3-Indolizin-2-ylquinoxalines and the derived monopodands*

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The reactions of 3-acetylquinoxalin-2-one with methyl- and benzylpyridines in the presence of iodine produce the corresponding 3-(2-alkylpyridinioacetyl)quinoxalin-2(1*H*)-one iodides. Treatment of the latter with triethylamine affords the corresponding 3-indolizin-2-ylquinoxalin-2-ones. Due to the presence of the endocyclic carbamoyl group, the reactions of these compounds with bisalkylating reagents give quinoxaline-containing monopodands and monoalkylation products containing spacers with different lengths and of different nature.

Key words: 3-acetylquinoxalin-2-one, pyridinium salts, Chichibabin reaction, indolizines, quinoxalines, monopodands, structure, IR spectra, 1D and 2D NMR spectroscopy.

Positions 1 and 3 of the indolizine system are characterized by high reactivity in electrophilic substitution reactions due to high local and overall π-excessive densities.[1] This fact was observed in studies of alkylation, acylation, nitration, nitrosation,[2,3] cycloaddition,[4] and Michael addition to electron-deficient olefins[5,6] and diazonium salts.[7] Certain indolizine derivatives were used for the preparation of dyes[8—11] and light-sensitive compounds in photoemulsions.[12] The synthesis of bis-indolizines is also of considerable interest. These compounds are reversible two-step redox systems,[13,14] which facilitate the occurrence of atropoisomerism[15] and serve as the starting compounds in the synthesis of heterocyclophanes and ligands[16,17] possessing the desired properties. The introduction of the indolizine fragment containing the free locally π-excessive active reaction centers C(1) and C(3) into functionalized heterocyclic systems will extend the synthetic potential of these compounds. The aim of the present study was to synthesize 3-indolizin-2-ylquinoxaline derivatives containing the C(1) and C(3) centers having high reactivity under the redox conditions and to prepare monopodands based on these compounds

Indolizine derivatives were synthesized by the modified Chichibabin method involving condensation of the 3-acetyl derivative of quinoxaline with 2-methyl- and 2-benzylpyridines in the presence of molecular iodine.

3-Acetylquinoxalin-2-(1*H*)one was transformed into 3-indolizinyl-substituted quinoxalines in several steps, such as halogenation, the reaction of the resulting iodide with α-picoline or 2-benzylpyridine giving rise to pyridinium salts, and subsequent intramolecular condensation of the latter.

Initially, we used a bromine—dioxane complex as a halogenating reagent. Bromination was performed in a dioxane solution at 10—15 °C for 1.5 h. 3-Bromoacetylquinoxalin-2-(1*H*)one was prepared in 30% yield. The reaction also afforded a compound containing two bromine atoms (one atom in the acetyl fragment and another atom in the benzo fragment of the quinoxaline system) as a by-product, whose percentage was 1—20% of the major product. Subsequent reactions always gave an impurity of the corresponding product containing the bromine atom in the benzo fragment of the quinoxaline system. We failed to separate these products. Attempts to change the reaction conditions of bromination (the reactions were performed in the presence of $AlCl_3$, in different solvents, with the use of a deficient amount of bromine, or at lower temperature) did not lead to the desired results. We only succeeded in increasing the yield of 3-picolinioacetylquinoxalin-2(1*H*)-one bromide from 27% (in the first procedure) to 50% by performing the one-pot reaction of 3-acetylquinoxalin-2-one with the bromine—dioxane complex followed by the addition of a twofold excess of picoline (to neutralize HBr) in chloroform. Hence, we used iodine instead of molecular bromine because iodine is a milder halogenating reagent, which reacts with 3-acetylquinoxalinone without heating and does not give a by-product, which could be formed as a result of halogenation at the benzo fragment of the quinoxaline system. Although we failed to isolate 3-iodoacetylquinoxalin-2-one, the one-pot reaction of 3-acetylquinoxalin-2-one (**1**)

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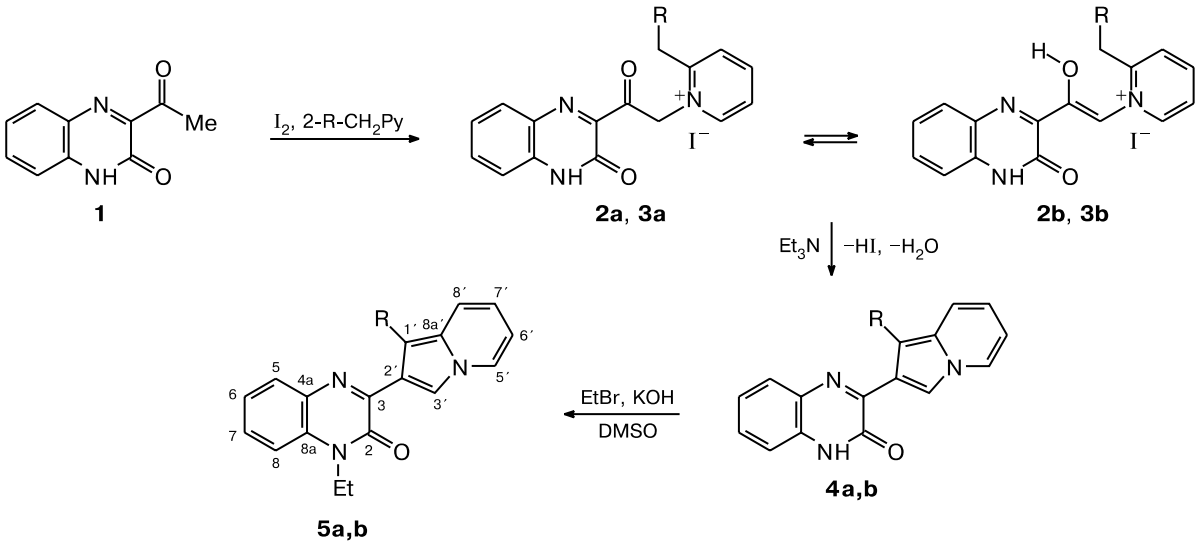
Scheme 1



R = H (**a**), Ph (**b**)

with a twofold excess of 2-methyl- or 2-benzylpyridine and one equivalent of iodine yielded crystalline products, *viz.*, 2-methylpyridinio- (**2a**) and 2-benzylpyridinio-acetylquinoxalin-2(1*H*)-one iodides (**3b**) in 75 and 32% yields, respectively (Scheme 1).

In the crystalline state and in a deuterated dimethyl sulfoxide solution, methylpyridinium salt **2** exists in keto form **2a**, whereas benzylpyridinium salt **3** exists in enol form **3b**, as evidenced by the presence of an absorption band ν(CO) = 1719 cm^{-1} in the IR spectrum of compound **2** and an absorption band ν(OH) = 3339 cm^{-1} in the IR spectrum of compound **3**. In addition, the ^1H NMR spectrum of compound **2** shows, along with other signals, two singlets at δ 6.42 and 12.90 corresponding to the protons of the CH_2 and NH groups, whereas the ^1H NMR spectrum of compound **3** has three singlets at δ 6.02, 11.82, and 12.36 assigned to the protons of the CH, OH, and NH groups. It should also be noted that the protons of the CH_2 group of the benzyl fragment in compound **3** are nonequivalent due to the presence of the double bond, with the result that these protons resonate as an AB system with large geminal coupling constants (J = 14.12 Hz).

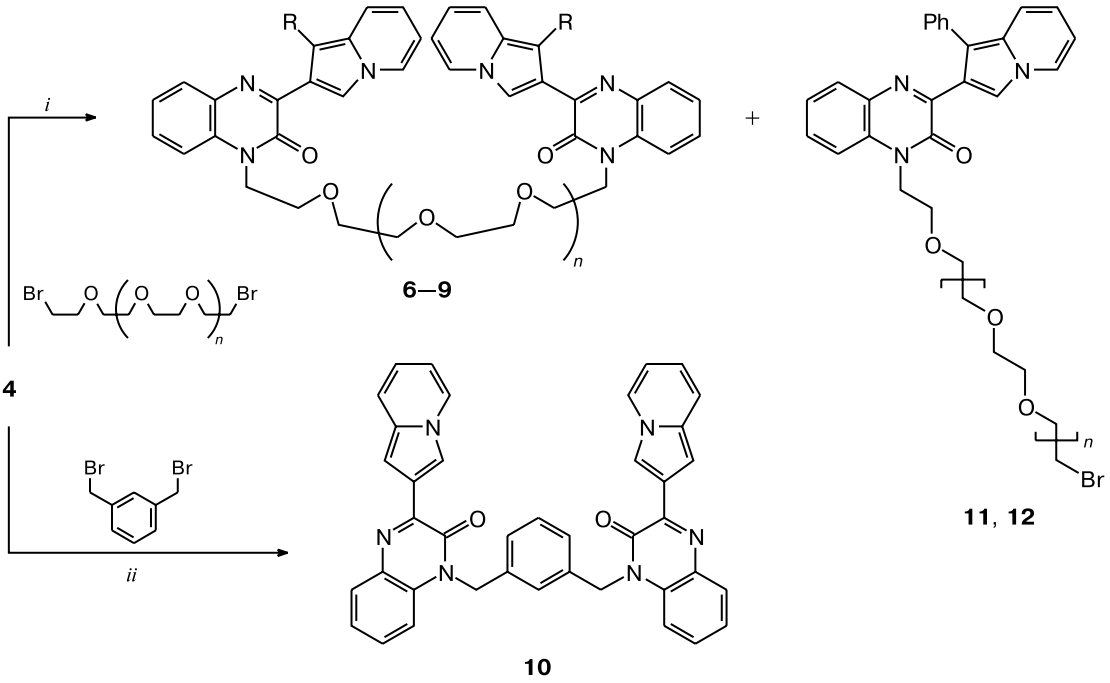
After stirring of pyridinium salts **2** and **3** in a 20% triethylamine solution in chloroform for 3 and 4 days, respectively, these compounds were transformed into indolizinylquinoxalines **4**, which were readily alkylated at the carbamoyl group with ethyl bromide in the presence of KOH in DMSO to give compounds **5a** and **5b** (see Scheme 1).

Alkylation of 3-indolizin-2-ylquinoxalinone **4** at the carbamoyl group with α,ω-dihalo derivatives made it possible to synthesize quinoxaline-containing monopodands with the π-excessive indolizine substituents. For example, the reactions of quinoxalinones **4a** and **4b** with such bisalkylating reagents as 1,5-dibromo-3-oxapentane, 1,11-dibromo-3,6,9-trioxaundecane, and α,α′-dibromo-*meta*-xylene at room temperature (in DMSO as the solvent) or in refluxing dioxane in the presence of KOH gave the bisalkylated derivative (**6—10**) as the major product and the monoalkylated derivative as a by-product. By-products **11** and **12**, which were obtained in the reaction with the phenylindolizinyl derivative of quinoxaline **4b**, were isolated and characterized (Scheme 2).

In most cases, the positions of the signals in the NMR spectra of indolizine derivatives strongly depend on the nature of the substituents.[13—18] Hence in the present study, we made the assignment of the signals in the ^1H and ^{13}C NMR spectra of the reaction products with the use of DEPT, 2D COSY, 2D HSQC, 2D HMBC,[19] and 1D DPFGNOE[20] experiments. Let us consider a detailed analysis of the assignment only for compound **5a**, whose structure was established by X-ray diffraction. The structures of the other compounds were determined analogously.

The geometry of molecule **5a** in the crystal structure is shown in Fig. 1. In this molecule, the indolizine fragment contains no bulky substituents and is planar to within experimental error (0.035(4) Å). In the quinoxaline fragment of molecule **5a**, the bicyclic system is slightly nonplanar. The bulky ethyl group and the indolizine fragment at the N(1) and C(3) atoms adjacent to the C(2)=O(2) carbonyl group cause substantial steric hindrances, the latter being reduced due to the perpendicular arrangement of the ethyl substituent with respect to the plane of the heterocycle, a slight twist of the quinoxaline fragment (the maximum deviation from the mean plane

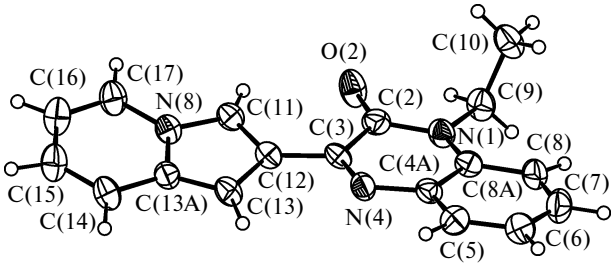
Scheme 2



Reagents: *i*. DMSO or dioxane, KOH; *ii*. DMSO, KOH.

R = H (**6**, **8**), Ph (**7**, **9**); *n* = 0 (**6**, **7**, **11**), 1 (**8**, **9**, **12**)

(−0.086(4) Å) is observed for the C(2) atom), a slight twist of the indolizine and quinoxaline fragments about the C(3)—C(12) bond (the C(2)—C(3)—C(12)—C(11) torsion angle is 14.3(5)° and the dihedral angle between the planes of these fragments is 14.1(1)°), and an increase in the exocyclic bond angles at the C(12) atom (the C(3)—C(12)—C(11) torsion angle (128.7(3)°) is larger than the C(3)—C(12)—C(13) torsion angle (123.3(3)°)).



Bond	*d*/Å	Bond	*d*/Å
O(2)—C(2)	1.222(4)	C(5)—C(6)	1.385(5)
N(1)—C(2)	1.397(4)	C(6)—C(7)	1.385(6)
N(1)—C(8a)	1.337(4)	C(7)—C(8)	1.377(6)
N(1)—C(9)	1.497(4)	C(8a)—C(8)	1.413(5)
N(4)—C(3)	1.295(4)	C(9)—C(10)	1.497(6)
N(4)—C(4a)	1.397(4)	C(11)—C(12)	1.372(5)
N(8)—C(11)	1.386(4)	C(12)—C(13)	1.416(5)
N(8)—C(13a)	1.380(4)	C(13)—C(13a)	1.360(5)
N(8)—C(17)	1.415(4)	C(13a)—C(14)	1.428(5)
C(2)—C(3)	1.492(5)	C(14)—C(15)	1.363(5)
C(3)—C(12)	1.474(5)	C(15)—C(16)	1.388(6)
C(4a)—C(5)	1.377(5)	C(16)—C(17)	1.358(6)
C(4a)—C(8a)	1.436(5)		

Fig. 1. Molecular geometry of compound **5a** in the crystal.

A system of intermolecular interactions in the crystal of compound **5a** consists, apparently, of C—H...O hydrogen bonds and π—π interactions between the aromatic systems. The molecules are linked into centrosymmetric dimers by pairs of identical hydrogen bonds between the O(2) atom of the carboxy group and the proton H(17′) of the fused pyridine ring with the following parameters: *d*(O(2)...H(17′)), 2.46 Å; *d*(O(2)...C(17′)), 3.420(5) Å; O(2)...H(17′)—C(17′), 162°; the symmetry code (2 − *x*, 1 − *y*, −*z*) (Fig. 2). The involvement of the O(2) atom in a bifurcated C—H...O hydrogen bond with the proton H(6″) of the fused benzene ring of another adjacent molecule results in the formation of two-layer chains (with an antiparallel arrangement of the molecules) consisting of hydrogen-bonded dimers along the crystallographic 0*y* direction, because each molecule is involved in two contacts (as a donor and an acceptor). The parameters of this interaction are as follows: *d*(O(2)...H(6″)), 2.66 Å; C(2)—O(2)...H(6″), 137°; the symmetry code (*x*, 1 + *y*, *z*).

The molecular packing of compound **5a** in the crystals can be described as a parallel packing of the above-de-

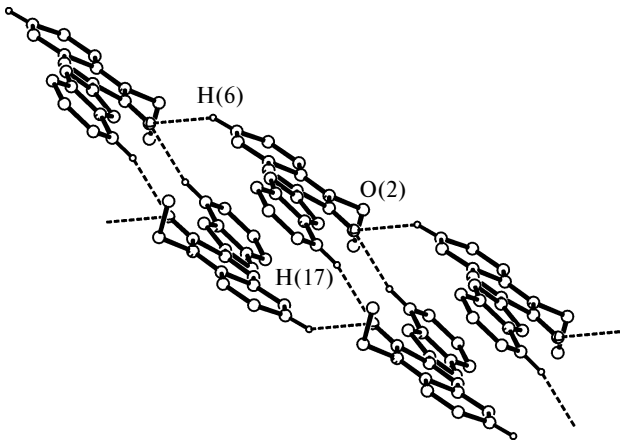


Fig. 2. Hydrogen bond network and π—π contacts in the crystal structure of compound **5a**. Only hydrogen atoms involved in hydrogen bonds (dashed lines) are shown.

scribed supramolecular structures along the crystallographic 0*y* axis so that the planes of the heterocyclic fragments of the molecules are coplanar with the crystallographic plane (−101) (Fig. 3). The aromatic fragments of the molecules in these chains form π—π contacts not only with fragments of the corresponding centrosymmetric molecules within the chain but also with the molecules of the adjacent chains. The shortest distances between the centers of the aromatic rings are in the range of 3.38—3.60 Å. Therefore, the supramolecular structure that exists in the crystals is characterized by the presence of different types of intermolecular interactions, C—H...O and π—π, in two mutually perpendicular directions.

In spite of the fact that the methyl group of the ethyl substituent at the N(1) atom deviates from the plane of the heterocycle, the packing coefficient of this crystal structure is rather high (71.1%), and the calculations provided evidence that there are no cavities accessible for solvent molecules.

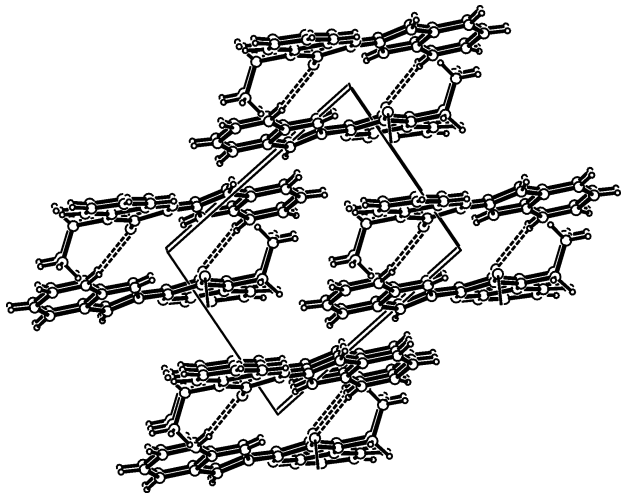


Fig. 3. Fragment of the molecular packing in the crystal structure of compound **5a** projected along the crystallographic 0*y* axis. Hydrogen bonds are indicated by dashed lines.

The ^{1}H NMR spectrum of compound **5a** has signals for the aromatic protons and signals for the protons of the ethyl group, which are observed at δ 4.48 and δ 1.32 as a doublet of quartet of quartets and a doublet of doublets, respectively, rather than the expected quartet and triplet. This is evidence for the presence of an A_3MX spin system associated, as mentioned above, with hindered rotation about the N(1)—CH_2 bond on the NMR time scale. The signals for the following three groups of protons are unambiguously distinguished in the aromatic region of the 2D COSY spectrum (Fig. 4, *a*): the quinoxaline fragment (H(5), H(6), H(7), and H(8)), the pyridine ring (H(5′), H(6′), H(7′), and H(8′)), and the pyrrole ring (H(1′) and H(3′)) of the indolizine fragment. Two singlets at δ 8.68 and 7.21 are assigned to the individual protons of the pyrrole ring of the indolizine fragment, the lower-

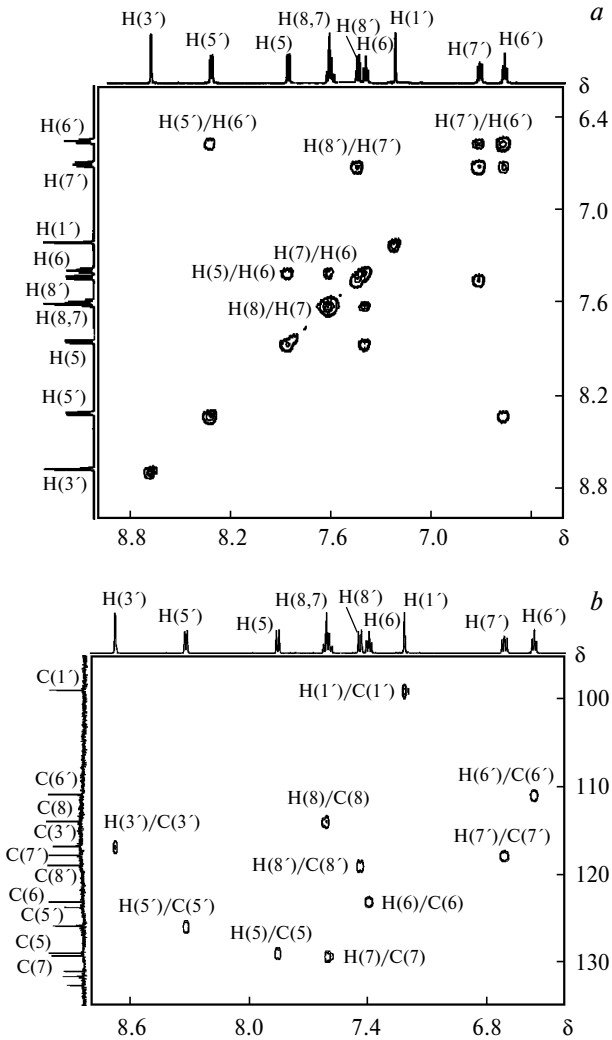


Fig. 4. Fragments of the 2D COSY (*a*) and 2D HSQC (*b*) spectra of compound **5a**.

field signal corresponding to the proton H(3′) in the α position with respect to the electron-withdrawing nitrogen atom.

The proton-containing carbon atoms can easily be determined with the use of DEPT and 2D HSQC spectra. For example, the resonance of the carbon atoms N(1)—CH_2, CH_3, C(3′), and C(1′) is revealed from the 2D HSQC spectrum (see Fig. 4, *b*).

The 2D HMBC spectrum (Figs 5 and 6) shows a cross-peak between H(3′) and the signal for the C(5′) atom of

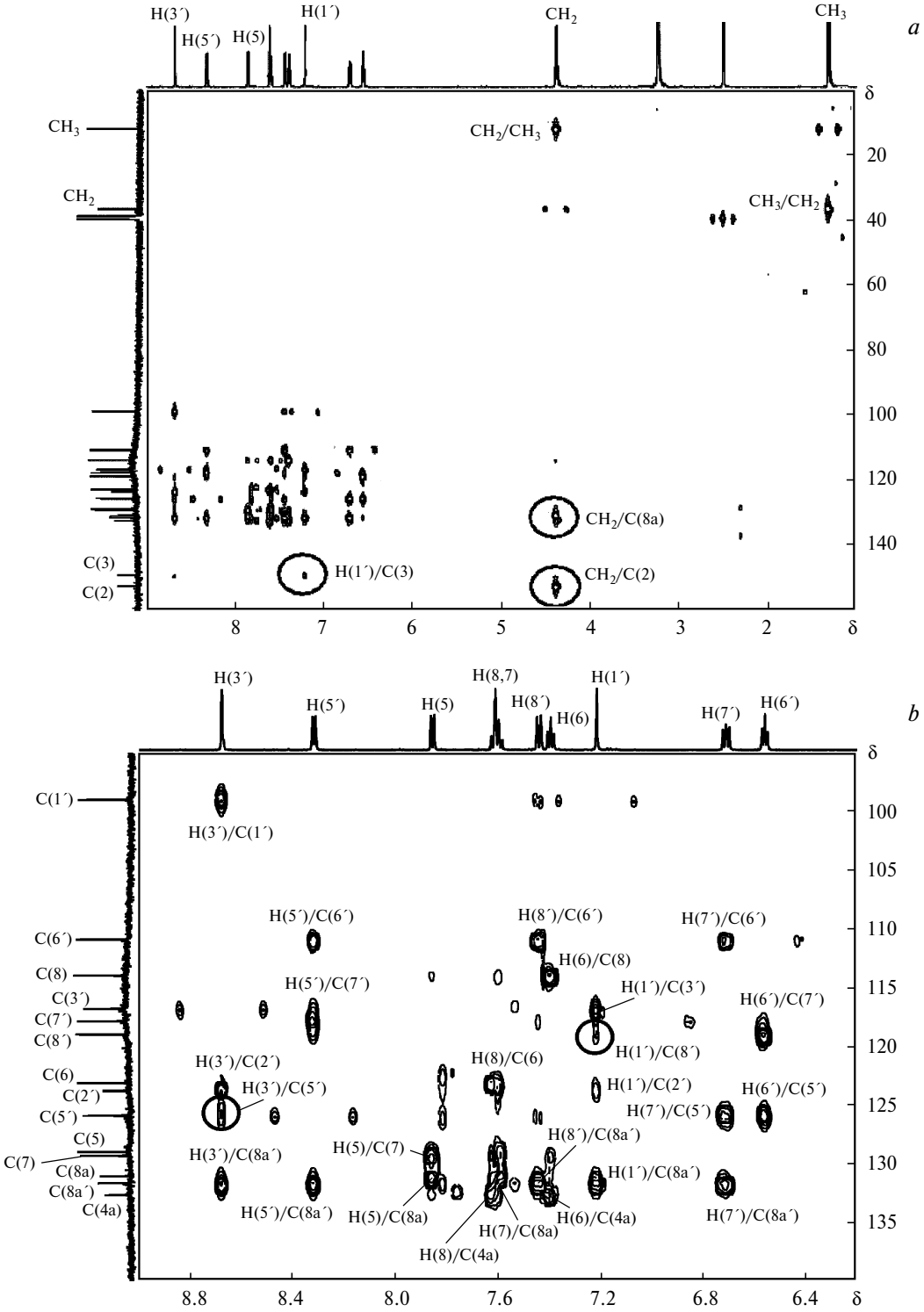


Fig. 5. 2D HMBC spectrum of compound **5a** (*a*) and its fragment (*b*).

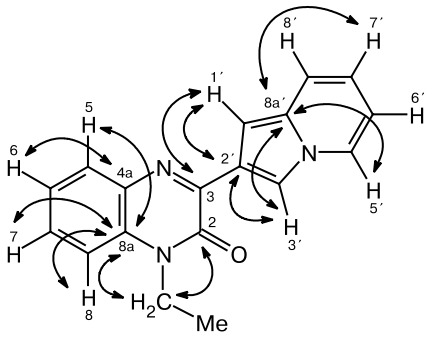


Fig. 6. Main HMBC correlations between the protons and the carbon atoms for compound **5a**.

the CH group at δ 125.90 as well as a cross-peak between H(1′) and the C(8′) carbon of the CH group at δ 119.00. This made it possible to unambiguously identify the C(5′) and C(8′) atoms. The assignment of the corresponding protons H(5′) (δ 8.32) and H(8′) (δ 7.44) was additionally confirmed using the 2D HSQC experiment. The other protons of the indolizine fragment (H(6′) and H(7′)) were determined from the COSY spectrum (see Fig. 4, *a*). Analysis of the 2D HSQC spectrum made it possible to differentiate the signals of the corresponding carbon atoms in the ^{13}C NMR spectrum (see Fig. 4, *b*). In the 2D HMBC spectrum (see Figs 5 and 6), there is a correlation between the protons H(1′), H(3′), H(5′), H(7′), and H(8′) and the resonance of the C(8a′) atom at δ 131.67 and a correlation between the signal for the protons H(3′) and H(1′) and the resonance of the C(2′) atom at δ 123.80. In addition, the 2D HMBC spectrum (see Figs 5, *a* and 6) shows a cross-peak between H(1′) and the resonance of the C(3) atom at δ 149.44. Therefore, we made the complete assignment of the signals of the indolizine fragment in the molecule.

We are coming now to the quinoxaline fragment. In the 2D HMBC spectrum (see Figs 5 and 6), there is a correlation between the signal for the protons of the N(1)—CH_2 group and two resonances of the quaternary carbon atoms (δ 152.89/131.08), which can be assigned to the C(8a)/C(2) (or vice versa) atoms because cross-peaks are observed only for these atoms, the intensity of the cross-peaks being proportional to the coupling constant. In the systems under consideration, the coupling constant ^3J is larger than $^{2,4}J$.[21] In addition, the presence of a cross-peak between the signal at δ 131.08 and two protons at δ 7.86 (dd) and δ 7.60 (m) allowed us to differentiate the C(8a) and C(2) atoms. Thus, the signal at δ 131.08 was assigned to the C(8a) atom, and the signal at δ 152.89 was attributed to the C(2) atom. Taking into account the multiplicities of the signals for the protons, the presence of the latter cross-peaks in the HMBC spectrum made it possible to identify H(5) (doublet, δ 7.86) and H(7) (multiplet, δ 7.60). Then, the signals for the H(6) and H(8) atoms of quinoxaline were determined using the 2D COSY spectrum. The resonances of the carbon atoms of this fragment were determined from the 2D HSQC spectrum (see Fig. 4, *b*). In addition, the 2D HMBC spectrum shows a cross-peak between the signals for the protons H(6) at δ 7.40 and H(8) at δ 7.61 and the resonance of the C(4a) atom at δ 132.70 (see Figs 5, *b* and 6). Therefore, we made the complete assignment of the signals of the quinoxaline fragment in **5a**.

In addition, the 2D HMBC experiment unambiguously confirmed the presence of covalent bonds between all fragments of the molecule (see Figs 5 and 6), *viz.*, between the indolizine and quinoxaline fragments and between the ethyl group and quinoxaline fragment.

To confirm the spatial proximity of the fragments in compound **5a**, we also performed nuclear Overhauser effect (NOE) experiments (Fig. 7).

As mentioned above, alkylation of the phenylindolizine derivative of quinoxaline **4b** with bisalkylating reagents ABr_2 (A = $(CH_2)_2O(CH_2)_2$ or $(CH_2)_2O(CH_2)_2O(CH_2)_2O(CH_2)_2$) afforded, along with the major products, monoalkylated derivatives as by-products. The formation of monoalkylated derivatives **11** and **12** is evidenced by the integrated intensities of the signals for the protons of the aromatic fragments and the methylene groups in the ^1H NMR spectrum as well as by the presence of a set of lines (24 signals in the spectrum of compound **11** and 28 signals in the spectrum of compound **12**) in the ^{13}C NMR spectrum. The fact that the 2D HMBC spectrum shows cross-peaks between the protons of $CH_2(1'')$ and the C(2) and C(8a) atoms of the quinoxaline system (Fig. 8) is indicative of the formation of *N*-alkylated rather than *O*-alkylated derivatives, as in the case of formation of bisalkylated compounds (podands).

The structure of the 11-bromo-3″,6″,9″-trioxaundecyl substituent was confirmed based on the 2D COSY and 2D HMBC spectra. The former shows a correlation between the methylene protons in the $O(CH_2)_2O$ unit. In

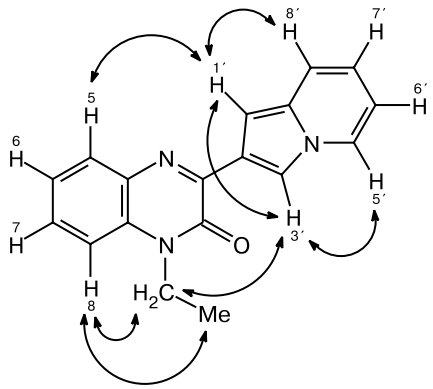
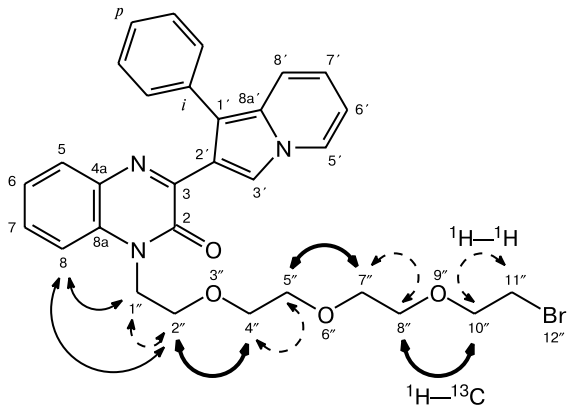


Fig. 7. Principal NOE and their correlations with the structure of **5a**.



12

Fig. 8. Principal correlations: HMBC (thick arrows, between the protons and the carbon atoms), COSY (dashed arrows), and NOE (thin solid arrows) for compound **12**.

the 2D HMBC spectrum there are correlations between the protons and the carbon nuclei (through three bonds) of the adjacent CH_2—O—CH_2 groups, which provides evidence for the presence of a covalent bond between the units through the oxygen atoms. For example, there are correlations between the $CH_2(1'')$ and $CH_2(2'')$ groups (2D COSY, see Fig. 8), between $CH_2(2'')$ and $CH_2(4'')$ (2D HMBC), between $CH_2(4'')$ and $CH_2(5'')$ (2D COSY), and then analogously up to $CH_2(11'')$ (see Fig. 8).

The attachement of the linear fragment to the quinoxaline system is additionally confirmed by the presence of NOE between the closely spaced protons of the $CH_2(1'')/CH_2(2'')$ groups and H(8) (see Fig. 8).

The chemical shifts of the triplets for the terminal methylene groups (δ = 3.77 and 3.50 for compounds **11** and **12**, respectively) are characteristic of this class of compounds,[21] which is indicative of the presence of the bromine atom in these groups.

The compositions of the reaction products were also confirmed by elemental analysis.

To summarize, we developed a convenient procedure for the synthesis of the indolizinylquinoxaline system and examined the possibilities of synthesizing quinoxaline-containing monopodands by alkylation with various bisalkylating reagents.

Experimental

The melting points were determined on a Boetius hot stage. The IR spectra of all compounds were recorded on a Bruker Vector-22 Fourier-transform spectrometer in Nujol mulls. The ^{1}H and ^{13}C NMR and 2D spectra, including COSY, HSQC, HMBC, and NOESY spectra, of compounds **4a**, **5a**, **6**, **9**, and **12** were measured on a Bruker AVANCE-600 Fourier-transform spectrometer operating at 600.00 (^{1}H) and 150.86 (^{13}C) MHz in DMSO-d_6 at 50 °C. The ^{1}H NMR spectra of compounds **2a**, **3b**, **4b**, **5b**, and **6—10** were recorded on a Bruker MSL-400 instrument operating at 400.13 MHz using the residual signal of DMSO as the internal standard (δ_H 2.54 and δ_C 40.45).

3-(2′-Methylpyridinioacetyl)quinoxalin-2(1*H*)-one iodide (2a). 2-Picoline (2.40 g, 25.8 mmol) was added to a solution of 3-acetylquinoxalin-2(1*H*)-one (2.40 g, 12.8 mmol) (**1**) in chloroform (25 mL). Then the reaction mixture was cooled to 15 °C, and I_2 (3.00 g, 11.8 mmol) was added. The reaction mixture was stirred at 15 °C for 1 h and allowed to stand for 7 days. The crystals that precipitated were filtered off and washed with chloroform. The yield was 3.9 g (75%), m.p. 205—207 °C. Found (%): C, 47.25; H, 3.63; N, 10.21; I, 31.02. $C_{16}H_{14}N_3O_2I$. Calculated (%): C, 47.19; H, 3.47; N, 10.32; I, 31.16. IR, ν/cm^{-1}: 472, 569, 591, 551, 895, 950, 1141, 1186, 1311, 1494, 1515, 1578, 1612, 1637, 1656, 1719, 2500—3220. ^{1}H NMR, δ: 6.42 (s, 2 H, CH_2); 7.46 (d, 1 H, H(8), J = 7.56 Hz); 7.47 (dd, 1 H, H(6), J = 8.70 and 7.56 Hz); 7.77 (dd, 1 H, H(7), J = 7.52 and 7.52 Hz); 7.96 (d, 1 H, H(5), J = 7.52); 8.10 (dd, 1 H, H(5) Py, J = 6.76 and 5.28 Hz); 8.18 (d, 1 H, H(3) Py, J = 7.52 Hz); 8.62 (dd, 1 H, H(4) Py, J = 7.52 and 7.56 Hz); 8.96 (d, 1 H, H(6) Py, J = 6.00 Hz); 12.90 (br.s, 1 H, NH).

3-[β-(2′-Benzylpyridinio)-α-hydroxyvinyl]quinoxalin-2(1*H*)-one iodide (3b). 2-Benzylpyridine (3.60 g, 21.30 mmol) was added to a solution of 3-acetylquinoxalin-2(1*H*)-one (**1**) (2.00 g, 10.63 mmol) in chloroform (15 mL). The reaction mixture was cooled to 15 °C, I_2 (3.00 g, 11.8 mmol) was added, and the mixture was stirred at 15 °C for 1 h and allowed to stand for 7 days. The crystals that precipitated were filtered off and washed with chloroform. The yield was 1.6 g (32%), m.p. 254—256 °C. Found (%): C, 56.55; H, 3.84; N, 8.76; I, 26.09. $C_{22}H_{18}N_3O_2I$. Calculated (%): C, 56.67; H, 3.75; N, 8.69; I, 26.26. IR, ν/cm^{-1}: 420, 473, 497, 637, 705, 746, 772, 824, 890, 929, 1097, 1151, 1167, 1237, 1302, 1345, 1497, 1560, 1578, 1616, 1629, 1666, 2500-3220, 3339. ^{1}H NMR, δ: 5.36 (d, 1 H, —C$\underline{H}_A$H$_B$Ph, J = 14.12 Hz); 5.61 (d, 1 H, —CH$_A\underline{H}_B$Ph, J = 14.12 Hz); 6.02 (s, 1 H, C$\underline{H}$COH); 7.08—7.18 (m, 1 H, H$_p$, Ph); 7.22—7.45 (m, 6 H, H(6), H(8), 2 H$_o$, 2 H$_m$, Ph); 7.64 (ddd, 1 H, H(7), J = 7.84, 7.72, and 0.96 Hz); 7.73 (d, 1 H, H(5), J = 7.84 Hz); 7.88 (d, 1 H, H(3) Py, J = 8.20 Hz); 8.15 (dd, 1 H, H(5) Py, J = 7.24 and 6.56 Hz); 8.58 (dd, 1 H, H(4) Py, J = 8.20 and 7.56 Hz); 9.27 (d, 1 H, H(6) Py, J = 5.92 Hz); 11.82 (br.s, 1 H, OH); 12.36 (br.s, 1 H, NH).

3-(Indolizin-2-yl)quinoxalin-2(1*H*)-one (4a). Triethylamine (10 mL) was added to a mixture of compound **2a** (2.0 g, 0.49 mmol) and chloroform (40 mL). The reaction mixture was stirred for 2 h and kept for 3 days. Then chloroform and Et_3N were evaporated *in vacuo*, and water (30 mL) was added to the residue. The crystals that precipitated were filtered off, washed with water, dried, suspended in chloroform (5 mL), passed through a column (300×25 mm) packed with silica gel (6 g), and eluted with chloroform (250 mL). The solvent was evaporated *in vacuo*, and analytically pure compound **4a** was obtained in a yield of 0.49 g (39%), m.p. 261—263 °C. Found (%): C, 73.49; H, 4.38; N, 16.03. $C_{16}H_{11}N_3O$. Calculated (%): C, 73.55; H, 4.24; N, 16.08. IR, ν/cm^{-1}: 421, 472, 543, 586, 639, 726, 745, 788, 813, 919, 1021, 1142, 1178, 1300, 1500, 1543, 1595, 1610, 1670. ^{1}H NMR, δ: 6.56 (dd, 1 H, H(6′), J = 7.02 and 6.60 Hz); 6.71 (dd, 1 H, H(7′), J = 6.96 and 6.50 Hz); 7.20 (s, 1 H, H(1′)); 7.31 (dd, 1 H, H(6), J = 8.34 and 6.96 Hz); 7.44 (d, 1 H, H(8′), J = 7.92 Hz); 7.36 (d, 1 H, H(8), J = 7.92 Hz); 7.48 (dd, 1 H, H(7), J = 7.92 and 7.44 Hz); 7.81 (dd, 1 H, H(5), J = 8.28 and 0.9 Hz); 8.33 (d, 1 H, H(5′), J = 7.02 Hz); 8.72 (s, 1 H,

H(3′)); 12.54 (s, 1 H, NH). ^{13}C NMR, δ: 98.74 (C(1′)), 110.84 (C(6′)), 114.81 (C(8)), 116.70 (C(3′)), 117.85 (C(7′)), 118.98 (C(8′)), 123.00 (C(6)), 123.66 (C(2′)), 125.91 (C(5′)), 127.81 (C(5)), 128.87 (C(7)), 131.01 (C(8a)), 131.68 (C(8a′)), 132.08 (C(4a)), 150.80 (C(3)), 154.00 (C(2)).

3-(3-Phenylindolizin-2-yl)quinoxalin-2(1*H*)-one (4b). Triethylamine (8 mL) was added to a mixture of compound **3b** (0.4 g, 0.083 mmol) and chloroform (32 mL). The reaction mixture was stirred for 2 h and kept for 3 days. Then chloroform and Et_3N were evaporated *in vacuo*, and water (20 mL) was added to the residue. The crystals that precipitated were filtered off, washed with water, dried, suspended in chloroform (10 mL), passed through a column (300×15 mm) packed with silica gel (2 g), and eluted with chloroform (80 mL). The solvent was evaporated *in vacuo*, and analytically pure compound **4b** was obtained in a yield of 0.2 g (71%), m.p. 243—245 °C. Found (%): C, 74.65; H, 5.28; N, 14.43. $C_{18}H_{15}N_3O$. Calculated (%): C, 74.72; H, 5.23; N, 14.52. IR, ν/cm^{-1}: 422, 472, 556, 594, 663, 702, 744, 769, 788, 912, 1149, 1176, 1276, 1317, 1490, 1544, 1597, 1666, 2500—3220. ^{1}H NMR, δ: 6.64 (dd, 1 H, H(6′), J = 6.80 and 6.76 Hz); 6.76 (dd, 1 H, H(7′), J = 6.76 and 6.08 Hz); 7.20 (dd, 1 H, H(6), J = 7.44 and 6.80 Hz); 7.26 (d, 1 H, H(8), J = 8.16 Hz); 7.30 (d, 1 H, H(5), J = 8.80 Hz); 7.31—7.40 (m, 6 H, Ph, H(5′)); 7.45 (dd, 1 H, H(7), J = 8.12 and 6.80 Hz); 8.38 (d, 1 H, H(5′), J = 6.76 Hz); 8.59 (s, 1 H, H(3′)); 12.33 (s, 1 H, NH).

1-Ethyl-3-(indolizin-2-yl)quinoxalin-2-one (5a). Ethyl bromide (0.046 mL, 0.62 mmol) was added to a mixture of compound **4a** (101 mg, 0.39 mmol), KOH (0.1 g, 1.8 mmol), and DMSO (1 mL). The reaction mixture was stirred for 5 h and kept for 2 days. The crystals that precipitated were filtered off and washed with water, and analytically pure compound **5a** was obtained. The filtrate was poured into water. The crystals that precipitated were filtered off and washed with water, and an additional amount of compound **5a** was obtained. The latter was dissolved in chloroform (1 mL), passed through a column (300×15 mm) packed with silica gel (1 g), and eluted with chloroform (40 mL). The solvent was evaporated *in vacuo*, and analytically pure compound **5a** was obtained in a yield of 0.62 g (55%), m.p. 167—168 °C. Found (%): C, 74.67; H, 5.26; N, 14.49. $C_{18}H_{15}N_3O$. Calculated (%): C, 74.80; H, 5.19; N, 14.53. IR, ν/cm^{-1}: 418, 427, 469, 549, 642, 651, 725, 742, 746, 780, 808, 1115, 1150, 1191, 1246, 1304, 1371, 1498, 1543, 1581, 1633, 1648. ^{1}H NMR, δ: 1.32 (dd, 3 H, CH_3, J = 7.28 and 6.94 Hz); 4.48 (dq, 2 H, CH_2, J = 7.28 and 6.94 Hz); 6.57 (dd, 1 H, H(6′), J = 6.52 and 6.16 Hz); 6.73 (dd, 1 H, H(7′), J = 6.52 and 6.48 Hz); 7.24 (s, 1 H, H(1′)); 7.37—7.44 (m, 1 H, H(6)); 7.44 (d, 1 H, H(8′), J = 8.92 Hz); 7.58—7.65 (m, 1 H, H(7)); 7.61 (dd, 1 H, H(8), J = 8.7 and 1.7 Hz); 7.86 (dd, 1 H, H(5), J = 7.88 and 1.0 Hz); 8.32 (d, 1 H, H(5′), J = 7.3 Hz); 8.68 (s, 1 H, H(3′)). ^{13}C NMR, δ: 12.08 (CH_3), 36.67 (CH_2), 98.97 (C(1′)), 110.88 (C(6′)), 113.97 (C(8)), 116.82 (C(3′)), 117.86 (C(7′)), 119.00 (C(8′)), 123.14 (C(6)), 123.80 (C(2′)), 125.90 (C(5′)), 129.00 (C(5)), 129.32 (C(7)), 131.08 (C(8a)), 131.67 (C(8a′)), 132.70 (C(4a)), 149.44 (C(3)), 152.89 (C(2)).

1-Ethyl-3-(3-phenylindolizin-2-yl)quinoxalin-2-one (5b) was prepared analogously to compound **5a** from phenylindolizin-2-ylquinoxalin-2-one (**4b**) (0.2 g, 0.59 mmol). The yield was 0.1 g (46%), m.p. 167—169 °C. Found (%): C, 78.96; H, 5.40; N, 11.39. $C_{24}H_{19}N_3O$. Calculated (%): C, 78.88; H, 5.24; N, 11.50. IR, ν/cm^{-1}: 419, 432, 463, 501, 584, 670, 701, 732, 745, 762, 1021, 1082, 1089, 1098, 1135, 1187, 1251, 1274, 1285, 1309, 1422, 1497, 1602, 1652. ^{1}H NMR, δ: 1.28 (dd, 3 H, CH_3, J = 7.04 and 6.63 Hz); 4.33 (dq, 2 H, CH_2, J = 7.04 and 6.63 Hz); 6.64 (dd, 1 H, H(6′), J = 6.68 and 5.84 Hz); 6.75 (dd, 1 H, H(7′), J = 6.28 and 6.28 Hz); 7.20—7.60 (m, 10 H, Ph, H(5), H(6), H(7), H(8), H(5′)); 8.37 (d, 1 H, H(5′), J = 7.04 Hz); 8.56 (s, 1 H, H(3′)).

1,5-Bis[3-(indolizin-2-yl)-2-oxoquinoxalin-1-yl]-3-oxapentane (6). 1,5-Dibromo-3-oxapentane (49 mg, 0.21 mmol) was added to a mixture of compound **4a** (100 mg, 0.39 mmol), KOH (0.1 g, 1.8 mmol), and DMSO (2 mL). The reaction mixture was stirred for 5 h and kept for 2 days. The crystals that precipitated were filtered off, washed with water, dried, dissolved in chloroform (1 mL), and passed through a column (300×15 mm) packed with silica gel (2 g) with the use of chloroform (60 mL) as the eluent. The solvent was removed *in vacuo*, and analytically pure compound **6** was obtained. The yield was 0.23 g (20%), m.p. 232—234 °C. Found (%): C, 72.85; H, 4.70; N, 14.26. $C_{36}H_{28}N_6O_3$. Calculated (%): C, 72.96; H, 4.76; N, 14.18. IR, ν/cm^{-1}: 421, 447, 550, 643, 730, 741, 753, 782, 810, 1107, 1120, 1224, 1305, 1364, 1499, 1545, 1603, 1659. ^{1}H NMR, δ: 3.86 (t, 2 H, OCH_2, J = 5.63 Hz); 4.49 (t, 2 H, NCH_2, J = 5.63 Hz); 6.57 (ddd, 1 H, H(6′), J = 7.17, 6.14, and 1.03 Hz); 6.77 (dd, 1 H, H(7′), J = 6.66 and 6.65 Hz); 7.22 (s, 1 H, H(1′)); 7.34 (dd, 1 H, H(6), J = 8.19 and 7.17 Hz); 7.45 (dd, 1 H, H(7), J = 7.46 and 7.45 Hz); 7.46 (d, 1 H, H(8′), J = 9.22 Hz); 7.56 (d, 1 H, H(8), J = 8.19 Hz); 7.79 (d, 1 H, H(5), J = 8.20 Hz); 8.31 (d, 1 H, H(5′), J = 6.15 Hz); 8.63 (s, 1 H, H(3′)). ^{13}C NMR, δ: 41.43 (NCH_2), 67.12 (OCH_2), 98.98 (C(1′)), 110.87 (C(6′)), 114.40 (C(8)), 116.79 (C(3′)), 117.84 (C(7′)), 118.99 (C(8′)), 123.13 (C(6)), 123.75 (C(2′)), 125.88 (C(5′)), 128.78 (C(5)), 128.95 (C(7)), 131.67 (C(8a)), 131.81 (C(8a′)), 132.55 (C(4a)), 149.30 (C(3)), 153.36 (C(2)).

1,5-Bis[2-oxo-3-(1-phenylindolizin-2-yl)quinoxalin-1-yl]-3-oxapentane (7) and **1-(5-bromo-3-oxapent-1-yl)-3-(1-phenylindolizin-2-yl)quinoxalin-2-one (11).** A mixture of compound **4b** (0.40 g, 1.19 mmol), KOH (0.10 g, 1.79 mmol), and dioxane (10 mL) was refluxed for 5 min. Then 1,5-dibromo-3-oxapentane (0.17 g, 0.73 mmol) was added. The reaction mixture was refluxed for 12 h, cooled, and poured into water (40 mL). The crystals that precipitated were filtered off and washed with water. The resulting mixture of compounds **4b**, **7**, and **11** was separated by silica gel column chromatography (m 20 g, L 100/160μ) using chloroform as the eluent.

The yield of compound **7** was 80 mg (18%), m.p. 138—140 °C. Found (%): C, 77.29; H, 4.81; N, 11.39. $C_{48}H_{36}N_6O_3$. Calculated (%): C, 77.40; H, 4.87; N, 11.28. IR, ν/cm^{-1}: 586, 670, 762, 1083, 1123, 1229, 1311, 1528, 1544, 1581, 1602, 1654. ^{1}H NMR, δ: 3.77 (t, 4 H, 2 OCH_2, J = 5.48 Hz); 4.40 (t, 4 H, 2 NCH_2, J = 5.48 Hz); 6.60 (ddd, 2 H, 2 H(6′), J = 7.56, 6.16, and 1.36 Hz); 6.73 (dd, 2 H, 2 H(7′), J = 7.52 and 6.80 Hz); 7.12—7.40 (m, 16 H, 2 Ph, 2 H(5), 2 H(6), 2 H(5′)); 7.37 (ddd, 2 H, H(7), J = 8.24, 6.88, and 1.40 Hz); 7.46 (d, 2 H, 2 H(8), J = 8.24 Hz); 8.29 (d, 2 H, 2 H(5′), J = 6.84 Hz); 8.49 (s, 2 H, H(3′)).

The yield of compound **11** was 58 mg (10%), m.p. 121—123 °C. Found (%): C, 64.01; H, 4.38; N, 8.43; Br, 16.25. $C_{26}H_{22}BrN_3O_2$. Calculated (%): C, 64.12; H, 4.51; N, 8.62; Br, 16.40. IR, ν/cm^{-1}: 672, 707, 752, 763, 1134, 1185, 1289, 1311, 1497, 1529, 1582, 1601, 1654. ^{1}H NMR, δ: 3.77 (t, 2 H, $N(CH_2)_2OCH_2C\underline{H}_2Br$, J = 5.48 Hz); 3.77 (t, 2 H,

$N(CH_2)_2OC\underline{H}_2CH_2Br$, J = 5.48 Hz); 3.82 (t, 2 H, $NCH_2C\underline{H}_2O(CH_2)_2Br$, J = 6.20 Hz); 4.51 (t, 2 H, $NC\underline{H}_2CH_2O(CH_2)_2Br$, J = 5.48 Hz); 6.64 (ddd, 1 H, H(6′), J = 6.86, 6.16, and 1.36 Hz); 6.76 (ddd, 1 H, H(7′), J = 9.24, 6.20, and 1.36 Hz); 7.18—7.40 (m, 8 H, Ph, H(5), H(6), H(5′)); 7.54 (ddd, 1 H, H(7), J = 8.24, 6.88, and 1.40 Hz); 7.65 (d, H, H(8), J = 8.20 Hz); 8.37 (d, 1 H, H(5′), J = 6.88 Hz); 8.54 (s, 1 H, H(3′)).

1,11-Bis(3-indolizin-2-yl-2-oxoquinoxalin-1-yl)-3,6,9-trioxaundecane (8) was prepared analogously to compound **7** from indolizinylquinoxaline **4a** (0.2 g, 0.76 mmol) and 1,11-dibromo-3,6,9-trioxaundecane (0.2 g, 0.62 mmol). The yield was 30 mg (11%), m.p. 70—71 °C. Found (%): C, 70.44; H, 5.37; N, 12.30. $C_{40}H_{36}N_6O_5$. Calculated (%): C, 70.57; H, 5.33; N, 12.35. IR, ν/cm^{-1}: 622, 742, 782, 810, 941, 1037, 1183, 1223, 1301, 1355, 1498, 1602, 1648. ^{1}H NMR, δ: 3.36—3.41 (m, 2 H, $N(CH_2)_2OCH_2C\underline{H}_2O$); 3.46—3.50 (m, 2 H, $N(CH_2)_2OC\underline{H}_2CH_2O$); 3.76 (t, 2 H, $NCH_2C\underline{H}_2O(CH_2)_2O$, J = 5.84 Hz); 4.49 (t, 2 H, $NC\underline{H}_2CH_2O(CH_2)_2O$, J = 5.84 Hz); 6.55 (dd, 1 H, H(6′), J = 6.88 and 6.16 Hz); 6.71 (dd, 1 H, H(7′), J = 8.92 and 6.16 Hz); 7.22 (s, 1 H, H(1′)); 7.36 (dd, 1 H, H(6), J = 7.52 and 6.88 Hz); 7.43 (d, 1 H, H(8′), J = 8.92); 7.53 (dd, 1 H, H(7), J = 8.24 and 7.52 Hz); 7.62 (d, 1 H, H(8), J = 8.24 Hz); 7.82 (d, 1 H, H(5), J = 8.20 Hz); 8.30 (d, 1 H, H(5′), J = 7.20 Hz); 8.66 (s, 1 H, H(3′)).

1,11-Bis[2-oxo-3-(1-phenylindolizin-2-yl)quinoxalin-1-yl]-3,6,9-trioxaundecane (9) and **1-(11-bromo-3,6,9-oxaundec-1-yl)-3-(1-phenylindolizin-2-yl)quinoxalin-2-one (12).** A mixture of compound **4b** (0.70 g, 2.09 mmol), KOH (0.18 g, 3.14 mmol), and dioxane (20 mL) was refluxed for 5 min. Then 1,5-dibromo-3-oxapentane (0.40 g, 1.25 mmol) was added. The reaction mixture was refluxed for 12 h, cooled, and poured into water (40 mL). The crystals that precipitated were filtered off and washed with water, and a mixture of compounds **4b**, **9**, and **12** was obtained. The compounds were separated by silica gel column chromatography (m 20 g, L 100/160μ) using chloroform as the eluent. The yield of compound **9** was 0.64 g (37%), m.p. 168—169 °C. Found (%): C, 75.07; H, 5.38; N, 10.00. $C_{52}H_{44}N_6O_5$. Calculated (%): C, 74.98; H, 5.32; N, 10.09. IR, ν/cm^{-1}: 670, 702, 753, 1007, 1125, 1183, 1228, 1289, 1311, 1494, 1529, 1581, 1602, 1652. ^{1}H NMR, δ: 3.37—3.41 (m, 2 H, $N(CH_2)_2OCH_2C\underline{H}_2O$); 3.45—3.49 (m, 2 H, $N(CH_2)_2OC\underline{H}_2CH_2O$); 3.71 (t, 2 H, $NCH_2C\underline{H}_2O(CH_2)_2O$, J = 5.50 Hz); 4.41 (t, 2 H, $NC\underline{H}_2CH_2O(CH_2)_2O$, J = 5.50 Hz); 6.60 (ddd, 1 H, H(6′), J = 6.81, 6.13, and 0.68 Hz); 6.72 (dd, 1 H, H(7′), J = 6.81, 6.13, and 0.68 Hz); 7.22—7.28 (m, 3 H, H(5), H(6), H_p); 7.29—7.38 (m, 5 H, H(8′), 2 H_o, 2 H_m); 7.46 (ddd, 1 H, H(7), J = 7.81, 7.80, and 1.41 Hz); 7.55 (d, 1 H, H(8), J = 7.82 Hz); 8.32 (d, 1 H, H(5′), J = 6.80 Hz); 8.52 (s, 1 H, H(3′)). ^{13}C NMR, δ: 41.47 ($N\underline{C}H_2CH_2OCH_2CH_2$), 66.90 ($NCH_2\underline{C}H_2OCH_2CH_2$), 69.47 ($NCH_2CH_2OCH_2\underline{C}H_2$), 69.74 ($NCH_2CH_2O\underline{C}H_2CH_2$), 113.79 (C(1′)), 114.46 (C(8)), 117.02 (C(3′)), 117.25 (C(8′)), 118.41 (C(7′)), 120.83 (C(2′)), 122.86 (C(6′)), 122.86 (C(6)), 125.17 (C_p), 125.79 (C(5′)), 127.25 (2 C_m), 128.58 (C(5)), 129.15 (C(7)), 129.54 (C(8a′)), 129.92 (2 C_o), 135.31 (C_i), 131.90 (C(8a)), 132.01 (C(4a)), 150.20 (C(3)), 153.37 (C(2)).

The yield of compound **12** was 24 mg (2%), m.p. 65—67 °C. Found (%): C, 62.48; H, 5.15; N, 7.32; Br, 13.73. $C_{30}H_{30}BrN_3O_4$. Calculated (%): C, 62.66; H, 5.21; N, 7.30; Br, 13.89. IR, ν/cm^{-1}: 672, 702, 752, 1015, 1184, 1226, 1248, 1288, 1311, 1529, 1581, 1601, 1654. ^{1}H NMR, δ: 3.41—3.44 (m, 2 H, C(7″)H_2); 3.45—3.48 (m, 4 H, C(5″)H_2, C(8″)H_2); 3.50 (t, 2 H, C(11″)H_2, J = 5.86 Hz); 3.54 (t, 2 H, C(4″)H_2, J = 5.86 Hz); 3.67 (t, 2 H, C(10″)H_2, J = 5.87 Hz); 3.75 (t, 2 H, C(2″)H_2, J = 5.87 Hz); 4.47 (t, 2 H, C(1″)H_2, J = 5.86 Hz); 6.63 (dd, 1 H, H(6′), J = 6.60 and 6.60 Hz); 6.75 (dd, 1 H, H(7′), J = 6.61 and 6.60 Hz); 7.22—7.29 (m, 3 H, H(5), H(6), H_p); 7.30—7.35 (m, 5 H, 2 H_o, 2 H_m, H(8′)); 7.53 (ddd, 1 H, H(7), J = 6.61, 6.60, and 2.20 Hz); 7.62 (d, 1 H, H(8), J = 8.07 Hz); 8.36 (d, 1 H, H(5′), J = 6.60 Hz); 8.53 (s, 1 H, H(3′)). ^{13}C NMR, δ: 31.79 (C(11)H_2), 41.58 (C(1)H_2), 67.01 (C(2)H_2), 69.34 (C(8)H_2), 69.54 (C(7)H_2), 69.57 (C(5)H_2), 69.85 (C(4)H_2), 70.13 (C(10)H_2), 111.34 (C(6′)), 113.85 (C(1′)), 114.58 (C(8)), 117.04 (C(3′)), 117.33 (C(8′)), 118.52 (C(7′)), 120.92 (C(2′)), 122.98 (C(6)), 125.25 (C_p), 125.88 (C(5′)), 127.35 (2 C_m), 128.67 (C(5)), 129.29 (C(7)), 129.60 (C(8a′)), 129.95 (2 C_o), 135.36 (C_i), 132.00 (C(8a)), 132.08 (C(4a)), 150.32 (C(3)), 153.47 (C(2)).

1,3-Bis[3-(indolizin-2-yl)-2-oxoquinoxalin-1-ylmethyl]benzene (10) was prepared analogously to compound **7** from indolizinylquinoxaline **4a** (100 mg) and α,α′-dibromo-*m*-xylene (52 mg). The yield was 67 mg (28%), m.p. 247—249 °C. Found (%): C, 76.99; H, 4.67; N, 13.63. $C_{40}H_{28}N_6O_2$. Calculated (%): C, 76.90; H, 4.52; N, 13.45. IR, ν/cm^{-1}: 530, 562, 644, 755, 783, 812, 1123, 1179, 1220, 1304, 1496, 1546, 1529, 1603, 1655. ^{1}H NMR (DMSO-d_6), δ: 5.62 (s, 4 H, CH_2); 6.58 (dd, 2 H, H(6′), J = 6.66 and 6.65 Hz); 6.74 (dd, 2 H, H(7′), J = 6.66 and 6.65 Hz); 7.27 (s, 2 H, H(1′)); 7.29—7.39 (m, 10 H, 2 H(6), 2 H(7), 2 H(8), C_6H_4); 7.43 (d, 2 H, H(8′), J = 8.19 Hz); 7.82 (d, 2 H, H(5), J = 6.65 Hz); 8.21 (d, 2 H, H(5′), J = 7.17 Hz); 8.67 (s, 2 H, H(3′)).

X-ray diffraction study of compound 5a was carried out on an automated four-circle Enraf-Nonius CAD-4 diffractometer. Pale-brown prismatic crystals of **5a**, $C_{18}H_{14}N_3O$, belong to the triclinic system, crystal dimensions were 0.3×0.3×0.3 mm. At 20 °C, a = 7.75(1), b = 9.49(1), c = 9.734(9) Å, α = 90.18(6), β = 97.68(6), γ = 89.96(5)°, V = 709(1) Å^3, Z = 2, d_{calc} = 1.35 g cm^{-3}, space group $P\bar{1}$. The unit cell parameters and the intensities of 2577 reflections, of which 1130 reflections were with $I \geq 3\sigma$, were measured at 20 °C (λ(Mo-Kα), graphite monochromator, ω/2θ scanning technique, θ ≤ 26.31°). The intensities of three check reflections showed no decrease in the course of X-ray data collection. The absorption correction was not applied because the absorption coefficient was small (μMo 0.81 cm^{-1}). The structure was solved by direct method using the SIR program[22] and refined first isotropically and then anisotropically using the MolEN program package.[23] Subsequently, the hydrogen atoms were located from difference electron density maps and included in the final steps of the refinement with fixed thermal and positional parameters. The final R factors were R = 0.059 and R_w = 0.068 based on 1130 reflections with $F^2 \geq 3\sigma$. The figures were drawn and intermolecular contacts were analyzed using the PLATON program.[24]

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