Synthesis, structure, and electrochemical properties of 1^2,4^2-dioxo-2^1,3^1-diphenyl-7,10,13-trioxa-1,4(3,1)-diquinoxalina-2(2,3),3(3,2)-diindolizinacyclopentadecaphane*

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The oxidative dehydrocyclization of the 3-(indolizin-2′-yl)-2-oxoquinoxaline monopodand performed either electrochemically or under the action of molecular iodine affords new redox-active heterocyclophane consisting of the redox-switchable biindolizine fragment combined with the polyether-bridged π-deficient quinoxaline systems. The single-crystal X-ray diffraction study showed that the trioxaundecane chain of heterocyclophane adopts an extended conformation, and one of the phenyl substituents of the molecule closes the pseudocavity formed by the spacer from one of the sides. The cyclic voltammetric study of heterocyclophane in MeCN and DMF showed the three-step oxidation of the indolizine fragments accompanied by the single-electron transfer in each step. The first and third steps are reversible, and the second step is irreversible. The oxidation at potentials of the first peak gives rise to stable radical cations detected by the ESR method (g = 2.0024, a_{2N} = 0.26 mT).

Key words: 3-(indolizin-2′-yl)quinoxalin-2-ones, 3-acetylquinoxalin-2-one, pyridinium salts, Ortoleva—King reaction, Chichibabin reaction, monopodands, UV spectra, 1D and 2D NMR spectroscopy, X-ray diffraction study, electrochemical oxidation, ESR.

In recent years, the synthesis of macrocyclic compounds, which can reversibly respond to external actions (thermal, photochemical, electrochemical, pH, *etc.*) by changing important properties and characteristics (the cavity size, the surface shape, the electronic structure, the complexing ability, *etc.*) due to the specially introduced functional groups or fragments, has taken a special place in supramolecular chemistry.[1] Such "sensitive" heterocyclophanes containing redox-active biindolizine systems can serve as molecular switches[2] and membrane carriers[3] and are of great interest in the design of new sensors for modern technologies based on molecular processes. Unlike redox-active compounds (ferrocenes,[4,5] tetrathiafulvalenes,[6,7] and quaternized 4,4′-bipyridines[8,9]), biindolizines have found little use as active regions, which make cyclophanes able to respond to external actions, in spite of the fact that biindolizines are quite stable two-step redox systems, whose electrochemical behavior has been studied in sufficient detail.[10—15]

Indolizines are π-rich compounds, which are readily oxidized (~0.2—0.3 V relative to $Fc^{0/+}$) to form radical cations.[10—14] The stability and subsequent transformations of radical cations are determined primarily by the presence of hydrogen atoms in the pyrrole ring of the indolizine system. The radical cations and dications of 3,3′-biindolizines, in which all hydrogen atoms in the five-membered ring are replaced by alkyl or aryl groups, are quite stable and can be isolated and characterized as perchlorates.[12] The electrochemical behavior of two diastereomers of macrocyclic biindolizines, in which both heterofragments are linked at positions 3,3′ and, through a bridge, at positions 1,1′, is different.[13] Thus, the diastereomer having the *anti* configuration is oxidized to form stable radical cations and dications, whereas the oxidation of the diastereomer having the *syn* configuration is followed by the intramolecular cyclization with the involvement of the C(5) and C(5′) atoms of the pyridine rings of the indolizine system having a favorable spatial arrangement.

In turn, if not all hydrogen atoms in the five-membered ring in indolizine molecules are replaced, the oxidation is accompanied by the coupling of the radical cations at the unsubstituted positions.[11,14] For example, the oxidation of 2,2′-diaryl-3,3′-biindolizines is accompanied by the coupling of the radical cations to form finally

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a polymeric film deposited on the electrode surface.[14] The properties of this film depend on the conditions of its formation. Films, which are prepared at the controlled potential of the first oxidation step or in the polycycling mode in the potential range of -0.3 V $\rightarrow$ $+0.8$ V $\rightarrow$ $\rightarrow -1.3$ V $\rightarrow -0.3$ V (relative to $Fc^{0/+}$), are redox-active and can undergo reversible oxidation to form stable paramagnetic states detected by the ESR method. The oxidation under more drastic conditions affords insulating films.

The formation of polymeric films having different properties is accompanied by oxidation of 2-arylmonoindolizines.[14] For 2-indolizinylquinoxalines, the nature of oxidation products depends on the presence or the absence of substituents at positions 1 and 3 of the five-membered ring of the indolizine system and at the nitrogen atom of the quinoxaline ring.[14] The behavior of alkyl-substituted 3-(indolizin-2-yl)quinoxalin-2-one is analogous to that of 2-arylindolizines. The oxidation of 3-(indolizin-2-yl)quinoxalin-2-ones containing the free carbamoyl group N—H affords insulating films regardless of the reaction conditions. If the phenyl group is introduced at position 1 of the indolizine fragment of 3-(indolizin-2-yl)quinoxalin-2-one, the oxidation does not give polymeric films regardless of the nature of the substituent at the nitrogen atom of the quinoxaline ring.[14]

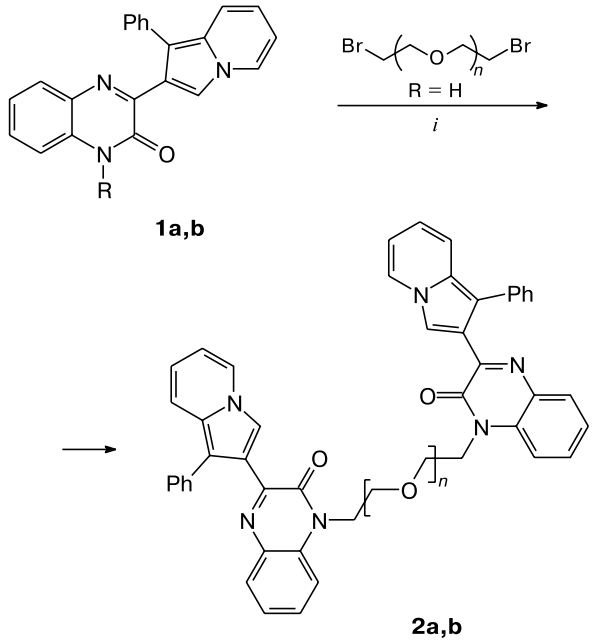
Two studies were published on cyclophanes containing redox-active biindolizine fragments, in which either the polymethylene or polyoxyethylene units[15] or, alternatively, the 1,4-phenylenebis[di(oxyethylene)] or 1,5-naphthylenebis[di(oxyethylene)] fragments[16] serve as spacers (units that link two indolizine systems at the terminal carbon atoms).

The complexing ability of these cyclophanes, particularly with respect to organic molecules, is not too high.[15,16] However, according to the terminal group concept,[17,18] the addition of heteroaromatic systems, which bear different types of atoms, at the ends of the oligo(ethylene glycol) chain substantially facilitates the complex formation. In addition, due to a combination of the π-systems of heteroaromatic rings with electron-rich indolizine fragments, the ability of such compounds to serve as active hosts with respect to guests containing electron-deficient aromatic moieties is substantially higher.[19]

The analysis of the data published in the literature[15,16] and our results[20] played the key role in the development of our strategy for the synthesis of indolizinylquinoxaline heterocyclophanes. Based on these data, the main requirements for the structure of podands, *viz.*, acyclic precursors, were defined: 1) two indolizinylquinoxaline fragments should be linked by a spacer of a particular length, 2) to perform the oxidative intramolecular cyclization, at least one of positions 1,3 in both indolizine systems should be unsubstituted, 3) to avoid polymerization, only one position of the five-membered ring of indolizine should be unsubstituted, 4) in the quinoxaline fragment, the hydrogen atom of the N—H group should be replaced by less mobile groups, 5) to increase the complexing ability of heterocyclophane, the indolizine fragments should be linked with the use of benzannelated aromatic heterocyclic systems.[21]

The designed synthesis of heterocyclophane containing the redox-active biindolizine systems is based on monopodand **2b** synthesized by the Williamson reaction[22] from the corresponding 1,11-dibromo-3,6,9-trioxaundecane and 3-(3-phenylindolizin-2-yl)quinoxalin-2(1*H*)-one (**1a**) (Scheme 1). Compound **1a** was synthesized according to the modified Chichibabin method[23] based on the condensation of 3-acetylquinoxalin-2(1*H*)-one with 2-benzylpyridine in the presence of molecular iodine[20] involving the formation of the pyridinium salt by the Ortoleva—King reaction[24] as the first step.

Scheme 1



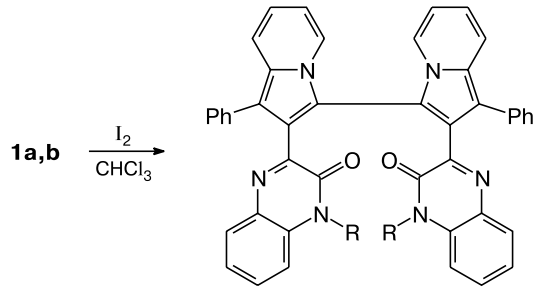
R = H (**1a**), Et (**1b**); *n* = 1 (**2a**), 3 (**2b**)

i. KOH/DMSO or dioxane.

Several methods for the oxidative dimerization of indolizines at unsubstituted position 3 were documented. However, all these methods have drawbacks. For example, the use of potassium hexacyanoferrate $K_3Fe(CN)_6$ leads to the formation of by-products,[11] the use of Fe^{3+} salts not always gives rise to the desired product,[25] and the use of platinum (Pt/C, 10% Pt) or palladium (Pd/C, 10% Pd) requires a long reaction time.[26] We found that molecular iodine can serve as an oxidation agent instead of the above-mentioned reagents. Model reactions of compounds **1a** and **1b** in chloroform in the presence of molecular I_2

produce analytically pure biindolizines **3a,b** in 30 and 31% yields, respectively, which stimulated us to apply this method to the oxidation of biindolizinylquinoxaline monopodand **2b** (Scheme 2).

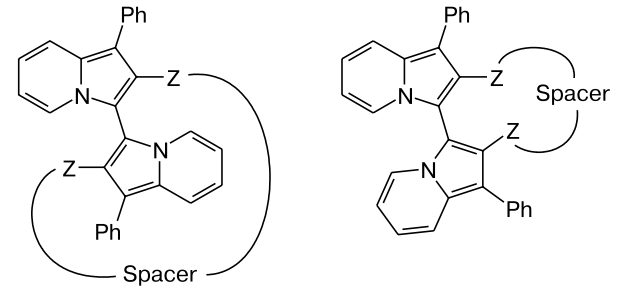
Scheme 2



3a,b

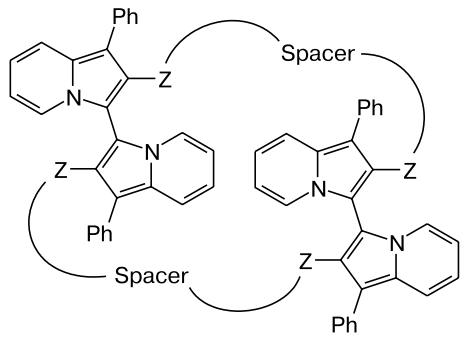
R = H (**a**), Et (**b**)

The treatment of compound **2b** with iodine in chloroform led to the oxidative dehydrocondensation giving rise to a mixture of intramolecular (**4**) and intermolecular cyclization products (**5**) in a ratio of 10 : 1, with the former predominating (two conformations, **4a** and **4b**, are considered). The ratio between the products remains virtually unchanged under the conditions of electrochemical oxidation of compound **2b** as well.



4a

4b



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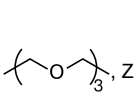
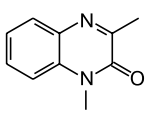
Spacer =  , Z = 

The presence of only two types of molecular ion peaks, MH^+ 831 and MH^+ 1662, in the MALDI TOF mass spectra, which were recorded for samples of the crude products of the chemical and electrochemical oxidation of compound **2b**, is evidence for the formation of impurity-free products **4** and **5**, with the former compound predominating regardless of the oxidation mode, whereas the latter compound being formed as a by-product in trace amounts. The electron impact mass spectrum of a sample purified by column chromatography shows, along with a 100% intensity molecular ion peak at m/z 830.2, molecular ion peaks at m/z 831.2 (61.8%), 832.3 (19.65%), and 833.2 (4.86%) containing isotopes.

The structure of the major product, *viz.*, cyclopentadecaphane **4**, was confirmed by IR, UV, and NMR spectroscopy and the X-ray diffraction study of a single crystal grown from DMF.

Structural characteristics of cyclopentadecaphane 4

IR spectra. A comparison of the IR spectra of biindolizine **3b** (see the Experimental section) and macrocyclic compound **4** (see Ref. 20) showed no substantial differences, which could serve as a diagnostic indication of the formation of cyclophane **4**.

UV spectra. The UV spectra of compounds **2b**, **4**, and **2a** in $CHCl_3$ in the 250—800 nm region show two intense absorption bands with maxima at ~290 and 350 nm and a third weak band as an inflection point near 430 nm (Table 1). Based on the assignments[27] for the spectrum of quinoxaline, two main maxima in the spectra of compounds **2b** and **2a** can be assigned to π-π* transitions; the long-wavelength maximum, to n-π* transitions. The π-π* bands of podands **2b** and **2a** have a vibrational structure, which is most pronounced in the spectrum of **2a**. The spectra of products **4** prepared by different methods (chemical and electrochemical) are completely identical. It should be noted that certain changes are observed in the spectra of **4** compared to those of podand **2b**. Thus, the band with a maximum at 359 nm is hypsochromically shifted by 9 nm, the intensities of both π-π* bands are lower, and their vibrational structure becomes less pronounced, which is, apparently, associated with a weakening of the conjugation in the strained cyclic molecule. The spectra of precursors **2b** and **2a** are virtually identical to the spectrum of indolizinylquinoxalinone **1** regardless of the spacer length.

NMR spectra. In the NMR spectra of indolizine derivatives, the positions of most signals strongly depend on the nature of the substituents,[11—13,15,16,26] which not always allows the comparison of the chemical shifts and the spin-spin coupling constants for their structure determi-

Table 1. UV spectra of compounds **1b**, **2a**, and **2b** and heterocyclophane **4**, which was synthesized by electrochemical oxidation (A) and oxidation with iodine (B), in $CHCl_3$

Compound	λ_{max}/nm (logε)		
	$\pi\rightarrow\pi^*$		$n\rightarrow\pi^*$
1b	282 (4.22) sh, 294 (4.31)	336 (4.24) sh, 353 (4.33) sh, 368 (4.36), 385 (4.20) sh	430 (3.19) sh
2a	281 (4.14), 290 (4.21)	323 (4.26) sh, 339 (4.34) sh, 355 (4.43) sh, 370 (4.47), 387 (4.36) sh	432 (3.73) sh
2b	282 (4.37) sh, 295 (4.46)	337 (4.36) sh, 355 (4.46) sh, 368 (4.47), 385 (4.32) sh	430 (3.46) sh
4 (A)	298 (4.07)	359 (3.91)	427 (3.08) sh
4 (B)	298 (4.12)	359 (3.94)	427 (3.05) sh
Quinoxaline[27]	280 (3.41)	316 (3.77)	339 (2.80)
Indolizine[28]	294.5 (3.56)	346.5 (3.29)	

nation. Hence, it is reasonable to present the assignment of the signals in the ^1H and ^{13}C NMR spectra of cyclopentadecaphane **4** based on 2D NMR methods.[29—31] A knowledge of the precise chemical shifts of the signals and their multiplicities, particularly, for the signals of the indolizine systems, can be useful for the analysis of NMR spectra of more complex compounds prepared based on compound **4**.

In the ^1H NMR spectrum of compound **4** at 323 K in DMSO-d_6, virtually all lines are broadened, particularly, in the region characteristic of the signals for the protons of the $-OCH_2$ groups. Moreover, signals were not observed in the ^{13}C NMR spectrum at 323 K due to a strong broadening and a low concentration of the sample. The observed broadening is most likely associated with the conformational exchange, whose rate appeared to be intermediate on the NMR time scale, although the formation of intermolecular complexes *via* π-π interactions between the aromatic rings of adjacent molecules **4** cannot be completely excluded solely based on the above-considered data.

To avoid complications in the spectra associated with the conformational exchange, all NMR experiments were carried out at high temperature, at which the exchange processes are fast on the NMR time scale and the spectra are simplified.

The ^1H NMR spectrum (DMF-d_7) of compound **4** at 333 K consists of well-resolved multiplets at low field belonging to protons of the aromatic rings and a series of complex multiplets at δ 4.1—3.3 assigned to the $C(1)H_2$, $C(2)H_2$, and $C(3)H_2$ methylene groups, in which the geminal protons are nonequivalent (Fig. 1).

The ^{13}C NMR spectrum of compound **4** at 333 K shows 20 signals at low field (the relative intensities of two signals correspond to two carbon atoms each) and four signals at δ 71—41.

Based on the 2D COSY NMR spectrum (Fig. 2), the spin systems belonging to the protons of the phenyl rings, the *ortho*-phenylene fragments of the quinoxaline system, and the pyridine fragments of the indolizine system, as well as of three $CH_2—CH_2$ groups (as an AA´BB´ spin system) were identified. Taking into account the 2D HSQC spectrum, the signals for the proton-containing carbon atoms of these fragments were determined.

The structures of these fragments were completely determined based on the 2D HMBC spectra (Fig. 3). In the 2D HMBC spectrum, the cross-correlations between the H(5) and H(7) atoms (δ 7.29 and 7.49) and the C(8a) atom (δ 134.06) and between the H(6) and H(8) atoms (δ 7.20 and 7.50) and the C(4a) atom (δ 133.52) are observed for the benzo fragment of quinoxaline, which allowed us to completely determine the

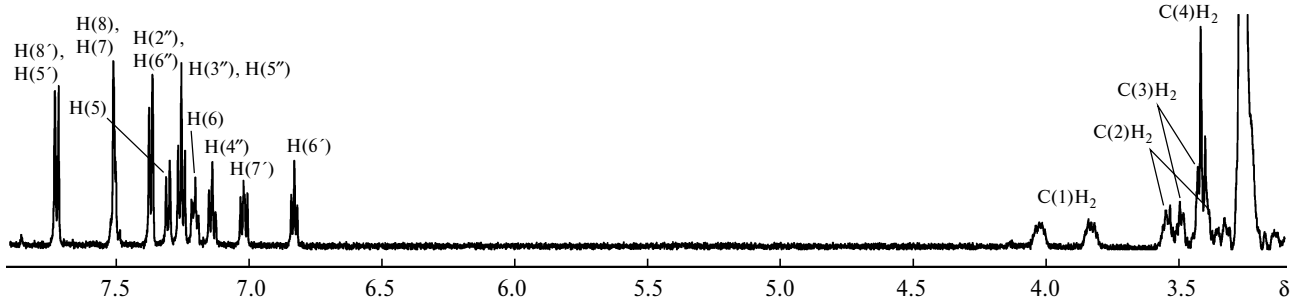


Fig. 1. ^1H NMR spectrum of compound **4** in DMF-d_7 at 333 K (the numbering of the nuclei is given in Fig. 4).

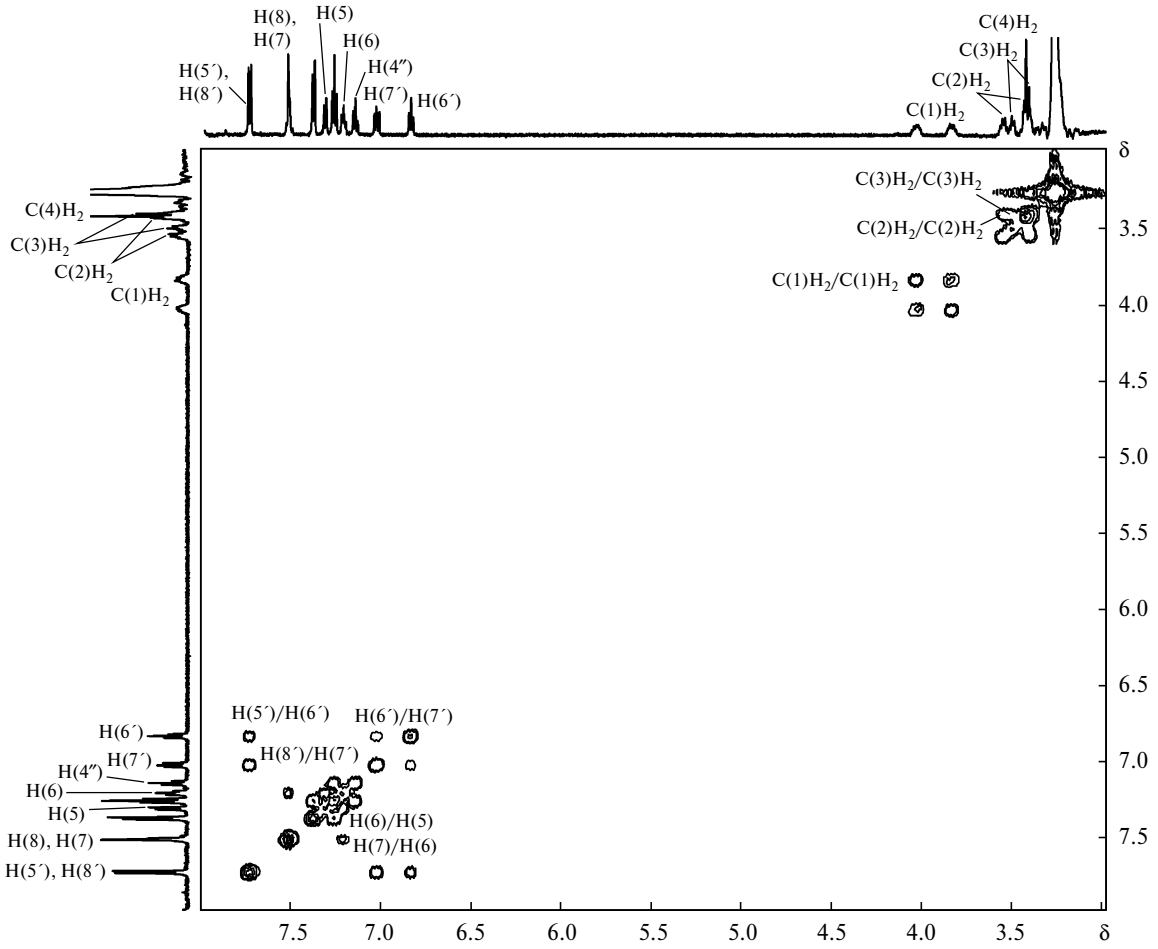


Fig. 2. 2D COSY spectrum of compound **4**.

structure of the carbocyclic moiety of the quinoxaline system (Fig. 4).

In addition, the 2D HMBC spectrum (see Fig. 3) shows the correlations between the H(5′) and H(7′) protons of the pyridine ring (δ 7.71 and 7.00) and the C(8a′) atom of the indolizine system (δ 131.42), between the H(5′) atom of the pyridine ring (δ 7.71) and the C(3′) atom of the pyrrole ring (δ 115.26), and between the H(8′) atom of the pyridine ring (δ 7.71) and the C(1′) atom of the pyrrole ring (δ 115.44), which allowed us to establish the structure of the indolizine system (see Fig. 4).

The cross-peaks between the H(3″) and H(5″) protons of the phenyl ring (δ 7.24) and the C(1″) atom (δ 136.01) and between the H(2″) and H(6″) protons (δ 7.36) and the C(1′) atom (δ 115.44) in the 2D HMBC spectrum unambiguously confirm the presence of the phenyl ring (see Fig. 3); besides, the presence of the latter cross-peak is indicative of the bond between the phenyl ring and the C(1′) atom of the indolizine system.

The cross-peaks between the $C(2)H_2$ protons (δ 3.53 and 3.39) and the $C(3)H_2$ carbon atom (δ 70.70) and between the $C(3)H_2$ protons (δ 3.48 and 3.42) and the $C(2)H_2$ carbon atom (δ 67.62) in the 2D HMBC spectrum are evidence for the presence of the bond between the CH_2—CH_2 fragments of the 3-oxapentane moiety (see Fig. 4); the cross-peaks between the $C(1)H_2$ protons (δ 4.01 and 3.82) and the C(8a) (δ 134.06) and C(2) (δ 154.24) carbon atoms confirm the presence of the bond between the 3-oxapentane spacer and the quinoxaline system (see Fig. 4).

The assignment of the signals at δ 147.98 and 125.11 in the ^{13}C NMR spectrum to the C(3) and C(2′) carbon atoms of the quinoxaline and indolizine systems, respectively, was made based on a comparison of their chemical shifts with the ^{13}C chemical shifts for compound **2b**,[20] in the spectrum of which the signals for C(3) and C(2′) are observed at δ 150.21 and 120.84, respectively. This assignment of the chemical shifts to the C(3) and C(2′) carbon atoms is in agreement with the results of calculations of the chemical shifts (GIAO B3LYP/6-31G(d)//RHF/6-31G [32—36]) performed for the simpler model compounds, *viz.*, 2-(1-methyl-2-oxo-1*H*-pyrazin-3-yl)indolizine (**5**) and 2,2′-(1-methyl-2-oxo-(1*H*)-pyrazin-3-yl)-3,3′-biindolizine (**6**), according to

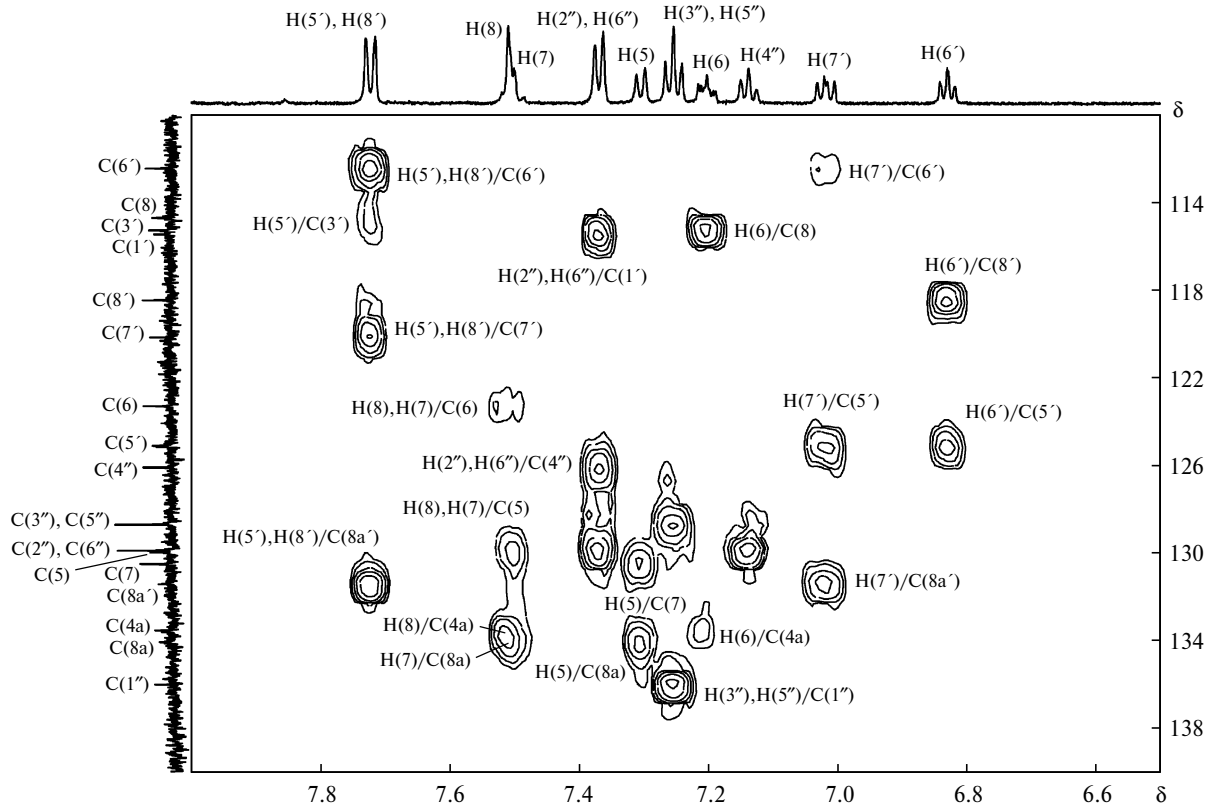


Fig. 3. Fragment of the 2D HMBC spectrum of compound **4**.

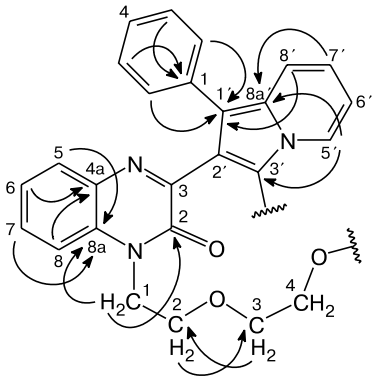
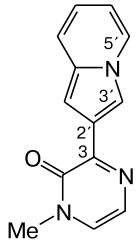


Fig. 4. Main HMBC correlations for compound **4** (one-half of the molecule is shown).

which the chemical shifts of C(3) and C(2′) should be 145 and 121 ppm, respectively. Taking into account that the ^{13}C chemical shifts are underestimated in calculations at this level of theory,[33,34,36] these chemical shifts are in agreement with the experimental values.

Therefore, based on different homo- ($^1H—^1H$) and heterocorrelation ($^1H—^{13}C$) experiments and quantum chemical calculations of the ^{13}C chemical shifts, we established that the compound under study consists of the quinoxaline and indolizine fragments with the phenyl ring



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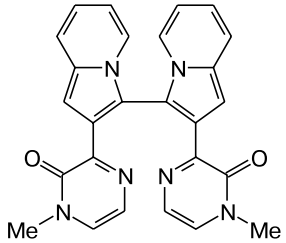

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bound to the latter fragment and the 3,6,9-trioxaundecane spacer attached to the quinoxaline system.

Taking into account the MALDI-TOF mass spectrometric data (for compound **4**, $MH^+ = 831$) and the NMR

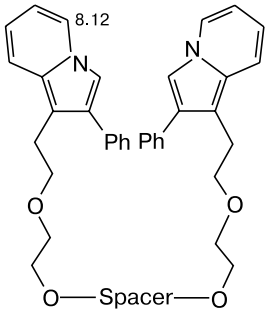
Table 2. Calculated ^1H and ^{13}C chemical shifts for 2-(1-methyl-2-oxo-1*H*-pyrazin-3-yl)indolizine (**5**) and 2,2′-(1-methyl-2-oxo-1*H*-pyrazin-3-yl)-3,3′-biindolizine (**6**)

Atom	δ	
	5	**6**
H(5′)	7.51	7.19
C(3′)	111.40	109.05
C(2′)	120.43	121.51
C(3)	145.00	145.53

spectroscopic data, it can be concluded that compound **4** consists of two fragments, and each fragment contains, along with other atoms, 26 carbon atoms and 21 hydrogen atoms. Most likely, these fragments are linked by the 3-oxapentane units through the oxygen bridge and through the C(3′) atoms of the indolizine systems to form the CH_2—O—CH_2— and C(3′)—C(3′) bonds.

This binding mode can be confirmed by the ^1H and ^{13}C chemical shifts. A comparison of the ^1H chemical shifts for product **2b** and macrocycle **4** shows that the signal for the H(5′) proton, which is most closely spaced to the C(3′)—C(3′) bond of all protons, is observed at 0.61 ppm higher field in the case of the macrocyclic structure compared to the open structure. This is attributed to the shielding effect of the indolizine systems in the macrocycle. For example, the estimation of δ ^1H for the model compounds **5** and **6** predicts the following effect: the difference in the chemical shifts in going from pyrazinylindolizine **5** to structure **6** containing the C(3′)—C(3′) bond is 0.32 ppm. In addition, the experimentally observed difference between the ^{13}C chemical shifts for C(3′) in the spectra of **2b** and **4** (1.77 ppm) is completely theoretically reproduced both in the order of magnitude and the sign (2.35 ppm).

The published data on the ^1H chemical shifts for analogous compounds having an open or macrocyclic structure,[15,16] *viz.*, biindolizine **7** and cyclophane **8**, respectively, is an additional evidence for the C(3′)—C(3′) bond formation. The presence of anisotropic groups in these compounds (the pyridine rings of the indolizine systems) and their influence on the ^1H chemical shifts are indications of the close proximity of the indolizine fragments. Thus, H(5′) in the ring of compound **8** is also more shielded (by 0.42 ppm) compared to the analogous proton in open structure **7**.[16]



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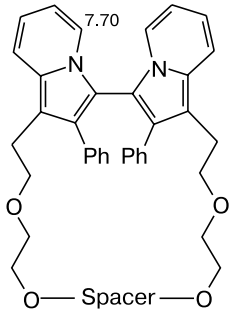

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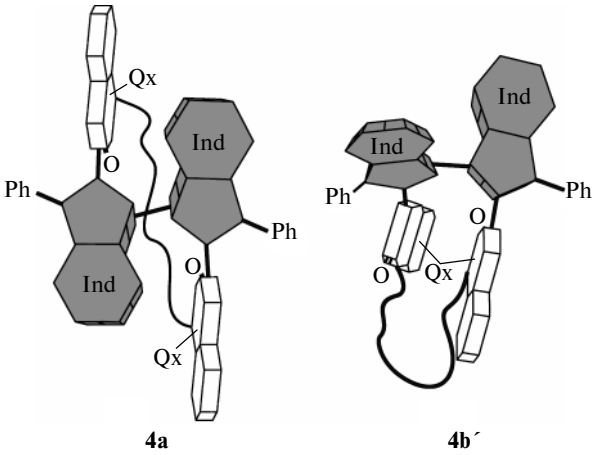
Therefore, based on the results of 2D NMR spectroscopy, mass spectrometric data, and the data published in the literature for model compounds, we established the structure of macrocyclic compound **4**.

Due to three axes of chirality, which coincide with the newly formed C(3′)—C(3′) bond between two indolizine systems and two C(3)—C(2′) bonds between the quinoxaline and indolizine systems that are fixed after the ring closure, eight isomers of heterocyclophane **4** can exist. Since the twisting about the C(3′)—C(3′) bond is impossible due to the steric hindrance caused by the H(5′) and H(5′) hydrogen atoms of the pyridine rings of the indolizine system and the quinoxaline fragments, either two *anti** (**4a,a′**) or two *syn* orientations* (**4b,b′**) of the indolizine fragments can exist, the quinoxaline systems being arranged so that their carbamoyl groups are directed in either the same or opposite directions.



4a **4b′**

Fig. 5. Schematic representation of the structures of isomers of compound **4** with the *anti* (**4a**) and *syn* orientations (**4b′**) with respect to the C(3′)—C(3′) bond in the indolizine fragments.

To reveal the details of the isomeric structure (*syn* or *anti*) of compound **4**, we calculated the ^1H and ^{13}C chemical shifts for diastereomers **4a** and **4b**.

Unfortunately, the large size of the macrocycle hinders the use of *ab initio* methods for the geometry optimization of possible structural isomers of **4**. Hence, we perfromed the geometry optimization by the MM method, and this geometry was then used to estimate the chemical shifts. This approach can be diagnostically valuable.[37,38] According to the MM calculations (with the force constants calculated by the MM2 method), the structure with the *syn* orientation (**4b′**) is energetically much more favorable than the structure with the *anti* orientation.

The main argument in favor of this conclusion is based on a comparison of the calculated chemical shifts for two isomers (GIAO B3LYP/6-31G(d)//MM2) with the experimental data. It can be noted that the chemical shifts should be substantially different for a number of nuclei (for example, for H(5), H(5′), H(6′), C(2), C(3), C(1′), C(2′), C(3′), and C(5′)) in going from one isomer to another. This can be employed for the spectra-structure correlations. Taking into account that the chemical shifts

* For the *syn* orientation, the dihedral angles between the pyridine rings of the indolizine systems are smaller than 90°; for the *anti* orientation, larger than 90°.

are underestimated at the B3LYP/6-31G(d)//MM2 level of theory, the experimental ^{1}H chemical shifts correlate well with the calculated values for the structure with the *syn* orientation ($R^2 = 0.99$), whereas the correlation for the structure with the *anti* orientation is substantially lower ($R^2 = 0.84$). Analogously, the ^{13}C chemical shifts are in good agreement with the experimental data for the *syn* isomer ($R^2 = 0.93$) and show much poorer agreement for the *anti* isomer ($R^2 = 0.87$).

Hence, the above-considered analysis allowed the conclusion that, in solution, compound **4** exists in the *syn* configuration (**4b´**).

To elucidate which configuration, *syn* or *anti*, is favorable in the crystal, we carried out the X-ray diffraction study of a single crystal of compound **4** grown by recrystallization from DMF.

X-ray diffraction study. The single-crystal X-ray diffraction study of cyclopentadecaphane **4** showed that compound **4** crystallizes with DMF molecules in a ratio of 1 : 2. One DMF molecule is disordered over two positions with relative occupancies of 0.59 and 0.41. In the crystal structure, molecules cyclopentadecaphane **4** occupy general positions. The molecular geometry is shown in Fig. 6. The quinoxaline and indolizine fragments are planar within 0.04(2) and 0.05(2) Å, respectively. The dihedral angle between the planes of two indolizine fragments linked to each other is 74.5°. The planes of the phenyl rings are twisted with respect to the planes of the indolizine fragments bound to these rings by approximately the same angle (the C(42)—C(43)—C(32)—C(31) torsion angle is −58.7(4)° and the C(56)—C(55)—C(31)—C(32) torsion angle is −43.3(5)°), whereas the quinoxaline rings are twisted with respect to these planes by substantially different angles (C(12)—C(13)—C(22)—C(21), −95.1(4)°; C(54)—C(49)—C(21)—C(22), −51.2(4)°). Two quinoxaline rings are virtually parallel to each other (the dihedral angle between their planes is 17.7°). The trioxaundecane chain adopts an extended conformation, and one of the phenyl substituents closes the pseudocavity formed by the spacer from one of the sides, thus restricting the complexing ability of this fragment (see Fig. 6, *b*).

Intermolecular interactions between the electronic systems of the aromatic fragments make the greatest contribution to the supramolecular organization of the crystal structure of compound **4**, only the quinoxaline fragments being involved in π-π interactions. We analyzed this type of interactions with the use of the Mercury and Platon programs, in which the following criteria of π-π interactions are included: the distances between the centers of aromatic rings shorter than 6 Å and the angle β between the normal to the plane of one ring and the vector linking the centers of the rings smaller than 60°. These parameters are consistent, for example, with those reported in the review.[39] In addition, the review[39] shows that interactions that exist in the case of the mutually perpendicular

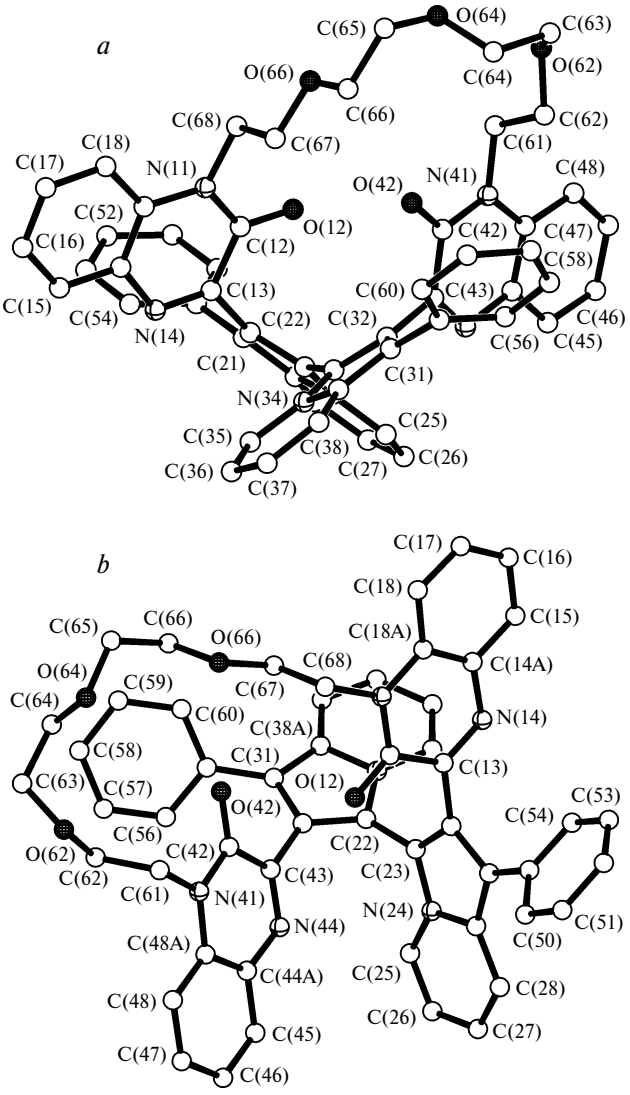


Fig. 6. Two projections of compound **4** in the crystal. The hydrogen atoms and the DMF molecules are omitted.

arrangement of the aromatic systems (the distances between the centers of the rings are, on the average, 4.96 Å) are the most often occurring and energetically favorable π-π interactions, the interactions between parallel systems shifted with respect to each other (the interplanar distances are 3.4—3.6 Å) are the next after the above interactions, and only a few structures containing completely overlapping aromatic systems were documented (this type of interactions is energetically least favorable). In the crystal of **4** under consideration, each quinoxaline fragment of the molecule is involved in head-to-tail interactions with the corresponding fragments of the adjacent molecules related to the original molecule by centers of symmetry and the translation ±1 along the *0x* axis. As a consequence, the dihedral angles between the aromatic systems are 0°, and the shortest distances between the planes of the quinoxaline rings of the adjacent molecules

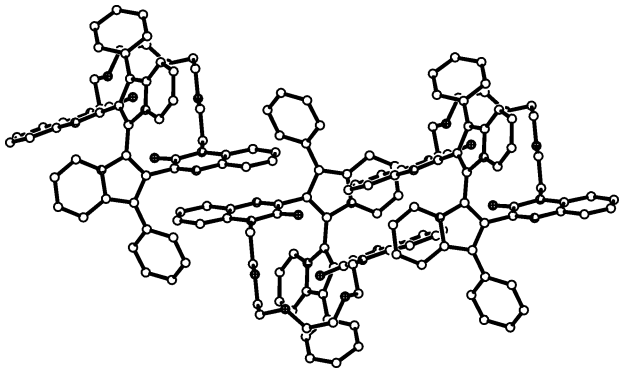


Fig. 7. The π-π interactions in the crystal structure of compound **4** (the hydrogen atoms and the DMF molecules are omitted).

are 3.54 Å for the planes of the ((N(11)—C(18a)) rings and 3.36 Å for the planes of the (N(41)—C(48a)) rings. In both cases, the angles β are smaller than 60°. As a result, infinite cylindrical supramolecular structures are formed (Fig. 7).

The C—H...O interactions between the hydrogen atoms of the phenyl substituents and the oxygen atoms of the carboxy groups (the O.....H distances are in the range of 2.44—2.55 Å) contribute to this situation.

Since compound **4** and its derivatives hold promise as selective extractants, we analyzed the crystal packing of the crystal solvate of **4**. On the whole, the cylindrical supramolecular structures are packed to form a hexagonal structure (Fig. 8), the solvent molecules being located in the cavities between the cylindrical structures. In spite of the presence of the solvent molecules, a high packing density is not achieved in the crystals of compound **4**. Thus, the packing coefficient calculated with the use of the PLATON program is 0.66. Apparently, it is possible to prepare crystal solvates of compound **4** containing larger molecules.

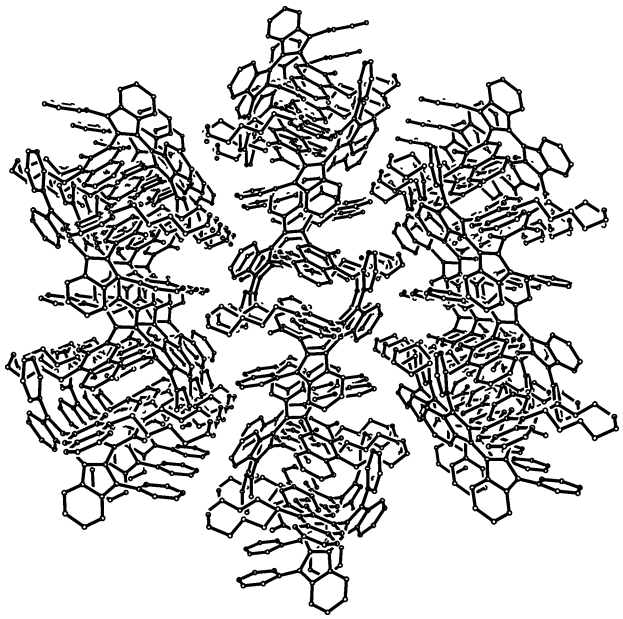


Fig. 8. Fragment of the molecular packing in the crystal of compound **4**. The hydrogen atoms and the solvent molecules are omitted. The projection along the *0c* axis.

Therefore, the single-crystal X-ray diffraction study of cyclopentadecaphane **4** showed that the indolizine fragments in the crystal structure are in the nearly *anti* orientation with respect to the C(3′)—C(3′) bond, as opposed to the *syn* orientation observed in solution. It should be noted that this mutual arrangement of the indolizine fragments observed in the crystal is unfavorable for their involvement in intramolecular π-π interactions.

Electrochemical properties of heterocyclophane 4 and compounds 2a, 2b, and 3b. The cyclic voltammograms of compounds **2a** and **2b** are completely identical to the corresponding curves for indolizinylquinoxaline **1b** studied earlier[14] under analogous conditions. For all these compounds, four irreversible oxidation peaks were recorded at virtually the same potentials on a glassy carbon electron in an acetonitrile/0.1 *M* Et_4NClO_4 system (Fig. 9, Table 3). The height of the first peak is larger than the one-electron level. The irreversibility of the first peak is

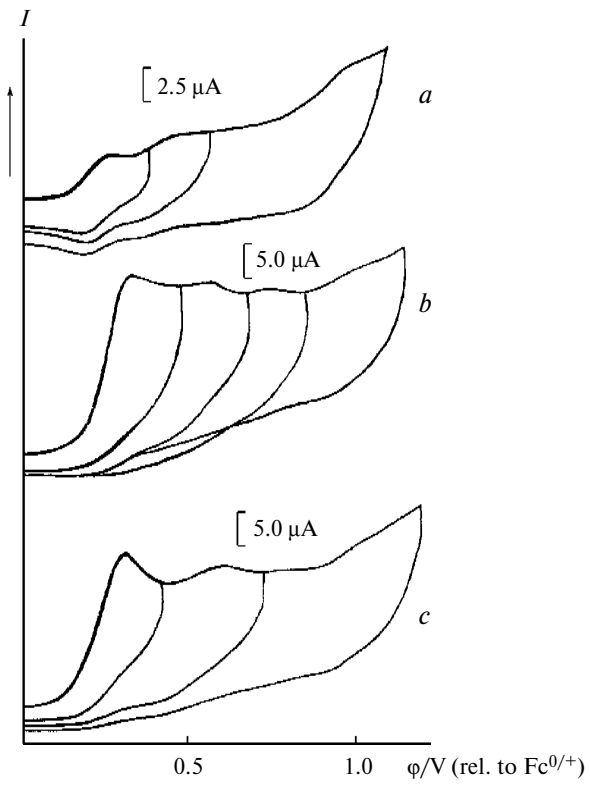


Fig. 9. Cyclic voltammograms of indolizinylquinoxalines **4** (*a*), **2a** (*b*), and **2b** (*c*) ($C_{\mathbf{2a,2b}} = 5 \cdot 10^{-4}$ mol L^{-1}, $C_{\mathbf{4}} = 1 \cdot 10^{-4}$ mol L^{-1}) in MeCN/0.1 *M* Et_4NClO_4 on a glassy carbon electrode ($\upsilon = 100$ mV s^{-1}).

Table 3. Cyclic voltammetry data for the oxidation of indolizines **1b**, **2a**, **2b**, **3b**, and **4** on a glassy carbon electrode in MeCN/0.1 *M* Et_4NClO_4*

Compound	$E^1_{p,ox}$ /V	n_1**	$E^2_{p,ox}$	$E^3_{p,ox}$	$E^4_{p,ox}$
			V		
1b	0.30	1.3	0.58	0.76	0.96
2a	0.32	1.7	0.60	0.78	1.05
2b	0.30	1.7	0.60	0.77	1.01
3b	0.29	1.0	0.49	0.98	1.31
4	0.26	1.0	0.46	0.97	—
4**	0.21	1.0	0.38	0.85	—

* The potentials were measured relative to the standard potential of the $Fc^{0/+}$ redox system (the internal standard) with the use of the Ag/0.01 *M* $AgNO_3$ reference electrode in MeCN; the potential scan rate was 100 mV s^{-1}; $C_{\mathbf{1b,2a,2b}} = 5 \cdot 10^{-4}$ mol L^{-1}, $C_{\mathbf{3b}} = 7 \cdot 10^{-4}$ mol L^{-1}, $C_{\mathbf{4}} = 1 \cdot 10^{-4}$ mol L^{-1}.
** The number of electrons was determined by comparing with the one-electron oxidation peak of ferrocene.
*** $C_{\mathbf{4}} = 5 \cdot 10^{-4}$ mol L^{-1} in DMF/0.1 *M* Et_4NClO_4.

indicative of the involvement of the radical cations of indolizinylquinoxalines **1b** and **2a,b** in subsequent fast chemical reactions. The potential of the first peak corresponds to the oxidation potential of indolizines, and the resulting radical cation is, apparently, involved in coupling reactions, which is typical of radical cations of simple indolizines.[11,14] For compound **1b**, the intermolecular coupling giving rise to dimers is the major process. For compounds **2a** and **2b**, both the intramolecular coupling of two indolizine fragments giving rise to macrocyclic products and the intermolecular coupling resulting in the formation of large rings and/or polymers can proceed. Since biindolizines are more easily oxidized than monoindolizines,[14] all resulting coupling products are further oxidized at potentials of the first peak, resulting in an increase in the current relative to the one-electron level ($n > 1$). The formation of polymeric products is easily observed by recording polycyclic voltammograms.[14] The oxidation of compounds **1b** and **2a,b**, unlike that of mono- and biindolizines studied earlier,[14] at potentials of the first peak in the multiple scan mode at a rate of 100 mV s^{-1} in the potential range of $-0.3 \rightarrow +0.4 \rightarrow \rightarrow -1.2 \rightarrow -0.3$ does not afford a polymeric film on the electrode surface, and the cyclic voltammograms remain virtually unchanged and are well-reproduced. This may be evidence that the electrolysis of compounds **2a** and **2b** at the generation potentials of radical cations under the particular reaction conditions used is accompanied primarily by the formation of low-molecular-weight macrocyclic products (monomers, dimers, *etc.*), which are soluble in MeCN to a certain extent. These results provide the first voltammetric argument for the possibility of the preparation of macrocyclic products by the electrooxidation of indolizines **2a** and **2b**. Based on this fact, we performed the preparative electrooxidation of compound **2b** on a platinum electrode in MeCN and obtained macrocyclic compound **4**.

Heterocyclophane **4** is much less soluble in MeCN than open precursor **2b**, and its limiting concentration at room temperature is $1 \cdot 10^{-4}$ mol L^{-1}. Three oxidation peaks are observed in the cyclic voltammograms of compound **4** (see Fig. 9). The shape and characteristics of the first peak differ from those for compound **2b**. First, the first oxidation peak of **4** is shifted by 40 mV to less positive potentials with respect to the first oxidation peak of **2b**, which indicates that the macrocyclic compound is more easily oxidized. This is clear because the oxidation of biindolizines proceeds more easily than that of monoindolizines.[14] Second, this peak is reversible, and its height corresponds to the one-electron transfer per molecule, which is evidence for the stability of the radical cation. An analogous situation is observed in DMF (see Table 3), in which compound **4** is much more readily soluble ($C = 5 \cdot 10^{-4}$ mol L^{-1}) and, correspondingly, the oxidation peaks are more pronounced (Fig. 10). The electrooxidation directly in a resonator of an ESR spectrometer at potentials of the first peak gives rise to the spectrum of the radical cation of compound **4** (Fig. 11). The same spectrum was recorded at room temperature and at lower temperature (−50 °C). Evidently, this spectrum belongs to the primary radical cation. The identical spectrum was

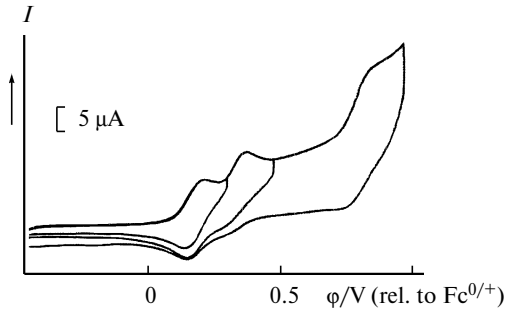


Fig. 10. Cyclic voltammograms of heterocyclophane **4** ($C = 5 \cdot 10^{-4}$ mol L^{-1}) in DMF/0.1 *M* Et_4NClO_4 on a glassy carbon electrode ($\upsilon = 100$ mV s^{-1}).

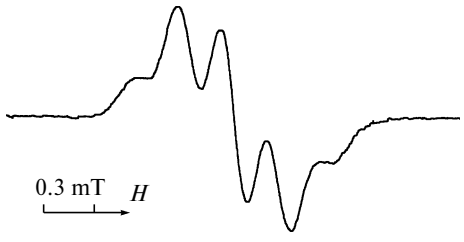
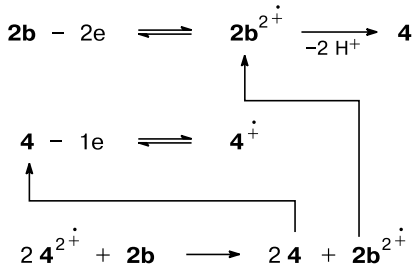


Fig. 11. ESR spectrum of the radical cation of heterocyclophane **4** electrochemically generated at the potential $E = +0.4$ V in MeCN/0.1 *M* Et_4NClO_4 on a Pt electrode ($C = 1 \cdot 10^{-4}$ mol L^{-1}).

recorded upon the chemical oxidation of macrocyclic compound **4** with iodine in CH_2Cl_2. The spectrum consists of five lines with an approximate intensity ratio between the lines of 1 : 2 : 3 : 2 : 1, which are associated with hyperfine couplings with the nuclei of two equivalent nitrogen atoms of the conjugated indolizine rings, and has the following characteristics: the *g* factor is 2.0024, a_{2N} = 0.26 mT.

Based on the above-considered results, the following scheme can be proposed for the description of the processes proceeding at potentials of the first oxidation peak of compound **2b** and giving rise to macrocyclic product **4** (Scheme 3). The first step involves the one-electron oxidation of each indolizine fragment of molecule **2b** to form the biradical dication followed by the intramolecular coupling and elimination of two protons to give compound **4**.

Scheme 3



Since compound **4** is more easily oxidized than the starting compound **2b** (40 mV), the former compound is rapidly oxidized to the radical cation. However, the reduction peak (E_p^{red} = +0.20 V) of the stable radical cation of heterocyclophane **4** is not observed in the cyclic voltammogram of compound **2b** (see Fig. 9), which can be attributed to the homogeneous intermolecular electron exchange between the radical cation of compound **4** and the starting compound **2b**. In other words, macrocyclic compound **4** produced in the reaction serves as a mediator of the electrochemical oxidation of biindolizine **2b**. The mediator properties combined with low solubility of macrocyclic product **4** result in the fact that the preparative oxidation of compound **2b** is not accompanied by accumulation of the radical cations of **4** in solution and their electrolysis culminates in the two-electron oxidation.

As mentioned above, the *syn* and *anti* diastereomers of macrocyclic biindolizines differ in the electrochemical properties.[13] The electrochemical behavior of compound **4** corresponds to none of the examples described in the literature.[13] The stability of the radical cations and the absence of any other paramagnetic species in the course of the prolonged electrolysis correspond to the *anti* diastereomer, whereas instability of the dication (the second peak is irreversible) and the appearance of additional oxidation peaks is attributed to the *syn* diastereomer. Unlike macrocyclic biindolizines described in the literature,[13] the bridge between two indolizine fragments in heterocyclophane **4** contains additionally two quinoxaline fragments. An increase in the length of the bridge leads to an increase in configurational flexibility, which can impart new properties, including electrochemical characteristics, to macrocyclic compounds. Hence, we studied also the electrochemical oxidation of model compound **3b**. The solubility of this compound in MeCN is substantially higher than that of macrocyclic product **4**; correspondingly, the cyclic voltammograms of the model compound are of better quality, and the anodic potential range is broader.

The cyclic voltammograms of compound **3b** show two reduction peaks of the quinoxaline fragments (at −2.08 and −2.32 V) and four one-electron oxidation peaks of the biindolizine system (Fig. 12). The first and third oxidation peaks are electrochemically reversible, whereas the second and fourth peaks are irreversible. The potentials of the first three peaks are consistent with the potentials of compound **4**. The electrolysis at the potentials of the first oxidation peak is accompanied by the formation of stable radical cations, whose ESR spectrum (*g* = 2.0024, a_{2N} = 0.26 mT) is identical to the spectrum of the radical cation of compound **4**. The absence of the fourth oxidation peak in the cyclic voltammogram of macrocyclic compound **4** is apparently associated with the fact that this peak is shielded by the discharge current of the supporting electrolyte due to a low concentration of compound **4**. A complete analogy between the cyclic voltammograms and the ESR spectra at the potentials of the first step for compounds **3b** and **4** indicates that the structures of the indolizine fragments of both compounds are identical.

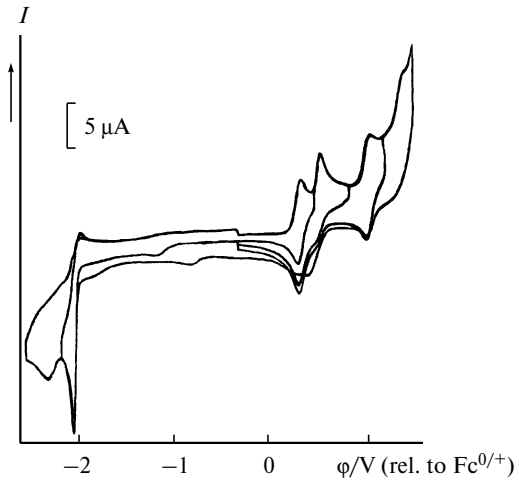


Fig. 12. Cyclic voltammograms of biindolizine **3b** ($C = 7 \cdot 10^{-4}$ mol L^{-1}) in MeCN/0.1 *M* Et_4NClO_4 on a glassy carbon electrode (υ = 100 mV s^{-1}). The scan begins at −0.45 V.

To conclude, we showed that, under the conditions of electrochemical oxidation or in the presence of molecular iodine, the oxidative dehydrocyclization of podand **2b** proceeds in an intra- and intermolecular fashion to form a mixture of heterocyclophanes, with the intramolecular cyclization product predominating, whereas the intermolecular cyclization product being formed as a by-product. The latter was detected only by mass spectrometry. We showed that cyclopentadecaphane **4** is a reversible redox-active system, and its one-electron oxidation affords the stable radical cation. The X-ray diffraction study of cyclopentadecaphane **4** demonstrated that in the crystal, the trioxaundecane chain of heterocyclophane adopts an extended conformation, and one of the phenyl substituents closes the pseudocavity formed by the spacer from one of the sides. This is promising for the synthesis of specific host molecules consisting of the redox-switchable biindolizine fragment combined with the π-deficient quinoxaline systems linked by a longer polyether bridge.

Experimental

The melting points were determined on a Boetius hot-stage apparatus. The IR spectra were measured on a Bruker Vector-22 Fourier-transform spectrometer in KBr pellets. The ^{1}H and ^{13}C NMR spectra were recorded on Bruker AVANCE-600 instrument (600.00 MHz for ^{1}H and 150.864 MHz for ^{13}C) for compound **4** in DMF-d_7 and on a Bruker MSL-400 instrument (400.13 MHz) for compounds **3** in DMSO-d_6 at 333 K. The residual signal of DMSO (δ_H 2.54) was used as the internal standard. The electron impact mass spectra (70 eV) were recorded on a Finnigan MAT-212 instrument. The MALDI-TOF mass spectra were obtained on a Finnigan Dynamo instrument with the use of 1,8,9-trihydroxyanthracene as the matrix.

The compounds were named according to the IUPAC phane nomenclature.[40,41]

The single-crystal X-ray diffraction study of **4**·DMF was performed on a NONIUS B.V. CAD-4 X-ray diffractometer. The crystals, $C_{52}H_{42}N_6O_5 \cdot 2(C_3H_7NO)$, are monoclinic; at 20 °C a = 13.028(5) Å, b = 24.559(5) Å, c = 16.374(4) Å, β = 103.28(2)°, V = 5099(3) Å^3, d_{calc} = 1.27 g cm^{-3}, Z = 4, space group $P2_1/n$. The unit cell parameters and the intensities of 10601 reflections, of which 5414 reflections were with $I \geq 2\sigma$, were measured at 20 °C (graphite monochromator, λCu-Kα, ω/2θ-scanning technique, θ ≤ 74.27°). The intensities of three check reflections showed no decrease in the course of the X-ray data collection. The absorption correction was applied using the azimuthal scan method (μCu 6.87 cm^{-1}). The structure was solved by direct methods with the use of the SIR program[42] and refined first isotropically and then anisotropically using the SHELXL program package.[43] The coordinates of the hydrogen atoms were calculated based on the stereochemical criteria and refined using a riding model. The final R factors were R = 0.0730, R_w = 0.1921 based on 5414 independent reflections with $F^2 \geq 4\sigma$. All calculations were carried out with the use of the MolEN[44] and WinGX[45] programs. The intermolecular interactions were analyzed and the figures were drawn with the use of the Mercury[46] and PLATON[47] programs. The X-ray diffraction data were deposited with the Cambridge Structural Database (CCDC 609481).

The cyclic voltammograms were recorded on a PI-50-1 potentiostat equipped with an H 307/2 X-Y recorder. A glassy-carbon disk electrode (∂ = 2 mm) pressed into Teflon served as the working electrode. Before each measurement, the electrode was subjected to mechanical polishing. The potential scan rate υ = 100 mV s^{-1}. The potentials were measured relative to the standard potential of the ferrocene—ferricinium ion redox system ($Fc^{0/+}$, internal standard) using an Ag/0.01 M $AgNO_3$ silver reference electrode (0.01 mol L^{-1}) in MeCN. The potentials for compound **1b** are 70 mV more positive that those determined by the external standard method.[14] Dissolved oxygen was removed by bubbling nitrogen through the solution at 295 K.

Studies by the ESR method (Radiopan SE/X-2544 spectrometer) combined with the *in situ* electrolysis (PI-50-1 potentiostat) were carried out on an instrument consisting of an ESR resonator and an electrochemical cell. A platinum plate served as the working electrode; a platinum wire, as the auxiliary electrode; a silver wire, as the reference electrode. The solutions were degassed by three freezing—evacuation—thawing cycles. The temperatures were 295 and 223 K.

2,2′-Di(2-oxo-1*H*-quinoxalin-3-yl)-1,1′-diphenyl-3,3′-biindolizine (3a). A solution of I_2 (100 mg, 0.4 mmol) in chloroform (3 mL) was added to a solution of compound **1a** (100 mg, 0.3 mmol) in chloroform (2 mL). The reaction mixture was stirred for 3 h and kept for 16 days. The black crystals that precipitated were filtered off, dried, and washed with a sodium carbonate solution and water. The residue was dried, refluxed in EtOH (10 mL) for 5 min, and cooled. The yellow crystals that formed were filtered off and washed with EtOH. The yield was 30 mg (30%), m.p. > 360 °C. IR, ν/cm^{-1}: 430, 473, 547, 602, 700, 729, 762, 961, 1029, 1098, 1152, 1211, 1236, 1247, 1272, 1344, 1418, 1520, 1563, 1611, 1670, 2500—3220. ^{1}H NMR, δ: 6.77 (ddd, 2 H, H(6′), J = 6.96 Hz, J = 6.64 Hz, J = 1.36 Hz); 6.90 (dd, 2 H, H(8), J = 8.28 Hz, J = 1.32 Hz); 6.94—7.02 (m, 4 H, H(7′), H(6)); 7.12 (dd, 2 H, H (*p*-Ph), J = 7.96 Hz, J = 7.32 Hz); 7.15 (d, 2 H, H(5), J = 8.28 Hz); 7.25 (dd, 4 H, H (*m*-Ph), J = 7.96 Hz, J = 7.28 Hz); 7.31—7.38 (m, 2 H, H(7)); 7.39 (dd, 4 H, H (*o*-Ph), J = ~8.3 Hz, J = 1.3 Hz); 7.59 (d, 2 H, H(8′), J = 6.96 Hz); 7.71 (d, 2 H, H(5′), J = 9.28 Hz); 11.78 (br.s, 2 H, NH). Found (%): C, 78.49; H, 4.07; N, 12.63. $C_{44}H_{28}N_6O_2$. Calculated (%): C, 78.56; H, 4.20; N, 12.49.

2,2′-Di(1-ethyl-2-oxo-1*H*-quinoxalin-3-yl)-1,1′-diphenyl-3,3′-biindolizine (3b). A solution of I_2 (22 mg, 0.09 mmol) in chloroform (10 mL) was added to a solution of compound **1b** (36 mg, 0.1 mmol) in chloroform (5 mL). The reaction mixture was stirred for 6 h and kept for 16 days. Chloroform was removed under reduced pressure, and the dark-brown resinous residue was washed with a sodium thiosulfate solution, a sodium carbonate solution, and water, dried, and chromatographed on a silica gel column (Silica gel L 100/160μ, $CHCl_3$ as the eluent). The yield was 11 mg (31%), m.p. 303—305 °C. IR, ν/cm^{-1}: 700, 741, 1099, 1159, 1218, 1283, 1347, 1461, 1526, 1583, 1602, 1653, 2854, 2924, 2955. ^{1}H NMR, δ: 1.06 (t, 6 H, Me, J = 7.20 Hz); 3.70—3.80 (m, 2 H, CH_2); 3.95—4.05 (m, 2 H, CH_2); 6.67 (ddd, 2 H, H(6′), J = 7.56 Hz, J = 6.15 Hz, J = 1.26 Hz); 6.86 (ddd, 2 H, H(7′), J = 8.25 Hz, J = 6.54 Hz, J = 1.08 Hz); 6.91 (dd, 2 H, H(6), J = 7.56 Hz, J = 7.32 Hz); 6.96 (d, 2 H, H(8), J = 8.10 Hz); 7.08 (d, 2 H, H(5), J = 8.40 Hz); 7.12 (dd, 2 H, H(*p*-Ph), J = 7.56 Hz, J = 7.32 Hz); 7.22 (dd, 4 H,

H (*m*-Ph), J = 7.86 Hz, J = 7.56 Hz); 7.30 (ddd, 2 H, H(7), J = 8.49 Hz, J = 7.02 Hz, J = 1.44 Hz); 7.40 (dd, 4 H, H (*o*-Ph), J = 7.56 Hz, J = 1.02 Hz); 7.63—7.73 (m, 4 H, H(5′), H(8′)). EI MS, *m/z* (%): 675.4 (4.0), 674.3 (14.0), 673.3 (55.4), 672.3 (100), 671.3 (2.7), 540.3 (1.5), 539.3 (3.35), 538.3 (1.30), 527.3 (1.32), 449.2 (0.4), 337.2 (4.6), 336.7 (7.8), 336.2 (16.8), 335.2 (3.3). Found (%): C, 79.01; H, 4.87; N, 11.63. $C_{48}H_{36}N_6O_2$. Calculated (%): C, 79.10; H, 4.98; N, 11.53.

1^2,4^2-Dioxo-2^1,3^1-diphenyl-7,10,13-trioxa-1,4(3,1)-diquinoxalina-2(2,3),3(3,2)-diindolizinacyclopentadecaphane (4). A solution of I_2 (300 mg, 1.18 mmol) in chloroform (100 mL) was added to a solution of compound **2b** (360 mg, 0.42 mmol) in chloroform (200 mL). The reaction mixture was stirred for 3 h, kept for 2 days, and washed with a sodium carbonate solution, a sodium thiosulfate solution, and water. Chloroform was removed under reduced pressure, and the brown resinous residue was chromatographed on a silica gel column (Silica gel L 100/160μ, $CHCl_3$: EtOH, 99 : 1, as the eluent). The yield was 250 mg (69%), m.p. >330 °C. IR, ν/cm^{-1}: 704, 729, 762, 1103, 1128, 1159, 1251, 1281, 1346, 1366, 1454, 1486, 1524, 1583, 1601, 1649, 2857, 2922. ^{1}H NMR, δ: 3.37—3.45 (m, 8 H, C(4)H_2, 1 H C(2)H_2, 1 H C(3)H_2); 3.48—3.52 (m, 2 H, C(3)H_2); 3.52—3.57 (m, 2 H, C(2)H_2); 3.99—4.05, 3.80—3.86 (m, 4 H, C(1)H_2); 6.83 (dd, 2 H, H(6′), J = 6.89 Hz, J = 6.67 Hz); 7.02 (dd, 2 H, H(7′), J = 9.42 Hz, J = 6.58 Hz); 7.14 (dd, 2 H, H (*p*-Ph), J = 7.38 Hz, J = 7.00 Hz); 7.20 (ddd, 2 H, H(6), J = 8.00 Hz, J = 5.73 Hz, J = 2.27 Hz); 7.25 (dd, 4 H, (*m*-Ph), J = 7.80 Hz, J = 7.58 Hz); 7.30 (d, 2 H, H(5), J = 7.90 Hz); 7.37 (d, 4 H, H (*o*-Ph), J = 7.56 Hz); 7.48—7.52 (m, 4 H, H(7), H(8)); 7.72 (d, 4 H, H(8′), H(5′), J = 8.67 Hz). ^{13}C NMR, δ: 154.24 (C(2)); 147.98 (C(3)); 133.52 (C(4a)); 129.99 (C(5)); 123.30 (C(6)); 130.52 (C(7)); 114.69 (C(8)); 134.06 (C(8a)); 115.44 (C(1′)); 121.32 (C(2′)); 115.26 (C(3′)); 125.13 (C(5′)); 112.43 (C(6′)); 120.15 (C(7′)); 118.46 (C(8′)); 131.42 (C(8a′)); 136.01 (C(1″)); 129.89 (C(2″)); 128.70 (C(3″)); 126.10 (C(4″)); 42.28 (CH_2(1)); 67.62 (CH_2(2)); 70.70 (CH_2(3)); 70.53 (CH_2(4)). MS of the crude product (MALDI TOF): $[MH]^+$ 831, $[MH]^+$ 1662. EI MS, *m/z* (I_{rel} (%)): 833.2 (4.9), 832.3 (19.7), 831.2 (61.1), 830.2 (100), 415.8 (4.6), 415.3 (13.3), 349.7 (3.4), 349.2 (3.1), 97.3 (5.3), 85.3 (4.1), 83.3 (5.7), 81.3 (6.0). Found (%): C, 75.25; H, 5.07; N, 10.03. $C_{52}H_{42}N_6O_5$. Calculated (%): C, 75.16; H, 5.09; N, 10.11.

The electrosynthesis of cyclopentadecaphane **4** was performed by the preparative electrochemical oxidation of compound **2b** using a PI-50-1 potentiostat in a diaphragm (cellulose) glass electrolytic cell on a platinum cylindrical electrode (S = 50.8 cm^2) in a galvanostatic mode at a controlled potential of the first oxidation peak ($E \leq$ +0.5 V relative to Ag/0.01 mol L^{-1} $AgNO_3$ in MeCN) in a MeCN/0.1 mol L^{-1} Et_4NClO_4 system at room temperature (22 °C). A platinum wire was used as the cathode. The working solution (50 mL) was prepared by dissolving compound **2b** (100 mg, 0.12 mmol) in a MeCN/0.1 mol L^{-1} Et_4NClO_4 system. The solution was magnetically stirred. The electrolysis was carried out for 3.88 h (I = 2 mA, τ = 3.22 h; I = 1.5 mA, τ = 0.12 h, I = 1.2 mA, τ = 0.12 h, I = 1.0 mA, τ = 0.42 h). The mass spectrometric study of the reaction mixture after the electrolysis showed the absence of the starting compound **2b** in the solution and the presence of two macrocyclic products, *viz.*, compound **4** (*m/z* = 830) and a dimeric macrocyclic compound (*m/z* = 1660). The solvent was evaporated, the supporting electrolyte was removed, and the residue was washed with water. Compound **4** was isolated and purified on silica gel as described above. The preparative yield was 40 mg (40%). All spectroscopic characteristics of compound **4** synthesized electrochemically were completely identical to those of compound **4** prepared by the chemical method.

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