# A new methodology of annelation of five- and seven-membered heterocycles to quinoxalines

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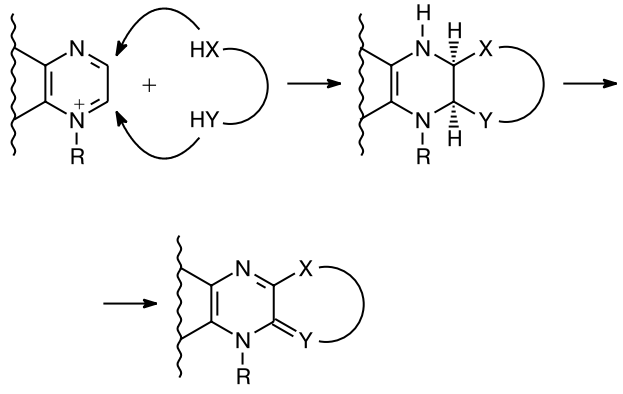
Pyrazolo[3,4-*b*]-, isoxazolo[4,5-*b*]-, benzo[2,3]-1,4-diazepino-, and benzo[2,3]-1,4-oxazepinoquinoxalines were prepared by reactions of 2-quinoxalinecarboxaldehyde with 1,2-*N*,*N*-, 1,2-*N*,*O* and 1,4-*N*,*N*- and 1,4-*N*,*O*-dinucleophiles.

**Key words:** 2-quinoxalinecarboxaldehyde, dinucleophiles, pyrazolo[3,4-b]quinoxalines, isoxazolo[4,5-*b*]quinoxalines, benzo[2,3]-1,4-diazepinoquinoxalines, benzo[2,3]-1,4-oxazepinoquinoxalines.

New methods for the construction of heterocycles have always attracted attention of organic chemists. In recent years, the research of cyclization processes of azines with 1,2-, 1,3-, or 1,4-bifunctional nucleophilic reagents has been developed successfully to allow one-step preparation of complex polycyclic heterocycles.[1—6] Quite a lot of examples of *ortho*-cyclization of 1,4-azines with dinucleophiles have been reported where cyclization products are formed through the tandem $S_N^{ipso}$—$S_N^{ipso}$ replacement of halogen atoms or other nucleofugal groups in positions 2 and 3 of the pyrazine ring.[7] The new strategies for the synthesis of fused azines developed to date are based on $A_N$—$A_N$ diaddition (Scheme 1), $A_N$—$S_N^{ipso}$ addition—substitution, $A_N$—$S_N^H$ addition—substitution, $S_N^H$-$S_N^H$ or $S_N^H$-$S_N^{ipso}$ disubstitution, and other tandem reactions.[1—6,8—10] Since the $A_N$—$A_N$ nucleophilic diaddition can be performed only for fairly π-deficient systems, the transformation of azines into cations through alkylation, protonation, or acylation (in some cases, *in situ*) is a common way of substrate activation (see Scheme 1). In addition, owing to the action of alkylating[8] or acylating[9,10] reagents, the reactions of azines with dinucleophiles furnish relatively stable cyclic adducts, which can be oxidized in some cases to give aromatic structures.[10,11]

**Scheme 1**




R = H, Alkyl, Acyl

The scope of annelation is markedly extended by using azines whose molecules contain an exocyclic electrophilic group. Cyclization can be carried out along two routes. In the first one (*A*), a dinucleophile first reacts with the exocyclic electrophilic group, and the subsequent activation of the azine induces the intramolecular reaction. In the other case (*B*), activation of the azine precedes the dinucleophile addition and the subsequent intramolecular cyclization (Scheme 2). In both cases, the process is a tandem reaction involving cyclization and intramolecular nucleophilic replacement of hydrogen, $S_N^H$. Examples of such transformation have been reported.[11—24]

This paper presents the results of the study of reactions of 2-quinoxalinecarboxaldehyde (**1**) with 1,2-*N*,*N*-, 1,2-*N*,*O*-, 1,4-*N*,*N*- and 1,4-*N*,*O*-dinucleophiles.

Since we failed to prepare the quaternary salt of quinoxalinecarboxaldehyde **1** due to the extremely low basicity of compound **1**, the subsequent study was arranged according to route *A* (see Scheme 2). As 1,2-*N*,*N*-dinucleophiles, we used monosubstituted hydrazines, which

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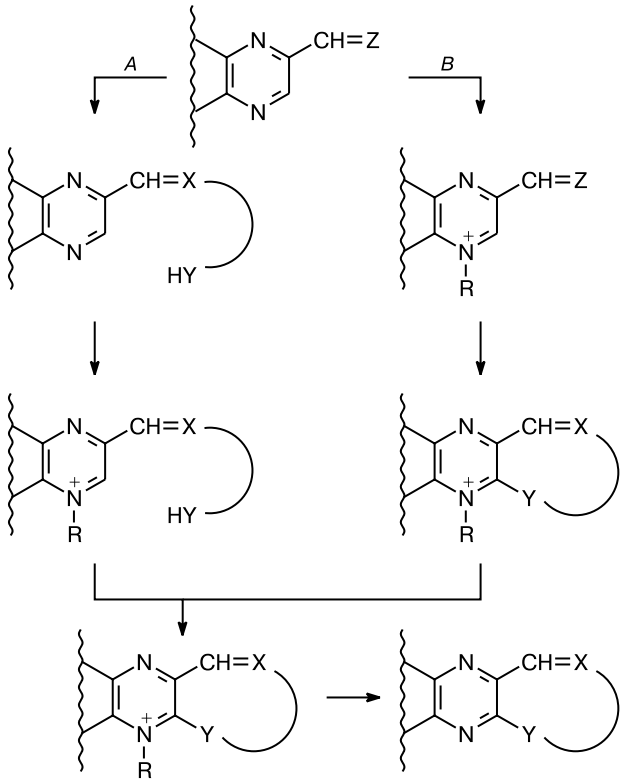
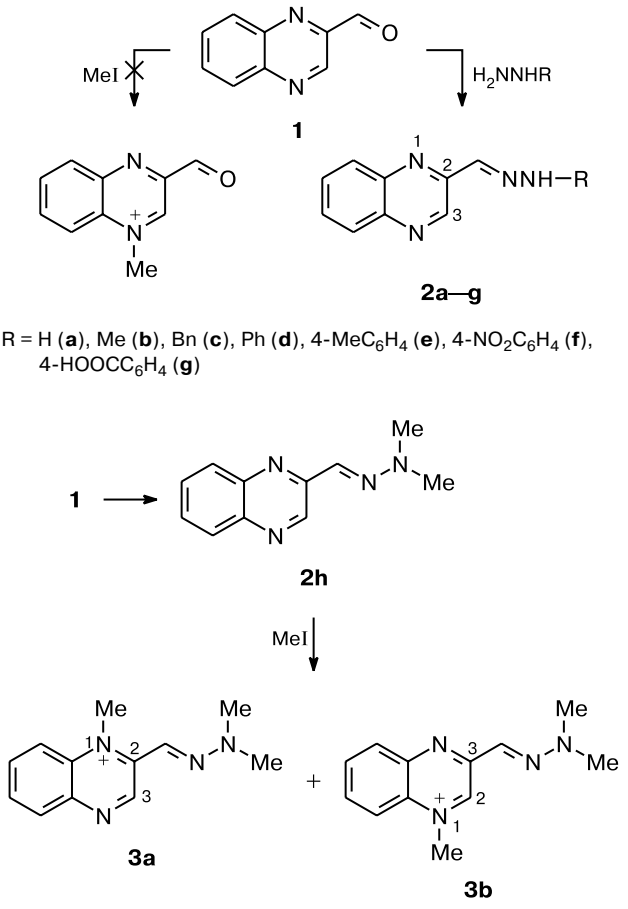
**Scheme 2**



**Scheme 3**



were condensed with aldehyde **1** to give hydrazones **2a**—**h** (Scheme 3).

The $^1$H NMR spectra of compounds **2** exhibit low-field singlets for the H(3) proton of the heterocyclic ring at 9.2—9.5 ppm and for the azomethine proton at 7.3—8.7 ppm (Table 1). With regard to the $^{13}$C NMR chemical shifts and the spin-spin coupling constants of the C(3) atom (142.9 ppm, $^1J_{C,H}$ = 186.3 Hz, $^3J_{C,H}$ = 4.0 Hz) and the azomethine carbon atom (134.3 ppm,

**Table 1.** $^1$H NMR data (DMSO-$d_6$) for compounds **2a**—**g**, **8**

| Compound | δ (*J*/Hz) | | | | | |
|---|---|---|---|---|---|---|
| | R | H(6), H(7) m, 2 H | H(5), H(8) m, 2 H | NH s, 1 H | H(3) s, 1 H | CH=N s, 1 H |
| **2a** | 7.35 (s, 2 H, $NH_2$) | 7.64—7.13 | 7.76—7.96 | — | 9.24 | 7.41 |
| **2b** | 3.00 (d, 3 H, Me, *J* = 5.0) | 7.58—7.75 | 7.81—8.99 | 8.40 (q, $J_{H,Me}$ = 5.0) | 9.20 | 7.40 |
| **2c** | 4.50 (d, 2 H, $CH_2$Ph, *J* = 5.0); 7.20—7.40 (m, 5 H, Ph) | 7.65—7.79 | 7.87—8.02 | 8.90 (t, $J_{H,CH_2}$ = 5.0) | 9.20 | 7.60 |
| **2d** | 6.85—7.35 (m, 5 H, Ph) | 7.70—7.90 | 7.90—8.10 | 11.91 | 9.51 | 8.01 |
| **2e** | 2.37 (s, 3 H, Me); 7.04—7.22 (m, 4 H, H(2′), H(3′), H(5′), H(6′)) | 7.60—7.81 | 7.88—8.01 | 11.09 | 9.45 | 7.92 |
| **2f** | 7.35 (d, 2 H, H(2′), H(6′), *J* = 9.1); 8.17 (d, 2 H, H(3′), H(5′), *J* = 9.1) | 7.76—7.89 | 8.00—8.12 | 11.80 | 9.50 | 8.20 |
| **2g** | 3.30—4.60 (br.s, 1 H, COOH); 7.30 (d, 2 H, H(2′), H(6′), *J* = 8.5); 7.92 (d, 2 H, H(3′), H(5′), *J* = 8.5) | 7.72—7.87 | 7.98—8.11 | 11.50 | 9.50 | 8.10 |
| **8** | 12.03 (s, 1 H, OH) | 7.80—8.00 | 8.05—8.25 | — | 9.35 | 8.33 |

$^1J_{C,H}$ = 166.4 Hz, $^3J_{C,H}$ = 3.7 Hz), the lower-field signal can be attributed to the carbon atoms of the pyrazine ring. This assignment is confirmed by full analysis of the $^1$H and $^{13}$C NMR spectra in terms of $^1$H—$^1$H COSY, $^{13}$C—$^1$H HETCOR, and $^1$H—$^{13}$C HMBC 2D experiments for compounds **2d**,**h** and by published data.[25]

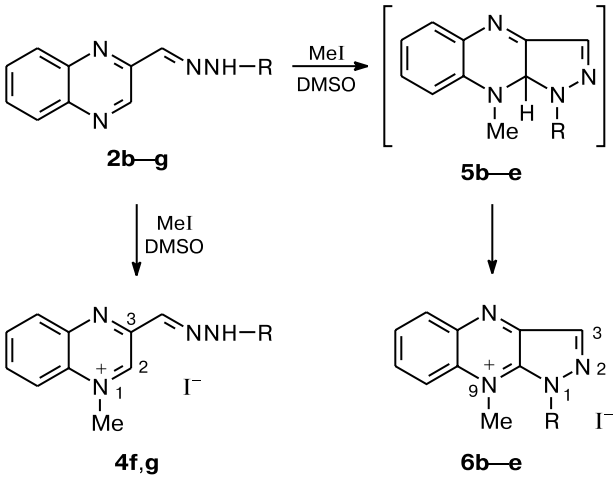
The intramolecular cyclization of hydrazones **2** requires activation of the N(4) atom of the azine ring. It was found that alkylation of *N*,*N*-dimethylhydrazone **2h** (model compound unable to undergo intramolecular cyclization) with methyl iodide results in a mixture of salts **3a** and **3b** in 1 : 9 ratio. These isomers cannot be isolated; however, by analyzing the $^1$H and $^{13}$C NMR, $^1$H—$^1$H NOESY, $^{13}$C—$^1$H HETCOR, and $^1$H—$^{13}$C HMBC spectra, we determined their ratio and spectral characteristics. Thus in the $^1$H NMR spectrum of salt **3b**, the signal of the *N*-methyl group at 4.66 ppm shows itself as a doublet ($^4J_{Me,H(2)}$ = 0.9 Hz) due to coupling with the H(2) proton, whereas in the case of the isomeric salt **3a**, the *N*-methyl group is responsible for a singlet at 4.25 ppm.

On treatment with methyl iodide in DMSO, hydrazones **2b**—**g** are transformed into two types of quaternary salts. Quaternization of hydrazones **2f**,**g** with electron-withdrawing *N*-aryl substituents affords quaternary *N*-methyl hydrazone salts **4f**,**g** (Scheme 4), but the reaction does not develop further. The $^1$H NMR spectra of salts **4f**,**g** exhibit a resonance signal due to the *N*-methyl group in the region of 4.7—4.8 ppm, but the singlets for the protons of the azomethine fragment (8.1—8.2 ppm) and the pyrazine ring (10.1 ppm) are still retained. The nucleophilicity of the NH fragment in compounds **2f**,**g** is much lower than in hydrazones **2b**—**e**; in the latter case, quaternization triggers intramolecular hydrogen displacement giving rise to pyrazolo[3,4-*b*]quinoxalinium salts **6b**—**e** *via* the intermediate σ-adducts **5b**—**e** (see Scheme 4).

In the $^1$H NMR spectra of salts **6b**—**e**, the signal for the quaternary *N*-methyl group occurs at 4.1—4.8 ppm, while the signal for the pyrazine ring proton is missing. The signal for H(3) is shifted downfield by 1.6—2.0 ppm due to the pyrazole ring formation. In conformity with known regularities of azine quaternization,[25] the $^{13}$C NMR spectrum of compound **6d** displays upfield shifts of the signals for C(8a) and C(9a) (by 10.9 and 5.3 ppm with respect to the C(4a) and C(3) signals of hydrazone **2d**); in addition, the signals of these carbon atoms are broadened due to coupling with the *N*-methyl group protons. The signal of the C(3a) atom shows itself as a doublet with $^2J_{C,CH}$ = 11.0 Hz at 145.8 ppm, whereas the signal of the corresponding C(2) atom in the starting compound **2d** is a doublet of doublets with $^2J_{C,CH}$ = 9.4 and $^2J_{C,CH}$ = 6.6 Hz recorded at 149.7 ppm. For unambiguous proof of the structure of pyrazoloquinoxalinium salts **6**, we performed an X-ray diffraction study of iodide **6d** (Fig. 1). The tricyclic system in cation **6d** was shown to be planar. The phenyl substituent linked to the pyrazole N(3) atom and the plane of the tricyclic system are arranged at a dihedral angle of 43.8°. The N(4)—C(8), N(2)—C(7), and N(1)—C(9) bond lengths in cation **6d** are 1.29, 1.30, and 1.28 Å, which is close to the usual length of the C=N multiple bonds in conjugated heterocycles;[26] this implies that the positive charge is mainly localized on the N(1) atom of the pyrazine nucleus.

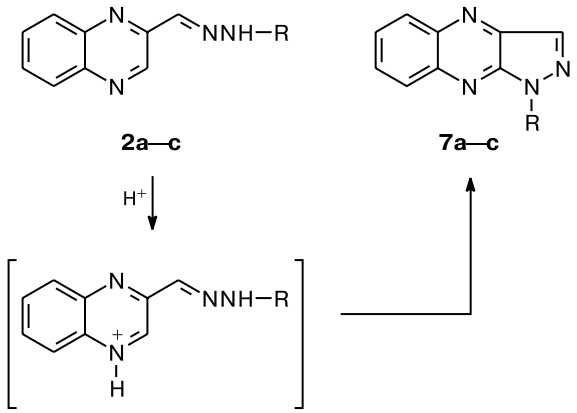
*N*-Alkylhydrazones **2a**—**c**, containing a more reactive nucleophilic center, can undergo intramolecular cyclization not only under *N*-alkylation but also under protonation of nitrogen. Thus refluxing of hydrazones **2a**—**c** in an acidic water—alcohol affords pyrazolo[3,4-*b*]quinoxalines **7a**—**c** in good yields (Scheme 5).

**Scheme 4**




R = Me (**b**), Bn (**c**), Ph (**d**), 4-$MeC_6H_4$ (**e**), 4-$NO_2C_6H_4$ (**f**), 4-$HOOCC_6H_4$ (**g**)

**Scheme 5**




R = H (**a**), Me (**b**), $CH_2Ph$ (**c**)

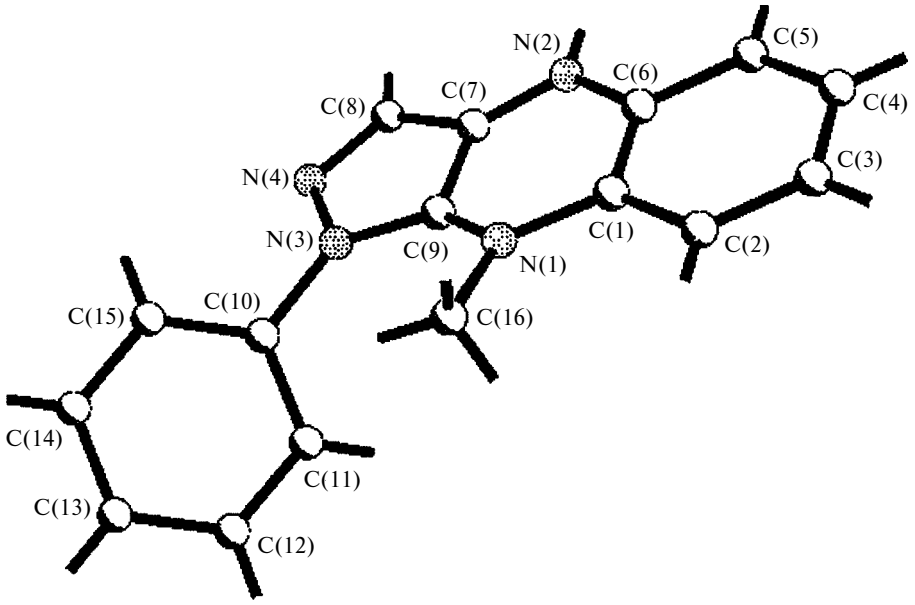
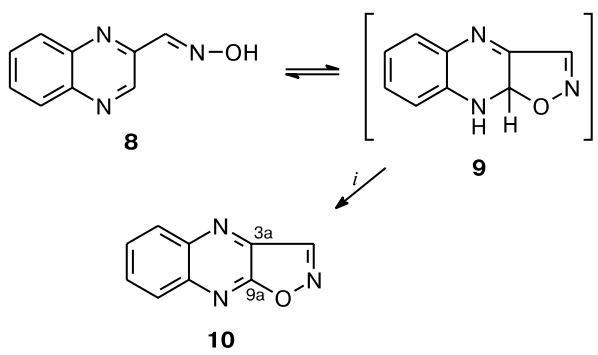



**Fig. 1.** Structure of cation **6d**.

As in the case of compounds **6b**—**e**, intramolecular cyclization is accompanied by nucleophilic displacement of hydrogen in which atmospheric oxygen serves as the oxidant, as indicated by the decrease in the reaction time observed with air bubbling. This reaction does not proceed in a neutral medium, which implies the necessity of acid catalysis. The $^1$H NMR spectra of compounds **7a**—**c** clearly show characteristic multiplets due to four protons of the benzene ring and the signal for the H(3) atom of the pyrazole ring, which shifts upfield by 1.2—1.3 ppm relative to that for the starting hydrazones (Table 2).

The annelation of an isoxazole ring to quinoxalines (Scheme 6) was accomplished by using the simplest 1,2-N,O-dinucleophile, hydroxylamine, which was trans-

**Scheme 6**

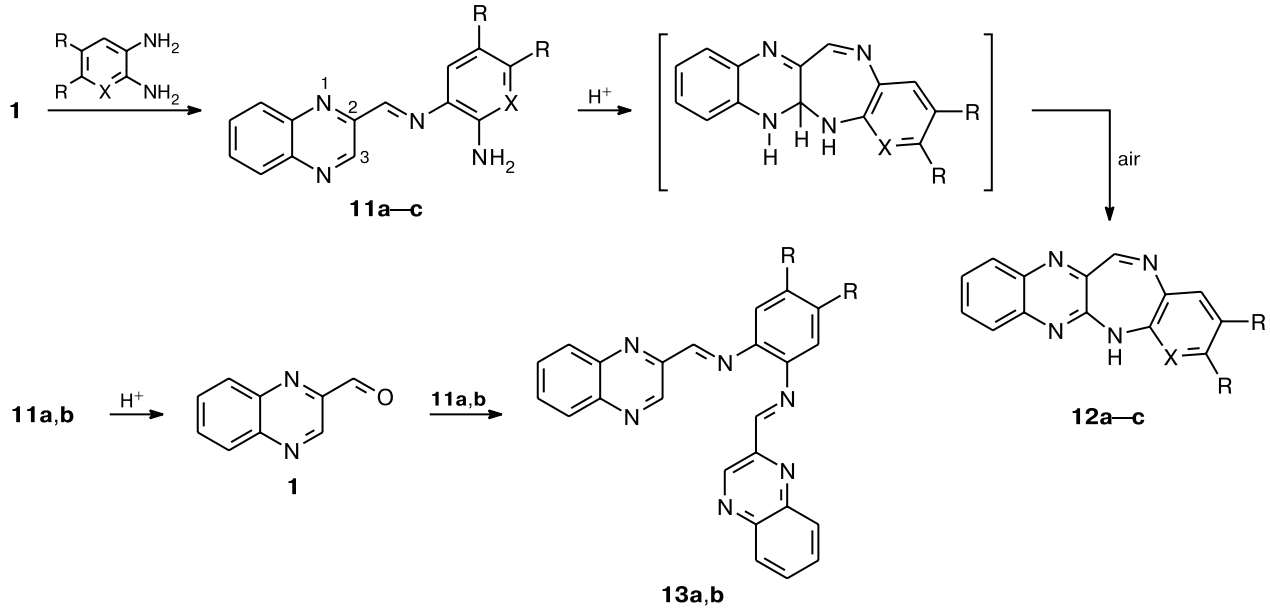



*i.* $KMnO_4$, acetone.

**Table 2.** $^1$H NMR data (DMSO-$d_6$, δ (*J*/Hz)) for 9-methylpyrazolo[3,4-*b*]-9-quinoxalinium iodides (**4b**—**e**), pyrazolo[3,4-*b*]quinoxalines (**5a**—**c**), and isoxazolo[4,5-*b*]quinoxaline (**10**)

| Compound | R | $N^+$Me s, 3 H | H(6), H(7) m, 2 H | H(5), H(8) m, 2 H | H(3) s |
|---|---|---|---|---|---|
| **4b** | 4.59 (s, 3 H, Me) | 4.83 | 8.09—8.50 | 8.55—8.78 | 9.28 |
| **4c** | 6.21 (s, 2 H, $CH_2$Ph); 7.32—7.48 (m, 5 H, Ph) | 4.65 | 8.11—8.50 | 8.62—8.76 | 9.52 |
| **4d** | 7.70—7.88 (m, 5 H, Ph) | 4.19 | 8.20—8.78 | | 9.61 |
| **4e** | 1.83—1.92 (m, 3 H, Me); 7.74 (d, 2 H, H(3′), H(5′), *J* = 7.5); 8.55 (d, 2 H, H(2′), H(6′), *J* = 7.5) | 4.18 | 8.17—8.78 | | 9.60 |
| **5a** | 14.07 (s, 1 H, NH) | — | 7.82—7.95 | 8.13—8.26 | 8.74 |
| **5b** | 4.18 (s, 3 H, Me) | — | 7.80—7.91 | 8.11—8.20 | 8.66 |
| **5c** | 5.88 (s, 2 H, $CH_2$Ph); 7.25—7.35 (m, 5 H, Ph) | — | 7.80—8.00 | 8.15—8.31 | 8.82 |
| **10** | — | — | 7.92—8.11 | 8.15—8.23 | 9.31 |

**Scheme 7**




R = H, X = CH (**a**), R = Me, X = CH (**b**), R = H, X = N (**c**)

formed into oxime **8** *via* condensation with 2-quinoxalinecarboxaldehyde.

The attempts to induce cyclization by quaternization or protonation of oxime **8** in the presence of atmospheric oxygen (by analogy with hydrazones) had not met with success until we used potassium permanganate in acetone, whereupon dihydroisoxazoloquinoxaline **9** was oxidized to give isoxazoloquinoxaline **10**.

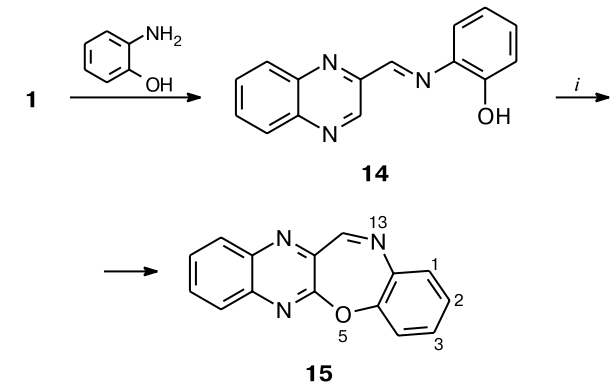
The cyclizations of quinoxalinecarboxaldehyde **1** with aromatic 1,2-diamines and 1,2-aminophenols acting as 1,4-*N*,*N*- and 1,4-*N*,*O*-dinucleophiles allow annelation of benzodiazepine and benzoxazepine fragments to quinoxalines. A vital difference between our procedure and the known condensation of 1,2-diamines with 1,3-dicarbonyl compounds[27,28] is the fact that this method allows the seven-membered ring to be closed inside the polycyclic chain, which opens new opportunities for the synthesis of biologically active compounds.

Azines **11a—c** were prepared by a standard procedure.[29] Intramolecular cyclization of compounds **11a—c** takes place on refluxing their alcohol solutions containing a mineral acid additive and results in fused diazepines **12a—c** (Scheme 7).

Cyclizations of derivatives **11a**,**b** were found to give side products, azomethines **13a**,**b**, the route leading to compounds **13a**,**b** becoming the major one with an increase in the medium acidity. This seems to be due to hydrolysis of azomethines **11a**,**b** to 2-quinoxalinecarboxaldehyde. This product enters into condensation with imines **11a**,**b** to give compounds **13a**,**b**. For compound **11c**, this process was not detected. The $^1$H NMR spectra of tetracyclic compounds **12a—c** do not exhibit signals for the H(3) protons or the amino group of the starting quinoxalines but instead, they contain a signal for the NH-group proton of the diazepine ring in the region of 10—13 ppm.

As in the case of oxime **8**, cyclization of compound **14**, resulting from condensation of aldehyde **1** with *ortho*-aminophenol, was possible only when potassium permanganate was used as the oxidant (Scheme 8). The $^{13}$C NMR spectra of compound **15** exhibit eight signals for the benzene ring carbon atoms with spin-spin coupling constants of 160—165 Hz, six signals for the quater-

**Scheme 8**




*i*. $KMnO_4$, acetone.

nary carbon atoms, and a signal for C(11a) as a doublet with a coupling constant of 189.6 Hz. The spectral data attest to the formation of benzo[2,3]-1,4-oxazepino[6,7-*b*]quinoxaline (**15**). The lack of reaction in an acid medium or oxidation with air is due to the same reasons as for oxime **8**.

Thus, on the basis of tandem reactions of quinoxalinecarboxaldehyde **1** with 1,2- and 1,4-dinucleophiles, we developed facile methods for the preparation of pyrazoloquinoxalines and their quaternary salts and fused isoxazolo-, benzodiazepino-, and oxazepinoquinoxaline structures.

## Experimental

$^1$H NMR spectra were recorded on a Bruker WM-250 spectrometer operating at 250 MHz and a Bruker DRX-400 instrument operating at 400 MHz; $^{13}$C NMR spectra were measured and 2D-experiments were done using a Bruker DRX-400 spectrometer with a frequency of 100 MHz. Tetramethylsilane was used as the internal standard. Mass spectra were run on a Varian MAT 311A spectrometer (accelerating voltage, 3 kV; cathode emission current, 300 μA, ionizing energy, 70 eV; direct sample injection to the source).

**Synthesis of 2-quinoxalinecarboxaldehyde hydrazones 2a—h (general procedure).** 2-Quinoxalinecarboxaldehyde (**1**) (1 g, 6.3 mmol) in 15 mL of ethanol was gradually added at 60—70 °C to a solution of the corresponding hydrazine or its hydrochloride (6.3 mmol or, in the case of hydrazine hydrate, 25 mmol) in 10 mL of water. The reaction mixture was kept at the given temperature for 3—5 min and cooled, and the precipitated hydrazone was filtered off and recrystallized.

$^1$H NMR spectra of compounds **2a—h** are given in Table 1.

**2-Quinoxalinecarboxaldehyde hydrazone (2a).** Yield 82%, m.p. 145—146 °C (from water). Found (%): C, 62.9; H 4.7; N, 32.4. $C_9H_8N_4$. Calculated (%): C, 62.8; H, 4.7; N, 32.5. MS (EI, 70 eV), *m/z* ($I_{rel}$ (%)): 172 $[M]^+$ (100), 171 (38), 145 (42), 144 (11), 143 (28), 118 (44), 102 (46).

**2-Quinoxalinecarboxaldehyde methylhydrazone (2b).** Yield 70%, m.p. 96—98 °C (from aqueous ethanol). Found (%): C, 64.8; H, 5.2; N, 29.6. $C_{10}H_{10}N_4$. Calculated (%): C, 64.5; H, 5.4; N, 30.0.

**2-Quinoxalinecarboxaldehyde benzylhydrazone (2c).** Yield 70%, m.p. 91—92 °C (from aqueous ethanol). Found (%): C, 73.1; H, 5.4; N, 20.9. $C_{16}H_{14}N_4$. Calculated (%): C, 73.3; H, 5.4; N, 21.4.

**2-Quinoxalinecarboxaldehyde phenylhydrazone (2d).** Yield 75%, m.p. 210—212 °C (from ethanol). Found (%): C, 72.5; H, 4.7; N, 22.5. $C_{15}H_{12}N_4$. Calculated (%): C, 72.6; H, 4.9; N, 22.6. $^{13}$C NMR (DMSO-$d_6$), δ: 112.77 (dd, C(2′), C(6′), $^1J_{C,H}$ = 160.5 Hz, $^3J_{C,H(4')}$ = 7.3 Hz); 120.31 (dd, C(4′), $^1J_{C,H}$ = 160.7 Hz, $^3J_{C,H(2')} = J_{C,H(6')}$ = 7.4 Hz); 128.35, 128.74, 128.94, 130.14 (all m, C(5), C(6), C(7), C(8)); 129.13 (dm, C(3′), C(5′), $^1J_{C,H}$ = 158.8 Hz); 134.37 (dd, HC=N, $^1J_{C,H}$ = 166.4 Hz, $^3J_{C,H(3)}$ = 3.7 Hz); 140.63 and 141.38 (both m, C(4a), C(8a)); 142.90 (dd, C(3), $^1J_{C,H}$ = 186.3 Hz, $^3J_{C,CHN}$ = 4.0 Hz); 143.95 (m, C(1′)); 149.68 (dd, C(2), $^2J_{C,CHN}$ = 9.4 Hz, $^2J_{C,C(3)H}$ = 6.6 Hz).

**2-Quinoxalinecarboxaldehyde *p*-tolylhydrazone (2e).** Yield 75%, m.p. 220—221 °C (from aqueous ethanol). Found (%): C, 73.5; H, 5.1; N, 21.1. $C_{16}H_{14}N_4$. Calculated (%): C, 73.3; H, 5.4; N, 21.4.

**2-Quinoxalinecarboxaldehyde 4′-nitrophenylhydrazone (2f).** Yield 63%, m.p. 255—256 °C (from glacial AcOH). Found (%): C, 61.3; H, 3.7; N, 23.7. $C_{15}H_{11}N_5O_2$. Calculated (%): C, 61.4; H, 3.8; N, 23.9.

**2-Quinoxalinecarboxaldehyde 4′-carboxyphenylhydrazone (2g).** Yield 87%, m.p. 338—340 °C (from glacial AcOH). Found (%): C, 65.8, H, 4.1, N, 19.1. $C_{16}H_{12}N_4O_2$. Calculated (%): C, 65.8; H, 4.1; N, 19.2.

**2-Quinoxalinecarboxaldehyde *N*,*N*-dimethylhydrazone (2h).** Yield 66%, m.p. 78—79 °C (from water). Found (%): C, 65.8; H, 6.3; N, 27.5. $C_{11}H_{12}N_4$. Calculated (%): C, 66.0; H, 6.0; N, 28.0. $^{13}$C NMR (DMSO-$d_6$), δ: 42.18 (dq, Me, $^1J_{C,H}$ = 137.2 Hz, $^3J_{C,CH_3}$ = 3.0 Hz); 127.07 (d.sept, CH=N, $^1J_{C,H}$ = 166.1 Hz, $^4J_{C,CH_3}$ = 1.3 Hz); 128.13 (dd, C(8), $^1J_{C,H}$ = 162.9 Hz, $^3J_{C,C(6)H}$ = 8.2 Hz); 128.28 (ddd, C(6), $^1J_{C,H}$ = 163.9 Hz, $^3J_{C,C(8)H}$ = 7.8 Hz, $^2J_{C,C(5)H}$ = 2.4 Hz); 128.73 (dd, C(5), $^1J_{C,H}$ = 162.5 Hz, $^3J_{C,C(7)H}$ = 7.4 Hz); 130.04 (dd, C(7), $^1J_{C,H}$ = 163.3 Hz, $^3J_{C,C(6)H}$ = 9.1 Hz); 140.19 (ddd, C(4a), $^3J_{C,C(8)H}$ = 11.4 Hz, $^3J_{C,C(3)H}$ = 9.4 Hz, $^3J_{C,C(6)H}$ = 5.5 Hz); 141.51 (dd, C(8a), $^3J_{C,C(5)H}$ = 9.4 Hz, $^3J_{C,C(7)H}$ = 5.6 Hz); 142.74 (dd, C(3), $^1J_{C,H}$ = 185.4 Hz, $^3J_{C,CHN}$ = 3.5 Hz); 150.52 (dd, C(2), $^2J_{C,CHN}$ = 9.5 Hz, $^2J_{C,C(3)H}$ = 6.3 Hz).

**Synthesis of *N*-methyl salts 3a,b, 4f,g, and 6b—e (general procedure).** A solution of the specified 2-quinoxalinecarboxaldehyde hydrazone **2** (2.0—2.5 mmol) in 2 mL of DMSO containing methyl iodide (2 mL) was heated on a water bath (40—50 °C) for 3 h. After cooling, the precipitated quaternary salt was filtered off, washed with ether, and recrystallized.

**A mixture of *N*-methyl salts 3a,b.** The major product formed upon methylation of compound **2h** was **3-dimethylhydrazonomethyl-1-methylquinoxalinium iodide (3b)**. $^1$H NMR (DMSO-$d_6$), δ: 3.31 (d, 6 H, Me, $^4J$ = 0.7 Hz); 4.66 (d, 3 H, $N^+$Me, $^4J$ = 0.9 Hz); 7.41 (s, 1 H, CH=N); 8.01 (ddd, 1 H, H(7), $^3J_{H,H(5)}$ = 8.7 Hz, $^3J_{H,H(6)}$ = 7.0 Hz, $^4J_{H,H(5)}$ =1.6 Hz); 8.08 (ddd, 1 H, H(6), *J* = 8.3 Hz, *J* = 7.0 Hz, *J* = 1.2 Hz); 8.17 (dd, 1 H, H(5), $^3J_{H,H(6)}$ = 8.3, $^4J_{H,H(5)}$ = 1.6); 8.41 (dd, 1 H, H(8), $^3J_{H,H(7)}$ = 8.7 Hz, $^4J_{H,H(6)}$ = 1.2 Hz); 9.72 (s, 1 H, H(2)). $^{13}$C NMR (DMSO-$d_6$), δ: 42.66 (br.q, Me, $^1J_{C,H}$ = 137.6 Hz); 45.49 (qd, $N^+$Me, $^1J_{C,H}$ = 145.8 Hz, $^3J_{C,H(2)}$ = 4.4 Hz); 119.29 (dd, C(8), $^1J_{C,H}$ = 169.0 Hz, $^3J_{C,C(6)H}$ = 7.5 Hz); 123.92 (dm, CH=N, $^1J_{C,H}$ = 170.8 Hz); 128.67 (m, C(8a)); 129.21 (dd, C(5), $^1J_{C,H}$ = 168.5 Hz, $^3J_{C,C(7)H}$ = 7.0 Hz); 131.72 (dd, C(7), $^1J_{C,H}$ = 167.3 Hz, $^3J_{C,C(5)H}$ = 8.6 Hz); 133.29 (dd, C(6), $^1J_{C,H}$ = 166.7 Hz, $^3J_{C,C(8)H}$ = 8.6 Hz); 140.81 (dm, C(2) $^1J_{C,H}$ = 196.4 Hz); 144.27 (dd, C(4a), $^3J_{C,C(8)H}$ = 9.3 Hz, $^3J_{C,C(6)H}$ = 5.7 Hz); 153.00 (dd, C(3), $^2J_{C,CHN}$ = 7.4 Hz, $^2J_{C,C(2)H}$ = 4.3 Hz).

The side product formed upon the methylation of compounds **2h** was **2-dimethylhydrazonomethyl-1-methylquinoxalinium iodide (3a).** $^1$H NMR (DMSO-$d_6$), δ: 3.33 (s, 6 H, Me); 3.65 (s, 3 H, $N^+$Me); 7.55 (s, 1 H, CH=N); 7.81—7.88 (m, 1 H, H(6)); 7.97—8.01 (m, 1 H, H(7)), 8.15—8.18 (m, 1 H, H(8)); 8.30 (dd, 1 H, H(5), $^3J_{H,H(6)}$ = 8.7 Hz, $^4J_{H,H(7)}$ = 1.4 Hz); 8.98 (s, 1 H, H(3)). $^{13}$C NMR (DMSO-$d_6$), δ: 37.30 (m, Me); 117.24 (dm, CH=N, $^1J_{C,H}$ = 170.8 Hz); 117.76, 129.14, 130,25, 133.10 (all m, C(5), C(6), C(7), C(8)); 128.7, 134.13 (both m, C(8a), C(4a)); 146.60 (dm, C(3), $^1J_{C,H}$ = 198.0 Hz); 155.77 (m, C(2)),

the signal of the quaternary $N^+Me$ group is in the region of the solvent signals.

**1-Methyl-3-(4-nitrophenylhydrazonomethyl)quinoxalinium iodide (4f).** Yield 67%, m.p. 314—315 °C (from AcOH—DMSO). Found (%): C, 44.1; H, 3.3; N, 16.4. $C_{16}H_{14}N_5O_2I$. Calculated (%): C, 44.2; H, 3.2; N, 16.1. $^1$H NMR (DMSO-$d_6$), δ: 4.79 (s, 3 H, Me); 7.56 (m, 2 H, H(2′), H(6′)); 8.16—8.28 (m, 2 H, H(3′), H(5′)); 8.16—8.59 (m, 4 H, H(5), H(6), H(7), H(8)); 8.31 (s, 1 H, CH=N), 10.13 (s, 1 H, H(2)); 12.26 (s, 1 H, NH). $^{13}$C NMR (DMSO-$d_6$), δ: 45.41 (qd, Me, $^1J_{C,H}$ = 146.1 Hz, $^3J_{C,H(2)}$ = 4.6 Hz); 113.06 (dm, C(2′), C(6′), $^1J_{C,H}$ = 167.1 Hz); 119.34, 129.96, 133.60 and 133.84 (all m, C(5), C(6), C(7), C(8)); 125.64 (dd, C(3′), C(5′), $^1J_{C,H}$ = 167.3 Hz, $^3J_{C,H(2')}$ = $^3J_{C,H(5')}$ = 4.9 Hz); 129.51 (m, C(4′)); 136.61 (dd, CH=N, $^1J_{C,H}$ = 172.2 Hz, $^3J_{C,H(2)}$ = 3.7 Hz); 140.54 (tt, C(4′), $^2J_{C,H(2')}$ = $^3J_{C,H(6')}$ = 9.5 Hz, $^2J_{C,H(3')}$ = $^3J_{C,H(5')}$ = 3.4 Hz); 140.99 (dm, C(2), $^1J_{C,H}$ = 201.2 Hz); 143.82 (dd, C(4a), $^3J_{C,C(8)H}$ = 8.6 Hz, $^3J_{C,C(6)H}$ = 5.5 Hz); 148.63 (m, C(8a)); 151.27 (dd, C(3), $^2J_{C,CHN}$ = 7.7 Hz, $^2J_{C,C(2)H}$ = 4.6 Hz).

**3-(4-Carboxyphenylhydrazonomethyl)-1-methyl-2-quinoxalinium iodide (4g).** Yield 62%, m.p. 360—362 °C (from AcOH—DMSO). Found (%): C, 46.7; H, 3.4; N, 12.6. $C_{17}H_{15}N_4O_2I$. Calculated (%): C, 47.0; H, 3.5; N, 12.9. $^1$H NMR (DMSO-$d_6$), δ: 4.0 (br.s, 1 H, COOH); 4.70 (s, 3 H, Me); 7.48 (d, 2 H, H(2′), H(6′), $^3J_{H,H(3')}$ = $^3J_{H,H(5')}$ = 8.6 Hz); 7.93 (d, 2 H, H(3′), H(5′), $^3J_{H,H(2')}$ = $^3J_{H,H(6')}$ = 8.6 Hz); 8.11—8.59 (m, 4 H, H(5), H(6), H(7), H(8)); 8.23 (s, 1 H, CH=N); 10.01 (s, 1 H, H(2)); 11.98 (s, 1 H, NH).

The data of the $^1$H NMR spectra of compounds **4b—e** are given in Table 2.

**1,9-Dimethylpyrazolo[3,4-*b*]-9-quinoxalinium iodide (6b).** Yield 43%, m.p. 186—187 °C (from aqueous $Pr^iOH$). Found (%): C, 40.1; H, 3.4; N, 16.9. $C_{11}H_{11}N_4I$. Calculated (%): C, 40.5; H, 3.4; N, 17.2.

**1-Benzyl-9-methylpyrazolo[3,4-*b*]-9-quinoxalinium iodide (6c).** Yield 74%, m.p. 186—187 °C (from propan-2-ol). Found (%): C, 50.4; H, 3.5; N, 13.7. $C_{17}H_{15}IN_4$. Calculated (%): C, 50.8; H 3.8; N 13.9.

**9-Methyl-1-phenylpyrazolo[3,4-*b*]-9-quinoxalinium iodide (6d).** Yield 62%, m.p. 206—208 °C (from water). Found (%): C, 49.4; H, 3.4; N, 14.2. $C_{16}H_{13}N_4I$. Calculated (%): C, 49.5; H, 3.4; N, 14.4. $^{13}$C NMR (DMSO-$d_6$), δ: 38.64 (q, Me, $^1J_{C,H}$ = 146.3 Hz); 117.76, 130.35, 131.28 and 132.53 (all m, C(5), C(6), C(7), C(8)); 127.86 (dm, C(2′), C(6′), $^1J_{C,H}$ = 166.1 Hz); 129.72 (m, C(8a)); 130.09 (dm, C(3′), C(5′), $^1J_{C,H}$ = 165.4 Hz); 132.98 (m, C(1′)); 137.60 (m, C(9a)); 137.86 (dm, C(4′), $^1J_{C,H}$ = 166.6 Hz); 140.31 (dd, C(4a), $^3J_{C,C(8)H}$ = 9.7 Hz, $^3J_{C,C(6)H}$ = 5.4 Hz); 140.37 (d, C(3), $^1J_{C,H}$ = 204.8 Hz); 145.80 (d, C(3a), $^2J_{C,H(3)}$ = 11.0 Hz).

**9-Methyl-1-(*para*-tolyl)pyrazolo[3,4-*b*]-9-quinoxalinium iodide (6e).** Yield 71%, m.p. 304—305 °C (from water). Found (%): C, 50.8; H, 3.5; N, 14.0. $C_{17}H_{15}N_4I$. Calculated (%): C, 50.8; H, 3.8; N, 13.9.

**Synthesis of pyrazolo[3,4-*b*]quinoxalines 7a,b,c (general procedure).** Dilute sulfuric acid (pH = 2) (10 mL) was added to a solution of the required hydrazone **2a—c** (2.5—3.0 mmol) in 10 mL of ethanol, and the mixture was refluxed with air bubbling for 4 h (in the case of **2a**, for 10 min). After cooling and neutralization with NaOH, the precipitate was filtered off and recrystallized.

The $^1$H NMR spectra of the products are given in Table 2.

**1*H*-Pyrazolo[3,4-*b*]quinoxaline (7a)**, yield 70%, m.p. >250 °C (from AcOH). Found (%): C, 63.1; H, 3.7; N, 32.5. $C_9H_6N_4$. Calculated (%): C, 63.5; H, 3.6; N, 32.9. MS (EI, 70 eV), *m/z* ($I_{rel}$ (%)): 170 $[M]^+$ (100), 143 (35), 116 (14).

**1-Methyl-1*H*-pyrazolo[3,4-*b*]quinoxaline (7b)**, yield 75%, m.p. 129—130 °C (from aqueous ethanol). Found (%): C, 65.3; H, 4.5; N, 30.4. $C_{10}H_8N_4$. Calculated (%): C, 65.2; H, 4.4; N, 30.4. MS (EI, 70 eV) *m/z* ($I_{rel}$ (%)): 184 $[M]^+$ (100), 183 (18), 130 (12), 129 (24), 103 (14), 102 (13). $^{13}$C NMR (DMSO-$d_6$), δ: 33.76 (q, Me, $^1J_{C,H}$ = 140.8 Hz); 127.55, 128.07, 129.65 and 130.65 (all m, C(5), C(6), C(7), C(8)); 132.70 (d, C(3), $^1J_{C,H}$ = 197.0 Hz); 136.34 (d, C(3a), $^2J_{C,H(3)}$ = 10.1 Hz); 140.32 (ddd, C(4a), $^3J_{C,C(8)H}$ = 9.9 Hz, $^3J_{C,C(6)H}$ = 5.4 Hz, $^2J_{C,C(5)H}$ = 1.3 Hz); 140.60 (dd, C(8a), $^3J_{C,C(5)H}$ = 10.4 Hz, $^3J_{C,C(7)H}$ = 5.8 Hz); 141.58 (dq, C(9a), $^3J_{C,CHN}$ = 4.1 Hz, $^3J_{C,Me}$ = 2.0 Hz).

**1-Benzyl-1*H*-pyrazolo[3,4-*b*]quinoxaline (7c)**, yield 80%, m.p. 113—114 °C (from aqueous ethanol). Found (%): C, 73.7; H, 4.3; N, 21.2. $C_{16}H_{12}N_4$. Calculated (%): C, 73.8; H, 4.7; N, 21.5.

**2-Quinoxalinecarboxaldehyde oxime (8).** Sodium acetate (0.27, 3.2 mmol) was added to a solution of hydroxylamine hydrochloride (0.25 g, 3.2 mmol) in 100 mL of water; then a solution of aldehyde **1** (0.5 g, 3.2 mmol) was added at a temperature of 70—75 °C. After keeping at this temperature for 10 min, the mixture was cooled and the precipitate formed was filtered off and recrystallized from water. Yield 78%, m.p. 195 °C. Found (%): C, 62.1; H, 4.5; N, 24.0. $C_9H_7N_3O$. Calculated (%): C, 62.4; H, 4.1; N, 24.3. The $^1$H NMR spectrum is presented in Table 1.

**Isoxazolo[4,5-*b*]quinoxaline (10).** A solution of $KMnO_4$ (0.67 g, 4.3 mmol) in acetone was gradually added with stirring at 50 °C to a solution of oxime **8** (0.3 g, 1.7 mmol) in 50 mL of acetone. The reaction mixture was cooled and $MnO_2$ was filtered off and washed with a large volume of acetone. The acetone solutions were combined and concentrated *in vacuo* to dryness. The product was purified by chromatography (silica gel, hexane—ethyl acetate solvent system). Yield 40%, m.p. >250 °C. Found (%): C, 63.3; H, 2.5; N, 24.1. $C_9H_5N_3O$. Calculated (%): C, 63.2; H, 2.9; N, 24.6. The $^1$H NMR spectrum is presented in Table 2.

**Synthesis of imines 11a—d (general procedure).** A solution of 2-quinoxalinecarboxaldehyde (**1**) (1 g, 6.3 mmol) in 15 mL of ethanol was added dropwise with stirring at 60 °C to a solution of the required amino derivative (8.2 mmol) in 15 mL of ethanol. After cooling the reaction mixture, the product was filtered off and recrystallized (in the case of compound **11b**, the reaction mixture was concentrated *in vacuo* to dryness and recrystallized).

The data of the $^1$H NMR spectra of compounds **11a—d** are presented in Table 3.

**2-[*N*-(2-Aminophenyl)formimidoyl]quinoxaline (11a).** Yield 82%, m.p. 121—123 °C (from acetonitrile). Found (%): C, 72.3; H, 4.9; N, 22.1. $C_{15}H_{12}N_4$. Calculated (%): C, 72.6; H, 4.9; N, 22.6.

**2[*N*-(Amino-4,5-dimethylphenyl)formimidoyl]quinoxaline (11b).** Yield 72%, m.p. 162—163 °C (from a hexane—acetone mixture). Found (%): C, 73.6 H, 5.8 N, 20.3. $C_{17}H_{16}N_4$. Calculated (%): C, 73.9; H, 5.8; N, 20.3.

**2[*N*-(2-Amino-3-pyridyl)formimidoyl]quinoxaline (11c).** Yield 65%, m.p. 219—220 °C (from ethanol). Found (%): C, 67.4; H, 4.6; N, 27.9. $C_{14}H_{11}N_5$. Calculated (%): C, 67.5; H, 4.5; N, 28.1.

**Table 3.** $^1$H NMR data (DMSO-$d_6$, δ (*J*/Hz)) of Schiff´s bases of 2-quinoxalinecarboxaldehyde **11a—d**

| Compound | Aryl | H(6), H(7) m, 2 H | H(5), H(8) m, 2 H | $NH_2$ s, 2 H | H(3) s, 1 H | CH=N s, 1 H |
|---|---|---|---|---|---|---|
| **11a** | 6.56—6.59 (m, 1 H, H(5´)); 6.79 (dd, 1 H, H(3´), $J_{H,H(4')}$ = 7.6, $J_{H,H(5')}$ = 0.7); 7.05—7.09 (m, 1 H, H(4´)); 7.39 (dd, 1 H, H(6´), $J_{H,H(5')}$ = 7.3, $J_{H,H(4')}$ = 0.7) | 7.90—7.92 | 8.15—8.19 | 5.69 | 9.92 | 8.88 |
| **11b** | 2.19 (s, 6 H, Me); 6.60 (s, 1 H, H(3´)); 7.23 (s, 1 H, H(6´)) | 7.92—7.98 | 8.17—8.19 | 5.44 | 9.88 | 8.84 |
| **11c** | 6.69 (dd, 1 H, H(5´), $J_{H,H(4')}$ = 7.5, $J_{H,H(6')}$ = 5.0); 7.67 (dd, 1 H, H(4´), $J_{H,H(5')}$ = 7.5); 7.85—7.98 (m, 3 H, H(6´), H(6), H(7)) | 7.85—7.98 | 8.09—8.21 | 6.36 | 9.93 | 8.91 |
| **11d** | 6.82—7.08 (m, 2 H, H(3´), H(5´)); 7.19—7.22 (m, 1 H, H(4´)); 7.50 (br.d, 1 H, H(6´), $J_{H,H(5')}$ = 7.9); 9.43 (s, 1 H, OH) | 7.85—8.00 | 8.11—8.25 | — | 9.55 | 9.00 |

**2-[*N*-(2-Hydroxyphenyl)formimidoyl]quinoxaline (11e).** Yield 82%, m.p. 219—220 °C (from AcOH). Found (%): C, 72.3; H, 4.3; N, 16.7. $C_{15}H_{11}N_3O$. Calculated (%): C, 72.3; H, 4.5; N, 16.9. $^{13}$C NMR (DMSO-$d_6$), δ: 116.64 (dd, C(3´), $^1J_{C,H}$ = 158.1 Hz, $^3J_{C,C(5')H}$ = 8.2 Hz); 119.51 (dd, C(6´), $^1J_{C,H}$ = 157.6 Hz, $^3J_{C,C(4')H'}$ = 8.2 Hz); 119.64 (dd, C(4´), $^1J_{C,H}$ = 161.6 Hz, $^3J_{C,C(6')H}$ = 8.5 Hz); 129.05, 129.34 (both m, C(5) and C(8)); 129.55 (dd, C(5´), $^1J_{C,H}$ = 158.6 Hz, $^3J_{C,CH}$ = 9.6 Hz); 130.77, 131.21 (both m, C(6) and C(7)); 135.68 (ddd, C(1´), $^3J_{C,C(3')H}$ = 10.5 Hz, $^3J_{C,C(5')H}$ = 8.9 Hz, $^3J_{C,C(6')H}$ = 5.9 Hz); 141.24 (dd, C(8a), $^3J_{C,C(5)H}$ = 8.4 Hz, $^3J_{C,C(7)H}$ = 5.1 Hz); 142.14 (ddd, C(4a), $^3J_{C,C(8)H}$ = 11.5 Hz, $^3J_{C,C(3)H}$ = 8.6 Hz, $^3J_{C,C(6)H}$ = 4.9 Hz); 144.49 (dd, C(3) $^1J_{C,H}$ = 189.0 Hz, $^3J_{C,CHN}$ = 3.7 Hz); 149.15 (dd, C(2´) $^3J_{C,C(4')H}$ = 9.3 Hz, $^3J_{C,C(6')H}$ = 9.3 Hz); 152.36 (dd, C(2), $^2J_{C,CHN}$ = 9.8 Hz, $^2J_{C,C(3)H}$ = 7.5 Hz); 156.77 (d, CH=N, $^1J_{C,H}$ = 167.9 Hz).

**Synthesis of compounds 12a—c (general procedure).** Compounds **11a—c** (2 mmol) were dissolved in 20 mL of methanol, 1 mL of glacial acetic acid was added, and the mixture was refluxed with air bubbling. After cooling, 10 mL of water was added, and the precipitate was filtered off and recrystallized.

**5*H*-Benzo[2,3]-1,4-diazepino[5,6-*b*]quinoxaline (12a)**, yield 65%, m.p. 241—242 °C (from aqueous methanol). Found (%): C, 73.3; H, 4.0; N, 22.9. $C_{15}H_{10}N_4$. Calculated (%): C, 73.2; H, 4.1; N, 22.8. $^1$H NMR (DMSO-$d_6$), δ: 7.21—7.35 (m, 2 H, H(2), H(3)); 7.62 (d, 1 H, H(4), *J* = 7.5 Hz); 7.77 (d, 1 H, H(1), *J* = 7.4 Hz); 7.85—7.98 (m, 2 H, H(8), H(9)); 8.10—8.25 (m, 2 H, H(7), H(10)); 9.80 (s, 1 H, H(12)); 13.40 (s, 1 H, NH). MS (EI, 70 eV), *m/z* ($I_{rel}$ (%)): 246 $[M]^+$ (100), 144 (89), 118 (23), 102 (8).

**5*H*-2,3-Dimethylbenzo[2,3]-1,4-diazepino[5,6-*b*]quinoxaline (12b)**, yield 65%, from aqueous methanol, m.p. >250 °C. Found (%): C, 74.6; H, 4.9; N, 20.7. $C_{17}H_{14}N_4$. Calculated (%): C, 74.4; H, 5.1; N, 20.4. $^1$H NMR (DMSO-$d_6$), δ: 2.35 (s, 6 H, Me); 7.79—7.86 (m, 1 H, H(4)); 7.89—7.98 (m, 2 H, H(8), H(9)); 8.04—8.09 (m, 1 H, H(1)); 8.13—8.21 (m, 2 H, H(7), H(10)); 9.77 (s, 1 H, H(12)); 13.42 (br.s, 1 H, NH).

**13*H*-Pyrido[3´,2´:2,3]-1,4-diazepino[5,6-*b*]quinoxaline (12c)**, yield 82%, m.p. 175—177 °C. Found (%): C, 68.2; H, 3.4; N, 28.0. $C_{14}H_9N_5$. Calculated (%): C, 68.0; H, 3.7; N, 28.3. $^1$H NMR (DMSO-$d_6$), δ: 7.88—8.12 (m, 3 H, H(2), H(3), H(4)); 8.13—8.38 (m, 4 H, H(8), H(9), H(10), H(11)); 9.33 (s, 1 H, H(6)); 10.19 (s, 1 H, NH).

**Preparation of compounds 13a,b (general procedure).** The required compound **12** (2 mmol) was dissolved in 15 mL of methanol, 10 mL of dilute sulfuric acid (pH = 2) was added, and the mixture was refluxed for 3 h. After cooling, the reaction mixture was neutralized with a solution of NaOH (25%) and the precipitate formed was filtered off and recrystallized.

***N*,*N*´-(Di-2-quinoxalylmethylene)-1,2-diaminobenzene (13a).** Yield 74%, m.p. 215—216 °C (from ethanol). Found (%): C, 74.3; H, 4.0; N, 21.1. $C_{24}H_{16}N_6$. Calculated (%): C, 74.2; H, 4.2; N, 21.6. $^1$H NMR (DMSO-$d_6$), δ: 6.45—6.62 (m, 2 H, H(4), H(5)); 7.32—7.50 (m, 2 H, H(3), H(6)); 7.61—8.19 (m, 10 H, quinoxaline protons); 9.15, 9.87 (both s, each 1 H, CH=N, CH=N´). MS (EI, 70 eV), *m/z* ($I_{rel}$ (%)): 388 $[M]^+$ (100), 259 (81), 194 (9).

***N*,*N*´-(Di-2-quinoxalylmethylene)-1,2-diamino-4,5-dimethylbenzene (13b).** Yield 68%, m.p. >250 °C. Found (%): C, 75.1; H, 4.5; N, 20.4. $C_{26}H_{20}N_6$. Calculated (%): C, 75.0; H, 4.8; N, 20.2. $^1$H NMR (DMSO-$d_6$), δ: 2.40 (s, 6 H, Me); 6.48—6.51 (m, 2 H, H(3), H(6)); 7.52—8.22 (m, 10 H, quinoxaline protons); 9.02, 9.83 (both s, each 1 H, CH=N, CH=N´).

**Benzo[2,3]-1,4-oxazepino[6,7-*b*]quinoxaline (15).** Potassium permanganate (2 g, 12.6 mmol) in acetone was added dropwise with stirring at 50 °C to compound **2c** (1 g, 4.02 mmol) in 100 mL of acetone. The reaction mixture was cooled and $MnO_2$ was filtered off and washed with a large amount of acetone. The acetone solutions were combined and concentrated to dryness *in vacuo*. The product was purified by chromatography (silica gel, hexane—acetone). Yield 0.42 g (42%), m.p. 173—175 °C. Found (%): C, 72.5; H, 3.9; N, 16.6. $C_{15}H_9N_3O$. Calculated (%): C, 72.9; H, 3.7; N, 17.0. $^1$H NMR (DMSO-$d_6$), δ: 7.42—7.64 (m, 2 H, H(9), H(8)); 7.85—8.08 (m, 4 H, H(1), H(2), H(3), H(4)); 8.11—8.34 (m, 2 H, H(7), H(10)); 9.71 (s, 1 H, H(12)). $^{13}$C NMR (DMSO-$d_6$), δ: 111.55, 120.71, 125.46, 127.10, 129.10, 129.60, 131.45, 131.95 (all m, C(1), C(2), C(3), C(4), C(7), C(8), C(9), C(10)); 140.97, 141.06, 142.13 (all m, C(6a), C(10a), C(13a)); 140.58 (d, C(11a), $^2J_{C,H(12)}$ = 3.6 Hz); 144.32 (d, C(12), $^1J_{C,H}$ = 189.0 Hz); 150.54 (m, C(4a)); 159.64 (s, C(5a)). MS (EI, 70 eV), *m/z* ($I_{rel}$ (%)): 247 $[M]^+$ (100), 173 (9), 145 (48), 129 (13), 119 (13), 102 (21).

**Table 4.** Basic bond lengths ($d$) in molecule **6d**

| Bond | $d$/Å | Bond | $d$/Å |
|---|---|---|---|
| N(1)—C(9) | 1.281(16) | C(3)—C(4) | 1.392(11) |
| N(1)—C(1) | 1.389(9) | C(4)—C(5) | 1.367(10) |
| N(1)—C(16) | 1.488(9) | C(5)—C(6) | 1.426(10) |
| N(2)—C(7) | 1.300(10) | C(7)—C(8) | 1.422(9) |
| N(2)—C(6) | 1.370(10) | C(7)—C(9) | 1.473(12) |
| N(3)—C(9) | 1.375(10) | C(10)—C(15) | 1.376(12) |
| N(3)—N(4) | 1.423(7) | C(10)—C(11) | 1.396(13) |
| N(3)—C(10) | 1.440(8) | C(11)—C(12) | 1.371(10) |
| N(4)—C(8) | 1.292(9) | C(12)—C(13) | 1.372(11) |
| C(1)—C(6) | 1.414(9) | C(13)—C(14) | 1.376(12) |
| C(1)—C(2) | 1.415(9) | C(14)—C(15) | 1.384(12) |
| C(2)—C(3) | 1.352(12) | | |

**Table 5.** Basic bond angles (ω) in molecule **6d**

| Angle | ω/deg | Angle | ω/deg |
|---|---|---|---|
| C(9)—N(1)—C(1) | 117.8(6) | C(1)—C(6)—C(5) | 119.2(7) |
| C(9)—N(1)—C(16) | 120.9(6) | N(2)—C(7)—C(8) | 132.1(6) |
| C(1)—N(1)—C(16) | 121.1(6) | N(2)—C(7)—C(9) | 122.2(7) |
| C(7)—N(2)—C(6) | 115.9(6) | C(8)—C(7)—C(9) | 105.6(7) |
| C(9)—N(3)—N(4) | 111.3(7) | N(4)—C(8)—C(7) | 111.8(6) |
| C(9)—N(3)—C(10) | 131.6(7) | N(1)—C(9)—N(3) | 134.6(8) |
| N(4)—N(3)—C(10) | 116.6(6) | N(1)—C(9)—C(7) | 121.4(6) |
| C(8)—N(4)—N(3) | 107.3(5) | N(3)—C(9)—C(7) | 103.9(10) |
| N(1)—C(1)—C(6) | 119.2(6) | C(15)—C(10)—C(11) | 120.8(7) |
| N(1)—C(1)—C(2) | 121.2(6) | C(15)—C(10)—N(3) | 119.0(9) |
| C(6)—C(1)—C(2) | 119.5(7) | C(11)—C(10)—N(3) | 120.1(8) |
| C(3)—C(2)—C(1) | 119.0(7) | C(12)—C(11)—C(10) | 118.1(7) |
| C(2)—C(3)—C(4) | 122.5(7) | C(11)—C(12)—C(13) | 121.3(7) |
| C(5)—C(4)—C(3) | 120.2(7) | C(14)—C(13)—C(12) | 120.4(8) |
| C(4)—C(5)—C(6) | 119.4(7) | C(13)—C(14)—C(15) | 119.3(8) |
| N(2)—C(6)—C(1) | 122.8(7) | C(10)—C(15)—C(14) | 119.9(8) |
| N(2)—C(6)—C(5) | 118.0(6) | | |

**X-ray diffraction study of compound 6d.** The X-ray diffraction experiment was carried out on a Bruker AXS SMART 1000 diffractometer equipped with a CCD detector ($\lambda$(Mo-K$\alpha$) = 0.71073 Å, graphite monochromator, 293 K, ω-scan mode, scan step 0.3°, frame measurement time 10 s, $2\theta_{max} = 60°$).

The crystals $C_{16}H_{13}IN_4$ were isolated from water, crystal dimensions 0.6×0.2×0.5, colored red, molecular mass 389.21, monoclinic system, space group *Cs*, $a$ = 6.689(3) Å, $b$ = 33.689(15) Å, $c$ = 7.224(3) Å, $\alpha = 90°$, $\beta = 112.416(10)°$, $\gamma = 90°$, $V$ = 1504.9(12) Å$^3$, $Z$ = 4, $d_{calc}$ = 1.713 g cm$^{-3}$, $F(000)$ = 760, $\mu$ = 2.126 cm$^{-1}$, the scanning range was 2.42—30.10°, the total number of measured reflections was 3863, the number of independent reflections was 2476, and $R_{int}$ = 0.026.

A semiempirical absorption correction was applied.[27] The structure was solved by the direct method using the SHELXS97 program package[28] and refined by the SHELXL97 package[29] using the least-squares method in the anisotropic (or isotropic for H atoms) approximation, the number of refined parameters was 190 for 2476 reflections. $R_1(I \geq 2\sigma(I)) = 0.0395$, $wR_2 = 0.0869$ (for 2476 reflections with $F^2 \geq 2\sigma$), $R_1(I \geq 2\sigma(I)) = 0.0499$, $wR_2 = 0.0899$ for all reflections. The positions of hydrogen atoms were calculated geometrically and refined isotropically according to the "rider" model. The bond lengths and angles are listed in Tables 4 and 5.

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