Benzimidazoles and related heterocycles
8.* Acid-catalyzed rearrangement of 3-aryl-1′*H*-spiro[2-pyrazoline-5,2′-quinoxalin]-3′(4′*H*)-ones as a new efficient method for the synthesis of 2-(pyrazol-3-yl)benzimidazoles**

V. A. Mamedov, A. M. Murtazina, A. T. Gubaidullin, E. A. Khafizova, I. Kh. Rizvanov, and I. A. Litvinov*

A. E. Arbuzov Institute of Organic and Physical Chemistry,
Kazan Scientific Center of the Russian Academy of Sciences,
8 ul. Akad. Arbuzova, 420088 Kazan, Russian Federation.
Fax: +7 (843) 273 2253. E-mail: mamedov@iopc.ru

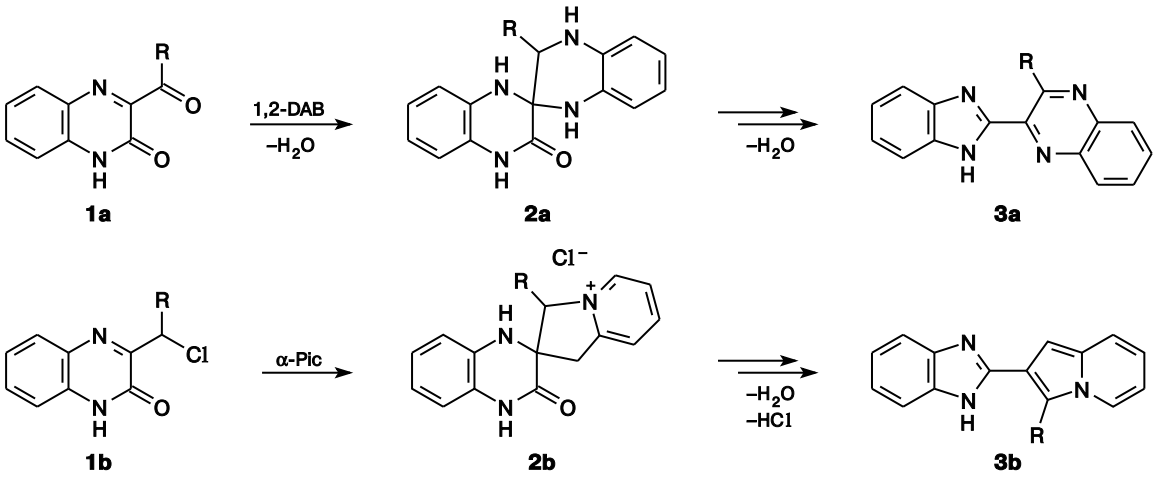
3-Aryl-1′*H*-spiro[2-pyrazoline-5,2′-quinoxalin]-3′(4′*H*)-ones, easily available by the reaction of 3-(2-aryl-2-oxoethylidene)-3,4-dihydroquinoxalin-2(1*H*)-ones with hydrazine hydrate (and phenylhydrazine), in boiling acetic acid undergo new acid-catalyzed rearrangement with the contraction of pyrazine ring of the quinoxaline system to form 2-(pyrazol-3-yl)benzimidazoles. Possible mechanisms of this rearrangement are considered.

Key words: 3-(2-aryl-2-oxoethylidene)-3,4-dihydroquinoxalin-2(1*H*)-ones, benzimidazole, pyrazine→imidazole ring contraction, 2-(pyrazol-3-yl)benzimidazoles, X-ray diffraction analysis.

Benzimidazole derivatives are parts of various biologically active compounds possessing antiviral, antihypertensive, and antitumor activity.[8,9] Compounds having a benzimidazole fragment exhibit pronounced activity against such viruses, as HIV,[10,11] herpes (VSV-1),[10,12] human cytomegalovirus (HCMV),[12] and flu virus.[13] Bisbenzimidazoles are the DNA-binding agents with antitumor activity.[14]

Earlier, we have found that the reactions of 3-(aroyl)- and 3-(alkanoyl)quinoxalin-2(1*H*)-ones[1—5] with 1,2-diaminobenzenes (1,2-DAB) and 3-(α-chlorobenzyl)-quinoxalin-2(1*H*)-ones[6,7] with α-picoline (α-Pic) proceed with a ring contraction and formation of 2-(benzimidazol-2-yl)-3-substituted quinoxalines and 2-(3-phenylindolizin-2-yl)benzimidazoles, respectively, due to the rearrangement of intermediate spiro compounds[5—7] (Scheme 1). It

Scheme 1



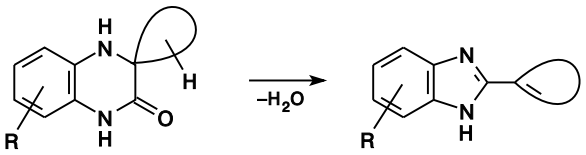
* For Parts 1—7, see Refs 1—7.
** Dedicated to Professor I. A. Nuretdinov on his 75th birthday.

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 8, pp. 1602—1611, August, 2010.
1066-5285/10/5908-1645

was shown that in both cases a key step leading to benzimidazole derivatives is the formation of spiro compounds of the type **2a** and **2b**, respectively, and a sequence of several-step processes resulted in conversion of these compounds to benzimidazole derivatives **3a**,**b**, which contain heterocyclic substituents being one of the spiro-jointed fragments in the intermediate compounds **2a** and **2b** (see Scheme 1).

These results allowed us to suggest a hypothesis on ability of any quinoxalin-3(4*H*)-one spiro derivative at least with one labile hydrogen atom in the spiro forming component to undergo rearrangement to the benzimidazole derivative, bearing one of the jointed fragments of the starting compound as a substituent at position 2 (Scheme 2).

Scheme 2



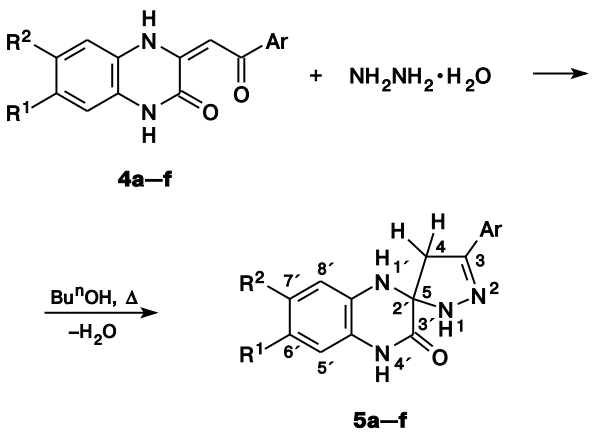
To show a generality of this hypothesis, which may be a method for the synthesis of benzimidazoles through spiro compounds, it is not necessary to use only either 3-aroyl-, or 3-alkanoyl- (**1a**), or chloroalkyl (**1b**) quinoxalin-2(1*H*)-one derivatives. Other derivatives capable to form spiro compounds of the type **2a,b** can be used as well.

The present work is devoted to the study of a possibility to use 3-(2-aryl-2-oxoethylidene)-3,4-dihydroquinoxalin-2(1*H*)-ones **4a—f** as the starting compounds for the synthesis of benzimidazole derivatives through the corresponding spiro compounds and, thereby, an evidence of the hypothesis suggested. The presence of an aroylvinylidene group in compounds **4a—f** allows one to introduce a spiropyrazole fragment in them by the method of pyrazole ring construction with the use of hydrazine hydrate, which is most widely used for this purpose.

The reaction of 3-(2-aryl-2-oxoethylidene)-3,4-dihydroquinoxalin-2(1*H*)-ones **4a—f**,[15] easily obtained from 4-aroyl-3-hydroxy-2(5*H*)-furanones, with hydrazine hydrate in boiling butanol leads to 3-aryl-1′*H*-spiro-[2-pyrazoline-5,2′-quinoxalin]-3′(4′*H*)-ones **5a—f** in good yields (Scheme 3).

Formation of spiro[2-pyrazoline-5,2′-quinoxalin]-3′(4′*H*)-ones can be recognized by characteristic upfield shift of the signals for the phenylene protons in the ^{1}H NMR spectrum, for example, to the region δ 6.70—6.85 for compound **5a**, as compared to the signals for the protons of the phenylene fragment (δ 7.54—7.61) in the starting compound **4a**,[7] which is an evidence of involvement of the sp^2-hybridized C(3) carbon atom of the quinoxaline system into the interaction, which results in its transformation to the sp^3-hybridized spiro carbon atom.[5—7] The spiro cyclization can be also recognized by the presence of two typical doublet signals for the AB-system at δ ~3.00 and ~3.90 with the constant $^2J \approx 17.4$ Hz in the ^{1}H NMR spectrum, characteristic[6] of quinoxalin-2(1*H*)-one spiro derivatives. The IR spectral data also indicate formation of spiro compounds **5a—f** (see Experimental) in the reaction considered. Structures of the spiro compounds were unambiguously established by X-ray diffraction of one of them and comparison of its spectral (IR and ^{1}H NMR) characteristics with the data for other compounds formed by the reaction of 3,4-dihydroquinoxalin-2(1*H*)-ones **4a—f** with hydrazine hydrate.

Scheme 3



$R^1 = R^2 = H$, Ar = Ph (**a**); $R^1 = R^2 = Me$, Ar = Ph (**b**);
$R^1 = Cl$, $R^2 = H$, Ar = Ph (**c**); $R^1 = H$, $R^2 = NO_2$, Ar = Ph (**d**);
$R^1 = R^2 = H$, Ar = C_6H_4Me-*p* (**e**); $R^1 = R^2 = H$, Ar = C_6H_4Cl-*p* (**f**)

Molecular geometry of spiro compound **5c** in the crystal is shown in Fig. 1. The chlorine atom in the molecule is disordered over two positions with relative populations 0.845 and 0.155.

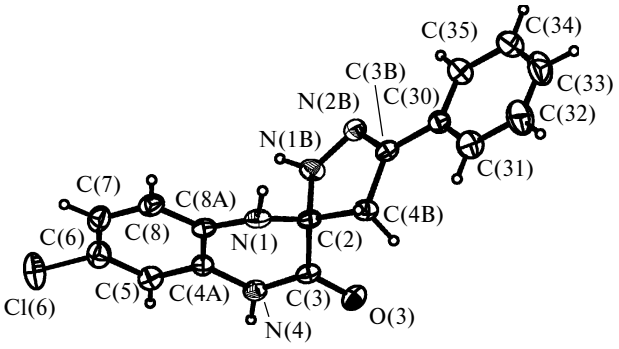


Fig. 1. Molecular geometry of compound **5c** in the crystal. Nonhydrogen atoms are represented by probability ellipsoids of thermal vibrations (p = 30%), hydrogen atoms, by spheres of arbitrary radii. The chlorine atom is shown in the position with higher population.

Planarity of the quinoxaline fragment of the molecule in crystal is disturbed, the six-membered diazine heterocycle is in the distorted boat conformation, the N(1)C(8A)C(4A)N(4) fragment fused with the benzene ring is planar within 0.027(3) Å, the C(2) and C(3) atoms come out of this plane on the same side by 0.637(3) and 0.183(4) Å, respectively. The dihedral angle between the plane of the pyrazole ring and the plane of the quinoxaline fragment is 85.5(2)°, whereas the phenyl substituent is virtually in the plane of the pyrazole ring (dihedral angle is 4.0(2)°). It should be noted that the compound under study is crystallized in the noncentrosymmetric space group $P2_12_12_1$. Thus, the crystal studied is optically active and contains only molecules of the diastereomer with the established configuration of the chiral atom (*R*)-C(2).

The presence of three N—H groups in the molecule of this compound leads to their active involvement into the hydrogen bonds N—H...O and N—H...N and formation of 2D-supramolecular structures, *viz.*, two-dimensional layers of hydrogen-bound molecules parallel to the crystallographic plane 0*ab* (Fig. 2, *a*). Parameters of hydrogen bonds are given in Table 1. Such a packing of the molecules in the crystal resulted in the formation of "pseudo-channels" from chlorine atoms, which have a zigzag-like location along the crystallographic axis 0*a* with the Cl—Cl distances equal to 3.470(2) Å (Fig. 2, *b*).

It should be noted that the conditions indicated, *i.e.* reflux of the corresponding 3,4-dihydroquinoxalin-2(1*H*)-ones **4a—f** with hydrazine hydrate in butanol, are the optimum for accomplishing this reaction. Its carrying out directly in hydrazine hydrate (though shorter time is required for its completion in this case) is accompanied by various side processes, including partial reduction of the carbonyl group of substituent and cleavage of 3-(2-aryl-2-oxoethylidene)-3,4-dihydroquinoxalin-2(1*H*)-ones at the C(3)—C_α bond to form, for example in the case of quinoxalin-2(1*H*)-one **4a**, 3-phenylethylenequinoxalin-2(1*H*)-one **6a** and quinoxaline-2,3(1*H*,4*H*)-dione **7a**, respectively, which is confirmed by the presence of the multiplet signals for the protons $—CH_2CH_2—$ of the AA´BB´-system of compound **6a** in the region δ 3.05—3.11 and the protons of the AA´BB´-system of the benzene ring of quinoxalin-2,3(1*H*,4*H*)-dione **7a** in the region δ 6.37—6.52.

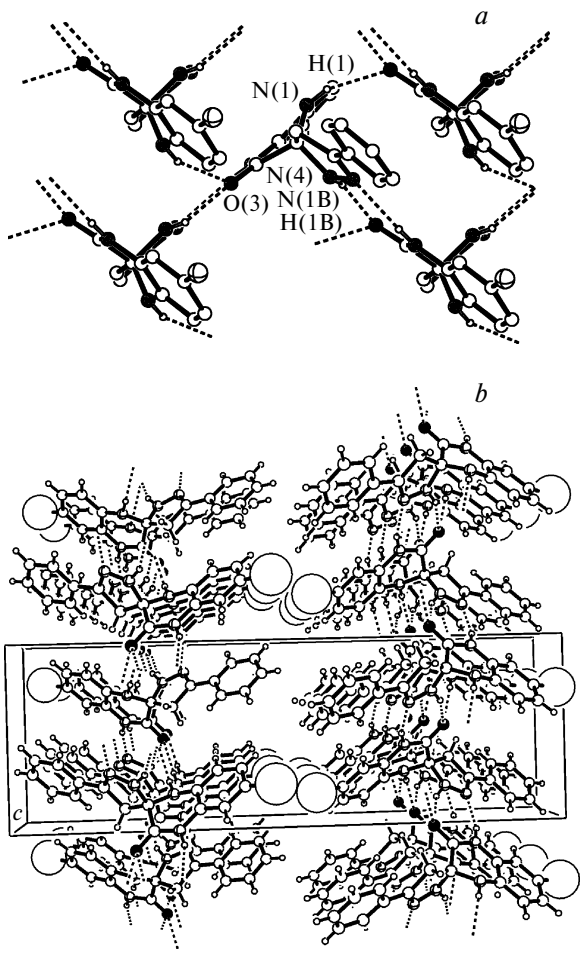
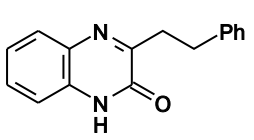
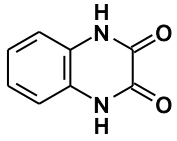


Fig. 2. (*a*) System of hydrogen bonds in the crystal of compound **5c**: the view is approximately along the 0*c* axis. The hydrogen atoms involved into the H bonds are only shown (dashed lines). (*b*) Perspective view of the **5c** crystal packing. The chlorine atoms are shown in the Van der Waals radii to highlight pseudochannels formed by them (the view is along the 0*a* axis).



6a



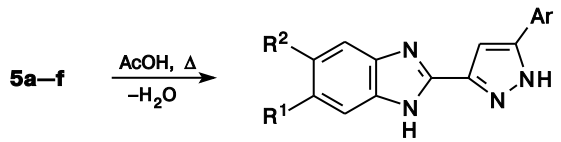
7a

Table 1. Parameters of hydrogen bonds in the crystal of compound **5c**

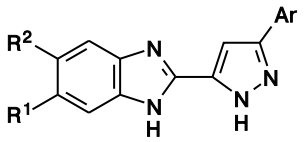
D—H...A	*d*/Å			Angle D—H—A/deg	Operation of symmetry
	D—H	H...A	D...A		
N(1)—H(1)...O(3´)	0.90(3)	2.16(3)	3.016(4)	159(3)	$1-x, 1/2+y, 3/2-z$
N(1B)—H(1B)...O(3″)	0.90(3)	2.07(3)	2.907(4)	155(3)	$-x, 1/2+y, 3/2-z$
N(4)—H(4)...N(2B″)	0.91(3)	2.26(3)	3.143(4)	162(3)	$-x, -1/2+y, 3/2-z$
C(4B)—H(4B(2))...O(3)	0.97	2.41	2.848(4)	107	—

Reflux of spiro[2-pyrazoline-5,2′-quinoxalin]-3′(4′*H*)-ones **5a—f** in acetic acid for 8 h leads to the corresponding 2-(pyrazol-3-yl)benzimidazoles **8a—f** in quantitative yields, which resulted from the acid-catalyzed rearrangement proceeding with the liberation of the water molecule (Scheme 4). As it is seen from the structures of compounds **8a—f**, formation of two new heterocyclic rings involves the C(2)—C(3)=CH—C(O)—Ar fragment of quinoxalin-2(1*H*)-ones **4a—f** and hydrazine hydrate. The ^{1}H NMR spectra of rearrangement products **8a—f** are characterized by the presence of a singlet signal for the proton H(4) of the pyrazole ring at δ 7.27—7.36 together with other signals for the protons of the phenylene fragment of the benzimidazole system at δ 7.21—8.16 and aryl substituent at position 5 of the pyrazole ring at δ 7.32—7.90. The IR spectroscopic and mass spectrometric data (see Experimental) do not contradict a suggestion on the formation of 2-(pyrazol-3-yl)benzimidazoles **8a—f** either, rather than isomeric to them 2-(pyrazol-5-yl)benzimidazoles **8′a—f**.

Scheme 4



8a—f



8′a—f

The structure of compound **8f** was established by X-ray diffraction study (Fig. 3). Molecules of **8f** crystallize with molecules of acetic acid in the ratio 1 : 2.

Benzimidazole fragment of the molecule is planar within 0.009(5) Å, whereas the planes of the pyrazole ring and its phenyl substituent form dihedral angles with the plane of the bicycle of 7.2(2) and 6.1(2)°, respectively. Thus, a molecule of **8f** on the whole is planar within 0.1 Å.

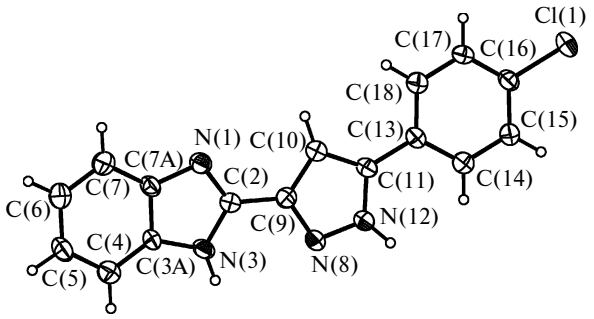


Fig. 3. Molecular geometry of compound **8f** in the crystal. Nonhydrogen atoms are represented by probability ellipsoids of thermal vibrations (p = 50%), hydrogen atoms, by spheres of arbitrary radii. Solvate molecules of acetic acid are not shown.

Due to the "classic" N—H...O and O—H...N hydrogen bonds in the crystal of pyrazolylbenzimidazole **8f**, centrosymmetric H-associates are formed, consisting of two molecules of **8f** and four molecules of acetic acid (Fig. 4). One of two independent molecules of acetic acid is involved in two hydrogen bonds only with one molecule of pyrazolylbenzimidazole ("intramolecular" H-bond), whereas the second molecule of acetic acid binds two molecules of **8f** due to the bridged H-bonds. Parameters of these hydrogen bonds are given in Table 2.

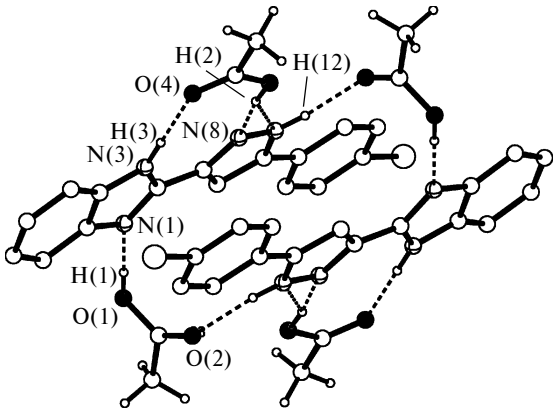


Fig. 4. Hydrogen-bound associates in the crystal of compound **8f**. Hydrogen atoms of solvate molecules and those involved in the H bonds are only shown (dashed lines).

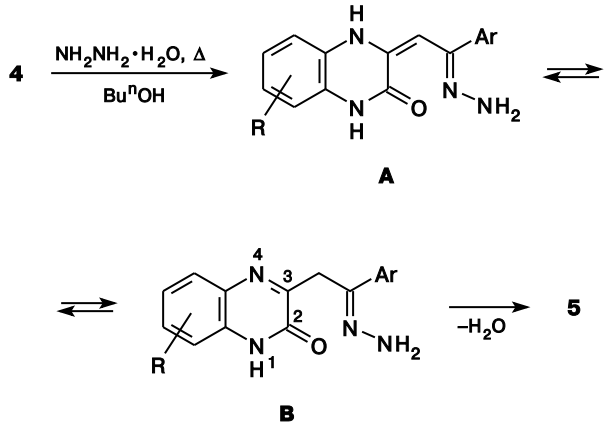
Table 2. Parameters of hydrogen bonds in the crystal of compound **8f**

D—H...A	d/Å			Angle D—H—A/deg	Operation of symmetry
	D—H	H...A	D...A		
O(1)—H(1)...N(1)	0.91(9)	1.75(8)	2.658(6)	180(11)	—
O(3)—H(2)...N(8)	1.05(6)	1.69(6)	2.732(6)	173(5)	—
O(3)—H(2)...N(12)	1.05(6)	2.48(6)	3.420(6)	148(5)	—
N(3)—H(3)...O(4)	0.87(2)	1.93(2)	2.797(6)	171(3)	—
N(12)—H(12)...O(2′)	0.88(3)	1.92(3)	2.791(6)	172(5)	$2-x$, $1-y$, $1-z$

Apparently, solvate molecules of acetic acid interfere close contacts of planar molecules. As a consequence, the distances between aromatic fragments are larger than the sum of Van der Waals radii of carbon atoms by 0.1—0.2 Å. The packing of the crystal of **8f** can be described as a parallel stacking of planar layers along the crystallographic axis 0*a*, but the distances between layers are >3.4 Å, that excludes the π—π-interactions between the aromatic systems. A low value of packing coefficient in the crystals of **8f**, 66.8%, should be also noted.

Proceeding from chemical properties of hydrazines,[16,17] ketones,[18,19] and quinoxalin-2(1*H*)-ones,[20,21] formation of spiro[2-pyrazoline-5,2′-quinoxalin]-3′(4′*H*)-ones **5** can be represented by Scheme 5. The initial step consists in nucleophilic addition of hydrazine to the carbonyl group of 3-(2-aryl-2-oxoethylidene) fragment of quinoxalin-2(1*H*)-one **4** with the formation of 3-(2-aryl-2-oxoethylidene)-3,4-dihydroquinoxalin-2(1*H*)-one hydrazone, the intermediate **A**. Tautomerization of the latter leads to the intermediate **B**, 5-*exo*-*trig*-cyclization of the intermediate **B** with subsequent nucleophilic attack by the amino group of the hydrazine fragment on the C(3) atom of quinoxalin-2(1*H*)-one gives spiro compound **5**.

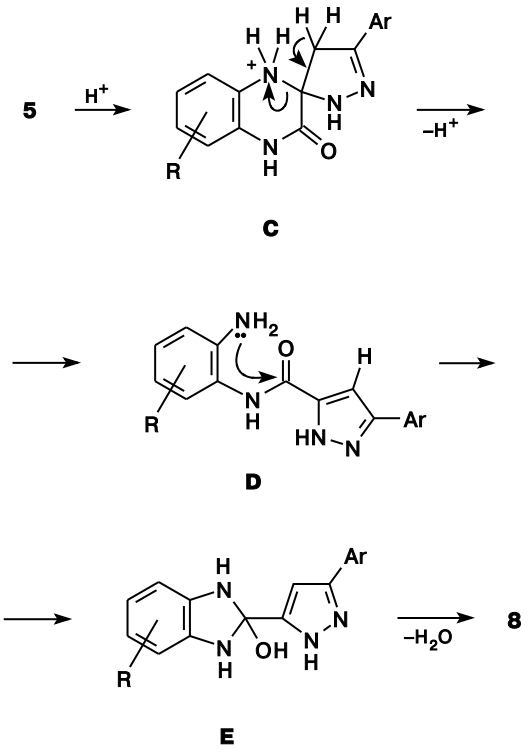
Scheme 5



Formation of the rearranged product from spiro-[2-pyrazoline-5,2′-quinoxalin]-3′(4′*H*)-ones **5** can be represented as a pyrazine ring contraction to imidazole ring resulting from the processes including a) the acid-catalyzed pyrazine ring opening in the intermediate compound **C** with the cleavage of the N(1)—C(2) bond and formation of pyrazole derivative **D**, b) intramolecular nucleophilic addition of the amine nitrogen atom to the carbonyl group with the formation of hydroxy derivative **E**, and c) elimination of water (Scheme 6).

It should be noted that formation of spiro compounds **5a—f** can be also explained by the Michael addition reaction of hydrazine hydrate[22] to more electrophilic carbon atom C(3) of the quinoxalinone in the first step with the

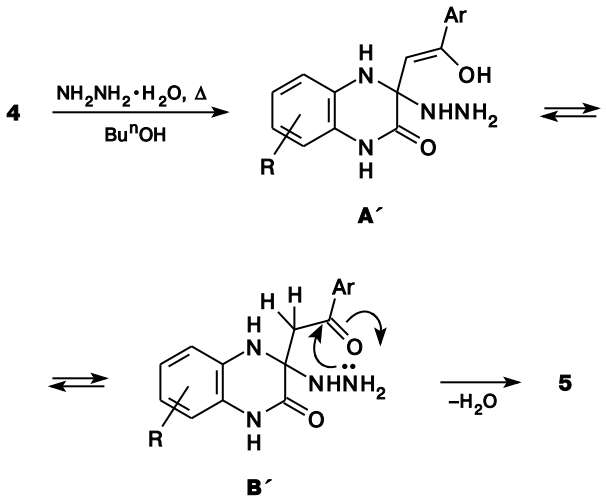
Scheme 6



formation of intermediate **A′**, also capable to exist in the keto form **B′**, in which nucleophilic attack by the amino group of the hydrazine fragment on the carbon atom of the carbonyl group of 2-aryl-2-oxoethylidene fragment takes place (Scheme 7).

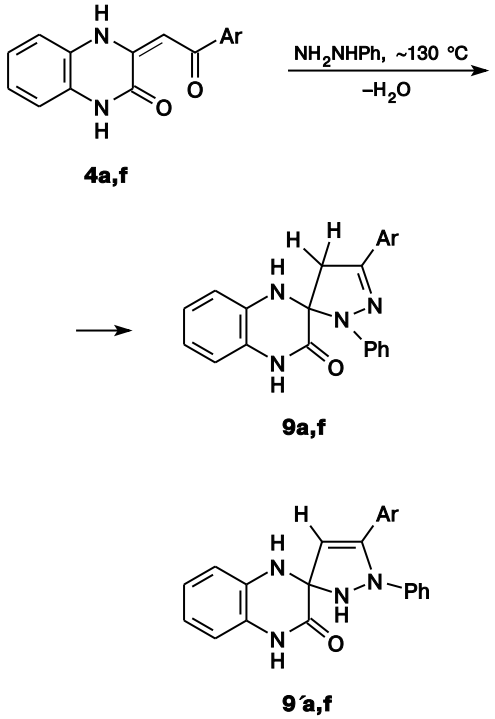
The scope of the reaction studied is not limited to the use of only hydrazine hydrate as a nucleophilic agent, since 3-(2-aryl-2-oxoethylidene)-3,4-dihydroquinoxalin-

Scheme 7



2(1*H*)-ones **4a—f** also react with phenylhydrazine, which is less strong base (pK_a = 5.27)[23] than hydrazine (pK_a = = 7.95),[23] but in this case higher temperature is required for the reaction to reach completion (Scheme 8). Carrying out the reaction in phenylhydrazine at ~130 °C is the optimum condition. Since the first step of these reactions can involve not only carbonyl carbon atom of the aroyl groups, but also imine carbon atom of the quinoxalin-2(1*H*)-one ring,[22] in the case when phenylhydrazine is used (as nonsymmetric reagent, in contrast to hydrazine hydrate), formation of two regioisomeric products of the type **9** and **9′** can be expected.

Scheme 8

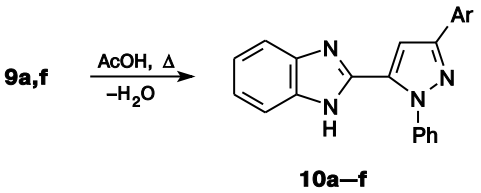


Ar = Ph (**a**), C_6H_4Cl-*p* (**f**)

The presence of two doublet signals for the AB-system at δ ~3.45 and ~3.95 with the constant $^2J \approx 17.5$ Hz in the ^{1}H NMR spectra of crude and purified products and absorption bands of stretching vibrations for the C=O and C=N groups with the frequencies 1683 and 1666 cm^{-1}, respectively, together with stretching vibrations of different NH groups at 3367 and 3314 cm^{-1} in the IR spectra, allows us to exclude structures **9′a,f** from consideration, since these compounds would have been characterized by the presence of the singlet signal for the CH proton of the pyrazoline fragment and three singlet signals for the NH groups in their ^{1}H NMR spectra.

The rearrangement of spiro[2-pyrazoline-5,2′-quinoxalin]-3′(4′*H*)-ones **9a,f** to the corresponding 2-(pyrazol-5-yl)benzimidazoles **10a,f** was carried out under conditions analogous to the rearrangement of spiro compounds **5a—f** to **8a—f** (Scheme 9).

Scheme 9



In the ^{1}H NMR spectra of compounds **10a,f**, formation of the pyrazole ring as a result of the rearrangement is characterized by the presence of a singlet signal for the phenylene proton H(4) in the same regions (δ 7.33 and 7.56) as in the spectra of compounds **8a—f** (δ 7.33, 7.28, 7.34, 7.40, 7.27, and 7.36).

The structure of compound **10a** was additionally confirmed by X-ray diffraction study (Fig. 5).

The benzimidazole fragment of the molecule is planar within 0.021(3) Å, whereas the plane of the pyrazole ring has a dihedral angle of 31.4(1)° with it. The planes of the phenyl substituents C(8)—C(17) and C(10A)—C(22) have dihedral angles of 52.2(1) and 17.3(1)°, respectively, with the plane of the central pyrazole ring of the molecule.

Due to the classic hydrogen bond of the type N—H...N, molecules of **10a** in the crystal form spirals along the screw axis 4_1 (Fig. 6, *a*). Parameters of the hydrogen bond N(3)—H(3)...N(1′): *d*(N(3)—H(3)) is 0.94(3) Å, *d*(H(3)...N(1′)) is 1.86(3) Å, *d*(N(3)...N(1′)) is 2.799(2) Å, the angle N(3)—H(3)...N(1′) is 171(2)°, operation of symmetry is 1/4 + *y*, 5/4 – *x*, 1/4 + *z*. The aromatic

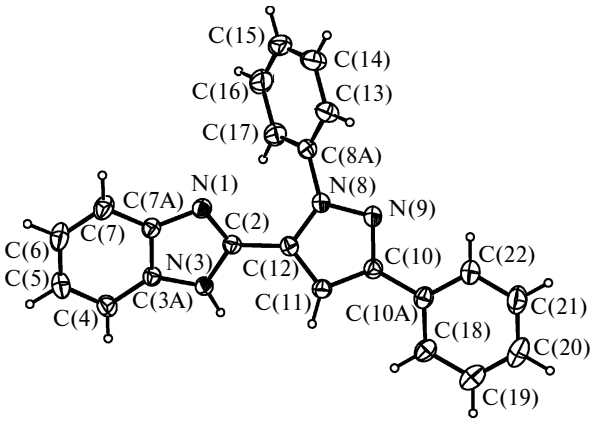


Fig. 5. Molecular geometry of the molecule of **10a** in the crystal. Nonhydrogen atoms are represented by probability ellipsoids of thermal vibrations (*p* = 50%), hydrogen atoms, by spheres of arbitrary radii.

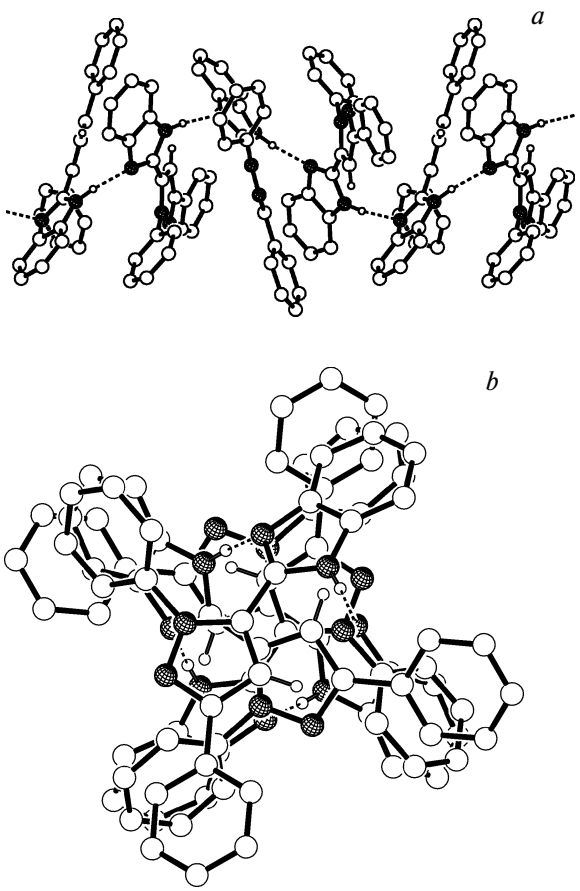


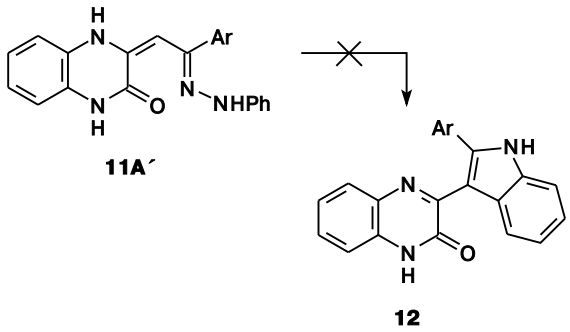
Fig. 6. Two projections of H-spiral formed in the crystal of compound **10a**. The hydrogen atoms involved into the H bonds are only shown (dashed lines): the view is along the *0b* (*a*) and 0*c* (*b*) axes.

fragments of the molecule are positioned on the external sides of the spiral cylinder supramolecular structures (Fig. 6, *a*, *b*). On the whole, the packing in the crystal is a parallel stacking of cylinders by a tetragonal type. Despite that calculations show no cavities in the crystal potentially available for additional molecule of a solvent, a coefficient of crystal packing has proved extremely low, *viz.*, 64%.

No expected intramolecular cyclization of the intermediately formed phenylhydrazones **11A´**, analogous to hydrazones **A** (see Scheme 5), according to the scheme of the Fischer reaction[24] to yield indole derivative **12** occurs (Scheme 10).

In conclusion, we have developed simple and efficient method for the synthesis of 2-(pyrazol-3-yl)benzimidazoles based on the new acid-catalyzed rearrangement of 3-aryl-1´*H*-spiro[2-pyrazoline-5,2´-quinoxalin]-3´(4´*H*)-ones, easily available by the reaction of 3-(2-aryl-2-oxoethylidene)-3,4-dihydroquinoxalin-2(1*H*)-ones with hydrazine hydrate and phenylhydrazine.

Scheme 10



Experimental

Melting points were measured on a Boetius heating stage. IR spectra were recorded on a Bruker Vector-22 Fourier spectrometer (KBr pellets). Mass spectra MALDI for compounds **8a,b,c,e,f** were recorded on an UltraFlex III MALDI TOF/TOF mass spectrometer (Bruker) using 2,5-dihydroxybenzoic acid as a matrix. ^{1}H NMR spectra for compounds **4b—e**, **5a,b**, **8a—d**, and **9f** were recorded on a Bruker MSL-400 spectrometer (400.13 MHz), for compounds **5c—f**, **8b,e,f**, **9a**, **10a,f**, on a Bruker Avance-600 spectrometer (600.13 MHz) (solutions in DMSO-d_6). Residual signal of DMSO (δ_H 2.50) was used as a reference.

3-(2-Aryl-2-oxoethylidene)-3,4-dihydroquinoxalin-2(1*H*)-ones 4a—f were synthesized according to the known procedure,[15] with compounds **4b—e** being obtained for the first time.

3-(2-Oxo-2-phenylethylidene)-3,4-dihydroquinoxalin-2(1*H*)-one (4a) was obtained from 4-benzoyl-3-hydroxy-2(5*H*)-furanone and *o*-phenylenediamine. The yield was 83%, m.p. 270—272 °C (*cf.* Ref. 15: 278—280 °C (ethanol)).

6,7-Dimethyl-3-(2-oxo-2-phenylethylidene)-3,4-dihydroquinoxalin-2(1*H*)-one (4b) was obtained from 4-benzoyl-3-hydroxy-2(5*H*)-furanone and 4,5-dimethyl-1,2-phenylenediamine. The yield was 81%, m.p. 298—299 °C. Found (%): C, 74.09; H, 5.46; N, 9.38. $C_{18}H_{16}N_2O_2$. Calculated (%): C, 73.95; H, 5.52; N, 9.58. IR, ν/cm^{-1}: 3444, 3153, 3100, 3062, 2936, 2916, 1685, 1608, 1583, 1538, 1459, 1402, 1358, 1309, 1248, 1062, 1025, 1005, 895, 863, 812, 786, 745, 707, 639, 596. ^{1}H NMR, δ: 2.21 (s, 3 H, C(7)CH_3); 2.22 (s, 3 H, C(6)CH_3); 6.78 (s, 1 H, H(1´)); 6.92 (s, 1 H, H(5)); 7.27 (s, 1 H, H(8)); 7.51—7.60 (m, 3 H, H_m, H_p); 7.97 (d, 2 H, H_o, J = 7.2 Hz); 11.94 (s, 1 H, NH).

7-Chloro-3-(2-oxo-2-phenylethylidene)-3,4-dihydroquinoxalin-2(1*H*)-one (4c) was obtained from 4-benzoyl-3-hydroxy-2(5*H*)-furanone and 4-chloro-1,2-phenylenediamine. The yield was 63%, m.p. 302—303 °C. Found (%): C, 64.46; H, 3.63; Cl, 11.92; N, 9.33. $C_{16}H_{11}ClN_2O_2$. Calculated (%): C, 64.33; H, 3.71; Cl, 11.87; N, 9.38. IR, ν/cm^{-1}: 3473, 3112, 3065, 1688, 1600, 1537, 1496, 1462, 1399, 1368, 1313, 1249, 1224, 1089, 1064, 1023, 946, 845, 815, 784, 706, 633, 603. ^{1}H NMR, δ: 6.84 (s, 1 H, H(1´)); 7.13—7.18 (m, 2 H, benzo fragment); 7.52—7.61 (m, 4 H, H_m, H_p, benzo fragment); 7.98—8.00 (m, 2 H, H_o); 12.06 (s, 1 H, NH).

6-Nitro-3-(2-oxo-2-phenylethylidene)-3,4-dihydroquinoxalin-2(1*H*)-one (4d) was obtained from 4-benzoyl-3-hydroxy-2(5*H*)-furanone and 4-nitro-1,2-phenylenediamine. The yield was 59%, m.p. 304—306 °C. Found (%): C, 62.28; H, 3.51; N, 13.61. $C_{16}H_{11}N_3O_4$. Calculated (%): C, 62.14; H, 3.58; N, 13.59. IR, ν/cm^{-1}: 3433, 3379, 3082, 2939, 1696, 1623, 1603, 1536, 1494, 1464, 1441, 1338, 1247, 1225, 1160, 1090, 1060, 1024, 875, 831, 807, 784, 746, 709, 573. ^{1}H NMR, δ: 6.89 (s, 1 H, H(1′)); 7.24 (d, 1 H, H(8), J = 8.8 Hz); 7.56—7.58 (m, 2 H, H_m); 7.62 (t, 1 H, H_p, J = 6.9 Hz); 7.97—8.02 (m, 3 H, H_o, H(7)); 8.61 (s, 1 H, H(5)); 12.41 (s, 1 H, NH); 13.29 (s, 1 H, NH).

3-[2-Oxo-2-(*p*-tolyl)ethylidene]-3,4-dihydroquinoxalin-2(1*H*)-one (4e) was obtained from 3-hydroxy-4-(4′-methylbenzoyl)-2(5*H*)-furanone and 1,2-phenylenediamine. The yield was 74%, m.p. 252—253 °C. Found (%): C, 73.46; H, 4.99; N, 10.10. $C_{17}H_{14}N_2O_2$. Calculated (%): C, 73.37; H, 5.07; N, 10.07. IR, ν/cm^{-1}: 3440, 3044, 3007, 2966, 2922, 2884, 1678, 1607, 1582, 1547, 1370, 1336, 1270, 1248, 1183, 1060, 801, 746, 570. ^{1}H NMR, δ: 2.40 (s, 3 H, Me); 6.82 (s, 1 H, H(1′)); 7.14—7.16 (m, 3 H, H(5), H(7), H(8)); 7.36 (d, 2 H, H_m, J = 8.2 Hz); 7.50—7.52 (m, 1 H, H(6)); 7.91 (d, 2 H, H_o, J = 8.2 Hz); 12.01 (s, 1 H, NH).

3-[2-(*p*-Chlorophenyl)-2-oxoethylidene]-3,4-dihydroquinoxalin-2(1*H*)-one (4f) was obtained from 4-(4′-chlorobenzoyl)-3-hydroxy-2(5*H*)-furanone and 1,2-phenylenediamine. The yield was 66%, m.p. 285—286 °C (*cf.* Ref. 15: m.p. 285—286 °C (ethanol)).

3-Phenyl-1′(*H*)-spiro[2-pyrazoline-5,2′-quinoxalin]-3′(4′*H*)-one (5a). A solution of 3,4-dihydroquinoxalin-2(1*H*)-one **4a** (0.13 g, 0.5 mmol) and $NH_2NH_2 \cdot H_2O$ (0.28 g, 5 mmol) (90%) in Bu^{n}OH (10 mL) after reflux for 16 h was kept for ~14 h. Crystals formed were filtered off, washed with EtOH (2×10 mL), and dried in air. The yield was 0.07 g (51%), m.p. 310—312 °C. The filtrate was half concentrated and kept for ~14 h at ~20 °C. Crystals of **5a** formed were filtered off, washed with EtOH (2×5 mL), dried in air. After recrystallization from MeCN, spiroquinoxaline **5a** was obtained (0.04 g, 30%). Found (%): C, 69.13; H, 4.92; N, 20.19. $C_{16}H_{14}N_4O$. Calculated (%): C, 69.05; H, 5.07; N, 20.13. IR, ν/cm^{-1}: 3445, 3318, 3261, 3080, 2960, 1664, 1617, 1604, 1504, 1446, 1413, 1377, 1356, 1312, 1218, 1062, 1002, 915, 871, 755, 735, 687. ^{1}H NMR, δ: 3.03 (d, 1 H, CH_AH_B, J = 17.4 Hz); 3.93 (d, 1 H, CH_AH_B, J = 17.4 Hz); 6.70 (dd, 1 H, H(6'), J = 7.5 Hz, J = 7.5 Hz); 6.74 (d, 1 H, H(8'), J = 7.2 Hz); 6.84 (dd, 1 H, H(7'), J = 7.5 Hz, J = 7.5 Hz); 6.85 (d, 1 H, H(5'), J = 7.5 Hz); 7.32 (br.s, 1 H, NH); 7.35 (t, 1 H, H_p, J = 7.5 Hz); 7.42 (dd, 2 H, H_m, J = 7.9 Hz, J = 7.2 Hz); 7.67 (d, 2 H, H_o, J = 7.2 Hz); 7.98 (br.s, 1 H, NH); 10.64 (br.s, 1 H, NH).

6′,7′-Dimethyl-3-phenyl-1′(*H*)-spiro[2-pyrazoline-5,2′-quinoxalin]-3′(4′*H*)-one (5b) was obtained similarly to **5a** from 3,4-dihydroquinoxalin-2(1*H*)-one **4b** (0.3 g, 1 mmol) and $NH_2NH_2 \cdot H_2O$ (0.55 g, 10 mmol) (90%). The yield was 0.232 g (76%), m.p. 237—240 °C. Found (%): C, 70.70; H, 5.88; N, 18.13. $C_{18}H_{18}N_4O$. Calculated (%): C, 70.57; H, 5.92; N, 18.29. IR, ν/cm^{-1}: 3440, 3308, 3264, 3104, 3054, 2968, 2916, 1679, 1660, 1605, 1516, 1448, 1401, 1356, 1308, 1245, 1062, 1003, 857, 753, 686. ^{1}H NMR, δ: 2.10 (s, 6 H, 2 Me); 3.01 (d, 1 H, CH_AH_B, J = 17.4 Hz); 3.90 (d, 1 H, CH_AH_B, J = 17.1 Hz); 6.54 (s, 1 H, H(8')); 6.63 (s, 1 H, H(5')); 7.04 (br.s, 1 H, NH); 7.34 (t, 1 H, H_p, J = 7.5 Hz, J = 7.2 Hz); 7.42 (dd, 2 H, H_m, J = 7.5 Hz, J = 7.2 Hz); 7.66 (d, 2 H, H_o, J = 7.2 Hz); 10.47 (br.s, 1 H, NH).

6′-Chloro-3-phenyl-1′(*H*)-spiro[2-pyrazoline-5,2′-quinoxalin]-3′(4′*H*)-one (5c) was obtained similarly to **5a** from 3,4-dihydroquinoxalin-2(1*H*)-one **4c** (0.12 g, 0.4 mmol) and $NH_2NH_2 \cdot H_2O$ (0.22 g, 4 mmol) (90%). The yield was 0.08 g (64%), m.p. 243—246 °C. Found (%): C, 61.52; H, 4.10; Cl, 11.30; N, 17.79. $C_{16}H_{13}ClN_4O$. Calculated (%): C, 61.45; H, 4.19; Cl, 11.34; N, 17.91. IR, ν/cm^{-1}: 3443, 3304, 3274, 3112, 2924, 1680, 1663, 1615, 1601, 1498, 1446, 1387, 1369, 1353, 1307, 1221, 1083, 1059, 1001, 871, 852, 812, 757, 688. ^{1}H NMR, δ: 3.05 (d, 1 H, CH_AH_B, J = 17.1 Hz); 3.91 (d, 1 H, CH_AH_B, J = 17.5 Hz); 6.73—6.75 (m, 1 H, H(8')); 6.86—6.88 (m, 2 H, H(7), NH); 7.35 (t, 1 H, H_p, J = 7.7 Hz, J = 7.2 Hz); 7.42 (dd, 2 H, H_m, J = 8.1 Hz, J = 7.2 Hz); 7.50 (s, 1 H, H(5')); 7.67 (d, 2 H, H_o, J = 7.2 Hz); 8.07 (br.s, 1 H, NH); 10.77 (br.s, 1 H, NH).

7′-Nitro-3-phenyl-1′(*H*)-spiro[2-pyrazoline-5,2′-quinoxalin]-3′(4′*H*)-one (5d) was obtained similarly to **5a** from 3,4-dihydroquinoxalin-2(1*H*)-one **4d** (0.15 g, 0.5 mmol) and $NH_2NH_2 \cdot H_2O$ (0.28 g, 5 mmol) (90%). The yield was 0.116 g (73%), m.p. 235—238 °C. Found (%): C, 59.57; H, 3.94; N, 21.52. $C_{16}H_{13}N_5O_3$. Calculated (%): C, 59.44; H, 4.05; N, 21.66. IR, ν/cm^{-1}: 3444, 3306, 3274, 1684, 1669, 1602, 1533, 1496, 1475, 1448, 1409, 1330, 1089, 880, 763, 744, 690. ^{1}H NMR, δ: 3.11 (d, 1 H, CH_AH_B, J = 17.6 Hz); 3.96 (d, 1 H, CH_AH_B, J = 17.5 Hz); 7.03 (d, 1 H, H(6'), J = 8.5 Hz); 7.38 (t, 1 H, H_p, J = 7.2 Hz); 7.44 (dd, 2 H, H_m, J = 7.7 Hz, J = 7.2 Hz); 7.60 (s, 1 H, H(8')); 7.68—7.70 (m, 3 H, H_o, H(5')); 7.97 (s, 1 H, NH); 8.21 (s, 1 H, NH); 11.30 (s, 1 H, NH).

3-(*p*-Tolyl)-1′(*H*)-spiro[2-pyrazoline-5,2′-quinoxalin]-3′(4′*H*)-one (5e) was obtained similarly to **5a** from 3,4-dihydroquinoxalin-2(1*H*)-one **4e** (0.4 g, 1.4 mmol) and $NH_2NH_2 \cdot H_2O$ (0.77 g, 14 mmol) (90%). The yield was 0.315 g (77%), m.p. 230—231 °C. Found (%): C, 69.98; H, 5.43; N, 19.05. $C_{17}H_{16}N_4O$. Calculated (%): C, 69.85; H, 5.52; N, 19.16. IR, ν/cm^{-1}: 3447, 3314, 3261, 3212, 3171, 3122, 3085, 3044, 2962, 2917, 1669, 1605, 1505, 1415, 1373, 1311, 1247, 1215, 1116, 1073, 1035, 1000, 916, 871, 812, 736. ^{1}H NMR, δ: 2.34 (s, 3 H, Me); 3.01 (d, 1 H, CH_AH_B, J = 17.1 Hz); 3.90 (d, 1 H, CH_AH_B, J = 17.1 Hz); 6.70 (dd, 1 H, H(6'), J = 7.7 Hz, J = 7.7 Hz); 6.74 (d, 1 H, H(8), J = 7.7 Hz); 6.83 (dd, 1 H, H(7), J = 7.7 Hz, J = 8.1 Hz); 6.85 (d, 1 H, H(5), J = 7.7 Hz); 7.23 (d, 2 H, H_m, J = 7.7 Hz); 7.29 (s, 1 H, NH); 7.56 (d, 2 H, H_o, J = 8.1 Hz); 7.83 (s, 1 H, NH); 10.60 (s, 1 H, NH).

3-(*p*-Chlorophenyl)-1′(*H*)-spiro[2-pyrazoline-5,2′-quinoxalin]-3′(4′*H*)-one (5f) was obtained similarly to **5a** from 3,4-dihydroquinoxalin-2(1*H*)-one **4f** (0.6 g, 2 mmol) and $NH_2NH_2 \cdot H_2O$ (1.1 g, 20 mmol) (90%). The yield was 0.454 g (73%), m.p. 235—237 °C. Found (%): C, 61.49; H, 4.09; Cl, 11.31; N, 17.84. $C_{16}H_{13}ClN_4O$. Calculated (%): C, 61.45; H, 4.19; Cl, 11.34; N, 17.91. IR, ν/cm^{-1}: 3445, 3314, 3249, 3171, 3126, 3081, 1668, 1666, 1619, 1605, 1505, 1374, 1311, 1090, 999, 824, 741, 647. ^{1}H NMR, δ: 3.02 (d, 1 H, CH_AH_B, J = 17.3 Hz); 3.91 (d, 1 H, CH_AH_B, J = 17.3 Hz); 6.71 (dd, 1 H, H(6'), J = 7.2 Hz, J = 7.7 Hz); 6.74 (d, 1 H, H(8'), J = 7.7 Hz); 6.84 (dd, 1 H, H(7), J = 7.2 Hz, J = 7.2 Hz); 6.86 (d, 1 H, H(5), J = 7.7 Hz); 7.32 (s, 1 H, NH); 7.47 (d, 2 H, H_m, J = 8.6 Hz); 7.68 (d, 2 H, H_o, J = 8.6 Hz); 8.12 (s, 1 H, NH); 10.64 (s, 1 H, NH).

2-(5-Phenyl-1*H*-pyrazol-3-yl)-1*H*-benzimidazole (8a). A solution of spiroquinoxaline **5a** (0.2 g, 0.7 mmol) in acetic acid (10 mL) after reflux for 8 h was kept for ~14 h. The solvent was evaporated *in vacuo*, a crystalline precipitate formed was

dried in air. The yield was 0.180 g (99%), m.p. 316—317 °C. Found (%): C, 73.96; H, 4.58; N, 21.50. $C_{16}H_{12}N_4$. Calculated (%): C, 73.83; H, 4.65; N, 21.52. IR, ν/cm^{-1}: 3427, 3212, 3167, 3110, 3026, 2605, 2526, 1693, 1566, 1499, 1456, 1438, 1419, 1363, 1280, 1267, 1196, 1025, 968, 889, 806, 762, 749. ^{1}H NMR, δ: 7.20—7.23 (m, 2 H, H(4), H(7)); 7.33 (s, 1 H, H(4′)); 7.40 (t, 1 H, H_p, J = 7.2 Hz, J = 7.5 Hz); 7.51 (dd, 2 H, H_m, J = 7.8 Hz, J = 7.2 Hz); 7.60 (br.s, 2 H, H(5), H(6)); 7.87 (d, 2 H, H_o, J = 7.5 Hz). MS MALDI, m/z: 261 $[MH]^+$.

5,6-Dimethyl-2-(5-phenyl-1*H*-pyrazol-3-yl)-1*H*-benzimidazole (8b) was obtained similarly to **8a** from spiroquinoxaline **5b** (0.15 g, 0.49 mmol). The yield was 0.147 g (99%), m.p. 264—265 °C. Found (%): C, 75.11; H, 5.51; N, 19.37. $C_{18}H_{16}N_4$. Calculated (%): C, 74.98; H, 5.59; N, 19.43. IR, ν/cm^{-1}: 3444, 3153, 3100, 3063, 2916, 1686, 1609, 1583, 1537, 1458, 1402, 1358, 1308, 1247, 895, 862, 812, 785, 745, 706, 638. ^{1}H NMR, δ: 2.34 (br.s, 6 H, 2 Me); 7.28 (s, 1 H, H(4′); 7.37 (br.s, 2 H, H(4), H(7); 7.39 (t, 1 H, H_p, J = 7.6 Hz, J = 7.2 Hz); 7.50 (dd, 2 H, H_m, J = 7.6 Hz, J = 7.6 Hz); 7.87 (d, 2 H, H_o, J = 7.2 Hz). MS MALDI, m/z: 289 [MH[$^+$.

6-Chloro-2-(5-phenyl-1*H*-pyrazol-3-yl)-1*H*-benzimidazole (8c) was obtained similarly to **8a** from spiroquinoxaline **5c** (0.1 g, 0.32 mmol). The yield was 0.092 g (98%), m.p. 305—307 °C. Found (%): C, 65.29; H, 3.73; Cl, 12.05; N, 19.05. $C_{16}H_{11}ClN_4$. Calculated (%): C, 65.20; H, 3.76; Cl, 12.03; N, 19.01. IR, ν/cm^{-1}: 3146, 3119, 3022, 1701, 1628, 1567, 1497, 1451, 1398, 1365, 1267, 1196, 1059, 1019, 966, 925, 807, 766. ^{1}H NMR, δ: 7.23 (dd, 1 H, H(5), J = 7.3 Hz, J = 2.1 Hz); 7.34 (s, 1 H, H(4′)); 7.41 (t, 1 H, H_p, J = 7.5 Hz); 7.52 (dd, 2 H, H_m, J = 7.8 Hz, J = 7.5 Hz); 7.58—7.62 (m, 2 H, H(4), H(7)); 7.87 (d, 2 H, H_o, J = 7.5 Hz). MS MALDI, m/z: 295 $[MH]^+$.

5-Nitro-2-(5-phenyl-1*H*-pyrazol-3-yl)-1*H*-benzimidazole (8d) was obtained similarly to **8a** from spiroquinoxaline **5d** (0.035 g, 0.1 mmol). The yield was 0.032 g (96%), m.p. 295—296 °C. Found (%): C, 63.11; H, 3.58; N, 22.88. $C_{16}H_{11}N_5O_2$. Calculated (%): C, 62.95; H, 3.63; N, 22.94. IR, ν/cm^{-1}: 3377, 3145, 1699, 1627, 1600, 1522, 1472, 1447, 1404, 1364, 1338, 1221, 1191, 1123, 1068, 1009, 964, 815, 760, 741, 692. ^{1}H NMR, δ: 7.41—7.44 (m, 2 H, H(4′), H_p); 7.53 (dd, 2 H, H_m, J = 7.8 Hz, J = 7.2 Hz); 7.71 (br.s, 1 H, H(7)); 7.90 (d, 2 H, H_o, J = 7.5 Hz); 8.16 (br.s, 2 H, H(4), H(6)); 8.55 (s, 1 H, NH); 11.93 (s, 1 H, NH). MS MALDI, m/z: 306 $[MH]^+$.

2-[5-(*p*-Tolyl)-1*H*-pyrazol-3-yl]-1*H*-benzimidazole (8e) was obtained similarly to **8a** from spiroquinoxaline **5e** (0.2 g, 0.68 mmol). The yield was 0.186 g (99%), m.p. 309—310 °C. Found (%): C, 74.55; H, 5.08; N, 20.36. $C_{17}H_{14}N_4$. Calculated (%): C, 74.43; H, 5.14; N, 20.42. IR, ν/cm^{-1}: 3231, 3145, 1690, 1510, 1448, 1422, 1366, 1280, 1267, 1190, 1025, 969, 887, 821, 798, 751, 625. ^{1}H NMR, δ: 2.37 (s, 3 H, Me); 7.21—7.22 (m, 2 H, H(4), H(7)); 7.27 (s, 1 H, H(4′)); 7.32 (d, 2 H, H_m, J = 8.1 Hz); 7.59 (br.s, 2 H, H(5), H(6)); 7.76 (d, 2 H, H_o, J = 8.1 Hz). MS MALDI, m/z: 275 $[MH]^+$.

2-[5-(*p*-Chlorophenyl)-1*H*-pyrazol-3-yl]-1*H*-benzimidazole (8f) was obtained similarly to **8a** from spiroquinoxaline **5f** (0.2 g, 0.6 mmol). The yield was 0.160 g (85%), m.p. 343—345 °C. Found (%): C, 65.27; H, 3.62; Cl, 11.99; N, 18.97. $C_{16}H_{11}ClN_4$. Calculated (%): C, 65.20; H, 3.76; Cl, 12.03; N, 19.01. IR, ν/cm^{-1}: 3435, 3228, 3159, 1701, 1648, 1492, 1448, 1415, 1352, 1272, 1194, 1092, 1014, 964, 830, 800, 754. ^{1}H NMR, δ: 7.22 (br.s, 2 H, H(4), H(7)); 7.36 (s, 1 H, H(4′)); 7.57 (d, 2 H, H_m, J = 7.9 Hz); 7.61 (br.s, 2 H, H(5), H(6)); 7.90 (d, 2 H, H_o, J = 7.9 Hz). MS MALDI, m/z: 295 $[MH]^+$.

1,3-Diphenyl-1′(*H*)-spiro[2-pyrazoline-5,2′-quinoxalin]-3′(4′*H*)-one (9a). Phenylhydrazine (2 mL) was added to 3,4-dihydroquinoxalin-2(1*H*)-one **4a** (0.1 g, 0.38 mmol) and the mixture was kept for 16 h at 130 °C, then treated with 10% aqueous HCl, and extracted with CH_2Cl_2 (2S15 mL). The organic layer was concentrated to obtain spiroquinoxaline **9a**. The yield was 0.13 g (49%), m.p. 186—188 °C. Found (%): C, 74.62; H, 5.07; N, 15.70. $C_{22}H_{18}N_4O$. Calculated (%): C, 74.56; H, 5.12; N, 15.81. IR, ν/cm^{-1}: 3449, 3315, 3058—2851, 1682, 1666, 1599, 1509, 1492, 1445, 1381, 1252, 1163, 1060, 757, 749, 691. ^{1}H NMR, δ: 3.47 (d, 1 H, CH_AH_B, J = 17.5 Hz); 3.96 (d, 1 H, CH_AH_B, J = 17.5 Hz); 6.63 (d, 1 H, H(8), J = 8.1 Hz); 6.66 (dd, 1 H, H(6), J = 7.7 Hz, J = 7.7 Hz); 6.80—6.84 (m, 3 H); 7.14—7.16 (m, 4 H); 7.40 (m, 2 H, H(*p*-NPh), NH); 7.46 (dd, 2 H, H(*m*-Ph), J = 7.7 Hz, J = 7.7 Hz); 7.77 (d, 2 H, H(*o*-Ph), J = 7.2 Hz); 10.86 (s, 1 H, NH).

3-(*p*-Chlorophenyl)-1-phenyl-1′(*H*)-spiro[2-pyrazoline-5,2′-quinoxalin]-3′(4′*H*)-one (9f) was obtained similarly to **9a** from 3,4-dihydroquinoxalin-2(1*H*)-one **4f** (0.1 g, 0.34 mmol) and phenylhydrazine (2 mL). The yield was 0.09 g (72%), m.p. 195—197 °C. Found (%): C, 68.08; H, 4.38; Cl, 9.23; N, 14.27. $C_{22}H_{17}ClN_4O$. Calculated: (%): C, 67.95; H, 4.41; Cl, 9.12; N, 14.41. IR, ν/cm^{-1}: 3425, 3055, 2922, 2852, 1671, 1599, 1493, 1379, 1251, 1091, 1010, 830, 748, 692. ^{1}H NMR, δ: 3.46 (d, 1 H, CH_AH_B, J = 17.8 Hz); 3.96 (d, 1 H, CH_AH_B, J = 18.1 Hz); 6.62—6.85 (m, 4 H); 7.13—7.17 (m, 5 H); 7.43 (s, 1 H, NH); 7.51 (d, 2 H, H(*o*-Ar), J = 8.5 Hz); 7.78 (d, 2 H, H(*m*-Ar), J = 8.5 Hz); 10.90 (s, 1 H, NH).

2-[1,3-Diphenyl-1*H*-pyrazol-5-yl]-1*H*-benzimidazole (10a). A solution of spiroquinoxaline **9a** (0.036 g, 0.1 mmol) in acetic acid (10 mL) after reflux for 8 h was kept for ~14 h. The solvent was evaporated *in vacuo*, a crystalline precipitate formed was dried in air. The yield was 0.029 g (86%), m.p. 164—167 °C. Found (%): C, 78.39; H, 4.71; N, 16.72. $C_{22}H_{16}N_4$. Calculated (%): C, 78.55; H, 4.79; N, 16.66. IR, ν/cm^{-1}: 3430, 3060, 2929, 2670, 1596, 1499, 1452, 1400, 1358, 1275, 1230, 1072, 958, 765, 746, 691. ^{1}H NMR, δ: 7.17 (br.s, 2 H, H(4), H(7)); 7.33 (s, 1 H, H(4′)); 7.33—7.35 (m, 2 H, H(5), H(6)); 7.39 (dd, 2 H, H(*m*-NPh), J = 7.7 Hz, J = 7.2 Hz); 7.42 (dd, 2 H, H(*m*-Ph), J = 7.2 Hz, J = 8.1 Hz); 7.48—7.49 (m, 4 H); 7.89 (d, 2 H, H(*o*-Ph), J = 7.2 Hz); 7.95 (s, 1 H, NH).

2-[3-(*p*-Chlorophenyl)-1-phenyl-1*H*-pyrazol-5-yl]-1*H*-benzimidazole (10f) was obtained similarly to **10a** from spiroquinoxaline **9f** (0.06 g, 0.17 mmol). The yield was 0.047 g (75%), m.p. 233—235 °C. Found (%): C, 71.14; H, 4.02; Cl, 9.61; N, 15.03. $C_{22}H_{15}ClN_4$. Calculated (%): C, 71.25; H, 4.08; Cl, 9.56; N, 15.11. IR, ν/cm^{-1}: 3434, 3057, 2963, 1597, 1498, 1451, 1419, 1353, 1275, 1229, 1091, 1014, 958, 805, 746, 691. ^{1}H NMR, δ: 7.24—7.26 (m, 2 H, H(4), H(7)); 7.44—7.51 (m, 5 H); 7.56 (s, 1 H, H(4′)); 7.57—7.59 (m, 4 H); 7.98 (d, 2 H, H(*m*-Ar), J = 8.0 Hz).

X-ray diffraction analysis of monocrystals of compounds **5c**, **8f**, and **10a** was performed in the Division of X-ray diffraction studies of the Community Center TsKP SATs on the basis of Laboratory of Diffraction Research Methods in the Institute of Organic and Physical Chemistry of the Kazan Scientific Center of the Russian Academy of Sciences. Crystallographic characteristics of compounds, parameters of experiments and structural refinements are given in Table 3. The X-ray diffraction experiment of crystals of **5c** and **8f** was carried out on a SMART Apex II automatic three-circle diffractometer (graphite monochromator, λ(Mo-Kα) = 0.71073 Å, at the temperature of

Table 3. Crystal parameters of compounds **5c**, **8f**, **10a** and conditions of X-ray diffraction experiments

Parameter	**5c**	**8f**	**10a**
Color, habit	Colorless, prismatic form	Rose, needle-like	Colorless, prismatic form
Molecular formula	$C_{16}H_{13}ClN_4O$	$C_{16}H_{11}ClN_4$, 2 ($C_2H_4O_2$)	$C_{22}H_{16}N_4$
Molecular weight	312.75	414.84	336.39
Crystal system	Orthorhombic	Monoclinic	Tetragonal
Space group	$P2_12_12_1$	$P2_1/n$	$I4_1/a$
a/Å	5.3749(9)	7.201(5)	22.0018(10)
b/Å	9.6037(15)	18.339(13)	22.0018(10)
c/Å	28.390(4)	15.269(11)	14.9106(9)
β/deg	—	92.638(10)	—
V/Å^3	1465.5(4)	2014(2)	7217.9(6)
Z	4	4	16
d_{calc}/g cm^{-3}	1.418	1.368	1.238
Absorption coefficient/cm^{-1}	2.68 (μ-Mo)	2.24 (μ-Mo)	5.94 (μ-Cu)
Allowance for absorption	Multi-scan	Multi-scan	Multi-scan
Irradiation (λ/Å)	Mo-Kα (0.71073)	Mo-Kα (0.71073)	Cu-Kα (1.54184)
F(000)	648	864	2816
Number of measured reflections	9274	16074	22636
R_{int}	0.0825	0.2344	0.0957
Number of observed independent reflections with $I > 2\sigma(I)$	1516	1404	1812
Values of divergence factors, $I > 2\sigma(I)$	$R = 0.0508$, $R_w = 0.0924$	$R = 0.0692$, $R_w = 0.1259$	$R = 0.0432$, $R_w = 0.1007$
Goodness of fit	0.925	0.965	0.998
Number of refined parameters	221	281	240
Region of measurements on indices	$-7 \le h \le 6$, $-11 \le k \le 12$, $-37 \le l \le 37$	$-9 \le h \le 9$, $-23 \le k \le 23$, $-19 \le l \le 20$	$-25 \le h \le 24$, $-23 \le k \le 25$, $-17 \le l \le 14$
Residual electron density/ e Å^{-3}, ρ_{max}/ρ_{min}	0.171/−0.162	0.234/−0.184	0.124/−0.139

296 K), of crystal of **10a**, on a Kappa Apex automatic four-circle diffractometer (graphite monochromator, λ(Cu—Kα) = = 1.54184 Å, at the temperature of 293 K). Collection and processing of the data and refinement of parameters of a unit cell were performed using the APEX2 program,[25] allowance for absorption was made using the SADABS program.[26] The structures were solved by the direct method and refined by the least squares method first in isotropic, then in anisotropic approximation (for all the nonhydrogen atoms) using the SHELXTL (see Ref. 27) and WinGX programs.[28] Hydrogen atoms of the hydroxy and amine groups were found from differential raws of electron density and refined in isotropic approximation. Coordinates of the rest of hydrogen atoms were calculated based on stereochemical criteria and refined using the corresponding riding models. Analysis of intermolecular interactions and figures were performed using the PLATON program.[29] Atomic oordinates of structures **5c**, **8f**, and **10a** and their temperature parameters were deposited with the Cambridge Structural Database (http://www.ccdc.cam.ac.uk; the deposit numbers are CCDC 740339, 740340, and 740341, respectively).

This work was financially supported by the Russian Foundation for Basic Research (Project No 10-03-00413-a), the Federal Purposed Program "Study and Elaboration on Priority Direction in Development of Russian Scientific and Technical Complex in 2007—2012" (State Contract No 02.512.11.2237), and the Council on Grants at the President of the Russian Federation (Program for the State Support of PhD Young Scientists, Grant MK-4008.2008.3).

References

1. A. A. Kalinin, V. A. Mamedov, Ya. A. Levin, *Khim. Geterotsikl. Soedin.*, 2000, 995 [*Chem. Heterocycl. Compd.* (*Engl. Transl.*), 2000, **36**, 882].
2. V. A. Mamedov, A. A. Kalinin, A. T. Gubaidullin, A. V. Chernova, I. A. Litvinov, Ya. A. Levin, R. R. Shagidullin, *Izv. Akad. Nauk, Ser. Khim.*, 2004, 159 [*Russ. Chem. Bull., Int. Ed.*, 2004, **53**, 164].
3. V. A. Mamedov, A. A. Kalinin, A. T. Gubaidullin, E. A. Gorbunova, I. A. Litvinov, *Zh. Org. Khim.*, 2006, **42**, 1543 [*Russ. J. Org. Chem.* (*Engl. Transl.*), 2006, **42**, 1532].
4. A. A. Kalinin, O. G. Isaikina, V. A. Mamedov, *Khim. Geterotsikl. Soedin.*, 2007, 1532 [*Chem. Heterocycl. Compd.* (*Engl. Transl.*), 2007, **43**, 1307].

5. V. A. Mamedov, D. F. Saifina, I. Kh. Rizvanov, A. T. Gubaidullin, *Tetrahedron Lett.*, 2008, **49**, 4644.
6. V. A. Mamedov, D. F. Saifina, A. T. Gubaidullin, A. F. Saifina, I. Kh. Rizvanov, *Tetrahedron Lett.*, 2008, **49**, 6231.
7. V. A. Mamedov, D. F. Saifina, A. T. Gubaidullin, A. F. Saifina, I. Kh. Rizvanov, V. R. Ganieva, *Izv. Akad. Nauk, Ser. Khim.*, 2009, 1924 [*Russ. Chem. Bull., Int. Ed.*, 2009, **58**, 1986].
8. D. A. Horton, G. T.Bourne, M. L. Sinythe, *Chem. Rev.*, 2003, **103**, 893.
9. M. Alamgir, St. C. D. Black, N. Kumar, *Top. Heterocycl. Chem.*, 2007, **9**, 87.
10. A. R. Porcari, R. V. Devivar, L. S. Kucera, J. C. Drach, L. B. Towsend, *J. Med. Chem.*, 1998, **41**, 1252.
11. T. Rath, M. L. Morningstar, P. L. Boyer, S. M. Hughes, R. W. Buckheitjr, C. J. Michejda, *J. Med. Chem.*, 1997, **40**, 4199.
12. M. T. Migawa, J. L. Girardet, J. A. Walker, G. W. Koszalska, S. D. Chamberlain, J. C. Drach, L. B. Townsend, *J. Med. Chem.*, 1998, **41**, 1242.
13. I. Tamm, *Science*, 1957, **126**, 1235.
14. J. Mann, A. Baron, Y. Opoku-Boahen, E. Johansson, G. Parkinson, L. R. Kelland, S. Neidle, *J. Med. Chem.*, 2001, **44**, 138.
15. A. Amer, M. Ventura, H. Zimmer, *J. Heterocycl. Chem.*, 1983, **20**, 359.
16. M. Behforouz, J. L. Bolan, M. S. Flynt, *J. Org. Chem.*, 1985, **50**, 1186.
17. J. Buckingham, *Q. Rev., Chem. Soc.*, 1969, **23**, 37.
18. M. B. Smith, J. March, *Advanced Organic Chemistry: Reactions, Mechanisms, and Structure*, 5th ed., Wiley-Interscience, New York, 2001, p. 2083.
19. C. D. Gutsche, *The Chemistry of Carbonyl Compounds*, Englewood Cliffs, Prentice Hall, New York, 1967, p. 141.
20. G. W. H. Cheeseman, R. F. Cookson, *Chemistry of Heterocyclic Compounds: Condensed Pyrazines*, Wiley-Interscience, New York, 1979, **35**, p. 135.
21. V. A. Mamedov, A. A. Kalinin, V. V. Yanilkin, A. T. Gubaidullin, Sh. K. Latypov, A. A. Balandina, O. G. Isaikina, A. V. Toropchina, N. V. Nastapova, N. A. Iglamova, I. A. Litvinov, *Izv. Akad. Nauk, Ser. Khim.*, 2005, 2534 [*Russ. Chem. Bull., Int. Ed.*, 2005, **54**, 2616].
22. S. Hoz, *Acc. Chem. Res.*, 1993, **26**, 69.
23. *The Chemistry of the Hygrazo, Azo and Azoxy Groups*, Ed. S. Patai, Part I, Wiley, London, 1975, p. 154.
24. H. Ishii, *Acc. Chem. Res.*, 1981, **14**, 275.
25. *APEX2 (Version 2.1), SAINTPlus. Data Reduction and Correction Program (Version 7.31A)*, Bruker Advansed X-ray Solutions, BrukerAXS Inc., Madison, Wisconsin, USA, 2006.
26. G. M. Sheldrick, *SADABS, Program for Empirical X-ray Absorption Correction*, Bruker-Nonius, 1990—2004.
27. G. M. Sheldrick, *SHELXTL v. 6.12, Structure Determination Software Suite*, Bruker AXS, Madison, Wisconsin, USA, 2000; G. M. Sheldrick, *SHELX-97, Release 97-2*, University of Göttingen, Göttingen, 1997.
28. L. J. Farrugia, *J. Appl. Cryst.*, 1999, **32**, 837.
29. A. L. Spek, *J Appl. Cryst.*, 2003, **36**, 7.

Received November 6, 2009;
in revised form May 6, 2010