalin-4(5*H*)-one (5b) and 8-nitro-3-phenyl-1-phenyliminothiazolo-[3,4-*a*]quinoxalin-4(5*H*)-one (6b) (a mixture of isomers **5b** + **6b** in a percentage ratio of 11 : 89). A solution of 4-hydroxythiazolidine **1a** (1 g, 2.60 mmol) and 1,2-diamino-4-nitrobenzene (**2d**) (0.40 g, 2.60 mmol) in AcOH (15 mL) was refluxed for 6 h. The orange crystals that formed were filtered off. A mixture **5b** + **6b** was obtained in a yield of 0.76 g (74%), m.p. 320—326 °C. IR, ν/cm^{-1}: 3180—3020 (NH), 1679 (C=O), 1628 (C=N), 1590, 1574, 1529, 1504. ^{1}H NMR, δ: 7.11—8.16 (m, 24 H, 4 Ph, 2 H(6), H(7), H(8)); 8.04 (d, 1 H, H(8), J = 9.2 Hz); 8.15 (d, 1 H, H(7), J = 8.9 Hz); 9.62 (d, 1 H, H(9), J = 8.9 Hz); 10.42 (s, 1 H, H(9)); 11.50 and 11.75 (both s, 1 H each, NH). The mixture of isomers **5b** + **6b** was recrystallized from DMF. Compound **6b** was obtained in a yield of 0.61 g (59%) as orange crystals, m.p. 344—346 °C. Found (%): C, 61.61; H, 4.31; N, 14.36; S, 6.58. $C_{22}H_{14}N_4O_3S \cdot$ DMF. Calculated (%): C, 61.77; H, 4.38; N, 14.53; S, 6.73. IR, ν/cm^{-1}: 3180—2853 (NH), 1678 (C=O), 1628 (C=N), 1590, 1573, 1529, 1502. ^{1}H NMR, δ: 7.13 (d, 2 H, 2 o-H phenylimine, J = 7.9 Hz); 7.20 (dd, 1 H, p-H phenylimine, J = 7.3 Hz, J = 7.3 Hz); 7.28 (d, 1 H, H(6), J = 8.6 Hz); 7.39—7.41 (m, 3 H, 2 o-H_{Ph} + p-H_{Ph}); 7.46 (dd, 2 H, 2 m-H phenylimine, J = 7.9 Hz, J = 7.6 Hz); 7.49—7.51 (m, 2 H, 2 m-H_{Ph}); 8.14 (dd, 1 H, H(7), J = 8.9 Hz, J = 2.1 Hz); 10.42 (d, 1 H, H(9), J = 2.1 Hz); 11.77 (s, 1 H, NH).

7-Methyl-3-phenyl-1-phenyliminothiazolo[3,4-*a*]quinoxalin-4(5*H*)-one (5a), 8-methyl-3-phenyl-1-phenyliminothiazolo-[3,4-*a*]quinoxalin-4(5*H*)-one (6a), 7-methyl-3-phenyl-1-(thiazol-2-yl)iminothiazolo[3,4-*a*]quinoxalin-4(5*H*)-one (9b), and 8-methyl-3-phenyl-1-(thiazol-2-yl)iminothiazolo[3,4-*a*]quinoxalin-4(5*H*)-one (9c) (a mixture of two pairs of isomers **5a**, **6a** and **9b**, **9c** in a percentage ratio of 5 : 2 : 65 : 28). A solution of 4-hydroxythiazolidine **1b** (0.5 g, 1.2 mmol) and 1,2-diamino-4-methylbenzene (**2c**) (0.15 g, 1.2 mmol) in AcOH (30 mL) was refluxed for 2 h. The yellow precipitate that formed was filtered off. The mixture **5a** + **6a** + **9b** + **9c** was obtained in a yield of 0.21 g (45%), m.p. 327—335 °C. IR, ν/cm^{-1}: 3200—2700 (NH), 1688 (C=O), 1605 (C=N), 1584, 1543. ^{1}H NMR, δ: 2.31, 2.32, 2.34, and 2.40 (all s, 3 H each, Me); 6.96—7.64 (m, 38 H, 6 Ph, 4 H(6), 2 H(7), 2 H(8)); 7.33 (d, 1 H, H(5) or H(4) thiazole, J = 3.7 Hz); 7.35 (d, 1 H, H(5) or H(4) thiazole, J = 3.7 Hz); 7.62 (d, 1 H, H(5) or H(4) thiazole, J = 3.7 Hz); 7.64 (d, 1 H, H(5) or H(4) thiazole, J = 3.7 Hz); 9.27 (s, 1 H, H(9)); 9.29 (d, 1 H, H(9), J = 8.9 Hz); 9.52 (s, 1 H, H(9)); 9.55 (d, 1 H, H(9), J = 8.4 Hz); 11.15, 11.18, 11.31, and 11.34 (all s, 1 H each, NH). The mixture **5a** + **6a** + **9b** + **9c** was recrystallized from DMF. Compound **9b** was obtained in a yield of 0.12 g (25%) as yellow crystals, m.p. >350 °C. Found (%): C, 61.15; H, 3.51; N, 14.30; S, 16.22. $C_{20}H_{14}N_4OS_2$. Calculated (%): C, 61.52; H, 3.61; N, 14.35; S, 16.40. IR, ν/cm^{-1}: 3020—2819 (NH), 1689 (C=O), 1605 (C=N), 1582, 1542. ^{1}H NMR, δ: 2.33 (s, 3 H, Me); 7.02 (s, 1 H, H(6)); 7.06 (d, 1 H, H(8), J = 8.6 Hz); 7.32 (d, 1 H, H(5) or H(4) thiazole, J = 3.6 Hz); 7.43—7.46 (m, 3 H, 2 o-H_{Ph} + p-H_{Ph}); 7.57—7.59 (m, 2 H, 2 m-H_{Ph}); 7.61 (d, 1 H, H(5) or H(4) thiazole, J = 3.7 Hz); 9.54 (d, 1 H, H(9), J = 8.6 Hz); 11.33 (s, 1 H, NH).

8-Nitro-3-phenyl-1-phenyliminothiazolo[3,4-*a*]quinoxalin-4(5*H*)-one (6b), 7-nitro-1-(thiazol-2-yl)imino-3-phenylthiazolo-[3,4-*a*]quinoxalin-4(5*H*)-one (9e), and 8-nitro-1-(thiazol-2-yl)imino-3-phenylthiazolo[3,4-*a*]quinoxalin-4(5*H*)-one (9d) (a mixture of **6b** and a pair of isomers **9e** and **9d** in a percentage ratio of 26 : 3 : 71). A mixture of 4-hydroxythiazolidine **1b** (0.25 g, 0.6 mmol) and 1,2-diamino-4-nitrobenzene (**2d**) (0.09 g, 0.6 mmol) was refluxed in AcOH (20 mL) for 4 h. The orange precipitate that formed was filtered off. A mixture **6b** + **9e** + **9d** was obtained in a yield of 0.07 g (28%), m.p. 324—332 °C. IR, ν/cm^{-1}: 3276—2854 (NH), 1681 (C=O), 1605 (C=N), 1593, 1573, 1525, 1504. ^{1}H NMR, δ: 7.11—7.59 (m, 20 H, 4 Ph); 7.25 (d, H(6), J = 8.9 Hz); 7.30 (d, H(6),

J = 8.9 Hz); 7.38 (d, 1 H, H(5) or H(4) thiazole, *J* = 3.7 Hz); 7.41 (d, 1 H, H(5) or H(4) thiazole, *J* = 3.4 Hz); 7.63 (d, 1 H, H(5) or H(4) thiazole, *J* = 3.7 Hz); 7.66 (d, 1 H, H(5) or H(4) thiazole, *J* = 3.4 Hz); 7.97 (d, 1 H, H(6), *J* = 2.7 Hz); 8.11 (dd, 1 H, H(7), *J* = 8.9 Hz, *J* = 2.5 Hz); 8.07 (dd, H(8), *J* = 9.4 Hz, *J* = 2.70 Hz); 8.18 (dd, 1 H, H(7), *J* = 8.9 Hz, *J* = 2.5 Hz); 9.84 (d, 1 H, H(9), *J* = 9.4 Hz); 10.39 (d, 1 H, H(9), *J* = 2.5 Hz); 10.69 (d, 1 H, H(9), *J* = 2.5 Hz); 11.65, 11.76, and 11.91 (all s, 1 H each, NH). The filtrate was concentrated, the residue was treated with diethyl ether, and the precipitate was filtered off. An additional amount of the mixture **6b** + **9e** + **9d** was obtained (0.05 g, 20%). The mixture **6b** + **9e** + **9d** was recrystallized from DMF. Compound **9d** was obtained in a yield of 0.07 g (29%), m.p. 342—343 °C. Found (%): C, 44.74; H, 2.04; N, 13.62; S, 12.48. $C_{19}H_{11}N_5O_3S \cdot$ DMF. Calculated (%): C, 44.89; H, 2.17; N, 13.78; S, 12.60. IR, ν/cm^{-1}: 3180—2852, 1698 (C=O), 1647, 1617, 1534. ^{1}H NMR, δ: 7.36 (d, 1 H, H(6), *J* = 8.5 Hz); 7.42 (d, 1 H, H(5) or H(4) thiazole, *J* = 3.6 Hz); 7.48—7.50 (m, 3 H, 2 *o*-H_{Ph} + *p*-H_{Ph}); 7.61—7.63 (m, 2 H, 2 *m*-H_{Ph}); 7.68 (d, 1 H, H(5) or H(4) thiazole, *J* = 3.6 Hz); 8.24 (dd, 1 H, H(7), *J* = 8.5 Hz, *J* = 2.5 Hz); 10.75 (d, 1 H, H(9), *J* = 2.5 Hz); 11.95 (s, 1 H, NH).

Single-crystal X-ray diffraction study of compounds **3b** and **9d** was carried out at the Department of X-ray Diffraction Studies of the Center of Collaborative Research on the basis of the Laboratory of X-ray Diffraction Methods of the A. E. Arbuzov Institute of Organic and Physical Chemistry, the Kazan Research Center of the Russian Academy of Sciences. The crystallographic characteristics and the X-ray data collection and refinement statistics are given in Table 2. The X-ray diffraction data were collected on an automated four-circle CAD-4 NONIUS B.V. diffractometer (graphite monochromator, Cu-Kα radiation) at 20 °C. The X-ray data were processed with the use of the MolEN program[29] on an AlphaStation 200. The intensities of three check reflections showed no decrease in the course of X-ray data collection. The empirical absorption correction was applied. All structures were solved by direct methods with the use of the SIR program[30] and refined first isotropically and then anisotropically using the SHELXL-97[31] and WinGX[32] program packages. The coordinates of the hydrogen atoms of the amino groups were located in difference electron density maps (the coordinates of the other hydrogen atoms were calculated based on the stereochemical criteria) and refined using a riding model. The intermolecular interactions were analyzed and the figures were drawn with the use of the PLATON program.[25] The atomic coordinates and displacement parameters for compounds **3b** and **9d** were deposited with the Cambridge Structural Database (http://www.ccdc.cam.ac.uk; CCDC 671888 and 671887, respectively).

Table 2. Crystallographic characteristics and the X-ray data collection and refinement statistics for compounds **3b** and **9d**

Parameter	**3b**	**9d**
Color and shape	Yellow, prismatic shape	
Molecular formula	$C_{24}H_{19}N_3OS \cdot \cdot C_2H_6OS$	$C_{19}H_{11}N_5O_3S_2 \cdot \cdot C_3H_7NO$
Molecular weight	475.61	494.54
Crystal system	Monoclinic	Triclinic
Space group	$P2_1/n$	$P\bar{1}$
a/Å	8.530(1)	7.0160(6)
b/Å	9.379(1)	12.718(1)
c/Å	29.260(6)	13.772(1)
α/deg	90	72.283(9)
β/deg	91.70(1)	87.253(8)
γ/deg	90	73.644(9)
V/Å^3	2339.9(6)	1122.25(17)
Z	4	2
d_{calc}/g cm^{-3}	1.350	1.464
μ/cm^{-1}	22.94	25.28
Absorption correction	Psi-scan	
F(000)	1000	512
Number of measured reflections	4699	4675
R_{int}	0.0000	0.0560
Number of observed reflections with $I > 2\sigma(I)$	3035	3513
R factors	$R = 0.0719$, $Rw = 0.2037$	$R = 0.0436$, $Rw = 0.1254$
Goodness-of-fit	1.038	1.033
Number of refined parameters	300	307

This study was financially supported by the Russian Foundation for Basic Research (Project Nos 07-03-00613-a and 05-03-33008-a), the Council on Grants of the President of the Russian Federation (Program for State Support of Leading Scientific Schools, Grant NSh-3758.2008.3), and the Federal Target Program "Research and Development in Priority Fields of Science and Technology in Russia in 2007—2012" (State Contract No. 02.512.11.2237).

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Received June 3, 2008;
in revised form September 22, 2008