Tetrahedron 69 (2013) 10675–10687

Contents lists available at ScienceDirect

Tetrahedron

journal homepage: www.elsevier.com/locate/tet

Efficient synthesis and structure peculiarity of macrocycles with bi-indolizinylquinoxalinone moieties

Vakhid A. Mamedov *, Aleksey A. Kalinin, Aidar T. Gubaidullin, Sergey A. Katsuba, Victor V. Syakaev, Il'dar K. Rizvanov, Shamil K. Latypov

A.E. Arbuzov Institute of Organic and Physical Chemistry, Kazan Research Center of the Russian Academy of Sciences, Arbuzov Str. 8, 420088 Kazan, Russian Federation

ARTICLE INFO

Article history:
Received 2 July 2013
Received in revised form 19 August 2013
Accepted 3 September 2013
Available online 11 September 2013

Keywords:
Oxidative dehydrogenation
Monoindolizinylquinoxalinepodands
Molecular iodine
Ring closure
Biindolizinacyclophanes
X-ray diffraction analysis
IR data
NMR data

ABSTRACT

Monoindolizinylquinoxalinepodands, easily available from indolizinylquinoxalines and various dihalides, undergo smooth oxidative dimerization in the presence of molecular iodine to afford corresponding macrocycles in good yields in a short reaction time. The use of inexpensive and readily available molecular iodine makes this method quite simple, more convenient, and practical. In solution the title macrocycles exist in an equilibrium of several conformations arising from restricted rotation around the Ind–Qx bonds (ca. C_2 symmetrical and nonsymmetrical forms). The population of the forms and exchange rate between them depends strongly on the spacer type (length).

1. Introduction

Recently, in connection with the creation of various electro-switched (electrochemically switched, redox-switched) nano-dimensional molecular devices, special attention has been paid to supramolecular systems based on macrocyclic compounds containing electrochemically active building blocks. A biindolizine fragment that can impart the ability to react to the external influences of heterocyclophanes has so far been little used,[16–18] as an active site, unlike ferrocenes,[1] tetratiofulvalens,[2–7] and quaternized-4,4′ dipyridyl,[6–9] hydroquinone,[9,10] anilines,[11,12] phenazine,[13] thiophenes.[13–15] This is probably due to the difficulty of introducing the indolizine fragment into macrocyclic systems of different sizes synthetically. It is also difficulty to perform the indolizine→biindolizine transformation in the presence of a common acceptor or heteroaryl substituents in the composition of indolizines.[16,19,20] 3,3′-Biindolizines are reversible two-step redox systems of theoretical and practical interest, which have attracted attention as a structural unit of cyclophanes[16–18] and as chiral ligands.[21–23] So far the methods used to synthesize biindolizines have been developed only with electron donating groups in good yields, despite the use of various dehydrating agents, such as $K_3[Fe(CN)_6]$,[24] Pd/C,[19,25–28] Pt/C[19] Fe (III)/O_2,[20] and electrochemically as well.[20,29] Indolizines with acceptor substituents are either unable to oxidize at all,[19] or the yields were very low[16,20] as in the cases of the heteroaryl substitutes of biindolizines. Recently, a new method for the oxidative dimerization of indolizines when exposed to $Pd(OAc)_2$[18] has been developed to produce high yields of biindolizines including acceptor substituents. At present, molecular iodine has received considerable attention in organic synthesis because of its low cost and ready availability. The mild Lewis acidity associated with iodine has enhanced its use in organic synthesis to perform several organic transformations with stoichiometric levels to catalytic amounts.[18,30–34] However, so far no examples are known in which molecular iodine was used as a mild oxidant for the transformation of the indolizine→biindolizine. Nevertheless, it should be noted that recently molecular iodine has been used as an excellent reagent-catalyst in the synthesis of the indolizine derivatives by 5-*endo*-*dig* cyclization.[35,36] In our previous paper[37] the molecular iodine and the binary system of the molecular iodine and the NaOAc (I_2–NaOAc) mediated one-pot process for the oxidative dimerization of indolizines under mild conditions have been described. The reaction afforded a variety of products from indolizines

* Corresponding author. Tel.: +7 843 2727304; fax: +7 843 2732253; e-mail address: mamedov@iopc.ru (V.A. Mamedov).

0040-4020/$ – see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.tet.2013.09.014

with acceptor groups in good to excellent yields. Macrocyclic systems with the biindolizine fragment(s) connected with 3-oxapentane, 3,6,9-trioxaundecane, 3,6,9,12-tetraoxatetradecane spacers have also been synthesized from monoindolizinylquinoxalinepodands under the same conditions. In our view, the application of molecular iodine for the dehydrogenation of indolizines, will allow us on the one hand to avoid the use of catalysts or toxic reagents, while on the other hand make it possible to carry out the reaction under mild conditions—at room temperature and with easily removable solvents, such as methylene chloride.

2. Results and discussion

2.1. Iodine mediated dehydrogenation of 3-(indolizin-2-yl) quinoxalin-2-ones 1

It is known that the complexing ability of macrocycles depend both on the size of the cavity and the number of atoms involved in the complex formation. In this connection the synthesis of biindolizine macrocycles with various lengthwise and number of oxygen atoms in the crown ether residues remains are of particular interest in designing new macrocyclic systems. As modified crown ethers and due to the biindolizine fragment they prove promising redox switchable ligands for different supramolecular systems.[16,17,19–21,38–43]

In continuation of our work on developing the indolizine chemistry and the macrocyclization of quinoxalinemonopodands, herein we report the use of the previously discovered new method.[37] The latter involves C–C bond creation (molecular iodine and the binary system (I_2–NaOAc) mediated oxidative coupling of indolizines) for the synthesis of new bi-indolizinylquinoxalinone macrocyclic systems with various crown ether residues, as well as the study of structural peculiarities of some obtained compounds.

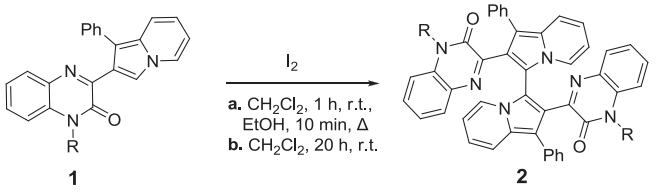
Initially, we attempted the oxidative dimerization of readily available indolizinylquinoxalines **1a**,**b** with the use of molecular iodine as a dehydrogenating reagent and the products, **2a** and **2b** were isolated in 92 and 70% yields, respectively (Table 1).

This result provided the incentive for further study of the mediated dehydrogenation with monoindolizinylquinoxalinepodands **4a**–**j**, which are easily available by the interaction of indolizinylquinoxaline **1a** with various dihalides **3**. These monoindolizinylquinoxalinepodands **4a**–**j** can be distinguished by the nature and length of the spacers (Table 2).

2.2. Synthesis of α,ω-bis-[3-(1-phenylindolizin-2-yl)quinoxalin-2-on-1-yl]oxaalkanes 4a–j

The interaction of 3-(1-phenylindolizin-2-yl)quinoxalin-2(1*H*)-one (**1**) with α,ω-dibromo- or ditosylatealkanes **3a**–**j** in boiling

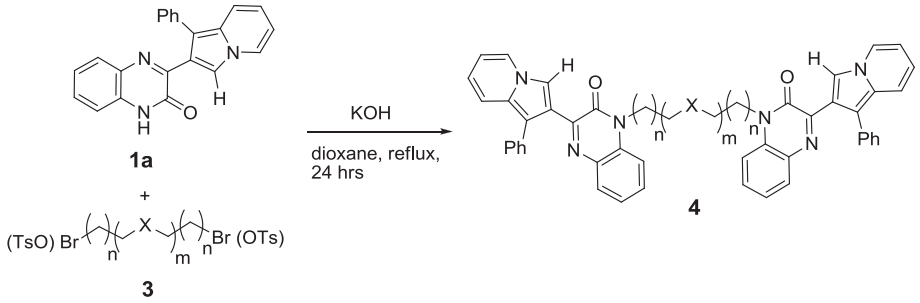
Table 1
A facile iodine mediated synthesis of biindolizines **1**



Entry	R	Yield (%) of biindolizine **2**
1 (**a**)	H	92
2 (**b**)[a]	Me	70

[a] The compound has been described in a previous paper[37] without detailed characteristics.

Table 2
The synthesis of α,ω-bis-[3-(1-phenylindolizin-2-yl)quinoxalin-2-on-1-yl]oxaalkanes **4a**–**j**



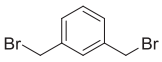
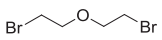
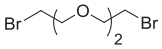
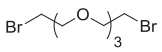
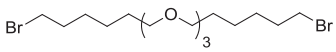
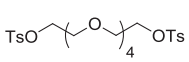
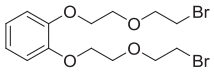
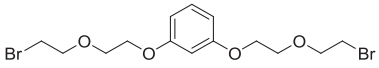
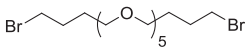
Entry	**3**	Product (yield, %)
1		**4a** (51)
2		**4b** (38)
3		**4c** (34)
4		**4d** (45)
5		**4e** (51)
6		**4f** (33)
7		**4g** (49)

Table 2 (*continued*)

Entry	3	Product (yield, %)
8		**4h** (36)
9		**4i** (31)
10		**4j**·H_2O (48)

dioxane in the presence of KOH for 24 h results in the formation of quinoxalinepodands **4a**–**j** with 28–51% yields. In this way compound **4a** is precipitated from the reaction mixture in an analytically pure form. Other α,ω-bis[(3-phenylindolizin-2-yl)quinoxalin-2-on-1-yl]alkanes **4b**–**j** were purified by column chromatography on silica gel.

The MALDI mass spectra of the compounds **4a**–**i** displayed ion peaks at appropriate MH^+ values. α,ω-Bis[(3-phenylindolizin-2-yl)quinoxalin-2-on-1-yl]alkane **4j** with longer spacers separated from the reaction mixture as hydrates. This was confirmed by its MALDI mass spectra, which displayed ion peaks at appropriate $[M+H_3O]^+$, and also by their elemental analysis data.

^1H NMR spectra of compounds **4b**–**j** contain the signals of the protons of phenylindolizin-2-ylquinoxalin-2-on-1-yle aromatic ring fragments resonating in the region of 6.5–8.5 ppm and the signals of the protons of spacers in the areas of 4.4 ppm, (NCH_2), 3.4–3.8 ppm, (OCH_2), and 1.2–1.8 ppm, (the remaining of CH_2 groups).

The symmetric structure of compounds **4b**–**j** indicates the relation of intensities of the signals of the NCH_2 and CH_2 groups, which is 1:4 for compounds **4b**; the signals of NCH_2 and OCH_2 groups are 1:1, 1:2, 1:3, and 1:4 for the compounds of **4c**–**e**,**h**,**i**, and **h** correspondingly; the signals of NCH_2, OCH_2, and CH_2 (the remaining) groups are 1:3:4 and 1:5:2 for the compounds of **4f** and **4j** correspondingly. These data, as well as the frequencies of the ν(C=O) group in IR spectra at 1654–1647 cm^{-1} indicates N-alkylation at the both quinoxalin-2(1*H*)-one fragments of the molecule and the formation of compounds **4b**–**j**.

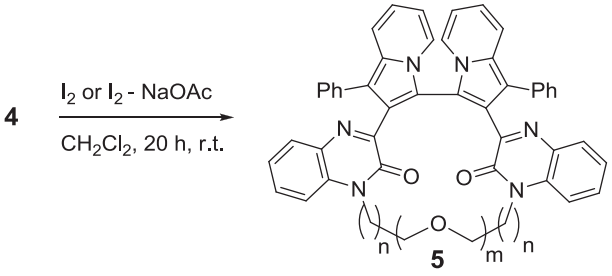
2.3. Iodine mediated oxidative cyclization of α,ω-bis-[3-(1-phenylindolizin-2-yl)-quinoxaline-2-one-1-yl]oxaalkanes 4a–j

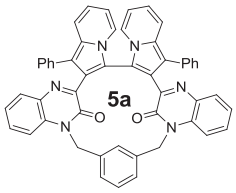
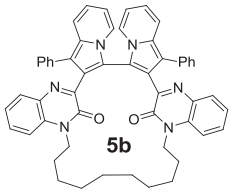
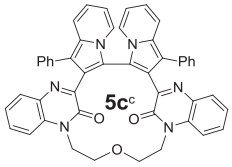
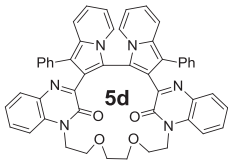
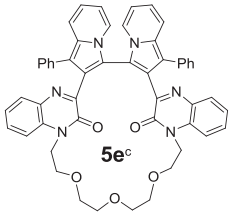
The interaction of α,ω-bis-[3-(1-phenylindolizin-2-yl)-quinoxaline-2-one-1-yl]oxaalkanes **4a**–**j** with molecular iodine at room temperature for 20 h in a solution of methylene chloride provides the formation of cyclophanes **5a**–**j** as the result of oxidative cyclization. The yields of the cyclophanes **5a**–**j** depending on the length of the spacer were in the range of 30–75% (Table 3).

It should be pointed out that an appreciable increase in yields (7–25%) occurs when the binary system (I_2–NaOAc) was used instead of molecular iodine.[37]

All the synthesized compounds were characterized by NMR, MS and IR spectra, and elemental analyses. Furthermore, the conformational behavior of the macrocycle **5e** in solid state and solutions by IR spectroscopic method and B3LYP/6-31G* optimization approach (see SD) and the structure of the macrocycle **5f** was further determined by X-ray crystallographic analysis of its complex with $Pb(ClO_4)_2$ as **5f**× $Pb(ClO_4)_2$ (see SD).

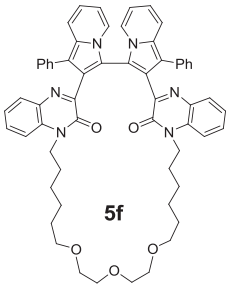
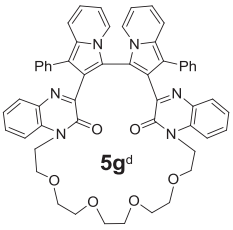
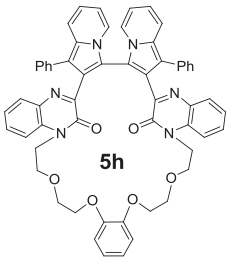
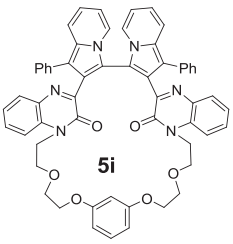
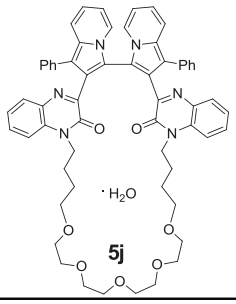
Table 3
A facile iodine mediated synthesis of diquinoxalinadiindolizinacyclophanes **5a**–**j**



Entry	Product	Yield, %[a] (%[b])
1		30 (50)
2		49 (59)
3		35 (60)
4		68 (74)
5		69 (92)

(*continued on next page*)

Table 3 (*continued*)

Entry	Product	Yield, %[a] (%[b])
6	 **5f**	79 (86)
7	 **5g**[d]	75 (86)
8	 **5h**	58 (67)
9	 **5i**	60 (69)
10	 $\cdot H_2O$ **5j**	60 (80)

[a] Yields of isolated products when molecular iodine was used as oxidative reagent.

[b] Yields of isolated products when the binary system (I_2–NaOAc) has been used instead of molecular iodine.

[c] The compounds have been described in previous paper[37] without characterization data.

[d] The compound has been described in previous paper[37] with characterization data.

2.4. Conformational peculiarities of the title macrocycles

In general, the ^{1}H NMR spectra of the title macrocycles reflect dependence of their conformational diversity and dynamics on the spacer type and their length in particular. Firstly, while in their precursors **4** the geminal protons of methylene groups of spacers in the ^{1}H NMR spectra are equivalent and resonate at 'normal' frequencies, these protons in macrocycles become nonequivalent in pairs. This is a clear indication that there is no mutual exchange between two conjugated conformations of the macrocycle **5** because of very a high barrier to rotation around the bond linking two indolizine fragments.[37] Secondly, the conversion of podands in macrocycles inevitably restricts the fluxionarity around other single bonds (e.g., Ind–Q), which leads to specific conformations in which the spacer protons fall within the shielding/deshielding zones of strongly anisotropic heteroaromatic groups. Therefore, some nuclei resonate at a higher field than in the source α,ω-bis-[3-(1-phenylindolizin-2-yl)-quinoxaline-2-one-1-yl]oxaalkanes **4a**–**j**.

If experimental data are considered in greater detail one can see that the compounds with a relative short spacer undergo a slow exchange (**5a**, **5c**), with well resolved lines for all the protons (Fig. 1a, b) that correspond to **5a** rigid (in the NMR time scale) structure. As soon as the spacers become longer there are characteristic broadenings in the ^{1}H NMR spectra for heteroaromatic and spacers moieties as well (Fig. 1c, d). Further elongation of the linkers (**5g**) produces a narrowing of the lines in the ^{1}H NMR spectra due to the exchange rate being higher in these cases, although the fast exchange regime in the NMR time scale has not been reached. The latter fact indicates that intramolecular dynamics depends not only on the spacer flexibility but on the restricted rotation around the heterocyclic Ind–Q units. In addition, it is also worth mentioning that from the point of view of heteroaromatic protons this influence of spacer's on the conformational characteristics is reflected on the H5 Ind and H5 Qx signals to a greater extent. It is assumed that these protons (in their environment) undergo changes more during conformational transformations.

The above spectral peculiarities for a variety of macrocycles can be well explained in the framework of the conformational exchange scheme outlined before for **5e** (Fig. 2).[44] These macrocycles can exist in several basic conformations due to their rotation around Ind–Qx bonds. There are ca. two C_2 symmetrical forms with both quinoxaline C=O bonds in-(SYM)[†] and out-(SYM*)[†] wardly directed in respect to the macrocycle annule (Fig. 2). In addition there are two nonsymmetrical and equivalent (in terms of the NMR) conformations in which the Qx C=O bonds directed only to one side (NSYM and NSYM*)[†] and therefore the two halves of the macrocycle have are nonequivalent.

2.5. Molecular structure of the complex 5f with $Pb(ClO_4)_2$

The molecular structure of compound **5f**·$Pb(ClO_4)_2$ was unambiguously established by a single-crystal X-ray analysis (Fig. 3). The crystals of **5f**·$Pb(ClO_4)_2$ were obtained by slow evaporation of the compound from chloroform solution. The single-crystal X-ray analysis reveled that, the molecule, possesses its own symmetry C_s, but loses it in the crystal and is located in a general positions of the monoclinic unit cell. The compound crystallizes with one cation complex, two ClO_4^- anions and two solvate chloroform molecules in the asymmetric part of the unit cell. Both solvate molecules are disordered in the crystal over two positions with relative occupancies 0.69:0.31 and 0.62:0.38. One of the two alkyl fragments (C6–C9) of the macrocycle is disordered over two positions with the relative occupancies 0.5:0.5.

[†] It means that there are set of conformations in fast exchange with characteristic orientation of C=O bonds.

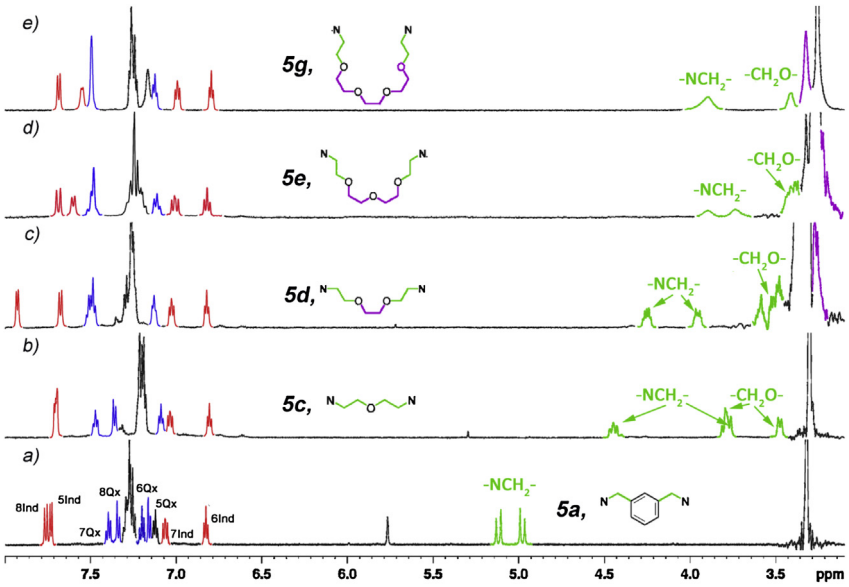


Fig. 1. ^{1}H NMR spectra of macrocycles **5a**, **c**–**e**, **g** in DMSO-d_6 at T=303 K.

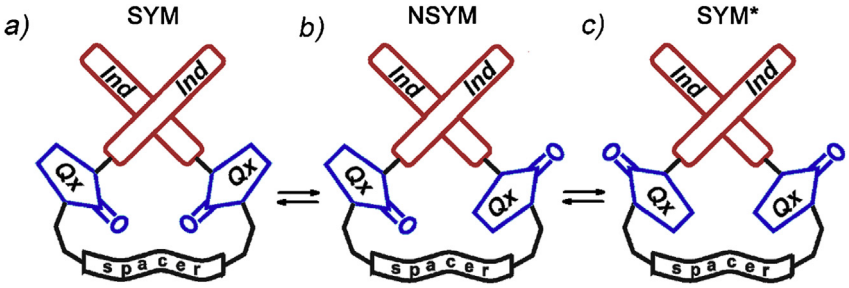


Fig. 2. Schematically presentation of the main conformer's geometries of **5**.

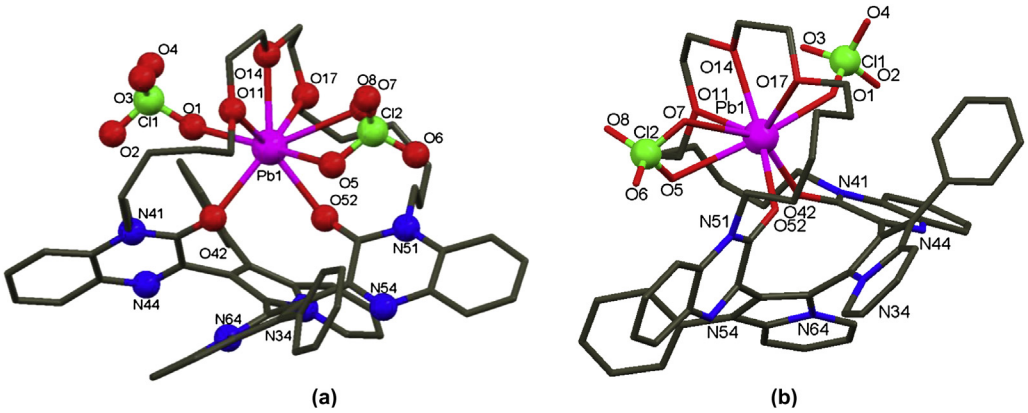


Fig. 3. Two projection of the molecular complex in the crystal **5f**·Pb(ClO$_4$)$_2$ and partial numbering scheme. (a) All heteroatoms are represented by sphere of arbitrary radii. The solvent $CHCl_3$ molecules and hydrogen atoms were omitted for clarity; (b) carbon, oxygen, and nitrogen atoms are represented by sticks.

The loss of symmetry of the macrocycle cation is connected, probably, with the realization of more favorable asymmetrical arrangement of its heterocyclic and alkyl fragments in the crystal. The dihedral angle between the planes of the two connected indolizine fragments is 125.7°, angles between the planes of bounded indolizine and quinoxaline fragments are 48.8° and 64.1° and between the planes of two pairs of bounded indolizine and phenyl fragments are 39.4° and 42.1°.

Within the complex **5f**·Pb(ClO$_4$)$_2$ the coordination number of lead cation is equal to 8 and two carboxyl groups, three ether oxygen atoms and oxygen atoms of two ClO_4^- anions are involved in its coordination. Two perchlorate anions are also located in the first coordination sphere of the cation, one of which take part in the direct interaction with the Pb^{2+} cation by one oxygen atom and another—by two oxygen atoms. Thus, the lead cation is completely encapsulated in the pseudocavity formed by the crown's basket,

heterocycles, and anions. The guest is, in this instance, not a cation, but a neutral $C_{60}H_{58}Cl_2N_6O_{13}Pb$ molecule. The space fill representation of the lead and oxygen atoms (Fig. 4) is noteworthy. Minimal distance between the centers of the nearest lead cations in the crystal is equal to 9.39 Å.

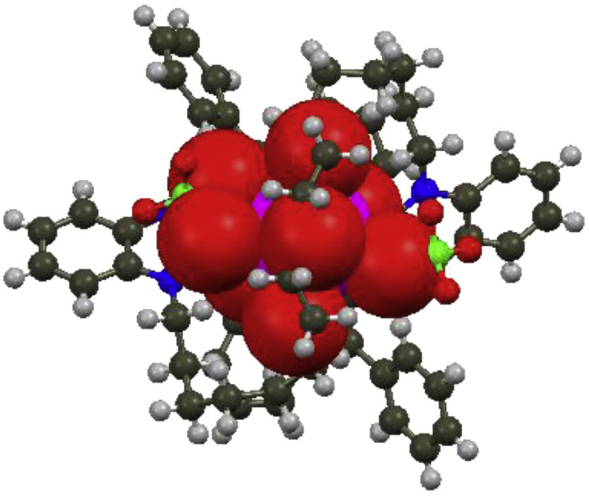


Fig. 4. Top view of the molecular complex in the crystal **5f**·$Pb(ClO_4)_2$. Pb atom and coordinated oxygen atoms are represented in 'space-fill' style. All other atoms are represented by 'ball-and-stick'. The solvent $CHCl_3$ molecules are omitted for clarity.

In the absence of classical hydrogen bonding supramolecular structure in the crystals of this compound is primarily determined by the intermolecular hydrogen bonds of C–H···O type and C–H···π and π···π contacts with a participation of electronic systems of the aromatic fragments. It should be mentioned that the C–H···Cl type interactions, as a whole interaction with the solvate chloroform molecules, apparently, are irrelevant for the formation of the supramolecular structure in the crystal, as evidenced by the disordered arrangement of chloroform molecules in the crystal. Probably, the role of the solvate molecules is more similar to 'void filling' aggregates in clathrate systems.[45]

CH–π and π–π type contacts are concentrated in one place of the unit cell (Fig. 5a—red circle) and form a supramolecular homosynthons—tetramers of the molecules. Relative position of two quinoxaline moieties belonged to adjacent molecules related by center of symmetry is favorable for dual π···π contacts between electron systems of its benzofragments. For this interaction *d*(Cg···Cg′) (centers of gravity of the aromatics)=3.90 Å, dihedral angle between aromatic planes is equal to 0°, and the shortest distance between these Ar···Ar planes is equal to 3.29 Å. At the same time the opposite side of this aromatic fragment takes part in the one else CH···π contact with the H704″ hydrogen atom belonged to the nearest molecule (H704″···Cg distance is equal to 3.43 Å, shortest distance 2.84 Å, symmetry operation 3/2−*x*,1/2+*y*,1/2−*z*). This type of supramolecular synthon links the molecules into a two-dimensional supramolecular structure—the goffered (wave-like) layers arranged parallel to the crystallographic planes (110) in the crystal (Fig. 5).

The second type of supramolecular homosynthon formed by the hydrogen bonds C–H···O type and brings together six molecules, four of which belong to the same coffered layer and two others are placed in the adjacent layers. Parameters of intermolecular C–H···O hydrogen bonds are summarized in Table 4. The first four C–H···O hydrogen bonds act in the same directions as π···π contacts. Thanks to central symmetry, these H-bonds are dual and stabilize the goffered layers. These layers are further linked into a 3D-structure by the other two dual hydrogen bonds.

Table 4
Parameters of the intermolecular H-bonds for complex **5f**·$Pb(ClO_4)_2$ in crystals

D–H···A	D–H, Å	H···A, Å	D···A, Å	∠DHA, °	Symmetry operation
C46–H46···O2	0.93	2.52	3.35(1)	149	1−*x*,2−*y*,1−*z*
C13–H131···O4	0.97	2.48	3.35(2)	149	1−*x*,1−*y*,1−*z*
C15–H152···O3		2.64		170	1−*x*,1−*y*,1−*z*
C68–H68···O8		2.63		131	3/2−*x*,1/2+*y*, 1/2−*z*
C56–H56···O6	0.93	2.41	3.28(1)	155	1−*x*,1−*y*,−*z*
C37–H37···O3		2.69		131	−1/2+*x*,3/2−*y*, −1/2+*z*

The mutual action of two type homosynthons—C–H···O H-bonds and C–H···π and π···π binding contacts—leads to formation of 3D supramolecular structure characterized by parallel arrangement of corrugated layers, two of which are shown in Fig. 5b. Disordered chloroform solvate molecules are distributed between the goffered layers and form cluster, consisting of four perchlorate moieties, with the shortest Cl···Cl distances into the cluster in the range 3.23–4.26 Å and Cl···Cl distances between cluster in the range 9.75–11.53 Å (Fig. 5c).

3. Conclusions

To summarize, we have described a new simple and efficient protocol for the intramolecular oxidative cyclization of mono-indolizinylquinoxalinepodands with molecular iodine as

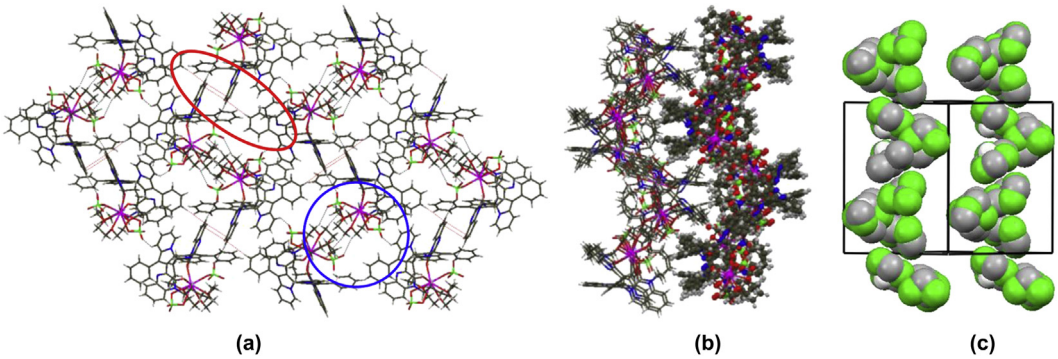


Fig. 5. Top (a) and bottom (b) view on the goffered layers of the complex in the crystal of **5f**·$Pb(ClO_4)_2$. (a) Two different supramolecular homosynthons are represented by red and blue circles. C–H···O intermolecular hydrogen bonds (blue) and C–H···π, π···π contacts (red) are shown by dashed lines. The solvent molecule in (a, b) was omitted for clarity; (c) 'space-fill' representation of the disordered solvent chloroform molecules arrangement .in the crystal, view along the 110 direction.

a dehydrogenating reagent. The remarkable features of this procedure are its efficiency, high conversion, operational simplicity, and the availability of reagents, all at low cost. In solution these macrocycles are in an equilibrium of several conformations due to restricted rotation around Ind–Qx bonds (ca. C_2 symmetrical and non-symmetrical forms), and their population and exchange rates depends on the spacer. It is anticipated that this methodology will have versatile applications in the practical syntheses of structural blockers for the various electroswitched nanodimensional molecular devices and machines with redox-active biindolizine and crown ethers moieties. Further expansion of the reaction scope and synthetic applications of this methodology are in progress in our laboratory.

4. Experimental section

4.1. General

The melting points were determined on a Boetius hot-stage apparatus and are uncorrected. Infrared (IR) spectra were recorded on a Bruker Vector-22 spectrometer. NMR experiments were carried out with Bruker spectrometers AVANCE-400 (400.1 MHz (^{1}H), 100.6 MHz (^{13}C)) and AVANCE-600 (600.1 MHz (^{1}H), 150.9 MHz (^{13}C)), equipped with a pulsed gradient unit capable of producing magnetic field pulse gradients in the *z*-direction of 53.5 G cm^{-1}. All spectra were acquired in a 5-mm gradient inverse broad band probe head. Chemical shifts are reported on the δ (parts per million) scale and are relative to the residual ^{1}H and ^{13}C signal of DMSO-d_6 and $CDCl_3$. The MALDI mass spectra were obtained on a Bruker UltraFlex III MALDI TOF/TOF instrument with 2,5-dihydroxybenzoic acid (2,5-DHB) as a matrix. Mass spectra Electronic ionization (EI) was measured on a TRACE MS spectrometer. The elemental analyses were carried out at the microanalysis laboratory of the Arbuzov Institute of Organic and Physical Chemistry, Russian Academy of Sciences. The 3-(1-phenylindolizin-2-yl)quinoxalin-2(1H)-one (**1a**) was synthesized according to the reported methods.[46,47]

The X-ray diffraction data for the crystal of **5f**·$Pb(ClO_4)_2$ (see Section 4.4.6) were collected on a Bruker Smart Apex II CCD diffractometer using graphite monochromated MoK_α (λ=0.71073 Å) radiation at 296(2) K. The structure was solved by direct method using SHELXS[48] program and refined by the full-matrix least-squares using SHELXL[49] programs. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were inserted at calculated positions and refined as riding atoms. Data collection: images were indexed and integrated using the APEX2 data reduction package.[50] All calculations were performed on PC using WinGX[51] suit of programs. Analysis of the intermolecular interactions was performed using the program PLATON.[52] Mercury program package[53] was used for figures preparation.

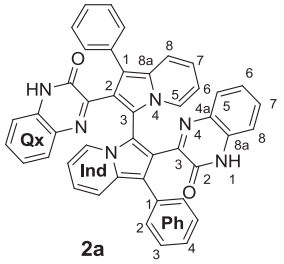
Crystallographic data (excluding structure factors) for the structure **5f**·$Pb(ClO_4)_2$ have been deposited in the Cambridge Crystallographic Data Centre as supplementary publication number CCDC 884152. Copies of the data can be obtained free of charge upon application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK, (fax: +44(0)1223 336033 or e-mail: deposit@ccdc.cam.ac.uk).

4.2. General procedure (*a*) for the synthesis of 1,1′-diphenyl-2,2′-di(quinoxalin-2-on-3-yl)-3,3′-biindolizines 2

A solution of I_2 (150 mg, 0.591 mmol) in CH_2Cl_2 (30 mL) at room temperature was added to a stirred solution of the appropriate indolizine **1** (0.40 mmol) in CH_2Cl_2 (15 mL).

When synthesizing **2a** while stirring the reaction mixture for 1 h at room temperature there occurs the precipitation of dark violet color crystals. EtOH (10 mL) was added to the reaction mixture and then refluxed. In the course of the reaction the crystals gradually dissolved during 10 min. After evaporation of the solvent the residue was washed with aqueous 5% $NaHCO_3$ (10 mL) and 5% $Na_2S_2O_3$ (10 mL), then filtered, and dried.

When synthesizing **2b**,**c** the reaction mixture was stirred for 20 h at this temperature and then was washed with aqueous 5% $NaHCO_3$ (10 mL) and 5% $Na_2S_2O_3$ (10 mL). The organic layer was dried over Na_2SO_4, then filtered, and evaporated under reduced pressure. The residue was purified by flash column chromatography on silica gel (hexane/CH_2Cl_2, 1:1 → CH_2Cl_2).



*4.2.1. 1,1′-Diphenyl-2,2′-di[quinoxalin-2(1H)-on-3-yl]-3,3′-biindolizine (**2a**).* Yellow powder, mp >360 °C. Found: C, 78.43; H, 4.28; N, 12.42. $C_{44}H_{28}N_6O_2$ requires: C, 78.56; H, 4.20; N, 12.49%. IR (ν_{max}, cm^{-1}, KBr): 3220–2500, 1670, 1611, 1563, 1520, 1418, 1344, 1272, 1247, 1236, 1211, 1152, 1098, 1029, 961, 762, 729, 700, 602, 547, 473, 430. δ_H NMR (600.1 MHz, DMSO-d_6): 6.79 (2H, ddd, *J* 7.2, 6.9, 1.0 Hz, H6 Ind), 6.85 (2H, dd, *J* 9.3, 1.3 Hz, H5 Qx), 6.98 (2H, ddd, *J* 9.3, 6.7, 1.1 Hz, H6 Qx), 7.00 (2H, ddd, *J* 9.1, 6.9, 1.0 Hz, H7 Ind), 7.11 (2H, m, H4 Ph), 7.14 (2H, dd, *J* 7.6, 1.1 Hz, H8 Qx), 7.26 (4H, dd, *J* 8.0, 7.6 Hz, H3 Ph), 7.31 (4H, dd, *J* 7.6, 1.5 Hz, H2 Ph), 7.38 (2H, ddd, *J* 7.6, 6.7, 1.3 Hz, H7 Qx), 7.53 (2H, dd, *J* 7.2, 1.0 Hz, H5 Ind), 7.70 (2H, dd, *J* 9.1, 1.0 Hz, H8 Ind), 12.01 (2H, s, H1 Qx); δ_C (151 MHz, DMSO-d_6): 111.9 (C6 Ind), 113.6 (C1 Ind), 113.8 (C3 Ind), 114.7 (C8 Qx), 117.6 (C8 Ind), 119.7 (C7 Ind), 122.6 (C6 Qx), 124.4 (C5 Ind), 125.1 (C2 Ind), 125.4 (C4 Ph), 128.2 (C3 Ph, C5 Qx), 129.0 (C2 Ph), 129.7 (C7 Qx), 130.2 (C8a Ind), 131.7 (C4a Qx), 131.8 (C8a Qx), 134.5 (C1 Ph), 153.9 (C3 Qx), 154.7 (C2 Qx). MS (EI, 70 eV): *m*/*z* (%) 673.3 (M^++1, 55.4), 672.3 (M^+, 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).

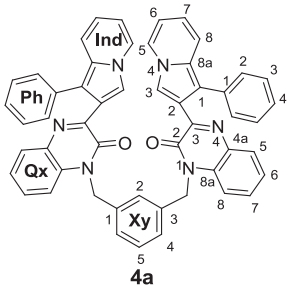
*4.2.2. 1,1′-Diphenyl-2,2′-di[5-methylquinoxalin-2-on-3-yl]-3,3′-biindolizine (**2b**).* Yellow powder, mp 317–319 °C. IR (ν_{max}, cm^{-1}, Nujol mull): 1662, 1602, 1586, 1522, 1339, 1312, 1280, 1235, 1220, 1161, 1101, 1089, 1035, 977, 953, 925, 890, 759, 730, 701, 538. Found: C, 78.77; H, 4.80; N, 11.87. $C_{46}H_{32}N_6O_2$ requires: C, 78.84; H, 4.60; N, 11.99. δ_H NMR (600.1 MHz, DMSO-d_6): 3.21 (6H, s, Me), 6.80 (2H, ddd, *J* 7.2, 6.9, 1.0 Hz, H6 Ind), 7.00 (2H, ddd, *J* 9.1, 6.9, 1.0 Hz, H7 Ind), 7.04 (2H, dd, *J* 7.5, 1.1 Hz, H5 Qx), 7.11 (2H, td, *J* 8.3, 1.5 Hz, H4 Ph), 7.13 (2H, ddd, *J* 7.7, 7.5, 1.0 Hz, H6 Qx), 7.23 (4H, dd, *J* 8.3, 7.6, Hz, H3 Ph), 7.26 (4H, dd, *J* 7.6, 1.5 Hz, H2 Ph), 7.36 (2H, dd, *J* 7.0, 1.0 Hz, H8 Qx), 7.49 (2H, ddd, *J* 7.7, 7.0, 1.1 Hz, H7 Qx), 7.51 (2H, d, *J* 7.2, 1.0 Hz, H5 Ind), 7.68 (2H, dd, *J* 9.1, 1.0 Hz, H8 Ind); δ_C (151 MHz, DMSO-d_6): 28.7 (Me), 112.1 (C6 Ind), 113.6 (C3 Ind), 113.9 (C1 Ind), 114.1 (C8 Qx), 117.7 (C8 Ind), 119.6 (C7 Ind), 122.6 (C6 Qx), 124.1 (C5 Ind), 125.4 (C4 Ph and C2 Ind), 128.1 (C3 Ph), 128.8 (C3 Ph), 129.0 (C5 Qx), 130.0 (C7 Qx), 130.1 (C8a Ind), 132.0 (C4a Qx), 133.0 (C8a Qx), 134.5 (C1 Ph), 153.1 (C3 Qx), 153.4 (C2 Qx). MS (MALDI TOF) $(MH)^+$ 729.

4.3. General procedure for the synthesis of α,ω-bis[3-(1-phenylindolizin-2-yl)quinoxalin-2-on-1-yl]oxaalkanes 4

A suspension of compound **1a** (0.55 g, 1.630 mmol), KOH (0.18 g, 3.214 mmol), dibromide **3** (0.80 mmol), and dioxane (25 mL) was refluxed for 24 h.

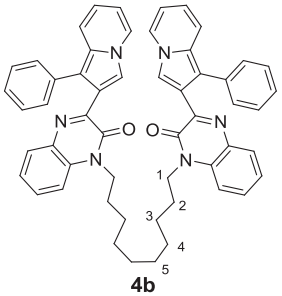
When synthesizing **4a** the reaction mixture was left overnight at room temperature, the yellow precipitate was filtrated and washed with EtOH (5 mL) and water (5 mL) and dried in vacuo to afford the product.

When synthesizing **4b**–**l** the temperature was allowed to slowly warm to room temperature, the reaction mixture was quenched with water (100 mL), and neutralized with AcOH. The yellow solid was filtrated and washed with water (5 mL), dried in vacuo and purified by flash column chromatography on silica gel (hexane/CH_2Cl_2, 3:1→CH_2Cl_2 (**a**–**c**); CH_2Cl_2→CH_2Cl_2/EtOH, 100:1 (**d**–**l**)).

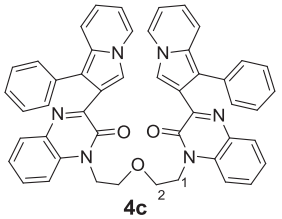


4a

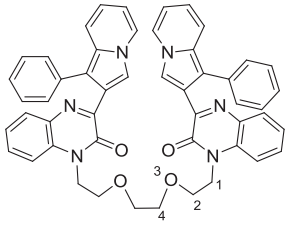
*4.3.1. 1,3-Bis[3-(1-phenylindolizin-2-yl)quinoxalin-2-on-1-yl]xylene (**4a**).* Yellow powder, mp 234–236 °C. Found: C, 80.29; H, 4.71; N, 10.89. $C_{52}H_{36}N_6O_2$ requires: C, 80.39; H, 4.67; N, 10.82%. IR (ν_{max}, cm^{-1}, KBr): 3055, 2957, 2912, 2886, 2853, 1647, 1600, 1577, 1549, 1525, 1494, 1450, 1438, 1422, 1365, 1314, 1284, 1251, 1227, 1177, 1121, 1082, 1047, 1007, 949, 874, 754, 704, 672, 583, 425. δ_H NMR (600.1 MHz, DMSO-d_6): 5.48 (4H, s, CH_2), 6.61 (2H, td, *J* 6.9, 1.0 Hz, H6 Ind), 6.75 (2H, dd, *J* 9.1, 6.9 Hz, H7 Ind), 7.11 (2H, dd, *J* 7.9, 1.0 Hz, H4 Xy), 7.20 (2H, t, *J* 7.5 Hz, H6 Qx), 7.21–7.42 (20H, ArH), 8.29 (2H, d, *J* 6.9 Hz, H5 Ind), 8.48 (2H, br s, H3 Ind); δ_C (151 MHz, DMSO-d_6): 44.8 (CH_2), 111.4 (C6 Ind), 113.9 (C1 Ind), 114.5 (C8 Qx), 117.2 (C3 Ind), 117.4 (C8 Ind), 118.6 (C7 Ind), 121.1 (C2 Ind), 123.2 (C6 Qx), 125.3 (C4 Ph), 125.5 (C2 Xy), 125.7 (C4 Xy), 125.9 (C5 Ind), 127.5 (C2 Ph), 128.9 (C5 Qx), 129.0 (C5 Xy), 129.4 (C7 Qx), 129.7 (C8a Ind), 130.0 (C3 Ph), 131.5 (C8a Qx), 132.3 (C4a Qx), 135.5 (C1 Ph), 136.4 (C1 Xy), 150.7 (C3 Qx), 153.7 (C2 Qx). MS (MALDI TOF) 777 (MH^+), 799 $(M+Na)^+$, 815 $(M+K)^+$.


4b

*4.3.2. 1,10-Bis[3-(1-phenylindolizin-2-yl)quinoxalin-2-on-1-yl]decane (**4b**).* Yellow powder, mp 221–223 °C. Found: C, 79.79; H, 5.99; N, 10.48. $C_{54}H_{48}N_6O_2$ requires: C, 79.78; H, 5.95; N, 10.34%. IR (ν_{max}, cm^{-1}, KBr): 3051, 2927, 2852, 1650, 1580, 1528, 1461, 1313, 1284, 1184, 1139, 764, 745, 700, 429. δ_H NMR (600.1 MHz, DMSO-d_6): 1.24–1.36 (12H, m, H3–H5), 1.60–1.69 (4H, m, H2), 4.24 (4H, t, *J* 7.1 Hz, H1), 6.62 (2H, td, *J* 6.9, 1.0 Hz, H6 Ind), 6.74 (2H, ddd, *J* 9.1, 6.9, 1.0 Hz, H7 Ind), 7.22–7.35 (16H, ArH), 7.54 (4H, m, H7 and H8 Qx), 8.35 (2H, d, *J* 6.9 Hz, H5 Ind), 8.53 (2H, s, H3 Ind); δ_C (151 MHz, DMSO-d_6): 26.0 (C3), 26.6 (C2), 28.4 (C4), 28.5 (C5), 41.5 (C1), 111.3 (C6 Ind), 113.9 (C1 Ind), 114.0 (C8 Qx), 117.1 (C3 Ind), 117.3 (C8 Ind), 118.5 (C7 Ind), 121.1 (C2 Ind), 122.9 (C6 Qx), 125.2 (C4 Ph), 125.9 (C5 Ind), 127.4 (C2 Ph), 128.9 (C5 Qx), 129.6 (C8a Ind), 129.7 (C7 Qx), 129.9 (C3 Ph), 131.5 (C8a Qx), 132.2 (C4a Qx), 135.4 (C1 Ph), 150.5 (C3 Qx), 153.3 (C2 Qx). MS (MALDI TOF) 813 (MH^+), 835 $(M+Na)^+$, 851 $(M+K)^+$.

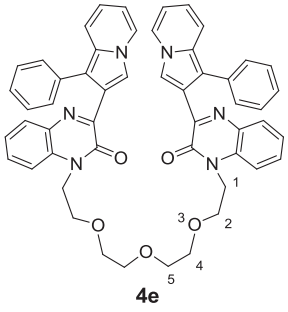

4c

*4.3.3. 1,5-Bis[3-(1-phenylindolizin-2-yl)quinoxalin-2-on-1-yl]-3-oxapentane (**4c**).* Yellow powder, mp 240–242 °C. Found: C, 77.29; H, 4.81; N, 11.39. $C_{48}H_{36}N_6O_3$ requires: C, 77.40; H, 4.87; N, 11.28%. IR (ν_{max}, cm^{-1}, Nujol mull): 1654, 1602, 1581, 1544, 1528, 1311, 1229, 1083, 1123, 762, 670, 586; δ_H NMR (600.1 MHz, DMSO-d_6): 3.76 (4H, t, *J* 5.7 Hz, H2), 4.40 (4H, t, *J* 5.7 Hz, H1), 6.61 (2H, td, *J* 7.0, 1.0 Hz, H6 Ind), 6.74 (2H, ddd, *J* 9.1, 7.0, 1.0 Hz, H7 Ind), 7.19 (2H, t, *J* 7.7, H6 Qx), 7.23 (4H, m, H5 Qx and H4 Ph), 7.29–7.38 (12H, ArH), 7.47 (2H, d, *J* 8.1 Hz, H8 Qx), 8.32 (2H, dd, *J* 7.0, 1.1 Hz, H5 Ind), 8.51 (2H, s, H3 Ind); δ_H (151 MHz, DMSO-d_6): 41.6 (C1), 67.2 (C2), 111.5 (C6 Ind), 113.9 (C1 Ind), 114.5 (C8 Qx), 117.2 (C3 Ind), 117.5 (C8 Ind), 118.7 (C7 Ind), 121.0 (C2 Ind), 123.1 (C6 Qx), 125.4 (C4 Ph), 126.0 (C5 Ind), 127.5 (C2 Ph), 128.8 (C5 Qx), 129.4 (C7 Qx), 129.7 (C8a Ind), 130.1 (C3 Ph), 132.1 (C8a Qx), 132.2 (C4a Qx), 135.5 (C1 Ph), 150.4 (C3 Qx), 153.6 (C2 Qx); MS (MALDI TOF) 745 (MH^+), 767 $(M+Na)^+$, 783 $(M+K)^+$.

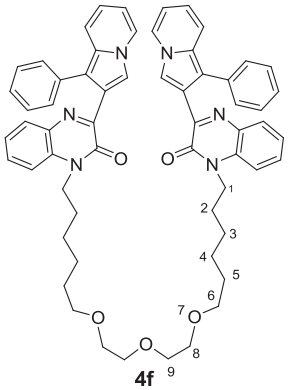

4d

*4.3.4. 1,8-Bis[3-(1-phenylindolizin-2-yl)quinoxalin-2-on-1-yl]-3,5-dioxaoctane (**4d**).* Yellow powder, mp 225–227 °C. Found: C, 76.20; H, 5.05; N, 10.48. $C_{50}H_{40}N_6O_4$ requires: C, 76.12; H, 5.11; N, 10.65%. IR (ν_{max}, cm^{-1}, KBr): 3143, 3045, 2961, 2923, 2894, 2870, 2855, 1654, 1600, 1581, 1527, 1492, 1452, 1440, 1310, 1280, 1255, 1182, 1124, 1102, 1082, 764, 750, 701, 672, 557. δ_H NMR (600.1 MHz, DMSO-d_6): 3.49 (4H, m, H4), 3.65 (4H, t, *J* 5.9 Hz, H2), 4.37 (4H, t, *J* 5.9 Hz, H1), 6.61 (2H, td, *J* 6.9, 1.0 Hz, H6 Ind), 6.74 (2H, ddd, *J* 9.1, 6.9, 1.0 Hz, H7 Ind), 7.19 (2H, t, *J* 7.7, H6 Qx), 7.20–7.38 (14H, ArH), 7.43 (2H, t, *J* 7.7 Hz, H7 Qx), 7.52 (2H, d, *J* 7.7 Hz, H8 Qx), 8.32 (2H, dd, *J* 6.9, 1.0 Hz, H5 Ind), 8.52 (2H, s, H3 Ind); δ_C (151 MHz, DMSO-d_6): 41.6 (C1), 67.1 (C2), 69.9 (C4), 111.4 (C6 Ind), 113.9 (C1 Ind), 114.6 (C8 Qx), 117.2 (C3 Ind), 117.4 (C8 Ind), 118.6 (C7 Ind), 120.9 (C2 Ind), 123.0 (C6 Qx), 125.3 (C4 Ph),

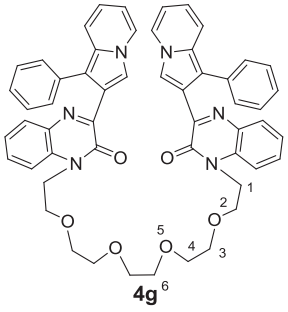
126.0 (C5 Ind), 127.4, 127.5 (C2 Ph), 128.7 (C5 Qx), 129.3 (C7 Qx), 129.6 (C8a Ind), 130.0 (C3 Ph), 132.0 (C8a Qx), 132.2 (C4a Qx), 135.4 (C1 Ph), 150.4 (C3 Qx), 153.5 (C2 Qx); MS (MALDI TOF) 789 (MH^+), 811 $(M+Na)^+$, 827 $(M+K)^+$.



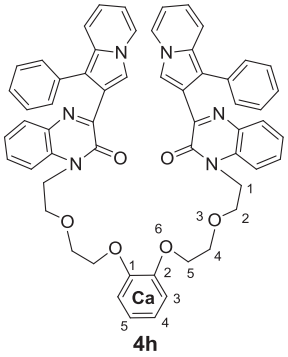
*4.3.5. 1,11-Bis[3-(1-phenylindolizin-2-yl)quinoxalin-2-on-1-yl]-3,6,9-trioxaundecane (**4e**).* Yellow powder, mp 192–194 °C. Found: C, 75.07; H, 5.38; N, 10.00. $C_{52}H_{44}N_6O_5$ requires: C, 74.98; H, 5.32; N, 10.09%. IR (ν_{max}, cm^{-1}, Nujol mull): 1652, 1602, 1581, 1529, 1494, 1311, 1289, 1228, 1183, 1125, 1007, 753, 702, 670. δ_H NMR (600.1 MHz, DMSO-d_6): 3.39 (2H, m, H5), 3.47 (2H, m, H4), 3.71 (2H, t, *J*=5.5 Hz, H2), 4.41 (2H, t, *J*=5.5 Hz, H1), 6.60 (1H, ddd, *J*=6.8, 6.1, 0.7 Hz, H6 Ind), 6.72 (1H, dd, *J* 6.8, 6.1, 0.7 Hz, H7), 7.22–7.28 (3H, m, H5 Qx, H6 Qx, and H4 Ph), 7.29–7.38 (5H, m, H8 Ind, H2 Ph, and H3 Ph), 7.46 (1H, td, *J*=7.8, 1.4 Hz, H7 Qx), 7.55 (1H, d, *J*=7.8 Hz, H8 Qx), 8.32 (1H, dd, *J*=6.8, 0.7 Hz, H5 Ind), 8.52 (1H, s, H3 Ind). δ_C NMR (150.9 MHz, DMSO-d_6): 41.5, 66.9, 69.5, 69.7, 113.8, 114.5, 117.0, 117.3, 118.4, 120.8, 122.9, 122.9, 125.2, 125.8, 127.3, 128.6, 129.2, 129.5, 129.9, 135.3, 131.9, 132.0, 150.2, 153.4. MS (MALDI TOF) 833 (MH^+), 855 $(M+Na)^+$, 871 $(M+K)^+$.



*4.3.6. 1,19-Bis[3-(1-phenylindolizin-2-yl)quinoxalin-2-on-1-yl]-7,10,13-trioxanonadecane (**4f**).* Yellow powder, mp 102–105 °C. Found: C, 76.08; H, 6.33; N, 8.82. $C_{60}H_{60}N_6O_5$ requires: C, 76.25; H, 6.40; N, 8.89%. IR (ν_{max}, cm^{-1}, KBr): 3048, 2930, 2857, 1649, 1600, 1579, 1552, 1528, 1494, 1457, 1369, 1311, 1283, 1247, 1221, 1187, 1122, 1086, 1038, 749, 700, 669, 646, 583, 561, 515, 464, 429. δ_H NMR (600.1 MHz, DMSO-d_6): 1.30–1.36 (8H, m, H3 and H4), 1.46 (4H, m, H5), 1.62 (4H, m, H2), 3.34 (4H, t, *J* 6.7 Hz, H6), 3.43 (4H, m, H8), 3.48 (4H, m, H9), 4.22 (4H, t, *J* 7.7 Hz, H1), 6.60 (2H, td, *J* 6.9, 1.0 Hz, H6 Ind), 6.72 (2H, ddd, *J* 9.1, 6.9, 1.0 Hz, H7 Ind), 7.24 (4H, m, H4 Ph and H6 Qx), 7.28–7.36 (12H, ArH), 7.51 (4H, m, H7 and H8 Qx), 8.33 (2H, dd, *J* 6.9, 1.0 Hz, H5 Ind), 8.53 (2H, s, H3 Ind); δ_C (151 MHz, DMSO-d_6): 25.2 (C4), 25.9 (C3), 26.7 (C2), 28.9 (C5), 41.6 (C1), 69.3 (C8), 69.7 (C9), 70.0 (C6), 111.4 (C6 Ind), 113.9 (C1 Ind), 114.1 (C8 Qx), 117.2 (C3 Ind), 117.4 (C8 Ind), 118.6 (C7 Ind), 121.1 (C2 Ind), 123.0 (C6 Qx), 125.3 (C4 Ph), 126.0 (C5 Ind), 127.4 (C2 Ph), 129.0 (C5 Qx), 129.6 (C7 Qx), 129.6 (C8a Ind), 130.0 (C3 Ph), 131.5 (C8a Qx), 132.2 (C4a Qx), 135.5 (C1 Ph), 150.5 (C3 Qx), 153.3 (C2 Qx); MS (EI, 70 eV): *m*/*z* (%) 945 (M^++1, 3), 945 (M^+, 5), 525 (19), 464 (22), 437 (25), 436 (48), 421 (20), 420 (17), 407 (18), 378 (15), 365 (11), 364 (26), 352 (10), 351 (30), 350 (11), 339 (17), 338 (62), 337 (70), 336 (34), 323 (13), 322 (30), 321 (12), 320 (22), 310 (12), 309 (28), 308 (100), 307 (39), 306 (15).

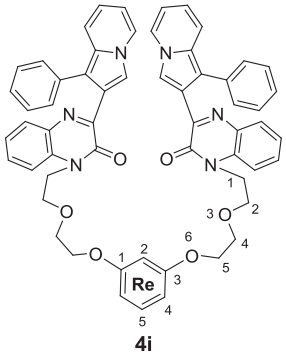


*4.3.7. 1,14-Bis[3-(1-phenylindolizin-2-yl)quinoxalin-2-on-1-yl]-3,6,9,12-tetraoxatetradecane (**4g**).* Yellow powder, mp 126–128 °C. Found: C, 73.87; H, 5.39; N, 9.63. $C_{54}H_{48}N_6O_6$ requires: C, 73.95; H, 5.52; N, 9.58%. IR (ν_{max}, cm^{-1}, KBr): 3046, 2866, 1653, 1600, 1580, 1527, 1494, 1451, 1310, 1286, 1226, 1182, 1124, 1099, 1082, 1037, 763, 752, 700, 671, 584, 561, 466, 428. δ_H NMR (400.1 MHz, $CDCl_3$): 3.52 (4H, s, H6), 3.52–3.57 (4H, m, H3), 3.59–3.61 (4H, m, H4), 3.83 (4H, t, *J* 6.2 Hz, H2), 4.50 (4H, t, *J* 6.2 Hz, H1), 6.51 (2H, td, *J* 6.8, 1.0 Hz, H6 Ind), 6.65 (2H, ddd, *J* 9.1, 6.8, 1.0 Hz, H7 Ind), 7.21 (2H, td, *J* 7.8, 1.0 Hz, H6 Qx), 7.25–7.52 (18H, ArH), 7.90 (2H, dd, *J* 6.8, 1.0 Hz, H5 Ind), 8.45 (2H, s, H3 Ind); δ_C NMR (100.6 MHz, $CDCl_3$) 42.5, 68.0, 70.5, 70.6, 70.8, 111.7, 114.2, 115.1, 116.9, 118.1, 118.6, 121.5, 123.4, 125.2, 125.6, 127.7, 129.2, 129.9, 130.6, 130.9, 132.4, 133.1, 136.0, 150.9, 154.5. MS (MALDI TOF) 877 (MH^+), 899 $(M+Na)^+$, 915 $(M+K)^+$.



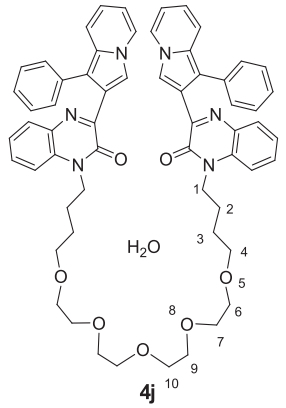
*4.3.8. 1,2-Bis{6-[3-(1-phenylindolizin-2-yl)quinoxalin-2-on-1-yl]-3-oxapentoxybenzene (**4h**).* Yellow powder, mp 104–106 °C. Found: C, 75.26; H, 5.25; N 9.14. $C_{58}H_{48}N_6O_6$ requires: C, 75.31; H, 5.23; N, 9.08%. IR (ν_{max}, cm^{-1}, Nujol mull): 1654, 1601, 1581, 1528, 1501, 1311, 1288, 1252, 1184, 1124, 1083, 1049, 1015, 960, 920, 763, 752, 704, 672. δ_H NMR (600.1 MHz, DMSO-d_6): 3.70 (4H, t, *J* 4.7 Hz, H4), 3.76 (4H, t, *J* 6.1 Hz, H2), 4.00 (4H, t, *J* 4.7 Hz, H5), 4.43 (4H, t, *J* 6.1 Hz, H1), 6.60 (2H, td, *J* 6.9, 1.0 Hz, H6 Ind), 6.72 (2H, ddd, *J* 9.1, 6.9, 1.0 Hz, H7 Ind), 6.82 (2H, m, H2 Ca), 6.88 (2H, m, H3 Ca), 7.17–7.35 (16H, ArH), 7.41 (2H, dd, *J* 8.6, 7.8 Hz, H7 Qx), 7.55 (2H, d, *J* 8.6 Hz, H8 Qx), 8.30 (2H, dd, *J* 6.9, 1.0 Hz, H5 Ind), 8.51 (2H, s, H3 Ind); δ_C (151 MHz, DMSO-d_6): 41.6 (C1), 67.2 (C2), 68.3 (C5), 69.1 (C4), 111.4 (C6 Ind), 113.9 (C1 Ind), 114.5 (C8 Qx), 114.8 (C4 Ca), 117.2 (C3 Ind), 117.4 (C8

Ind), 118.6 (C7 Ind), 120.9 (C2 Ind), 121.2 (C3 Ca), 123.0 (C6 Qx), 125.3 (C4 Ph), 125.9 (C5 Ind), 127.4 (C2 Ph), 128.7 (C5 Qx), 129.3 (C7 Qx), 129.6 (C8a Ind), 130.1 (C3 Ph), 132.0 (C8a Qx), 132.1 (C4a Qx), 135.4 (C1 Ph), 148.4 (C1 Ca), 150.3 (C3 Qx), 153.5 (C2 Qx); MS (MALDI TOF) 789 (MH^+), 811 $(M+Na)^+$, 827 $(M+K)^+$.



4i

*4.3.9. 1,3-Bis{6-[3-(1-phenylindolizin-2-yl)quinoxalin-2-on-1-yl]-3-oxapentoxybenzene (**4i**).* Yellow powder, mp 116–118 °C. Found: C, 75.28; H, 5.20; N, 9.15. $C_{58}H_{48}N_6O_6$ requires: C, 75.31; H, 5.23; N, 9.08%. IR (ν_{max}, cm^{-1}, Nujol mull): 1653, 1601, 1582, 1528, 1491, 1311, 1287, 1248, 1227, 1182, 1157, 1126, 1082, 1057, 856, 763, 751, 723, 702, 668. δ_H NMR (600.1 MHz, DMSO-d_6): 3.72 (4H, t, *J* 4.0 Hz, H4), 3.79 (4H, t, *J* 6.2 Hz, H2), 3.97 (4H, t, *J* 4.0 Hz, H5), 4.47 (4H, t, *J* 6.2 Hz, H1), 6.37 (1H, t, *J* 2.0 Hz, H2 Re), 6.42 (2H, td, *J* 8.3, 2.0 Hz, H4 Re), 6.61 (2H, td, *J* 6.6, 0.8 Hz, H6 Ind), 6.73 (2H, ddd, *J* 9.1, 6.6, 1.0 Hz, H7 Ind), 7.07 (1H, t, *J* 8.3 Hz, H5 Re), 7.20–7.36 (16H, ArH), 7.47 (2H, td, *J* 8.4, 1.7 Hz, H7 Qx), 7.60 (2H, d, *J* 8.4 Hz, H8 Qx), 8.33 (2H, dd, *J* 6.6, 1.0 Hz, H5 Ind), 8.52 (2H, s, H3 Ind); δ_C (151 MHz, DMSO-d_6): 41.6 (C1), 67.0 (C5), 67.1 (C2), 68.9 (C4), 101.2 (C2 Re), 106.8 (C4 Re), 111.4 (C6 Ind), 113.9 (C1 Ind), 114.6 (C8 Qx), 117.2 (C3 Ind), 117.4 (C8 Ind), 118.6 (C7 Ind), 121.0 (C2 Ind), 123.1 (C6 Qx), 125.3 (C4 Ph), 126.0 (C5 Ind), 127.4 (C2 Ph), 128.8 (C5 Qx), 129.4 (C7 Qx), 129.6 (C8a Ind), 129.6 (C5 Re), 130.0 (C3 Ph), 132.0 (C8a Qx), 132.2 (C4a Qx), 135.4 (C1 Ph), 150.4 (C3 Qx), 153.5 (C2 Qx), 159.5 (C1 Re); MS (MALDI TOF) $(MH)^+$=925.



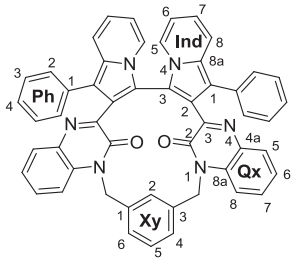
4j

*4.3.10. 1,21-Bis[3-(1-phenylindolizin-2-yl)quinoxalin-2-on-1-yl]-5,8,11,14,17-pentaoxaheneicosane monohydrate (**4j**).* Yellow powder, mp 132–134 °C. Found: C, 71.39; H, 6.38; N, 8.33. $C_{60}H_{62}N_6O_8$ requires: C, 72.41; H, 6.28; N, 8.44%. IR (ν_{max}, cm^{-1}, KBr): 2937, 2865, 1650, 1559, 1579, 1526, 1460, 1449, 1282, 1249, 1220, 1180, 1121, 1086, 1066, 1039, 1005, 763, 751, 702, 672, 645, 582, 563, 516, 466, 433. δ_H NMR (600.1 MHz, $CDCl_3$): 1.72–1.77 (4H, m, H2), 1.83–1.88 (4H, m, H3), 3.55 (4H, t, *J* 6.2 Hz, H4), 3.59–3.65 (8H, m, H6 and H7), 3.66–3.71 (8H, m, H9 and H10), 4.33 (4H, t, *J* 7.6 Hz, H1), 6.50 (2H, ddd, *J* 6.8, 6.6, 0.9 Hz, H6 Ind), 6.64 (2H, ddd, *J* 9.2, 6.6, 0.9 Hz, H7 Ind), 7.22 (2H, dd, *J* 7.8, 7.3 Hz, H6 Qx), 7.27–7.47 (18H, m, ArH), 7.90 (2H, dd, *J* 6.8, 0.9 Hz, H5 Ind), 8.45 (2H, s, H3 Ind). δ_C NMR (150.9 MHz, $CDCl_3$): 24.2, 26.9, 42.2, 61.8, 70.3, 70.5, 70.8, 72.5, 111.7, 113.4, 115.1, 116.9, 118.1, 118.6, 121.6, 123.3, 125.2, 125.6, 127.7, 129.4, 130.2, 130.6, 130.9, 131.8, 133.3, 136.0, 151.0, 154.4; MS (MALDI TOF) $(M+H_2O)H^+$ = 995. MS (EI, 70 eV): *m/z* (%) 977 (M^++1, 0.2), 976 (M^+, 0.3), 499 (15), 498 (23), 497 (71), 453 (11), 452 (19), 436 (21), 423 (13), 409 (21), 408 (28), 393 (19), 392 (18), 379 (17), 378 (35), 365 (16), 364 (25), 352 (11), 351 (30), 350 (11), 339 (21), 338 (58), 337 (58), 336 (39), 323 (18), 322 (37), 321 (16), 320 (31), 310 (15), 309 (34), 308 (100), 307 (49), 306 (22).

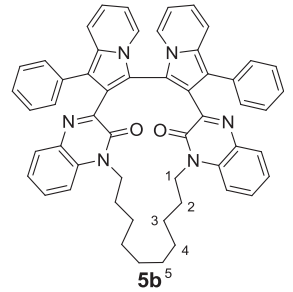
4.4. General procedure (*a*) $2^1,3^1$-diphenyl-$1^2,4^2$-dioxo-1,4(3,1)-diquinoxalina-2(2,3),3(3,2)-diindolizinacycloalkaphanes 5

A solution of I_2 (100 mg, 0.424 mmol) in CH_2Cl_2 (30 mL) at room temperature was added to a stirred solution of the appropriate α,ω-bis-[3-(1-phenylindolizin-2-yl)quinoxalin-2-on-1-yl]oxaalkane **4** (0.20 mmol) in CH_2Cl_2 (150 mL). The reaction mixture was stirred for 20 h at this temperature and then was washed with aqueous 5% $NaHCO_3$ (10 mL) and 5% $Na_2S_2O_3$ (10 mL). The organic layer was dried over Na_2SO_4, filtered, and evaporated under reduced pressure. The residue was purified by flash column chromatography on silica gel (hexane/CH_2Cl_2, 1:1→CH_2Cl_2 (**a**–**c**); CH_2Cl_2→CH_2Cl_2/EtOH, 50:1 (**d**–**j**)).

*4.4.1. $2^1,3^1$-Diphenyl-$1^2,4^2$-dioxo-1,4(3,1)-diquinoxalina-2(2,3),3(3,2)-diindolizina-6-(1,3)benzacyclo-heptaphane (**5a**).* Yellow powder, mp >360 °C. Found: C, 80.77; H, 4.48; N, 10.72. $C_{52}H_{34}N_6O_2$ requires: C, 80.60; H, 4.42; N, 10.85%. IR (ν_{max}, cm^{-1}, KBr): 3047, 2923, 2852, 1666, 1602, 1581, 1519, 1488, 1440, 1364, 1348, 1307, 1281, 1250, 1237, 1196, 1164, 1148, 1100, 1065, 1046, 1013, 944, 757, 728, 700, 671, 567, 429. δ_H NMR (400.1 MHz, DMSO-d_6): 4.98 and 5.12 (4H, d, *J* 16.0 Hz, CH_2), 5.76 (1H, s, H2 Xy), 6.83 (2H, dd, *J* 7.1, 6.9 Hz, H6 Ind), 7.06 (2H, dd, *J* 9.1, 6.9 Hz, H7 Ind), 7.12 (2H, dd, *J* 6.9, 6.6 Hz, H6 Qx), 7.15 (2H, d, *J* 6.9 Hz, H5 Qx), 7.16–7.33 (13H, m, ArH), 7.34 (2H, d, *J* 7.9 Hz, H8 Qx), 7.39 (2H, t, *J* 7.9 Hz, H7 Qx), 7.73 (2H, d, *J* 7.1 Hz, H5 Ind), 7.76 (2H, d, *J* 9.1 Hz, H8 Ind); δ_C (151 MHz, DMSO-d_6): 44.3, 109.7, 110.0, 112.4, 113.9, 114.6, 114.7, 117.9, 120.7, 121.7, 123.8, 125.1, 125.7, 125.9, 126.7, 128.5, 128.8, 129.9, 130.7, 132.5, 133.1, 136.0, 136.3, 153.1, 153.4. MS (MALDI TOF) $(MH)^+$ 775.



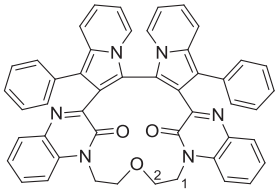
5a



5b[5]

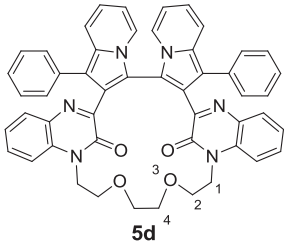
*4.4.2. $2^1,3^1$-Diphenyl-$1^2,4^2$-dioxo-1,4(3,1)-diquinoxalina-2(2,3),3(3,2)-diindolizinacyclotetradecaphane (**5b**).* Yellow powder,

mp >360 °C. Found: C, 80.07; H, 5.68; N, 10.43. $C_{54}H_{46}N_6O_2$ requires: C, 79.97; H, 5.72; N, 10.36%. IR (ν_{max}, cm^{-1}, KBr): 3072, 2928, 2855, 1650, 1601, 1584, 1521, 1487, 1456, 1364, 1348, 1226, 1159, 1097, 760, 728, 706. δ_H NMR (400.1 MHz, DMSO-d_6): 0.90–1.45 (16H, m, H2–H5), 3.69 (4H, m, H1), 6.82 (2H, dd, *J* 7.2, 6.7 Hz, H6 of Ind), 7.01 (2H, ddd, *J* 8.2, 6.7 Hz, H7 of Ind), 7.09 (2H, m, H6 of Qx), 7.15–7.35 (12H, m, ArH), 7.45 (2H, d, *J* 8.0 Hz, H8 of Qx), 7.51 (2H, dd, *J* 8.0, *J* 7.5 Hz, H7 of Qx), 7.66 (2H, d, *J* 8.2 Hz, H8 of Ind), 7.83 (2H, d, *J* 7.2 Hz, H5 of Ind); δ_C (151 MHz, DMSO-d_6): 25.3, 26.4, 26.8, 27.6, 41.6, 110.0, 111.8, 113.3, 114.3, 114.9, 117.8, 120.5, 123.4, 125.9, 126.6, 128.7, 128.9, 129.7, 130.7, 130.7, 132.8, 133.1, 135.4, 153.4, 154.2. MS (MALDI TOF) $(MH)^+$ 811.



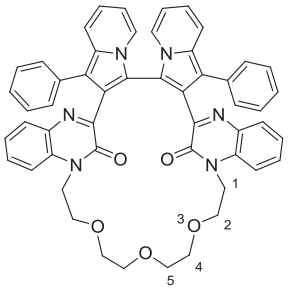
5c

*4.4.3. $2^1,3^1$-Diphenyl-$1^2,4^2$-dioxo-7-oxa-1,4(3,1)-diquinoxalina-2(2,3),3(3,2)-diindolizinacyclononaphane (**5c**).* Yellow powder, mp >360 °C. Found: C, 77.49; H, 4.67; N, 11.44. $C_{48}H_{34}N_6O_3$ requires: C, 77.61; H, 4.61; N, 11.31%. IR (ν_{max}, cm^{-1}, KBr): 3072, 3048, 2952, 2854, 1663, 1602, 1583, 1520, 1489, 1459, 1440, 1363, 1346, 1310, 1280, 1249, 1235, 1164, 1123, 1093, 1074, 1038, 1008, 758, 727, 700, 560. δ_H NMR (400.1 MHz, DMSO-d_6): 3.47 (2H, m, H2), 3.76 (2H, m, H2), 3.79 (2H, m, H1), 4.45 (2H, m, H1), 6.80 (2H, t, *J* 6.9 Hz, H6 Ind), 7.04 (2H, dd, *J* 8.2, 6.9 Hz, H7 Ind), 7.09 (2H, m, H6 Qx), 7.15–7.20 (12H, m, ArH), 7.37 (2H, d, *J* 6.7 Hz, H8 Qx), 7.47 (2H, td, *J* 6.7, 3.0 Hz, H7 Qx), 7.68–7.81 (4H, m, H5 and H8 Ind); δ_C (151 MHz, DMSO-d_6): 40.4, 67.1, 112.4, 113.7, 114.3, 114.6, 117.9, 120.5, 123.2, 124.8, 125.8, 127.2, 128.5, 128.7, 130.1, 130.5, 130.7, 132.8, 133.1, 135.9, 153.5, 153.7. MS (MALDI TOF) $(MH)^+$=743.



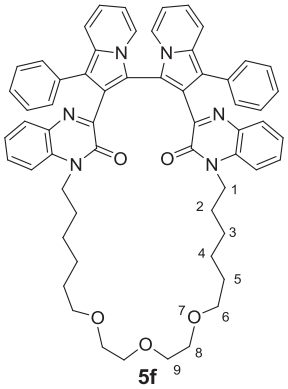
5d

*4.4.4. $2^1,3^1$-Diphenyl-$1^2,4^2$-dioxo-7,10-dioxa-1,4(3,1)-diquinoxalina-2(2,3),3(3,2)-diindolizinacyclododecaphane (**5d**).* Yellow powder, mp >360 °C. Found: C, 76.46; H, 4.78; N, 10.54. $C_{50}H_{38}N_6O_4$ requires: C, 76.32; H, 4.87; N, 10.68%. IR (ν_{max}, cm^{-1}, KBr): 2960, 1651, 1601, 1520, 1486, 1448, 1365, 1309, 1274, 1252, 1162, 1095, 1050, 986, 760, 703. δ_H NMR (400.1 MHz, DMSO-d_6): 3.30–3.80 (8H, m, H2 and H3), 3.96 and 4.25 (4H, m, H1), 6.83 (2H, t, *J* 6.5 Hz, H6 Ind), 7.04 (2H, dd, *J* 9.1, 6.5 Hz, H7 Ind), 7.13 (2H, m, H6 Qx), 7.14–7.25 (12H, m, ArH), 7.46–7.57 (4H, m, H7 and H8 Qx), 7.67 (2H, d, *J* 9.1, H8 Ind), 7.92 (2H, d, *J* 6.5, H5 Ind); δ_C (151 MHz, $CDCl_3$ (50%)+DMSO-d_6 (50%)): 42.0, 67.3, 70.6, 111.5, 113.5, 114.6, 114.7, 117.9, 120.6, 123.4, 123.6, 126.0, 126.2, 127.0, 128.9, 129.1, 130.3, 130.7, 131.3, 133.3, 136.2, 153.7, 154.5. MS (MALDI TOF) $(MH)^+$=787, $(M+Na)^+$=809, $(M+K)^+$=825.



5e

*4.4.5. $2^1,3^1$-Diphenyl-$1^2,4^2$-dioxo-7,10,13-trioxa-1,4(3,1)-diquinoxalina-2(2,3),3(3,2)-diindolizinacyclopentadecaphane (**5e**).* Yellow powder, mp >330 °C. Found: C, 75.03; H, 5.01; N, 10.02. $C_{52}H_{42}N_6O_5$ requires: C, 75.16; H, 5.09; N, 10.11%. IR (ν_{max}, cm^{-1}, KBr): 2922, 2857, 1649, 1601, 1583, 1524, 1486, 1454, 1366, 1346, 1281, 1251, 1159, 1128, 1103, 762, 729, 704. δ_H NMR (400.1 MHz, DMF-d_7): 3.40–3.49 (10H, m, H5, H2 and H3), 3.50 (2H, m, H3), 3.55 (2H, m, H2), 3.83 and 4.02 (4H, m, H1), 6.83 (2H, dd, *J*=6.9, 6.7 Hz, H6 Ind), 7.02 (2H, dd, *J*=9.4, 6.7 Hz, H7 Ind), 7.14 (2H, d, *J* 7.4 Hz, H4 Ph), 7.20 (2H, ddd, *J*=8.0, 5.7, 2.3 Hz, H6 Qx), 7.25 (4H, dd *J*=7.8, 7.4 Hz, H3 Ph), 7.30 (2H, d, *J*=8.0 Hz, H5 Qx), 7.37 (4H, d, *J*=7.8 Hz, H2 Ph), 7.48–7.52 (4H, m, H7 Qx and H8 Qx), 7.62 (2H, d, *J*=6.9 Hz, H5 Ind), 7.72 (2H, d, *J*=9.4 Hz, H8 Ind). δ_C NMR (150.9 MHz, DMF-d_7): 42.3, 67.6, 70.5, 70.7, 112.4, 114.7, 115.4, 115.3, 118.5, 120.2, 121.3, 123.3, 125.1, 126.1, 128.7, 129.9, 129.9, 130.5, 131.4, 133.5, 134.1, 136.0, 147.9, 154.2. MS (MALDI TOF) $(MH)^+$=831. MS (EI, 70 eV): *m*/*z* (%) 831.2 (M^++1, 61), 830.2 (M^+, 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).

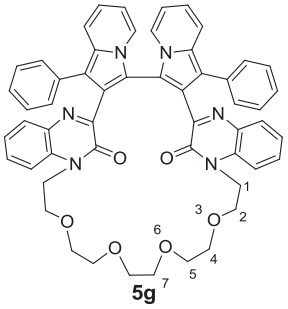


5f

*4.4.6. $2^1,3^1$-Diphenyl-$1^2,4^2$-dioxo-11,13,17-trioxa-1,4(3,1)-diquinoxalina-2(2,3),3(3,2)-diindolizinacyclotricosaphane (**5f**).* Yellow powder, mp 293–295 °C. Found: C, 76.27; H, 6.17; N, 8.90. $C_{60}H_{58}N_6O_5$ requires: C, 76.41; H, 6.20; N, 8.91%. IR (ν_{max}, cm^{-1}, KBr): 2928, 2854, 1647, 1601, 1526, 1454, 1365, 1348, 1307, 1278, 1261, 1097, 1040, 760, 703, 553, 461, 431. δ_H NMR (400.1 MHz, DMSO-d_6): 0.85–1.43 (16H, m, H2–H5), 3.31 (4H, m, H6), 3.44 (4H, m, H9), 3.51 (4H, m, H8), 3.64 (4H, m, H1), 6.79 (2H, t, *J* 6.4 Hz, H6 Ind), 6.98 (2H, dd, *J* 8.9, 6.4 Hz, H7 Ind), 7.10 (2H, t, *J* 7.0 Hz, H6 of Qx), 7.19–7.24 (12H, m, ArH), 7.41 (2H, d, *J* 7.9 Hz, H8 Qx), 7.51 (2H, dd, *J* 7.9, 7.0 Hz, H7 Qx), 7.59 (2H, d, *J* 6.4 Hz, H5 Ind), 7.66 (2H, d, *J* 8.9 Hz, H8 Ind); δ_C 151 MHz, DMSO-d_6: 25.5, 26.0, 26.5, 29.2, 41.0, 69.8, 70.3, 70.4, 112.2, 113.5, 114.2, 114.4, 117.9, 120.0, 123.0, 124.7, 125.7, 126.2, 128.4, 129.0, 129.7, 130.4, 130.5, 132.6, 132.8, 134.9, 153.3, 153.8. MS (EI,

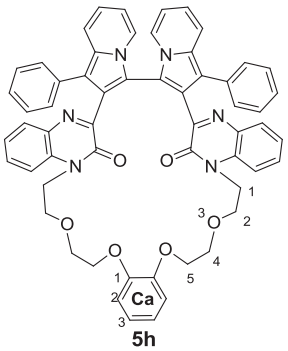
70 eV): *m*/*z* (%) 943 (M^++1, 41), 942 (M^+, 100), 472 (11), 471 (16), 377 (12), 336 (14), 335 (21).

Crystallographic data for **5f**× $Pb(ClO_4)_2$: $C_{60}H_{58}Cl_2N_6O_{13}Pb$, $2CHCl_3$, colorless prism crystal, M=1587.96, monoclinic, a=16.943 (6) Å, b=17.939 (7) Å, c=22.611 (9) Å, β=99.753 (5)°, V=6773 (4) Å^3, T=296 (2) K, space group $P2_1/n$, Z=4, $\mu(\lambda MoK_\alpha)$=2.871 mm^{-1}, ρ_{calcd}=1.557 g cm^{-3}, $F(000)$=3184, 66,586 reflections measured, 15,678 independent reflections (R_{int}=0.0935), full-matrix least-squares on F^2, parameters=835, restraints=795. Final indices $R1$=0.0569 ($I>2\sigma(I)$), $wR2$=0.1174 ($I>2\sigma(I)$), $R1$=0.1679 (all data), $wR2$=0.1567 (all data), goodness-of-fit on F^2=0.962.



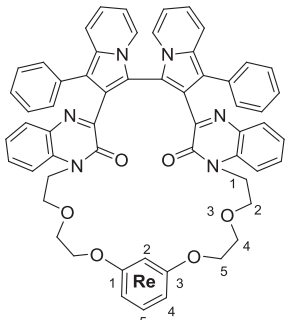
5g

*4.4.7. 2^1,3^1-Diphenyl-1^2,4^2-dioxo-7,10,13,16-tetraoxa-1,4(3,1)-diquinoxalina-2(2,3),3(3,2)-diindolizinacyclooctadecaphane (**5g**).* Yellow powder, mp 309–311 °C (DMSO-d_6). Found: C, 74.04; H, 5.17; N, 9.65. $C_{54}H_{46}N_6O_6$ requires: C, 74.13; H, 5.30; N, 9.60%. IR (ν_{max}, cm^{-1}, KBr): 3072, 2923, 2868, 1654, 1602, 1583, 1529, 1520, 1488, 1444, 1363, 1347, 1308, 1278, 1424, 1125, 768, 727, 700, 608, 560, 507, 434. δ_H NMR (400.1 MHz, DMSO-d_6): 3.32–3.39 (12H, m, H4, H5 and H7), 3.41 (4H, m, H2), 3.88–4.09 (4H, m, H1), 6.79 (2H, dd, *J* 7.2, 5.4 Hz, H6 of Ind), 6.99 (2H, dd, *J* 8.9, 7.2 Hz, H7 of Ind), 7.12 (2H, t, *J* 6.9 Hz, H6 of Qx), 7.13–7.22 (12H, m, ArH), 7.49 (4H, m, H7 and H8 Qx), 7.55 (2H, d, *J* 5.4 Hz, H5 Ind), 7.68 (2H, d, *J* 8.9 Hz, H8 Ind); δ_C (151 MHz, DMSO-d_6): 41.5, 67.0, 69.8, 70.1, 70.2, 112.3, 113.7, 114.4, 114.9, 1187.0, 120.1, 123.0, 124.5, 125.6, 126.0, 128.5, 129.1, 129.5, 130.2, 130.4, 132.6, 133.3, 135.1, 153.4, 153.5. MS (MALDI TOF) $(MH)^+$ 875, $(M+Na)^+$=897, $(M+K)^+$=913.



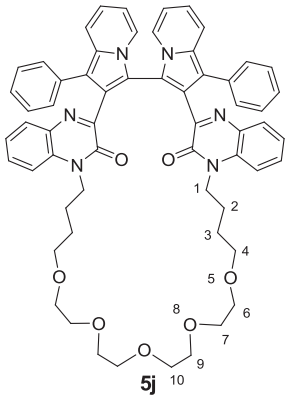
5h

*4.4.8. 2^1,3^1-Diphenyl-1^2,4^2-dioxo-7,10,12,15-tetraoxa-1,4(3,1)-diquinoxalina-2(2,3),3(3,2)-diindolizina-11(1,2)-benzenacycloheptadecaphane (**5h**).* Yellow powder, mp 220–222 °C. Found: C, 75.39; H, 5.06; N, 9.08. $C_{58}H_{46}N_6O_6$ requires: C, 75.47; H, 5.02; N, 9.10%. IR (ν_{max}, cm^{-1}, Nujol mull): 1649, 1600, 1583, 1560, 1520, 1504, 1366, 1350, 1308, 1281, 1257, 1222, 1158, 1126, 1040, 1024, 958, 933, 761, 729, 705. δ_H NMR (400.1 MHz, DMSO-d_6): 3.28–3.59 (8H, m, H2 and H4), 3.89–4.05 (8H, m, H1 and H5), 6.79 (2H, dd, *J* 7.0, 7.2 Hz, H6 Ind), 6.85–6.95 (4H, m, H2 and H3 Ca), 6.99 (2H, dd, *J* 9.3, 7.2 Hz, H7 of Ind), 7.07 (2H, t, *J* 6.9 Hz, H6 Qx), 7.13–7.31 (12H, m, ArH), 7.42–7.49 (4H, m, H7 and H8 Qx), 7.65 (2H, d, *J* 7.0 Hz, H5 Ind), 7.67 (2H, d, *J* 9.3 Hz, H8 Ind); δ_C (151 MHz, DMSO-d_6): 41.8, 67.7, 69.3, 69.6, 110.0, 112.4, 113.6, 114.4, 115.2, 118.1, 120.4, 121.9, 123.4, 124.9, 125.9, 126.4, 128.7, 129.2, 129.6, 130.6, 130.7, 132.7, 133.5, 135.2, 149.2, 153.7, 154.0. MS (MALDI TOF) $(MH)^+$=923.



5i

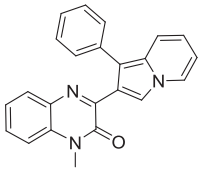
*4.4.9. 2^1,3^1-Diphenyl-1^2,4^2-dioxo-7,10,12,15-tetraoxa-1,4(3,1)-diquinoxalina-2(2,3),3(3,2)-diindolizina-11(1,3)-benzenacycloheptadecaphane (**5i**).* Yellow powder, mp 249–251 °C. Found: C, 75.37; H, 5.07; N, 9.16. $C_{58}H_{46}N_6O_6$ requires: C, 75.47; H, 5.02; N, 9.10%. IR (ν_{max}, cm^{-1}, Nujol mull): 1654, 1602, 1559, 1522, 1508, 1489, 1344, 1307, 1285, 1181, 1154, 1128, 1038, 758, 727, 702. ^{1}H NMR (400.1 MHz, $CDCl_3$): δ_H NMR (400.1 MHz, DMSO-d_6): 3.48–3.62 (12H, m, H2, H4 and H5), 4.01 (4H, m, H1), 5.49 (1H, br s, H2 Re), 6.28 (2H, d, *J* 6.2 Hz, H4 Re), 6.79 (2H, t, *J* 6.6 Hz, H6 Ind), 6.91–7.29 (17H, m, ArH), 7.34 (2H, m, H7), 7.43 (2H, m, H8 Qx), 7.52 (2H, d, *J* 6.6 Hz, H5 Ind), 7.68 (2H, d, *J* 9.3 Hz, H8 Ind); δ_C (151 MHz, DMSO-d_6): 42.0, 67.2, 67.9, 69.5, 101.3, 107.9, 110.0, 112.7, 114.4, 115.2, 118.2, 120.3, 123.1, 124.7, 125.8, 126.0, 128.7, 129.2, 129.6, 129.7, 130.2, 130.6, 132.7, 133.3, 135.1, 153.3, 153.9, 159.8. MS (MALDI TOF) $(MH)^+$=923.



5j

*4.4.10. 2^1,3^1-Diphenyl-1^2,4^2-dioxo-9,12,15,18,21-pentaoxa-1,4(3,1)-diquinoxalina-2(2,3),3(3,2)-diindolizinacyclopentacosaphane monohydrate (**5j**).* Yellow powder, mp 130–132 °C. Found: C, 72.43; H, 5.95; N, 8.36. $C_{60}H_{60}N_6O_8$ requires: C, 72.56; H, 6.09; N, 8.46%. IR (ν_{max}, cm^{-1}, KBr): 2924, 2855, 1644, 1600, 1582, 1519, 1455, 1365, 1348, 1307, 1278, 1221, 1093, 1068, 761, 704, 559, 446, 463, 430. δ_H NMR (400.1 MHz, DMSO-d_6): 1.25–1.51 (8H, m, H2 and H3), 3.36–3.48 (20H, m, H4, H6, H7, H8, H9 and H10), 3.76 and 3.91 (4H, m, H1), 6.80 (2H, t, *J* 6.7 Hz, H6 Ind), 6.88 (2H, d, *J* 6.8 Hz, H5 Qx), 6.99 (2H, dd, *J* 9.1, 6.7 Hz, H7 of Ind), 7.01 (2H, dd, *J* 7.7, 6.8 Hz, H6 Qx), 7.07–7.31 (10H, m, ArH), 7.39 (2H, d, *J* 8.1 Hz, H8 Qx), 7.44 (2H, dd, *J* 8.1, 7.7 Hz, H7 of Qx), 7.51 (2H, d, *J* 6.7 Hz, H5 of Ind), 7.67 (2H, d, *J* 9.1 Hz, H8 Ind); δ_C (151 MHz, DMSO-d_6): 23.9, 26.4, 41.3, 60.7, 69.9, 70.1, 70.2, 72.8, 110.0, 112.6, 114.4, 114.5, 114.6, 118.3, 120.0, 123.2,

124.8, 125.9, 128.6, 129.6, 129.7, 130.4, 130.8, 132.5, 132.8, 135.0, 153.5, 153.7. MS (MALDI TOF) $(M+H_3O)^+$=993.



1b

4.5. 5-Methyl-3-(1-phenylindolizin-2-yl)quinoxalin-2-one (1b)

A solution of MeI (0.2 g, 1.409 mmol) in DMSO (1 mL) at room temperature was added to a stirred solution of the quinoxalinone **1a** (0.30 g 0.889 mmol) in DMSO (3 mL). The reaction mixture was stirred for 6 h at this temperature and left overnight. The precipitate was filtrated and washed with EtOH (3 mL) and water (10 mL) and to dryness in air to afford the product. Yield (0.24 g, 77%). Yellow powder, mp 223–225 °C. Found: C, 76.55; H, 4.53; N, 11.87. $C_{23}H_{17}N_3O$ requires: C, 78.61; H, 4.88; N, 11.96%. IR (ν_{max}, cm^{-1}, KBr): δ_H NMR (400.1 MHz, $CDCl_3$): 3.76 (3H, s, CH_3), 6.50 (2H, ddd, *J* 7.2, 6.6, 1.0 Hz, H6 Ind), 6.64 (2H, ddd, *J* 9.2, 6.6, 0.7 Hz, H7 Ind), 7.20–7.50 (4H, m, ArH), 7.90 (2H, dd, *J* 7.2, 0.7 Hz, H5 Ind), 8.45 (2H, s, H3 Ind). MS (MALDI TOF) $(MH)^+$=352.

Acknowledgements

This work was supported by the Russian Foundation for Basic Research (grants No. 13-03-00123-a, 09-03-99011-r-ofi, 13-03-97073) and by the Federal Agency of Science and Innovation (the state contract No. 02.740.11.0633: 8432).

Supplementary data

Supplementary data associated with this article can be found in the online version, at http://dx.doi.org/10.1016/j.tet.2013.09.014. These data include MOL files and InChiKeys of the most important compounds described in this article.

References and notes

1. Allgeier, A. M.; Slone, C. S.; Mirkin, C. A.; Liable-Sands, L. M.; Yap, G. P. A.; Rheingold, A. L. *J. Am. Chem. Soc.* **1997**, *119*, 550–559.
2. Jeppesen, J. O.; Takimiya, K.; Becher, J. *Org. Lett.* **2000**, *2*, 2471–2473.
3. Nielsen, K. A.; Jeppesen, J. O.; Levillain, E.; Thorup, N.; Becher, J. *Org. Lett.* **2002**, *4*, 4189–4192.
4. Lau, J.; Blanchard, P.; Riou, A.; Jubault, M.; Cava, M. P.; Becher, J. *J. Org. Chem.* **1997**, *62*, 4936–4942.
5. Christensen, C. A.; Batsanov, A. S.; Bryce, M. R. *J. Org. Chem.* **2007**, *72*, 1301–1308.
6. Takimiya, K.; Imamura, K.; Shibata, Y.; Aso, Y.; Ogura, F.; Otsubo, T. *J. Org. Chem.* **1997**, *62*, 5567–5574.
7. Devonport, W.; Blower, M. A.; Bryce, M. R.; Goldenberg, L. M. *J. Org. Chem.* **1997**, *62*, 885–887.
8. Cordova, E.; Bissel, R. A.; Kaifer, A. E. *J. Org. Chem.* **1995**, *60*, 1033–1038.
9. Asakawa, M.; Ashton, P. R.; Boyd, S. E.; Brown, C. L.; Gillard, R. E.; Kocian, O.; Raymo, F. M.; Stoddart, J. F.; Tolley, M. S.; White, A. J. P.; Williams, D. J. *J. Org. Chem* **1997**, *62*, 26–37.
10. Kim, H. G.; Lee, C. W.; Yun, S.; Hong, B. H.; Kim, Y. O.; Kim, D.; Ihm, H.; Lee, J. W.; Lee, E. C.; Tarakeshwar, P.; Park, S. M.; Kim, K. S. *Org. Lett.* **2002**, *4*, 3971–3974.
11. Hauck, S. I.; Lakshmi, K. V.; Hartwig, J. F. *Org. Lett.* **1999**, *1*, 2057–2060.
12. Selby, T. D.; Blackstock, S. C. *Org. Lett.* **1999**, *1*, 2053–2055.
13. Memminger, K.; Oeser, T.; Muller, T. J. J. *Org. Lett.* **2008**, *10*, 2797–2800.
14. Baxter, P. N. W. *J. Org. Chem.* **2004**, *69*, 1813–1821.
15. Sakai, T.; Satou, T.; Kaikawa, T.; Takimiya, K.; Otsubo, T.; Aso, Y. *J. Am. Chem. Soc.* **2005**, *127*, 8082–8089.
16. Kreher, T.; Sonnenschein, H.; Costisella, B.; Schneider, M. *J. Chem. Soc., Perkin Trans. 1* **1997**, 3451–3458.
17. Sonnenschein, H.; Kreher, T.; Gründemann, E.; Krüger, R.-P.; Kunath, A.; Zabel, V. *J. Org. Chem.* **1996**, *61*, 710–714.
18. Xia, J. B.; Wang, X. Q.; You, S. L. *J. Org. Chem.* **2009**, *74*, 456–458.
19. Sonnenshein, H.; Kosslick, H.; Tittelbach, F. *Synthesis* **1998**, 1596–1598.
20. Andruzzi, R.; Cardellin, L.; Greci, L.; Stipa, P.; Poloni, M.; Trazza, A. *J. Chem. Soc., Perkin Trans. 1* **1988**, 3067–3070.
21. Theil, F.; Sonnenschein, H.; Kreher, T. *Tetrahedron: Asymmetry* **1996**, 3365–3370.
22. Sonnenschein, H.; Theil, F.; Kreher, T.; Kockritz, A. *Chem. Commun.* **1997**, 551–552.
23. Kockritz, A.; Sonnenschein, H.; Bischoff, S.; Theil, F.; Gloede, J. *Phosphorus, Sulfur Silicon Relat. Elem.* **1998**, *132*, 15–19.
24. Hünig, S.; Linhart, F. *Tetrahedron Lett* **1971**, 1273–1276.
25. Kakehi, A.; Ito, S.; Hamaguchi, A.; Okano, T. *Bull. Chem. Soc. Jpn.* **1981**, 2833–2834.
26. Kreher, T.; Sonnenschein, H.; Schmidt, L.; Hunig, S. *Liebigs Ann. Chem.* **1994**, 1173–1176.
27. Leitner, M. B.; Kreher, T.; Sonnenschein, H.; Costisella, B.; Springer, J. *J. Chem. Soc., Perkin Trans. 2* **1997**, 377–382.
28. Hunig, S. *J. Prakt. Chem./Chem.-Ztg.* **1994**, *336*, 38–42.
29. Hünig, S.; Linhart, F. *Liebigs Ann. Chem.* **1976**, 317–335.
30. Togo, H.; Iida, S. *Synlett* **2006**, 2159–2175.
31. Lin, X.-F.; Cui, S.-L.; Wang, Y. G. *Tetrahedron Lett.* **2006**, *47*, 4509–4512.
32. Chen, W.-Y.; Lu, J. *Synlett* **2005**, 1337–1339.
33. Royer, L.; De, S. K.; Gibbs, R. A. *Tetrahedron Lett.* **2005**, *46*, 4595–4597.
34. Stavber, S.; Jereb, M.; Zupan, M. *Synthesis* **2008**, 1487–1513.
35. Kim, I.; Choi, J.; Won, H. K.; Lee, G. H. *Tetrahedron Lett.* **2007**, *48*, 6863–6867.
36. Mamedov, V. A.; Kalinin, A. A.; Rizvanov, I. H.; Bauer, I.; Habicher, W. D. *Izv. Akad. Nauk, Ser. Khim.* **2009**, *58*, 1450–1459.
37. Mamedov, V. A.; Kalinin, A. A.; Samigullina, A, . I.; Mironova, E. V.; Krivolapov, D. B.; Gubaidullin, A. T.; Rizvanov, I. K. *Tetrahedron Lett.* **2013**, *54*, 3348–3352.
38. Fyfe, M. C. T.; Glink, P. T.; Menzer, S.; Stoddart, J. F.; White, A. J. P.; Williams, D. J. *Angew. Chem., Int. Ed.* **1997**, *36*, 2068–2070.
39. Megiatto, J. D.; Spencer, R.; Schuster, D. I. *Org. Lett.* **2009**, *11*, 4152–4155.
40. Sandanayaka, A. S. D.; Sasabe, H.; Araki, Y.; Kihara, N.; Furusho, Y.; Takata, T.; Ito, O. *J. Phys. Chem. A* **2010**, *114*, 5242–5250.
41. Collin, J.-P.; Durola, F.; Lux, J.; Sauvage, J.-P. J. *Angew. Chem., Int. Ed.* **2009**, *48*, 8532–8535.
42. Jiang, Q.; Zhang, H.-Y.; Han, M.; Ding, Z.-J.; Liu, Y. *Org. Lett.* **2010**, *12*, 1728–1731.
43. Chuang, C.-J.; Li, W.-S.; Lai, C.-C.; Liu, Y.-H.; Peng, S.-M.; Chao, I.; Chiu, S.-H. *Org. Lett.* **2009**, *11*, 385–388.
44. Balandina, A.; Mamedov, V.; Latypov, S. *J. Mol. Struct.* **2008**, *889*, 89–97.
45. Steed, J. W.; Atwood, J. L. *Supramolecular Chemistry*; John Wiley & Sons, Ltd: Chichester, UK, 2009.
46. Mamedov, V. A.; Kalinin, A. A.; Yanilkin, V. V.; Gubaidullin, A. T.; Latypov, S. K.; Balandina, A. A.; Isaikina, O. G.; Toropchina, A. V.; Nastapova, N. V.; Iglamova, N. A.; Litvinov, I. A. *Russ. Chem. Bull.* **2005**, *54*, 2616–2625.
47. Mamedov, V. A.; Kalinin, A. A.; Gubaidullin, A. T.; Isaikina, O. G.; Litvinov, I. A. *Russ. J. Org. Chem.* **2005**, *41*, 599–606.
48. APEX2 (Version 2.1), SAINTPlus. Data Reduction and Correction Program (Version 7.31A), Bruker Advanced X-ray Solutions; Bruker-AXS: Madison, Wisconsin, USA, 2006.
49. Sheldrick, G. M. *SADABS: Program for Empirical X-ray Absorption Correction*; Bruker-Nonius: Dordrecht, The Netherlands, 1990–2004.
50. Sheldrick, G. M. *SHELXTL Version 6.12, Structure Determination Software Suite*; Bruker-AXS: Madison, Wisconsin, USA, 2000.
51. Farrugia, L. J. *J. Appl. Crystallogr.* **1999**, *32*, 837–838.
52. Spek, A. L. *Acta Crystallogr.* **2003**, *36*, 7–13.
53. Macrae, C. F.; Edgington, P. R.; McCabe, P.; Pidcock, E.; Shields, G. P.; Taylor, R.; Towler, M.; van de Streek, J. *J. Appl. Crystallogr.* **2006**, *39*, 453–457.