Russian Journal of Organic Chemistry, Vol. 39, No. 1, 2003, pp. 131–140. Translated from Zhurnal Organicheskoi Khimii, Vol. 39, No. 1, 2003, pp. 141–150.

Fused Nitrogen-Containing Heterocycles: IV.* 3-Benzoyl-2-oxo-1,2-dihydroquinoxaline Hydrazones and Flavazoles Derived Therefrom

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Received June 27, 2001

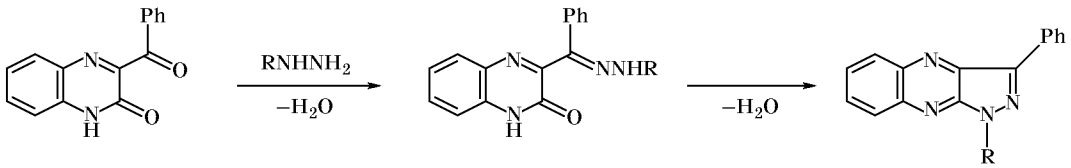
Abstract—3-Benzoyl-1,2-dihydroquinoxalin-2-one reacts with hydrazine and thiosemicarbazide to give the corresponding hydrazone and thiosemicarbazone. The reaction with arylhydrazines yields 3-(α-arylazobenzylidene)-1,2,3,4-tetrahydroquinoxalin-2-ones which are tautomeric to the respective arylhydrazones. On heating in boiling acetic acid, the products of both types undergo intramolecular cyclocondensation with formation of 3-phenylpyrazolo[3,4-*b*]quinoxalines (3-phenylflavazoles). 3-Benzoyl-1,2-dihydroquinoxalin-2-one thiosemicarbazone gives rise to flavazole structure only in the presence of methyl 3-chloro-2-oxo-3-phenylpropionate as a trap of thiocarbamoyl moiety. The cyclization of 3-(α-hydrazonobenzyl)-1,2-dihydroquinoxalin-2-one is accompanied by formation of quinoxalyl ketone azine.

The β-dicarbonyl fragment in 3-benzoyl-1,2-dihydroquinoxalin-2-one (**I**) contains both ketone and lactam carbonyl groups; therefore, this compound seems to be very promising from the viewpoint of fusion of various heterocyclic systems to its pyrazine ring. Ketone **I** has become accessible as a result of our studies [2–4]. In the present work we examined the possibility for preparation of hydrazones **II** and their subsequent intramolecular cyclization to 3-phenylpyrazolo[3,4-*b*]quinoxalines **III** (phenylflavazoles) [5].

The reactions of ketone **I** with hydrazine, phenyl-, 4-tolyl-, and 2,4-dinitrophenylhydrazines, and thiosemicarbazide afforded products whose elemental compositions were similar to those expected for hydrazones **II** (Scheme 1, Table 1). Unsubstituted hydrazone **IIa** was obtained in high yield by reaction in dioxane at room temperature. Arylhydrazones **IIb** and **IIc** were formed in boiling dioxane, and the reaction with thiosemicarbazide required heating in boiling acetic acid. The synthesis of dinitrophenylhydrazone **IIe** from less reactive and poorly soluble 2,4-dinitrophenylhydrazine was performed in a mixture of acetic amd sulfuric acids.

Judging by the presence in the IR spectra of strong absorption bands in the region 1660–1675 cm^{-1}

Scheme 1.



I **IIa–IIe** **IIIa–IIIc**

R = H (**a**), Ph (**b**), 4-MeC_6H_4 (**c**), 2,4-$(O_2N)_2C_6H_3$ (**d**), $C(S)NH_2$ (**e**).

* For communication III, see [1].

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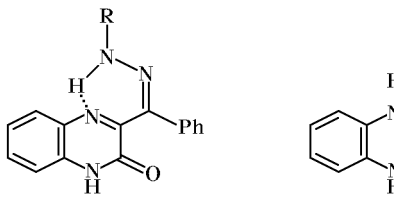
Table 1. Yields, melting points, and elemental analyses of quinoxaline derivatives **IIa**–**IIe**, **IIIa**–**IIIc**, **V**, and **VI**

Comp. no.	Yield, % (method)	mp, °C (solvent)	Found, %			Formula	Calculated, %		
			C	H	N		C	H	N
IIa	80	152–154[a]	68.05	4.58	21.32	$C_{15}H_{12}N_4O$	68.17	4.66	21.20
IIb	99	266–268 (AcOH)[b]	74.19	4.58	16.44	$C_{21}H_{16}N_4O$	74.10	4.74	16.46
IIc	80	234–236 (MeCN)	74.35	5.20	15.76	$C_{22}H_{18}N_4O$	74.56	5.12	15.81
IId	93	329–331 (*i*-PrOH)	59.41	4.03	21.16	$C_{21}H_{14}N_6O_5$	59.42	4.05	21.66
IIe[c]	89	266–269 (DMSO)	58.75	2.86	18.85	$C_{16}H_{13}N_5OS$	58.61	3.28	19.53
IIIa	80 (*a*) 28 (*b*)	262–263 (AcOH)	73.05	4.05	22.97	$C_{15}H_{10}N_4$	73.16	4.09	22.75
IIIb	78 (*a*) 74 (*b*)	235–237 (DMSO–MeCN, 2 : 1)[d]	78.34	4.57	17.08	$C_{21}H_{14}N_4$	78.24	4.38	17.38
IIIc	62 (*a*) 95 (*b*) 74 (*c*)	208–210 (DMSO–MeCN, 2 : 1)	74.72	4.67	16.74	$C_{22}H_{16}N_4$	78.55	4.79	16.66
V[e]	35	>360[a]	–	–	–	$C_{30}H_{20}N_6O_2$	–	–	–
VI[f]	81	252–254 (AcOH)	67.57	3.68	15.20	$C_{26}H_{17}N_5O_2S$	67.37	3.70	15.11

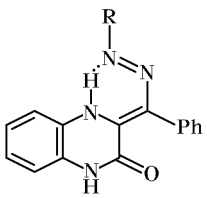
[a] The product was washed with isopropyl alcohol.
[b] Published data [6]: mp 248–250°C.
[c] Found, %: S 9.67. Calculated, %: S 9.91.
[d] Published data [7]: mp 233–234°C.
[e] Mass spectrum, *m*/*z*: 496.1661 $[M]^+$. Calculated: *M* 496.1647.
[f] Found, %: S 6.42. Calculated, %: S 6.92.

(Table 2), compounds **IIa**–**IIe**, as well as initial ketone **I** [2–4], have lactam structure. As concerns fine details of the structure of the hydrazone and pyrazine fragments, some conclusions may be drawn from analysis of the electron absorption and ^{1}H NMR spectra (Tables 2, 3).

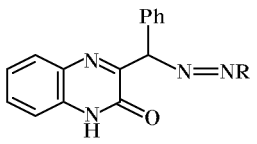
Hydrazones derived from aromatic and heterocyclic ketones [Ar_2CO, Het_2CO, HetC(O)Ar] and having at least one hydrogen atom on the amino nitrogen atom are capable of existing as the corresponding azo tautomers [8]. Hydrazones like Het(Ar)CNNHR (**II**) could give rise to a greater number of tautomers due to proton transfer not only to the imino carbon atom but also to the quinoxaline N^4 atom which is a member of the conjugated −HN−N=C−C=N− pentad. Therefore, depending on the nature of the R substituent, aggregate state, and solvent, compounds **II** can exist as hydrazone (**A**), azoenamine (**B**), and azo tautomer (**C**). For each of the above structure, *E*/*Z* isomerism with respect to the exocyclic C=N and/or N=N bonds is possible. *Z*,*Z*-Hydrazone and *E*,*E*-azoenamine tautomers can be stabilized by intramolecular hydrogen bonds (just these structures are shown for tautomers **A** and **B**).



A



B



C

Compounds **IIa**–**IIe** were assigned structures like **A**, **B**, and **C** without distinguishing stereoisomeric forms and modes of intramolecular hydrogen bonding. The structure of hydrazones derived from 3-acyl-1,2-dihydroquinoxalin-2-ones (which were synthesized by azo coupling of 3-methyl- and 3-R-CH_2-substituted 1,2-dihydroquinoxalin-2-ones or, more seldom, by reaction of 3-formyl-1,2-dihydroquinoxalin-2-ones with arylhydrazines) was discussed in [9–22]. The ^{1}H NMR spectra of **IIa**–**IIe** contain no signal from proton at sp^3-hybridized carbon atom (δ 6.0–6.5 ppm, Table 2), which is typical of 3-(α-X-benzyl)-1,2-di-

Table 2. IR and ^{1}H NMR spectra of quinoxaline derivatives **IIa**–**IIe**, **IIIa**–**IIIc**, **V**, and **VI**

Comp. no.	IR spectrum, ν, cm^{-1}	^{1}H NMR spectrum, δ, ppm (solvent)
IIa	1125, 1480, 1530, 1610, 1660, 2500–3100 br, 3205 br, 3270 br, 3380 br	7.21–7.81 m (10H, 5-H, 6-H, 7-H, C_6H_5, NH_2), 7.83 d (1H, 8-H, J = 7.96 Hz), 12.45 br.s (1H, NH) (DMSO-d_6)
IIb	1105, 1140, 1153, 1230, 1242, 1430, 1495, 1520, 1540, 1598, 1670, 2500–3100 br	6.78–6.81 m (1H, *p*-H in NPh), 7.16–7.65 m (12H, 5-H, 6-H, 7-H; CC_6H_5; *o*-H, *m*-H in NPh), 7.85 d (1H, 8-H, J = 7.28 Hz), 9.80 s (1H, 4-H), 12.48 br.s (1H, 1-H) (CD_3CN)
IIc	1103, 1230, 1255, 1525, 1623, 1675, 2350–3100 br	2.25 s (3H, Me), 7.03 d (2H, *o*-H in MeC_6H_4, J = 8.10 Hz), 7.09 d (2H, *m*-H in MeC_6H_4, J = 8.10 Hz), 7.26–7.69 m (8H, 5-H, 6-H, 7-H, C_6H_5), 7.90 d (1H, 8-H, J = 7.30 Hz), 9.28 s (1H, 4-H), 10.41 br.s (1H, 1-H) (CD_3CN)
IId	1090, 1315, 1340, 1420, 1495, 1590, 1615, 1660, 3105, 2400–3300 br	7.45–7.50 m (5H, C_6H_5), 7.72–7.79 m (3H, 12H, 5-H, 6-H, 7-H), 8.00 d.d (1H, 8-H, J = 7.13, 1.29 Hz), 8.25 d (1H, 6-H in C_6H_3, J = 9.55 Hz), 8.47 d.d (1H, 5-H in C_6H_3, J = 9.55, 8.60 Hz), 8.85 d (1H, 3-H in C_6H_3, J = 2.60 Hz), 12.28 s (1H, 4-H), 12.90 br.s (1H, 1-H) (DMSO-d_6)
IIe	1075, 1265, 1290, 1430, 1445, 1490, 1520, 1605, 1630, 1665, 2000–3200 br, 3090, 3180, 3260, 3300, 3415	7.75–7.91 m (DMSO-d_6)
IIIa	980, 1132, 1210, 1300, 1345, 1460, 1505, 1598, 2700–3300 br	7.56–7.75 m (3H, *m*-H, *p*-H), 7.95 d.d.d. (1H, 7-H, $J_{7,8}$ = 8.4, $J_{7,6}$ = 8.3, $J_{7,5}$ = 2.2 Hz), 8.05 d.d.d. (1H, 6-H, $J_{6,7}$ = 8.3, $J_{6,5}$ = 8.5, $J_{6,8}$ = 1.6 Hz), 8.27 d.d.d. (1H, 8-H, $J_{8,7}$ = 8.4, $J_{8,6}$ = 1.6, $J_{8,5}$ = 1.0 Hz), 8.45 d.d.d. (1H, 5-H, $J_{5,6}$ = 8.5, $J_{5,7}$ = 2.2, $J_{5,8}$ = 1.0 Hz), 8.70–8.73 m (2H, *o*-H), 14.28 br.s (1H, 1-H) (DMSO-d_6)
IIIb	1130, 1360, 1420, 1490, 1560, 1590	7.85–8.90 m (DMSO-d_6)
IIIc	992, 1120, 1135, 1207, 1260, 1360, 1430, 1495, 1515, 1565, 1615	2.44 s (3H, Me), 7.41 d (2H, *m*-H in C_6H_4, J = 8.34 Hz), 7.45–7.62 m (3H, *m*-H, *p*-H in C_6H_5), 7.82 d.d.d (1H, 6-H or 7-H, J = 7.71, 5.95, 1.39 Hz), 7.91 d.d.d. (1H, 7-H or 6-H, J = 7.63, 5.92, 1.36 Hz), 8.24 d.d (1H, 5-H or 8-H, J = 8.34, 1.12 Hz), 8.38 d.d (1H, 8-H or 5-H, J = 8.34, 1.14 Hz), 8.42 d (2H, *o*-H in C_6H_4, J = 8.34 Hz), 7.75–8.81 m (2H, *o*-H in Ph) (CD_3COOD)
V	1288, 1420, 1572, 1600, 1654, 1690	7.73–8.07 m (DMSO-d_6)
VI	1080, 1135, 1160, 1175, 1200, 1260, 1270, 1330, 1355, 1410, 1470, 1500, 1520, 1535, 1585, 1722	3.73 s (3H, Me), 7.45–7.70 m (8H, 5′-C_6H_5, *m*-H and *p*-H in 3-C_6H_5), 7.89 d.d (1H, 6-H or 7-H, J = 7.81, 7.39 Hz), 7.98 d.d (1H, 7-H or 6-H, J = 7.81, 7.39 Hz), 8.31 br.d (1H, 5-H or 8-H, J = 8.48 Hz), 8.41 br.d (1H, 8-H or 5-H, J = 8.50 Hz), 7.75–8.82 m (2H, *o*-H in 3-C_6H_5) (CD_3COOD)

hydroquinoxalin-2-ones (X = Cl, SCN, N_3, NHPh) [1, 2, 23]; therefore, azobenzyl structure **C** can be ruled out. Compounds **IIa**–**IIe** can be divided into two groups according to their color and electron absorption spectra (Table 3). The first group consists of hydrazone **IIa** and thiosemicarbazone **IIe**. They show in the electron absorption spectra a strong band in the long-wave UV region or short-wave visible region. The visible region of the spectrum contains neither absorption maxima nor shoulders. The second group includes red–orange products **IIb**–**IId** obtained from arylhydrazines. Their electron absorption spectra in dioxane are characterized by the presence of strong bands in the region λ 440–460 nm ($\log\varepsilon$ ~4).

Table 3. Electron absorption spectra of compounds **IIa**–**IIe**, λ_{max}, nm ($\log \varepsilon$)

Comp. no.	Dioxane	Ethanol
IIa	227 (4.41), 276.5 (4.11), 341 sh (3.72), 355 (3.76), 369 sh (3.69)	225 (4.42), 248 sh (4.09), 257 (4.07), 275 (4.05), 347 sh (3.94), 358 (3.98), 369 sh (3.94)
IIb	232 (4.55), 291 (4.21), 296 (4.22), 331 (4.29), 440 (3.69), 461 sh (3.68)	232 (4.67), 296 (4.35), 336 (4.45), 425 (3.76), 454 sh (3.69)
IIc	233 (4.55), 296 (4.26), 336 (4.29), 459 (3.73)	231 (4.57), 296 (4.29), 339 (4.36), 436 (3.74), 488 sh (3.59)
IId	226 (4.64), 286 (4.23), 365 sh (4.38), 388 (4.34), 440 sh (4.17)	
IIe[a]	315 (4.41), 361 sh (3.98)	

[a] In DMSO.

Like hydrazones of the first group, light yellow color is characteristic of 3-formyl-2-oxo-1,2-dihydroquinoxaline hydrazones obtained from *N*-methyl-*N*-phenylhydrazine and *N*-acetyl-*N*-phenylhydrazine [9]. These compounds have fixed structure **A**, while tautomers like **B** and **C**, having a chromophoric azo group, cannot be formed. Therefore, unsubstituted hydrazone **IIa** and thiosemicarbazone **IIe** were assigned structure **A**. This assignment is supported by the presence in the IR spectrum of **IIa** of three medium-intensity bands which can be attributed to stretching vibrations of the NH_2 group: 3380 (ν_{as}), 3270 (ν_{as}), and 3205 cm^{-1} (ν_s).

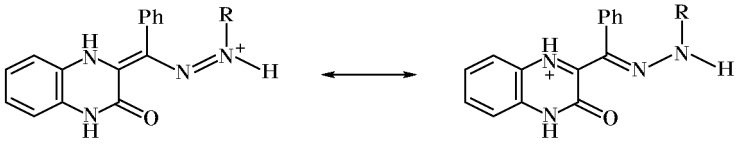
Red–orange derivatives **IIb**–**IIe** characterized by strong absorption in the visible region of the electron spectra are likely to have azoenamine structure **B** or, at least, azoenamine tautomer should be present in the isomer mixture (in Experimental, compounds **IIb**–**IIe** are named as tautomers **B**). The IR spectra of **IIb** and **IIc** contain no other NH bands than that typical of lactam moiety (a very broad absorption band with a complex shape in the region 2400–3100 cm^{-1}). Finally, in the downfield region of the ^1H NMR spectra of **IIb**–**IId**, unlike hydrazone **IIa**, we observed a broadened singlet at δ 10.4–12.9 ppm from the lactam NH group and a narrow one-proton singlet at δ 9.3–12.3 ppm. Presumably, the latter belongs to the 4-H proton in azoenamine structure **B**. An analogous signal was present in the spectra of azoenamine arylhydrazone tautomers [21]. The chemical shift of 4-H in **IIb**–**IId** is considerably influenced by the substituent in the benzene ring at the azo group. Strong electron-acceptor substituents (e.g., nitro groups in **IId**) induce a downfield shift of that signal relative to the corresponding signal in the spectra of **IIb** and **IIc** (δ 9.3–9.8 ppm). In the series of 3-formyl-2-oxoquinoxaline hydrazones, the maximal chemical shift of 4-H was observed for the 4-nitrophenyl derivative, δ 11.9 ppm [21]. The shape of the 4-H signal in the ^1H NMR spectra of **IIb**–**IId** suggests either stability of tautomer **B** under the conditions of spectral measurements or, by contrast, fast interconversion of tautomers (NH protons of different tautomers give a common signal). Distinctive features of tautomers **A** and **B** require further studying; nevertheless, all the above stated suggests structure **B** for compounds **IIb**–**IId**.

Judging by the presence in the ^1H and ^{13}C NMR spectra of signals typical of both hydrazone and enamine structures, most 3-acyl-2-oxo-1,2-dihydroquinoxaline arylhydrazones studied so far exist in solution as equilibrium mixtures of hydrazone and azoenamine tautomers **A** and **B** [12, 14–22]. By contrast, the ^1H NMR spectra of compounds **IIa**–**IId** (Table 2) indicate the presence of only one tautomer. The spectra of **IIb**–**IId** lack HNAr signal from arylhydrazone moiety, which was observed in a very weak field (δ 14.4–15.2 ppm) for tautomeric mixtures of arylhydrazones derived from 2-oxo-3-formyl-1,2-dihydroquinoxaline [21].

Acid solutions of arylhydrazones **IIb**–**IId** having structure **B**, as well as of other structurally related compounds [10, 18–20], are violet due to charge delocalization in the protonated species which may be represented by canonical structures **IV** (Scheme 2).

Like hydrazones derived from other 3-acyl-2-oxo-1,2-dihydroquinoxalines [6, 9, 22, 24–27], heating of compounds **IIa**–**IIc** in boiling acetic acid leads to intramolecular ring closure with loss of water molecule and formation of pyrazolo[3,4-*b*]quinoxalines (flavazoles) **IIIa**–**IIIc** (Scheme 1, Table 1). Dinitrophenylhydrazone **IId** did not undergo analogous transformation even in polyphosphoric acid. The intramolecular cyclization of hydrazone **IIa** was accom-

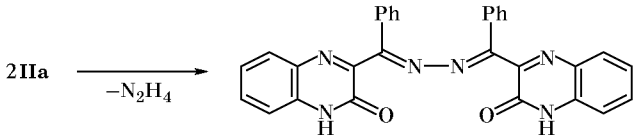
Scheme 2.



IV

panied by formation of the corresponding ketone azine **V** (Scheme 3). Compounds **IIIa**–**IIIc** can be obtained directly from ketone **I** and excess hydrazine in boiling acetic acid or by heating ketone **I** with excess arylhydrazine hydrochloride in boiling dioxane. Here, the presence of excess hydrazine prevents formation of ketone azine **V**.

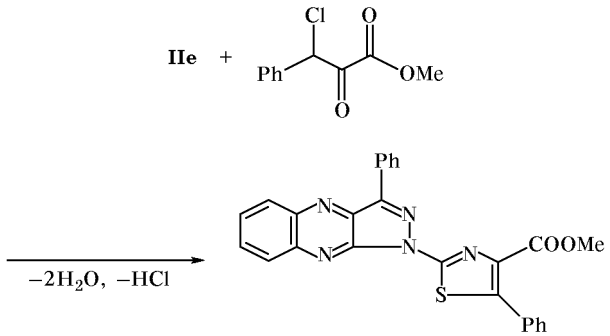
Scheme 3.



V

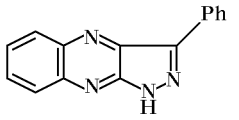
Our attempts to synthesize flavazole **IIIe** by dehydration of thiosemicarbazone **IIe**, as well as by one-step procedure from ketone **I**, were unsuccessful. Presumably, the reason is the presence of a thiocarbamoyl moiety which can be involved in various side pocesses. Nevertheless, thiosemicarbazone **IIe** was converted into the corresponding flavazole structure by heating in dioxane in the presence of methyl 3-chloro-2-oxo-3-phenylpropionate as a trap for thiocarbamoyl functionality. This compound is known to readily react with thioamides, affording thiazole derivatives [28, 29]. As a result, we obtained 1-thiazolyl-substituted pyrazoloquinoxaline **VI** in high yield (Scheme 4). The cyclization occurred especially readily in boiling dioxane, i.e., under the conditions

Scheme 4.

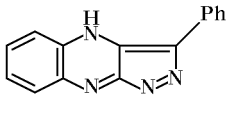


VI

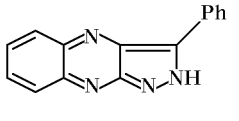
corresponding to formation of hydrazones **II**. We failed to isolate thiazolyl analog of **II** in the above reaction. The structure of flavazoles **IIIa**–**IIIc** and **VI** was confirmed by elemental analyses and spectral data (Tables 1, 2). The presence of a labile hydrogen atom in molecule **IIIa** gives rise to five possible tautomeric structures **D**–**H** where this proton is localized on N^1, N^2, N^4, N^9, or C^3.



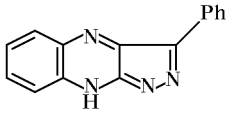
D



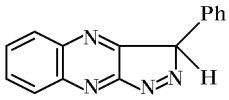
E



F



G



H

The ^{1}H NMR spectrum of a solution of **IIIa** in DMSO-d_6 (Table 2) lacks CH proton signal but contains a downfield signal at δ 14.28 ppm (NH). These data allow us to rule out tautomer **H**. The multiplicities of signals from protons of the quinoxaline fragment originate from couplings between only four nonequivalent protons in the aromatic moiety without participation of the NH proton. Therefore, structures **E** and **G** with NH proton localized in the pyrazine fragment are less probable than **D** and **F** where that proton appears in the pyrazole fragment. In order to refine the chemical shifts and coupling constants, the ^{1}H NMR spectrum of **IIIa** was sumulated using PANIC program (correlation coefficient R = 0.997); the resulting values are given in Table 2. Analogous conclusions may be drawn for a solution in $CDCl_3$.

The structure of compound **IIIa** in crystal was established by X-ray analysis. Crystals of **IIIa** are rhombic with one molecule in the symmetrically

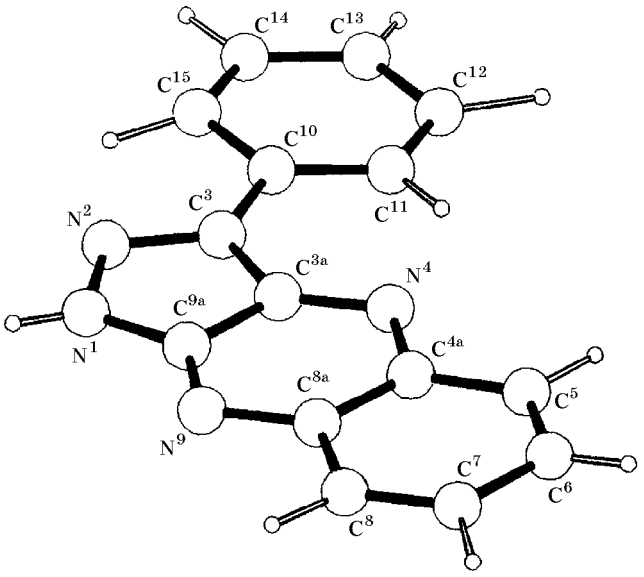


Fig. 1. Structure of the molecule of 3-phenylpyrazolo-[3,4-*b*]quinoxaline (**IIIa**).

independent part. The structure of molecule **IIIa** is shown in Fig. 1. The position of the labile hydrogen atom (on N^1) was unambiguously determined from the difference synthesis of electron density. The pyrazoloquinoxaline ring system is planar within experimental error [0.07(1) Å], and the phenyl substituent lies almost in the same plane [the corresponding dihedral angle is 6.2(2)°]. Two C–H···N intramolecular hydrogen bonds are formed between H^{15} and N^2 and between H^{11} and N^4. Also, there are two intermolecular hydrogen bonds with identical parameters: they are formed by the H^1 hydrogen atom and N^9 atom of the pyrazole fragment with the corresponding nitrogen and hydrogen atoms of two neighboring molecules which are related to the first molecule through a second-order screw axis (Fig. 2). The following hydrogen bond parameters were obtained for the systems donor(hydrohen)···acceptor (D–H···A) using the standard criterion for H-bonding, $d(D\cdots A) < R(D) + R(A) + 0.50E$, $d(H\cdots A) < R(H) + R(A) - 0.12E$, $\angle DHA > 100.00°$ (here, R is van der Waals radius of the corresponding atom).

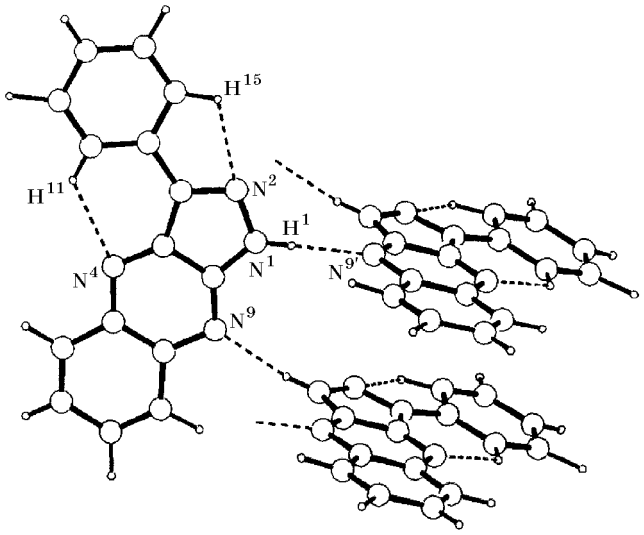


Fig. 2. Intra- and intermolecular hydrogen bonds (dashed lines) in the crystalline structure of 3-phenylpyrazolo-[3,4-*b*]quinoxaline (**IIIa**).

DHA triad	$C^{11}H^{11}N^4$	$C^{15}H^{15}N^2$	$N^1H^1N^9$
D–H, Å	0.97(4)	1.04(4)	0.86(3)
H···A, Å	2.45(3)	2.36(4)	2.05(3)
D···A, Å,	3.157(5)	2.842(6)	2.906(4)
∠DHA, deg	130(2)	107(2)	169(3)

Molecules of **IIIa** in crystal are linked by hydrogen bonds to form infinite chains along the crystallographic *x* axis which coincides with the second-order screw axis. The mode of crystal packing is strongly affected by π,π interactions between electron systems of the pyrazoloquinoxaline fragments. The resulting supramolecular structure can be described as follows: an almost planar molecule of **IIa** participates in π,π interactions with two neighboring molecules which are related to the former through +1 and –1 translation along the crystallographic *x* axis, i.e., an infinite stack of molecules along that axis is obtained. Here, the ring planes are not orthogonal to the *x* axis, and no hydrogen bonding exists between molecules in the stack. The stacks of molecules constrained through second-order screw axis are linked in pairs by hydrogen bonds (Fig. 3). The tightest crystal packing is attained via parallel laying of the H-bonded stack pairs along the 0*x* crystallographic axis. This leads to anisotropic properties of the crystal.

EXPERIMENTAL

The melting points were determined on a Boetius device. The IR spectra were measured on a UR-20 spectrometer from samples dispersed in mineral oil. The ^1H NMR spectra of compounds **IIe**, **IIIa**–**IIIc**, and **V** were recorded on a Bruker WM-250 instrument at 250.1 MHz, and of the other products, on a Bruker MSL-400 spectrometer at 400.1 MHz. The chemical shifts were measured relative to the residual proton signals of the deuterated solvent. The electron absorption spectra were measured on a Specord UV-Vis spectrophotometer. The mass spectrum of **V** (electron

Table 4. Bond lengths *d* (Å), bond angles ω (deg), and torsion angles τ (deg) in the molecule of 3-phenylpyrazolo-[3,4-*b*]quinoxaline (**IIIa**)

Bond	*d*, Å	Bond	*d*, Å	Bond	*d*, Å	Bond	*d*, Å
N^1-N^2	1.387 (5)	$C^{3a}-C^3$	1.436 (6)	C^6-H^6	0.93 (3)	$C^{11}-H^{11}$	0.97 (3)
N^1-C^{9a}	1.341 (6)	$C^{3a}-C^{9a}$	1.420 (5)	C^7-C^8	1.350 (6)	$C^{12}-C^{13}$	1.387 (8)
N^1-H^1	0.87 (3)	C^3-C^{10}	1.456 (6)	C^7-H^7	1.09 (4)	$C^{12}-H^{12}$	1.20 (5)
N^2-C^3	1.326 (5)	$C^{4a}-C^5$	1.400 (6)	$C^{8a}-C^8$	1.439 (6)	$C^{13}-C^{14}$	1.389 (8)
N^4-C^{3a}	1.322 (5)	$C^{4a}-C^{8a}$	1.418 (5)	C^8-H^8	1.07 (3)	$C^{13}-H^{13}$	0.98 (5)
N^4-C^{4a}	1.381 (5)	C^5-C^6	1.351 (6)	$C^{10}-C^{11}$	1.372 (6)	$C^{14}-C^{15}$	1.376 (7)
N^9-C^{8a}	1.361 (5)	C^5-H^5	1.03 (3)	$C^{10}-C^{15}$	1.402 (7)	$C^{14}-H^{14}$	1.07 (5)
N^9-C^{9a}	1.315 (6)	C^6-C^7	1.405 (6)	$C^{11}-C^{12}$	1.384 (7)	$C^{15}-H^{15}$	1.05 (3)
Angle	**ω, deg**	**Angle**	**ω, deg**	**Angle**	**ω, deg**	**Angle**	**ω, deg**
$N^2N^1C^{9a}$	111.8 (3)	$N^2C^3C^{10}$	120.8 (4)	$C^6C^7H^7$	123.0 (2)	$N^9C^{9a}C^{3a}$	125.5 (4)
$N^2N^1H^1$	116.0 (3)	$C^{3a}C^3C^{10}$	130.8 (3)	$C^8C^7H^7$	116.0 (2)	$C^3C^{10}C^{11}$	120.5 (4)
$C^{9a}N^1H^1$	132.0 (3)	$N^4C^{4a}C^5$	119.5 (3)	$N^9C^{8a}C^{4a}$	123.8 (4)	$C^3C^{10}C^{15}$	120.2 (4)
$N^1N^2C^3$	107.6 (3)	$N^4C^{4a}C^{8a}$	121.3 (4)	$N^9C^{8a}C^8$	118.0 (3)	$C^{11}C^{10}C^{15}$	119.2 (4)
$C^{3a}N^4C^{4a}$	114.4 (3)	$C^5C^{4a}C^{8a}$	119.2 (4)	$C^{4a}C^{8a}C^8$	118.2 (4)	$C^{10}C^{11}C^{12}$	121.4 (5)
$C^{8a}N^9C^{9a}$	112.6 (3)	$C^{4a}C^5C^6$	121.0 (4)	$C^7C^8C^{8a}$	120.1 (4)	$C^{11}C^{12}C^{13}$	119.4 (5)
$N^4C^{3a}C^3$	131.2 (3)	$C^{4a}C^5H^5$	119.0 (2)	$C^7C^8H^8$	123.0 (2)	$C^{12}C^{13}C^{14}$	119.6 (5)
$N^4C^{3a}C^{9a}$	122.4 (4)	$C^6C^5H^5$	120.0 (2)	$C^{8a}C^8H^8$	117.0 (2)	$C^{10}C^{15}C^{14}$	119.6 (4)
$C^3C^{3a}C^{9a}$	106.4 (3)	$C^5C^6C^7$	120.6 (4)	$N^1C^{9a}N^9$	128.8 (4)	$C^{13}C^{14}C^{15}$	120.7 (5)
$N^2C^3C^{3a}$	108.4 (3)	$C^5C^6H^6$	116.0 (2)	$N^1C^{9a}C^{3a}$	105.7 (4)	$C^6C^7C^8$	120.7 (4)
$C^7C^6H^6$	123.0 (2)						
Angle	**τ, deg**	**Angle**	**τ, deg**	**Angle**	**τ, deg**	**Angle**	**τ, deg**
$C^{9a}N^1N^2C^3$	0 (4)	$C^{8a}N^9C^{9a}C^{3a}$	1.9 (6)	$C^{4a}C^5C^6H^6$	179.0 (2)	$C^3C^{10}C^{11}C^{12}$	178.5 (5)
$H^1N^1N^2C^3$	178.0 (2)	$N^4C^{3a}C^3N^2$	–177.2 (4)	$H^5C^5C^6C^7$	179.0 (2)	$C^{15}C^{10}C^{11}C^{12}$	0.8 (7)
$N^2N^1C^{9a}N^9$	–179.8 (4)	$N^4C^{3a}C^3C^{10}$	3.7 (8)	$H^5C^5C^6H^6$	–1.0 (3)	$C^3C^{10}C^{15}C^{14}$	–177.0 (4)
$N^2N^1C^{9a}C^{3a}$	0.7 (5)	$C^{9a}C^{3a}C^3N^2$	1.0 (5)	$C^5C^6C^7C^8$	0.7 (7)	$C^{11}C^{10}C^{15}C^{14}$	0.6 (6)
$H^1N^1C^{9a}N^9$	2.0 (3)	$C^{9a}C^{3a}C^3C^{10}$	–178.1 (4)	$C^5C^6C^7H^7$	177.0 (2)	$C^{10}C^{11}C^{12}C^{13}$	–1.8 (8)
$H^1N^1C^{9a}C^{3a}$	–177.0 (3)	$N^4C^{3a}C^{9a}N^1$	177.4 (4)	$H^6C^6C^7C^8$	–179.0 (2)	$C^{11}C^{12}C^{13}C^{14}$	1.3 (8)
$N^1N^2C^3C^{3a}$	–0.6 (4)	$N^4C^{3a}C^{9a}N^9$	–2.1 (7)	$H^6C^6C^7H^7$	–3.0 (3)	$C^{12}C^{13}C^{14}C^{15}$	0.1 (8)
$N^1N^2C^3C^{10}$	178.6 (3)	$C^3C^{3a}C^{9a}N^1$	–1.1 (5)	$C^6C^7C^8C^{8a}$	–1.8 (6)	$C^{13}C^{14}C^{15}C^{10}$	–1.1 (7)
$C^{4a}N^4C^{3a}C^3$	179.5 (4)	$C^3C^{3a}C^{9a}N^9$	179.5 (4)	$C^6C^7C^8H^8$	–176.0 (2)	$C^5C^{4a}C^{8a}N^9$	179.6 (4)
$C^{4a}N^4C^{3a}C^{9a}$	1.5 (5)	$N^2C^3C^{10}C^{11}$	–173.9 (4)	$H^7C^7C^8C^{8a}$	–178.0 (2)	$C^5C^{4a}C^{8a}C^8$	–2.6 (6)
$C^{3a}N^4C^{4a}C^5$	–179.5 (4)	$N^2C^3C^{10}C^{15}$	3.8 (6)	$H^7C^7C^8H^8$	7.0 (3)	$C^{4a}C^5C^6C^7$	–0.6 (7)
$C^{3a}N^4C^{4a}C^{8a}$	–1.2 (6)	$C^{3a}C^3C^{10}C^{11}$	5.2 (7)	$N^9C^{8a}C^8C^7$	–179.3 (4)	$C^{8a}C^{4a}C^5C^6$	1.6 (6)
$C^{9a}N^9C^{8a}C^{4a}$	–1.5 (6)	$C^{3a}C^3C^{10}C^{15}$	–177.2 (5)	$N^9C^{8a}C^8H^8$	–4.0 (2)	$C^{8a}C^{4a}C^5H^5$	–179.0 (2)
$C^{9a}N^9C^{8a}C^8$	–179.4 (4)	$N^4C^{4a}C^5C^6$	179.9 (4)	$C^{4a}C^{8a}C^8C^7$	2.7 (6)	$N^4C^{4a}C^{8a}N^9$	1.3 (6)
$C^{8a}N^9C^{9a}N^1$	–177.4 (4)	$N^4C^{4a}C^5H^5$	0 (2)	$C^{4a}C^{8a}C^8H^8$	178.0 (2)	$N^4C^{4a}C^{8a}C^8$	179.1 (4)

impact, 70 eV) was obtained on an MKh-1310 instrument at a resolution *R* of 15000 (electron collector current 60 μA; ion source temperature 120°C; direct sample admission into the ion source using an SVP-5 direct inlet probe).

The X-ray diffraction data for a single crystal of **IIIa** were obtained on an Enraf–Nonius CAD-4 four-circle automatic diffractometer. Rhombic crystals, $C_{15}N_4H_{11}$; unit cell parameters (20°C): a = 4.8275 (6), b = 19.294 (4), c = 12.954 (3) Å; V = 1206.5 (4) Å^3;

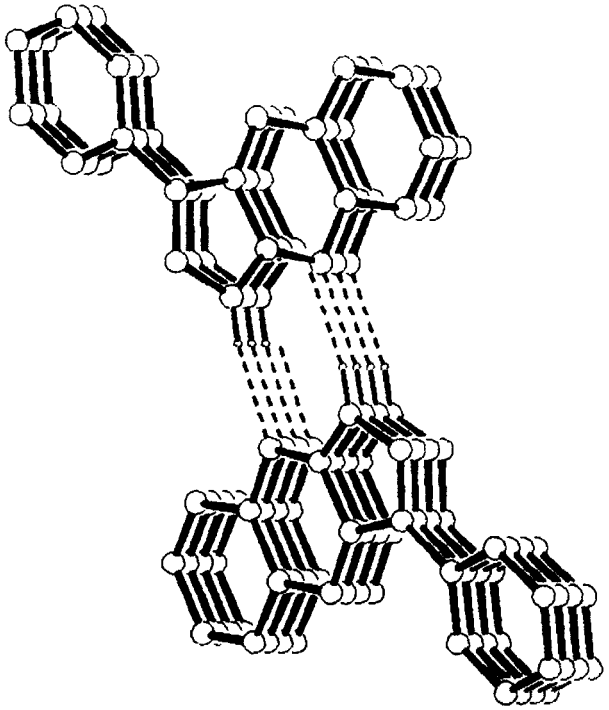


Fig. 3. Hydrogen bonded stacks of molecules in the crystalline structure of 3-phenylpyrazolo[3,4-*b*]quinoxaline (**IIIa**). Only the H^1 hydrogen atom is shown, which is involved in intermolecular contacts (dashed lines). A view approximately along the 0*x* crystallographic axis.

$Z = 4$; $\rho_{calc} = 1.36$ g/cm^3; space group $P2_12_12_1$. The unit cell parameters and intensities of 1643 reflections (749 of which with $I \geq 3\sigma$) were measured at 20°C; λMoK_α, graphite monochromator, $\omega/2\theta$ scanning, $\theta \leq 26.3°$. No reduction in intensity of three control reflections was observed during the measurements. The structure was solved by the direct method using SIR program [30] and was refined first in isotropic and then in anisotropic approximation. Hydrogen atoms were visualized from the difference series of electron density; in the final cycles of the least-squares procedure, their positions were refined in isotropic approximation. The final divergence factors were $R = 0.0419$ and $R_w = 0.042$ (from 882 reflections with $F^2 \geq 3\sigma$). All calculations were performed with the aid of MolEN software [31] on an Alpha-Station 200 computer. Some geometric parameters of molecule **IIIa** are listed in Table 4. The molecular structure and crystal packing shown in Figs. 1–3 were plotted, and the parameters of intra- and intermolecular interactions were calculated, using PLATON software [32].

When the same compound was synthesized by different methods, the identity of the products was established on the basis of their physical and spectral properties and the absence of depression of the melting point of a mixed sample.

3-(α-Hydrazonobenzyl)-1,2-dihydroquinoxalin-2-one (IIa). A suspension of 0.50 g (2.0 mmol) of ketone **I** in a mixture of 1 ml of 60% hydrazine hydrate and 6 ml of dioxane was stirred for 24 h at room temperature. The initial compound dissolved, and crystals of the product separated. The precipitate was filtered off and washed with isopropyl alcohol.

3-(α-Phenylazobenzylidene)-1,2,3,4-tetrahydroquinoxalin-2-one (IIb). A solution of 0.30 g (1.2 mmol) of ketone **I** and 0.5 ml of phenylhydrazine in 15 ml of dioxane was heated for 2 h under reflux. The mixture was cooled, and the precipitate was filtered off and washed with isopropyl alcohol.

3-[α-(4-Tolylazo)benzylidene]-1,2,3,4-tetrahydroquinoxalin-2-one (IIc). A suspension of 0.50 g (2.0 mmol) of ketone **I**, 0.63 g (4.0 mmol) of 4-tolylhydrazine hydrochloride, and 0.20 g (3.6 mmol) of potassium hydroxide in 20 ml of dioxane was heated for 1 h under reflux. The mixture was filtered, the filtrate was poured into water acidified with acetic acid, and the precipitate was filtered off and washed with water.

3-[α-(2,4-Dinitrophenylazo)benzylidene]-1,2,3,4-tetrahydroqunoxalin-2-one (IId). 2,4-Dinitrophenylhydrazine, 0.30 g (1.5 mmol), was dissolved in 6 ml of concentrated sulfuric acid, 6 ml of water was carefully added with stirring, and a boiling solution of 0.30 g (1.2 mmol) of ketone **I** in 10 ml of acetic acid was added to the warm mixture. Red crystals separated, and the mixture was left overnight. It was then diluted with 12 ml of water, and, after 1 h, the crystals were filtered off and washed with water and isopropyl alcohol.

3-(α-Thiosemicarbazonobenzyl)-1,2-dihydroquinoxalin-2-one (IIe). A solution of 0.40 g (1.60 mmol) of ketone **I** and 0.16 g (1.76 mmol) of thiosemicarbazide in 7 ml of acetic acid was heated for 3 h under reflux. The mixture was cooled, and the precipitate was filtered off and washed with isopropyl alcohol.

3-Phenylpyrazolo[3,4-*b*]quinoxaline (IIIa) and *N*,*N*′-Bis[phenyl(2-oxo-1,2-dihydroquinoxalin-3-yl)-methylene]hydrazine (V). *a.* A solution of 0.50 g (2 mmol) of ketone **I** and 1 ml of 60% hydrazine hydrate in 7 ml of acetic acid was heated for 2 h under reflux. The mixture was cooled, and the crystals of pyrazoloquinoxaline **IIIa** were filtered off and washed with isopropyl alcohol and water.

b. A solution of 0.20 g (0.76 mmol) of hydrazone **IIa** in 3 ml of acetic acid was heated for 1.5 h under

reflux. The mixture was cooled, and the precipitate (a mixture of compounds **IIIa** and **V**) was filtered off. The product mixture was heated for 2 min in 15 ml of boiling acetic acid, and the precipitate of ketone azine **V** was filtered off from the hot mixture and washed with isopropyl alcohol. The filtrate was cooled, and the crystals of pyrazoloquinoxaline **IIIa** were filtered off and washed with isopropyl alcohol and water.

1,3-Diphenylpyrazolo[3,4-*b*]quinoxaline (IIIb). *a*. A solution of 0.20 g (0.80 mmol) of ketone **I** and 0.7 ml of phenylhydrazine in 15 ml of acetic acid was heated for 9 h under reflux and was then left overnight. The precipitate was filtered off and washed with isopropyl alcohol.

b. A solution of 0.20 g (0.60 mmol) of hydrazone **IIb** in 15 ml of acetic acid was heated for 9 h under reflux; the initially dark red solution turned orange. The mixture was cooled, and the precipitate was filtered off and washed with isopropyl alcohol.

3-Phenyl-1-(4-tolyl)pyrazolo[3,4-*b*]quinoxaline (IIIc). *a*. A mixture of 1.00 g (4.0 mmol) of ketone **I**, 1.26 g (8.0 mmol) of 4-tolylhydrazine hydrochloride, and 0.5 ml of triethylamine in 50 ml of acetic acid was heated for 7 h under reflux and was then left overnight. The precipitate was filtered off and washed with water and isopropyl alcohol.

b. A solution of 0.10 g (0.28 mmol) of hydrazone **IIc** in 15 ml of acetic acid was heated for 4 h under reflux; the initially dark red solution turned orange. The mixture was cooled and left overnight. The precipitate was filtered off and washed with isopropyl alcohol.

c. A suspension of 0.80 g (3.2 mmol) of ketone **I** and 1.01 g (6.4 mmol) of 4-tolylhydrazine hydrochloride in 40 ml of dioxane was heated for 2.5 h under reflux. The mixture was filtered while hot, the filtrate was poured into water, and a solution of sodium carbonate was added. The precipitate was filtered off and washed with water and isopropyl alcohol.

Methyl 5-phenyl-2-(3-phenylpyrazolo[3,4-*b*]-quinoxalin-1-yl)thiazole-1-carboxylate (VI). A mixture of 0.30 g (1.0 mmol) of thiosemicarbazone **IIe** and 0.24 g (1.1 mmol) of methyl 3-chloro-2-oxo-3-phenylpropionate in 20 ml of dioxane was heated for 3 h under reflux and was left overnight. Crystals separated and were filtered off and washed in succession with isopropyl alcohol, a solution of sodium carbonate, water, and isopropyl alcohol again. The filtrate was poured into isopropyl alcohol to isolate an additional amount of the product.

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