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Chromophoric Macrocycles from the Oxidation of Bis(aminofurazanylic) Ethers of 1,2-Diols

Aleksei B. Sheremetev,[1] Elena V. Shatunova,[1] Boris B. Averkiev,[2] Dmitrii E. Dmitriev,[1] Viktor A. Petukhov,[1] and Mikhail Yu. Antipin[2]

[1]*N. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences, 47, Leninsky Prosp., 119991 Moscow, Russia*

[2]*A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, 28 Vavilov Street B-334, 119991 Moscow, Russia*

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ABSTRACT: *A series of chromophoric azofurazan-containing macrocycles* **6a–c** *and* **7a–d** *were synthesized from bis(aminofurazanylic) ethers of 1,2-diols* **4a–d** *by dibromoisocyanurate oxidation. The macrocycle closure is a result of N=N bond formation. An ion-binding ability of these compounds was tested. The macrocycles were characterized by NMR, MS, IR, and UV spectroscopy. The X-ray crystal structures of the macrocycles* **6a, 7c**, *and linear counterpart* **12** *are reported.* © 2004 Wiley Periodicals, Inc. Heteroatom Chem 15:131–145, 2004; Published online in Wiley InterScience (www.interscience.wiley.com). DOI 10.1002/hc.10226

INTRODUCTION

The classical synthetic route to crown ethers involves cyclizations between appropriate polyethylene glycol dichloride or ditosylate and a compound incorporating two-hydroxy units. Common cryptand synthesis involves reaction of appropriately functionalized dicarboxylic acid chlorides with diamines, following reduction of the amide. Both these routes were utilized in the synthesis of chromophoric ligands possessing azobenzene bridge [1–6]. Diazotization of bis(aminophenyl) ether of glycols followed by azo coupling with a suitable substrate is another route to analogous ligands [7–11]. Azobenzene crown ethers have been also synthesized by reductive macrocyclization of corresponding bis(nitrophenoxy) oxa alkanes [12,13]. These macrocycles change their binding ability for ammonium salts and metal cations in response to photoirradiation. This is a result of the cavity volume changing of the macrocycle by the photoinduced *E–Z* isomerism of the azobenzene subunit. Chromophoric ligands are also interesting analytical reagents for colorimetry and metal-ion indication [14–18].

However, realization of these approaches is often difficult and total yields are poor. Furthermore, high-dilution technique is necessary, in most cases to perform such reactions, to obtain reasonable yields because of a tendency to form linear oligomers. It should be noted that analogous macrocycles where the benzene ring is replaced by any heteroaromatic ring are unknown. At the same time the presence of additional heteroatoms in the subunit can evidently

Correspondence to: Aleksei B. Sheremetev; e-mail: sab@cacr.ioc.ac.ru.
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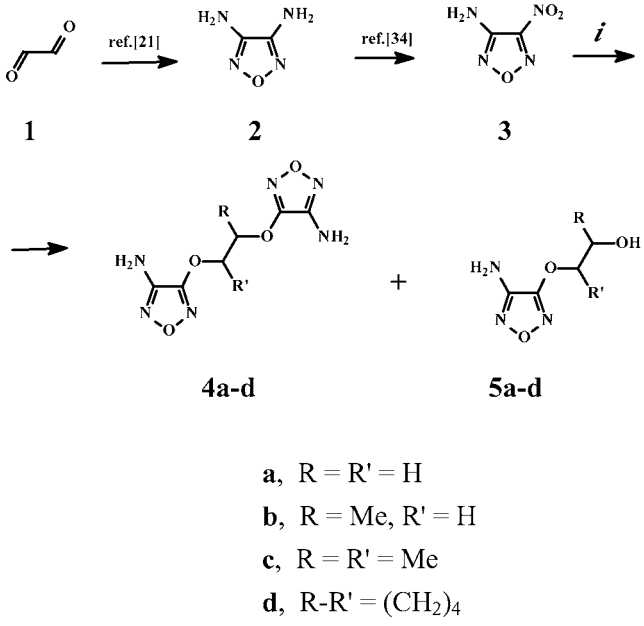
induce some corrections into their ability to complexation [19].

The goal of our work was to replace a part of this structure, namely the benzene ring, by a heterocyclic subunit. To this end we designed a series of furazan derivatives. In our earlier communication we disclosed results on synthesis of zero-hydrogen furazan macrocycles with oxy and azo bridges via ether bond formation [20]. It has been shown that some of azofurazan macrocycles are useful as ingredients to explosives and rocket propellants [21,22]. A series of macrocycles incorporating few azofurazan subunits was found to be effective inhibitors of soluble guanylate cyclase [23].

In 1991 we developed and exploited over the past time an alternative synthetic methodology to chromophoric macrocycles, which involves the prior synthesis of linear bis(aminofurazanylic) ether followed by final oxidative cyclization via N=N bond formation [24–27]. Following our report, Makhova et al. [28] and Batog et al. [29–33] reported the synthesis of a series of macrocycles incorporating only furazan rings and azo bridges.

This is the first detailed paper describing a projected strategy.



Reagents and conditions: ***i***, 0.5 mol of 1,2-diol, K_2CO_3, 75–80°C

SCHEME 1

RESULTS AND DISCUSSION

We prepared several bis(aminofurazanylic) ethers of 1,2-glycols **4** as outlined in Scheme 1. Starting from glyoxal **1** or a suitable glyoxal equivalent, 3,4-diaminofurazan **2** was prepared in a one-pot synthesis following literature procedures [21]. Hydrogen peroxide oxidation of **2** afforded 3-amino-4-nitrofurazan **3**, as we have previously described [34].

Reaction of the di-sodium salt of glycol with **3** gave a mixture of 1,2-bis(3-aminofurazan-4-oxy) ethane **4a** and 2-(3-aminofurazan-4-oxy) ethanol **5a** from which **4a** was isolated in 17% yield. However, more successful preparation of **4a** was achieved utilizing K_2CO_3 in DMSO in the reaction of **3** with glycol at 75–80°C. Thus, when 2 equiv of **3** was allowed to react with 1 equiv of glycol, the diamine **4a** was the major product. The extent of the reaction was followed by a combination of TLC and electrospray mass spectrometry (ESMS). The reaction was completed after 6 h, and no further significant change in distribution was seen, even after 3 days. Compound **4a** was isolated as an amorphous off-white powder in good yield.

We were interested in studying the effect of the steric factors of the bridging unit at invariable length (four-atom linker between furazan rings). An assortment of different 1,2-dioles was examined. These were also chosen to modify physical properties of the products (e.g., solubility, reactivity, partition coefficient). A series of diamines **4** containing modified bridging units was prepared in a straightforward manner following the above procedure.

The steric factors play an important role in the reaction. The main product (84%) in this reaction was the diamine **4a** at R = R′ = H. The presence of the methyl group in starting glycol (R = H, R′ = CH_3) resulted in diamine **4b** with 68% yield. The 2,3-butanediol produced diamine **4c** (R = R′ = CH_3) in 45% yield. The highest sterically overcrowded diol, such as 1,2-cyclohexanediol, in the reaction with **3** gave corresponding diamine **4d** with only 30% yield.

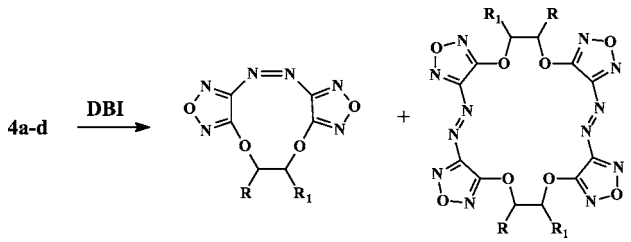
For all products **4a–d**, the presence of the amino group was confirmed from the $\nu(NH_2)$ doublet at ca. 3450 and ca. 3350 cm^{-1} in the infrared spectra. The ^1H and ^{13}C NMR spectra of the diamines and amino alcohols were all consistent with the structures shown in Scheme 1. For each compound, two quaternary furazan ring carbons were discernible at ca. δ 149 for C—O and ca. δ 158 for C—N in the ^{13}C spectra, similar to those reported for the analogous furazan derivatives [35].

The macrocyclization is a key step of the study and results in the formation of N=N bond. This step is based on the oxidative condensation of two amino groups. Various methods for the oxidative

cyclization of diamines **4a–d** to the corresponding macrocycles were examined.

There are several methods available for the oxidation of aminofurazans to azofurazans. The common reagent systems consisting of $KMnO_4$, NaOCl, or NaOBr in acidic or basic conditions gave usually linear azofurazans in excellent yields [36]. In our case, however, these classical procedures were unsuccessful; the colorless starting material **4a** produced red-orange insoluble material, which was probably either a mixture of linear azo polymer and inorganic residue or a coordination compound of oligomeric azofurazans [37]. The last hypothesis provoked us to utilize an oxidizer that did not contain inorganic cation. The preferred reagent was dibromoisocyanurate (DBI). DBI was first introduced by Semenov et al. in the synthesis of linear azo compounds [38].

We found that a mixture of 10-membered macrocycles **6a** and dimeric 20-membered macrocycle **7a** can be easily prepared by the reaction of **4a** with DBI (Scheme 2). It turned out that stirring of a suspension of the reagents in CH_2Cl_2 at ambient temperature gave desired macrocycles in moderate yields by simple filtration of the reaction mixture (separation of cyanuric acid and a polymer) and evaporation of the solvent. Monitoring of the cyclization by ESMS showed initial formation of some open chain dimer, which then disappeared to give cyclic dimer. The course of reaction was followed by the disappearance of the IR bands due to $\nu(NH_2)$ and was also evident from the red-brown coloring of the initially white suspension. The 10-membered cycle **6a** was obtained in 23% yield [39] by silica gel flash chromatography. The 20-membered macrocycle was isolated as a mixture of three isomers in a ratio of 5:7:1 (**7a′**:**7a″**:**7a‴**) and in a combined 38% yield. These



a, R = R' = H
b, R = Me, R' = H
c, R = R' = Me
d, R-R' = $(CH_2)_4$

SCHEME 2

isomers were also separated by chromatography on silica gel. It should be noted that any individual isomer readily isomerized at storage giving a mixture of three isomers that was clearly seen from TLC.

The isomers **7a′, 7a″,** and **7a‴** showed the same molecular ion in MS and elemental composition at microanalysis but different melting points and TLC spots; also no structural difference were observed by ^1H and ^{13}C NMR [40].

For azofurazan moiety four cis and four trans conformers [41] (at $R^1 \neq R^2$) are possible with respect to the N=N bond. All these eight possible conformers may be classified by indicating a relative orientation (cis and trans) of the N=C and N=N bonds (with respect to single C–N bonds) and these bonds in the system N=C–N=N–C=N [42]. In our work we used notations from Klyne and Prelog [43] (see Fig. 1).

A similar notation to define the conformation of azofurazans of interest was used [44], when the conformation of C–N bond with respect to azo group is indicated and then (in brackets) two letters D(cis) and P(trans) are noted, which characterize a relative orientation of the N=N and C=N bonds. For example, trans(P,D) means *ap–ap–sp*. The Klyne and Prelog nomenclature allows one to describe the molecular conformation more definitely because the torsion angle between bonds may deviate significantly from 0° or 180°, and in such a case notations *ac* and *sc* may be used instead of *ap* and *sp*, respectively. Usage of notations by Klyne and Prelog is more convenient because symbols *ac* and *sc* may be used at strong distortion of the azofurazan fragment in the N=C–C=N part.

However, only *trans*-azofurazans were isolated and characterized by X-ray analysis at present [27,30,32,33,42,44,45]. Most probably, in the solid state these conformers are most stable; that is for solutions, mutual conformational changes are possible, which makes identification of the conformers more difficult.

The observed abundance of possible isomers (conformers) for macrocycles **7** is a result of the presence of two azofurazan moieties, which allows an existence of one more type of the isomer differing by mutual orientation of these fragments in the molecule (Fig. 2). Because of a quite short alkyl spacer that links the heterocycles, a mutual interconvertion of such isomers should be prohibited.

When **4b** was used as precursor for the reaction, a small amount of intramolecular cyclization product **6b** (9%) was obtained along with the mixture of dimeric product **7b** (49%) and a polymer. In this case it was possible to expect a formation of a large number of isomeric macrocycles **7b**. Indeed, in addition

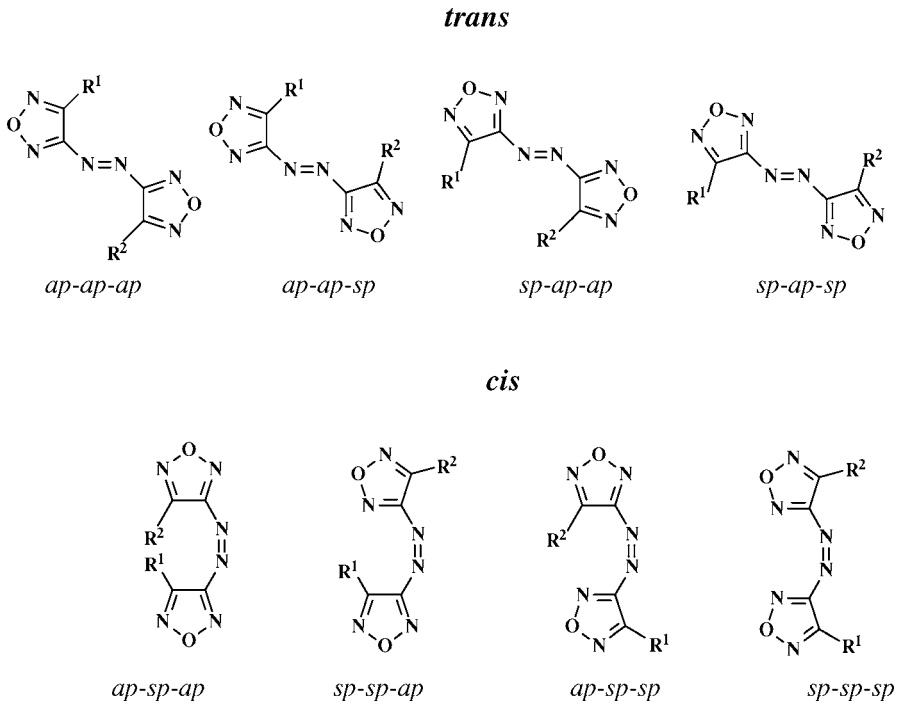


FIGURE 1 Possible conformers for the azofurazan frame.

to conformational isomers, which were found for **7a**, two positional isomers **7ba** and **7bb** are also possible (Fig. 3). However, column chromatography resulted in only three fractions for the dimeric product with an approximate ratio of 5:2:1. All these fractions contained two positional isomers **7ba** and **7bb** in comparable quantities as determined by the NMR spectra. This means that conformational isomerism of the macrocycles produces more effect on their properties than positional changes of the methyl group.

Oxidation of diamine **4c** in analogous manner afforded only 0.5% yield of intramolecular cyclization product **6c**. A mixture of four isomeric 20-membered macrocycles, **7c′, 7c″, 7c‴**, and **7c′ᵛ**, was obtained in 51% yield.

In the case of compound **4d**, corresponding macrocycle **6d** was not formed. In the reaction only a mixture of the dimers **7d′, 7d″**, and **7d‴** (68% yield) was obtained.

An alternate route to similar macrocycles based on nucleophilic displacement of nitro groups in 4,4′-dinitroazofurazan **8** [46] by glycolate was investigated (Scheme 4). A variety of reaction conditions similar to those employed previously by us [35] have been examined. However, the reaction failed to give **6a** or **7a**.

Macrocycles **6** and **7** are yellow to red amorphous powders or crystals and were found to be stable when kept at room temperature for a long time. They are highly stable to acids and heat. In

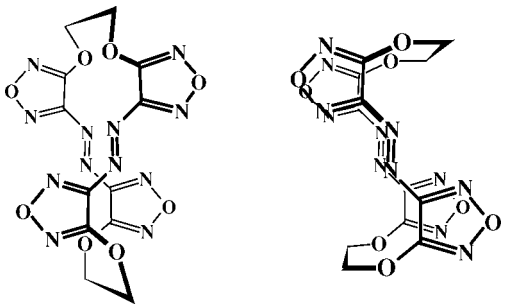


FIGURE 2 Possible orientation of the azofurazan moieties in the molecule **7a**.

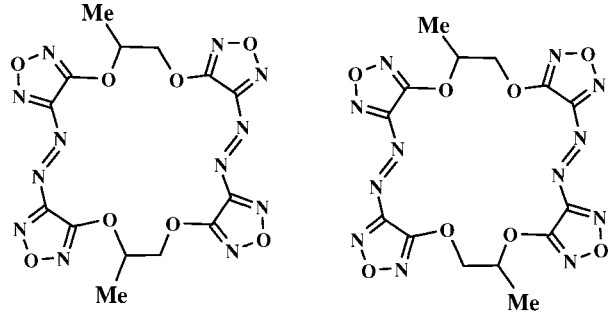
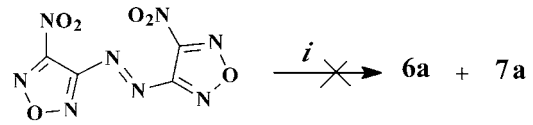


FIGURE 3 Positional isomers **7ba** and **7bb**.



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SCHEME 3

2 months 30–50% of the compounds were hydrolyzed in glim by 5% aqueous KOH. Macrocycles **6** and **7** are soluble in common organic solvents; 10-membered cycles **6** display better solubility than the corresponding 20-membered cycles **7**, and more substituted macrocycles exhibit higher solubility. All macrocycles are not soluble in water.

NMR Spectroscopy of Macrocycles

We next needed to establish the structure of the macrocycles. Here, the literature on ^{13}C NMR of furazans was very helpful [35,47].

It should be noted that most favorable existence of compounds **6** in the *ap–ap–sp* conformation proved by X-ray data (see below) must result (at low conformational flexibility) in the absence of the cycle symmetry relative to the plane normal to the azo-bond. In the ^{13}C NMR spectra of such compounds, four signals of the furazan carbon atoms must be observed. However, the spectra involved only two signals. Moreover, low-temperature ^{13}C data for the compound **6a** had demonstrated that until $-70^{\circ}C$ its symmetry was held in a solution. This allows one to make a suggestion about relatively small rigidity of the azofurazan moiety in a solution. Presence of some relatively stable forms of 20-membered cycles **7a–d** may result from the combination of different isomeric types.

The 10-membered cycles **6a–c** and 20-membered cycles **7a–d** could be distinguished by their ^{13}C NMR spectra. The peak attributable to the carbon of the furazan ring bonded to the oxygen atom was at δ 160.3–163.2 for **6a–c**, whereas the same peak was shifted upfield to 157.7–159.0 for **7a–d** (Table 1). The peaks attributable to the carbons of the furazan ring bonded to the azo moiety for both cycles **6a–c** and **7a–d** were observed in common region at *ca*. δ 155.5.

We had used ^{13}C NMR to examine the distinction of the individual isomeric macrocycles **7**. The peaks attributable to similar carbon atoms differed in 0.5–2 ppm. It may be noted that the deviations were comparable to those from solvent effects. Assignment of peaks to different conformers is impossible [48].

TABLE 1 ^{13}C NMR Data for Macrocycles **6** and **7**

	Furazan			
	C–O	*C–N*	*R*	*Solvent*
6a	160.9	155.8	72.9 (CH_2)	$CDCl_3$
	161.6	156.3	72.4	DMSO-d_6
	162.9	157.7	73.8	Acetone-d_6
	163.2	158.1	74.4	CD_3OD
6b	160.3	155.8	82.0 (CH_2)	$CDCl_3$
	160.5	156.0	79.2 (CH)	
			21.3 (CH_3)	
6c	160.7	156.2	81.3 (CH)	$CDCl_3$
			19.7 (CH_3)	
7a	158.1	155.1	70.7 (CH_2)	DMSO-d_6
7b	158.0	155.0	78 (CH)	
	159.0	156.0	75 (CH_2)	DMSO-d_6,
			14 (CH_3)	
7c	157.8	155.0	85.0 (CH)	$CDCl_3$
			15.9 (CH_3)	
7d	157.7	155.0	87.6 (CH)	$CDCl_3$
				23.3; 29.9 (CH_2)

MS Analysis

The mass spectrum of all macrocycles by electron impact ionization at 70 eV showed the expected molecular ion peak together with the characteristic fragmentation. The fragmentation was additional support for this series of structure [35]. For example, MS of **6a** confirmed the sequence by the fragment ion peaks shown in Fig. 4. The product ion peaks at *m/z* 194 ($M^+ - 30$) confirmed the presence of furazan unit [49]. The presence of the azo linkage in the product ion peaks at *m/z* 166 ($M^+ - 30 - 28$) was confirmed.

Similar fragmentation was also observed for **6b** and **6c**. Dimeric macrocycles showed more complicated mass spectra. The spectra for all compounds also showed the molecular ion and peaks corresponding to the loss of NO and N_2, giving rise to signals with *m/z* values for ($M^+ - NO$) and ($M^+ - NO - N_2$). For example, MS data for **7a′** showed ion peaks at *m/z* 448 (M^+), 390, 363,

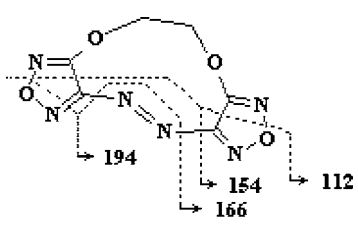
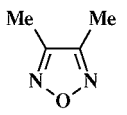


FIGURE 4 MS fragmentation ways for macrocycles **6a**, *m/z* 224 (M^+).

and 166, the same as for **7a″** or **7a‴**, and corresponded to a molecular formula of $C_{12}H_8N_{12}O_8$. Fragmentation of isomers **7b**, **7c**, and **7d** characterized the similar picture. The product ion peaks useful for structure assignment are listed in Experimental section.

UV–Vis Absorption Spectroscopy

Worthy of comment from the spectroscopic data we have collected on the basic macrocycles described above are the UV–vis spectra. The observed trends are listed in Table 2 along with the data for simple furazans **9–12** for comparison. The main results are as following: (i) As expected, the presence of two disconnected azofurazan subunits in macrocycles **7** increases the λ_{max} by about twice as compared to macrocycles **6**. (ii) For all macrocycles, the furazan ring has absorption bands with a constant λ_{max} of 208–220 nm and 242–252 nm ($\pi \rightarrow \pi^*$ transition) [49], azo group displayed maximum absorption in the 420–440 nm region ($n \rightarrow \pi$ transition). (iii) In contrast to linear compound **12**, these bands for higher macrocycle **7** are less clear; for macrocycle **6**, the band at λ_{max} of about 440 nm was apparent in the UV–vis spectrum as a broad low-energy tail. Probably, this effect is manifested by the conformation of azofurazan moiety.



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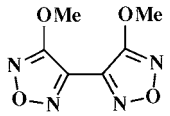

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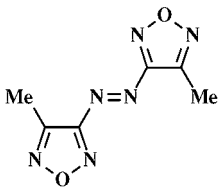

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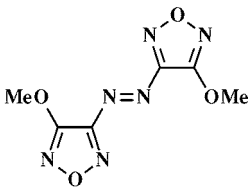

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It should be noted that all of our attempts to establish *E*,*Z*-isomerism for macrocycles **6** and **7**, as well as for linear compound **11** and **12** by UV–vis spectroscopic analysis failed. For example, refluxing a sample of macrocycle **7a** in methanol, ethyl acetate, and nitromethane or irradiation with a medium-pressure Hg lamp (360 nm) gave no changes in the UV spectrum.

Ion-Binding Ability

We were also interested in determining the possibility to utilize the macrocycles **6** and **7** as complexing agents. Reactions of **7a** with nitrate (NO_3^-), perchlorate (ClO_4^-), dinitramide ($N_3O_4^-$) [50], and nitroformate ($CN_3O_6^-$) salts (Na^+, K^+, NH_4^+, NH_3OH^+, $N_2H_5^+$, and $N_2H_6^{+2}$) were attempted by adding **7a** (dissolved in the reaction solvent) to 1–15 ml of a solution containing 20–100 mg of a salt in methanol, acetonitrile, acetone, or nitromethane. Mole ratios of **7a** to salt varied from 3:1 to 1:1. However, the solution gave no color changes or a precipitate separation. No detectable changes of the UV spectrum were observed.

Alkali metal picrate extraction studies were performed using a CH_2Cl_2/H_2O extraction system for 10-membered cycle **6a** (where a sandwich-type interaction is possible) and 20-membered macrocycle **7a** (where host–guest complex formation is possible). These compounds display no extraction of the salt from aqueous solution.

In contrast, coordination of $PdCl_2$ to the macrocycle **7a** results in the formation of an intense metal-to-ligand transition in the visible spectrum (λ_{max} ca. 450 and 680). During the addition of $PdCl_2$, the reaction proceeded through a series of notable color changes to afford the final precipitate. The complex $[(C_{12}H_8N_{12}O_8)\cdot 2PdCl_2]$ was isolated as an amorphous khaki powder.

The following factors may be responsible for this result: (i) The electron-withdrawing azofurazan unit absorbs the lone electron pairs of the oxygen atoms in the bridging unit, denuding them of donor properties. (ii) The combination of large and rigid azofurazan unit with small flexible ethylene glycol unit is unfavorable for coordination geometry of the donor centers. (iii) The alkali metal salts used are weak partners as acceptors to the macrocycles **6** and **7**. (iv) Preliminary studies on the transition metal salt, namely $PdCl_2$, indicate powerful interaction with the azofurazan macrocycles.

Crystal Structure of **6a, 7c**, *and* **12**

Single crystals for X-ray diffraction analysis were grown for macrocycles **6a, 7c**, and related linear azofurazan **12**. General view of molecules **6a, 7c**, and **12** and atom numbering scheme are presented in Figs. 5–7. Important bond lengths and crystal data are listed in Tables 3 and 4. Molecules **7c** and **12** in crystal occupy the centers of symmetry. In the crystal of **6a** (diffraction data at 110 K) there are two independent molecules having very similar geometry, and a phase transition has been observed at ca.

TABLE 2 UV-Vis Data of Macrocycles and Related Furazans

	λ_{max} (nm)	ε	λ_{max} (nm)	ε	λ_{max} (nm)	ε	λ_{max} (nm)	ε
6a	450	54	310	6300			215	8550
6b	445	62	310	3500	245	4900	220	5250
6c	445	63	310	4220	250	6400	220	6800
7a′	445	280	300	11200	250	9300	208	12300
7a″	445	342	300	11700	252	13500	212	14600
7b′	450	343	302	11500	247	14400	208	14700
7b″	450	282	302	14300	252	13600	215	17400
7b‴	450	308	302	15300	249	14400	215	14800
7c	445	223	314	13000	250	10700	215	14250
7c′	445	394	306	14700	250	14200	215	18900
7c″	447	265	310	14600	248	14000	206	22000
7c‴	455	216	312	13000	252	10500	216	14500
7c^{IV}	450	260	312	12700	250	12600	210	23100
7d′	445	248	306	12400	252	14900	216	21800
7d″	445	140	310	6600	242	9700	205	11100
7d‴	445	214	306	7300	251	8450	213	9400
9							215	2700
10					257	5700		
11	438	80			270	10300	204	7250
12	445	187	302	8600	247	6550	212	9050

295 K to the orthorhombic modification **6a*** where the molecule is disordered in the crystal.

The 10-membered cycle **6a** has the *sc–ap* conformation. The small value of the macrocycle cavity of the cycle **6a** results in the molecule strain that might increase bond and torsion angles. The azofurazan moiety in **6a** is strongly deformed: torsion angles N(6)—C(7)—N(8)—N(9) and N(8)—N(9)—C(10)—N(11) are equal to 32° and 167° (data at 110 K). Similar torsion angles in less strained 20-membered cycle **7c**, having *sp–ap* configuration, are equal to 23° and 171°, respectively. It is clear that larger distortion of the torsion angle N=C—N=N at the cis-position to the double bond in comparison to the trans-position in molecules **6a** and **7c** is related to steric effects.

Unfortunately, because of crystal disorder of the alkoxy bridge in the structure **7c** we cannot discuss molecular geometry in details.

When passing from strained macrocycle **6a** to its linear unstrained counterpart **12** (having a *ap–ap* configuration), bond lengths at the oxygen

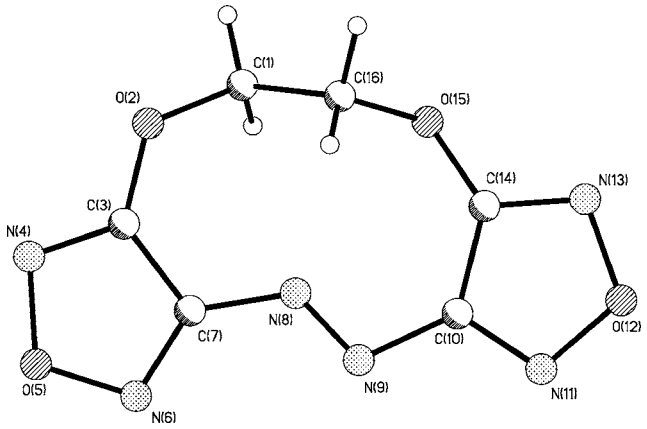

FIGURE 5 General view of one independent molecule of **6a**.

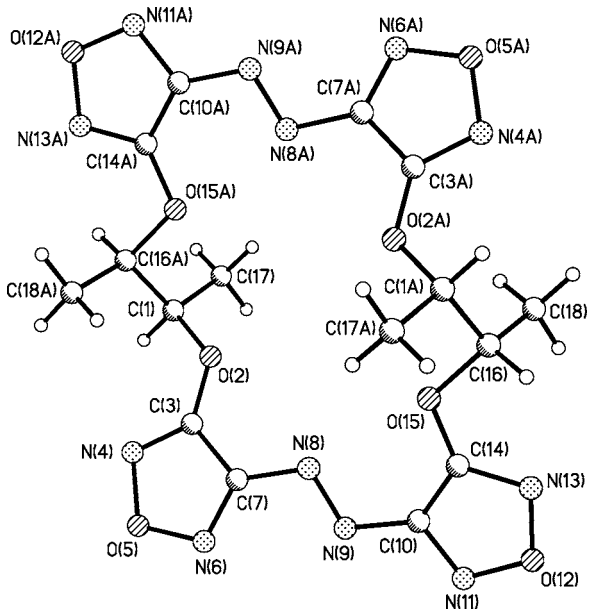

FIGURE 6 General view of molecule **7c**.

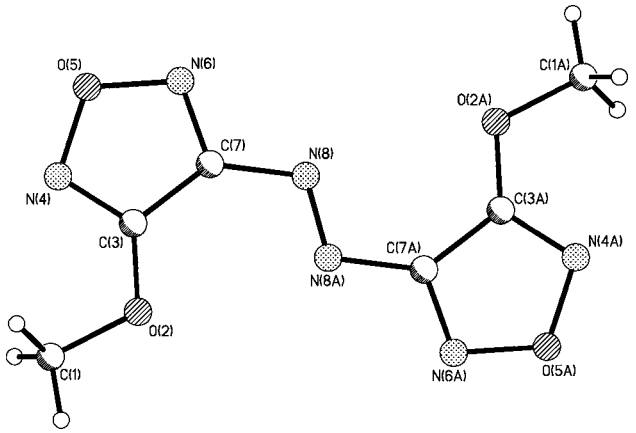

FIGURE 7 General view of molecule **12**.

atoms bonded to furazan ring are shortening by 0.01 Å. The strength of the macrocycle **6a** is evidence in distortion of the azo-group; torsion angle C(7)–N(8)–N(9)–C(10) is equal to 171°. For molecules **7c** and **12** these angles are equal to 178° and 180°, respectively.

Geometry of the furazan ring in all the three structures is similar. Bond lengths N–O are in the interval 1.357–1.406 Å that corresponds to the single N–O bond. So, lone pairs of the oxygen atoms do not participate in formation the π-system of the furazan ring or its contribution is small; the electronic conjugation is realized mostly in the N=C–C=N system. It has been noted earlier that in the furazan ring the length of the N–O bond proximate to an electron-donating substituent is longer than that proximate to an electron-withdrawing substituent [51,52]. In molecules **6a, 7c**, and **12** the difference in corresponding N–O bonds is equal 0.007–0.034 Å.

As may be expected, the bond length C–N between the furazan ring and azo group (see, Table 3) is intermediate between the single bond (1.47 Å) and the double (1.29 Å) [53] one, which might be related to conjugation between these fragments. On increasing the torsion angle N=N–C=N, the bond length N–C increases from 1.404 Å in **12** (torsion angle 179°) to 1.419 Å for N(7)–N(8) in **7c** (torsion angle 23°).

TABLE 3 Important Bond Lengths (Å) and Bond Angles (°) in Molecules **6a, 7c**, and **12**

	Compounds			
Bond	**6a***(I)*[a]	**6a***(II)*[b]	**7c**	**12**
C(1)–O(2)	1.464(3)	1.467(3)	1.480(6)	1.451(3)
O(2)–C(3)	1.338(3)	1.328(3)	1.309(6)	1.319(3)
C(3)–N(4)	1.305(3)	1.308(3)	1.298(6)	1.292(3)
C(3)–C(7)	1.431(3)	1.434(3)	1.433(6)	1.426(3)
N(4)–O(5)	1.406(3)	1.404(3)	1.391(6)	1.394(3)
O(5)–N(6)	1.376(2)	1.383(3)	1.385(5)	1.360(3)
N(6)–C(7)	1.305(3)	1.306(3)	1.274(6)	1.305(3)
C(7)–N(8)	1.390(3)	1.391(3)	1.419(5)	1.404(3)
N(8)–N(9)	1.257(3)	1.262(3)	1.254(5)	1.244(4)[b]
N(9)–C(10)	1.413(3)	1.411(3)	1.407(6)	–
C(10)–N(11)	1.304(3)	1.304(3)	1.309(6)	–
C(10)–C(14)	1.444(3)	1.446(3)	1.399(7)	–
N(11)–O(12)	1.372(3)	1.372(3)	1.357(6)	–
O(12)–N(13)	1.397(3)	1.398(3)	1.379(6)	–
N(13)–C(14)	1.304(3)	1.302(3)	1.319(6)	–
C(14)–O(15)	1.332(3)	1.342(3)	1.322(6)	–
O(15)–C(16)	1.462(3)	1.460(3)	1.473(7)	–
C(7)–N(8)–N(9)	119.4(2)	118.6(2)	110.4(3)	112.3(2)
N(8)–N(9)–C(10)	105.8(2)	106.0(2)	112.5(3)	–
C(1)–O(2)–C(3)	118.6(2)	118.4(2)	–[c]	115.3(2)
C(14)–O(15)–C(16)	120.8(2)	120.1(2)	–[c]	–
C(16)–C(1)–O(2)	113.7(2)	112.5(2)	–[c]	–
C(1)–C(16)–O(15)	108.9(2)	109.0(2)	–[c]	–
C(7)–N(8)–N(9)–C(10)	−171.0(2)	−167.9(2)	177.6(3)	180
O(2)–C(1)–C(16)–O(15)	143.6(2)	146.4(2)	–[c]	–

[a](I) refers to the first independent molecule and (II) refers to the second independent molecule of low-temperature modification of **6a**.
[b]N(8)–N(8A) bond.
[c]This part of molecule **7c** is disordered.

TABLE 4 Crystal Data for Compounds **6a, 7c**, and **12**

	6a	**6a**[a]	**7c**	**12**
Empirical formula	$C_6H_4N_6O_4$	$C_6H_4N_6O_4$	$C_{16}H_{16}N_{12}O_8$	$C_6H_6N_6O_4$
Molecular weight	224.14	224.14	504.38	226.15
T (K)	110	300	293	110
Crystal system	Monoclinic	Orthorhombic	Monoclinic	Triclinic
Space group	$P2_1/c$	$Pbca$	$P2_1/c$	$P1$bar
a (Å)	20.528(7)	20.745(9)	11.009(4)	4.246(4)
b (Å)	11.794(4)	11.597(5)	15.52(1)	7.190(6)
c (Å)	7.187(2)	7.454(3)	6.656(2)	7.830(7)
$\alpha(^\circ)$	90	90	90	85.55(1)
$\beta(^\circ)$	92.18(1)	90	103.52(2)	78.57(2)
$\gamma(^\circ)$	90	90	90	79.50(2)
V (Å^3)	1739(1)	1793(2)	1105.7(9)	230.2(3)
Z	8	8	2	1
μ(Mo-K_α) (mm^{-1})	0.142	0.142	0.125	0.139
D_x (g cm^{-3})	1.713	1.660	1.515	1.632
Scan method	ω	ω	$\theta/2\theta$	ω
$2\theta_{max}$ ($^\circ$)	60	50	54	46
Crystal size (mm)	0.35 × 0.20 × 0.15	0.35 × 0.20 × 0.15	0.20 × 0.15 × 0.05	0.15 × 0.10 × 0.05
Reflections measured	11407	8015	2602	965
Unique reflections	4973	1583	2393	647
R_{int}	0.025	0.034	0.061	0.040
Reflections with $I \geq 2\sigma(I)$	3390	1094	1002	547
Refined variables	321	143	159	74
$R(F^2 \geq 2\sigma(F^2))$	0.055	0.050	0.080	0.048
Goodness-of-fit	1.05	1.084	0.96	1.08
$wR(F^2)$, all data	0.165	0.1495	0.255	0.129

[a]For high-temperature modification of compound **6a**.

Crystal packing of the compounds **6a, 7c**, and **12** is different. The planar molecules of the linear azofurazan **12** form layers parallel to (11$\bar{1}$) plane (Fig. 8). The shortest interplanar distances between molecular layers does not exceed significantly the Van-der-Waals distances [54], so we may conclude that there is no specific intermolecular interactions in the crystal. Molecules of the 20-membered macrocycle **7c** form parquet-like motif parallel to (100) plane (Fig. 9). Furazan rings of the neighboring

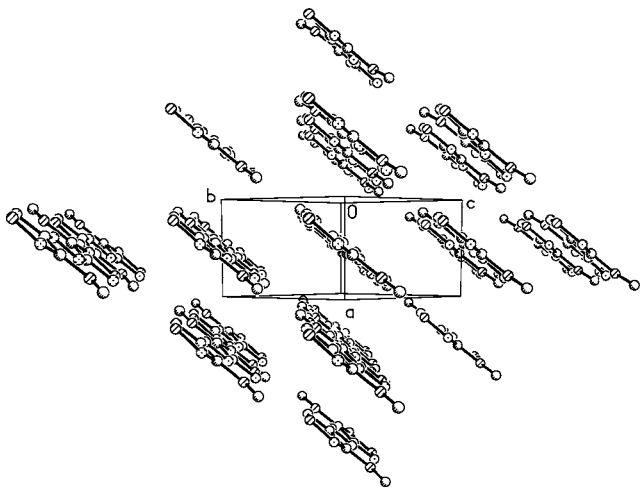

FIGURE 8 The crystal packing diagram for compound **12** (projection on the (011) plane).

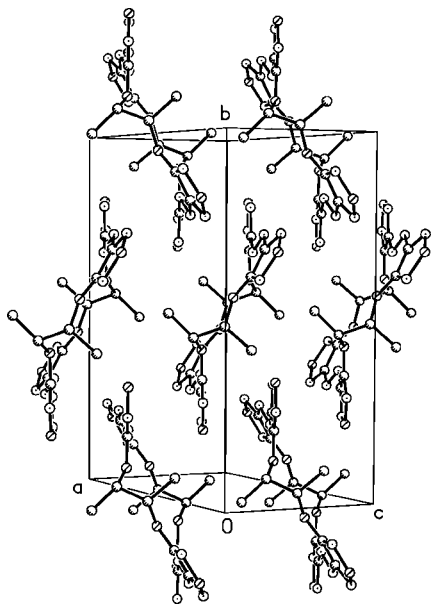

FIGURE 9 The crystal packing diagram for compound **7c** (projection on the (101) plane).

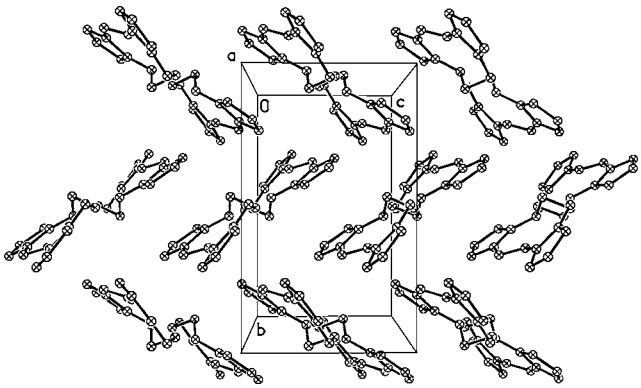

FIGURE 10 The crystal packing diagram for compound **6a** (projection on the (100) plane).

molecules are parallel, which may be related to their stacking interaction in the crystal.

Crystal packing of the 10-membered macrocycle **6a** (Fig. 10) is close to that in the compound **7c**; however, the "parquet" motif is formed by the two molecules forming a centrosymmetric dimer. Shortest intermolecular distances in these dimers (O(15)···O(15′) for one independent molecule and O(2)···O(2′) for the second one) are equal to 2855 and 2918 Å, respectively.

A multitemperature X-ray diffraction analysis of the crystal structure **6a** was performed in the wide temperature interval 110–335 K. The full data set were measured at 110, 240, 270, and 300 K, and in addition, unit cell parameters were measured (from one single crystal sample) at 14 points between 110 and 335 K.

These data are presented in Fig. 11, and they indicate a continuous and reversible phase transition in compound **6a** with changing crystal symmetry from monoclinic ($P2_1/c$, $Z = 8$) to the orthorhombic one (*Pbca*, $Z = 8$) at ca. 295 K. Crystal structure analysis at different temperatures has revealed that on increasing the temperature from 110 K (where azo groups are ordered), a graduate increasing of their disorder by two positions is observed in both independent molecules.

At 295 K both orientations of the azo group became equivalent and each molecule attains C_2-symmetry (Fig. 12). The crystal symmetry change also from monoclinic ($P2_1/c$) to orthorhombic one (*Pbca*) as a result of the appearance new crystal 2_1-axis, which related two independent (in the monoclinic modification) molecules. Details of the phase transition in the macrocycle **6a** will be described elsewhere.

CONCLUSION

A number of novel crown ether analogs, 10- and 20-membered macrocycles incorporating azofurazan subunit, have been synthesized. We have demonstrated that oxidative cyclization of bis(aminofurazanylic) ethers of 1,2-diols by dibromoisocyanurate provided a new and versatile approach to the synthesis of chromophoric macrocycles. Their structures were studied by X-ray crystallography, MNR, MS, and UV analysis. Nevertheless, these methods do not allow one to get clear understanding of the nature of observed isomerism.

Our current efforts are focused on the further applications of this methodology to the formation of related macrocycles. For a further study of

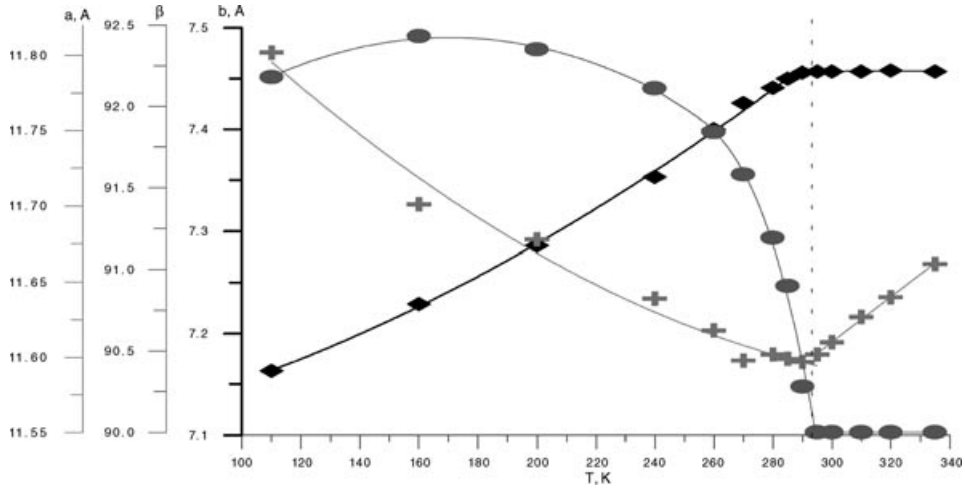

FIGURE 11 Temperature dependence of some crystall parameters in macrocycle **6a**. +: a (Å); ●: angle β; ◆: b (Å).

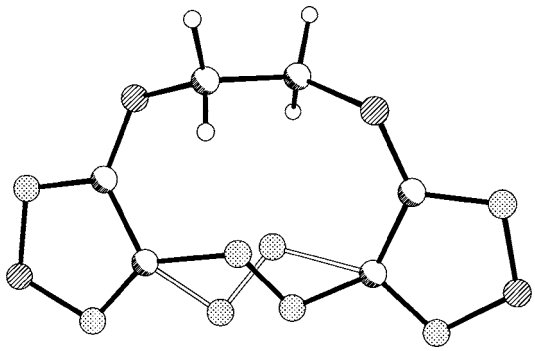

FIGURE 12 General view of disordered macrocycle **6a**.

structure–properties relations within this series, we are investigating structural requirements of the bridge linking the azofurazan subunits.

EXPERIMENTAL

Melting points were uncorrected. Infrared spectra were determined in KBr pellets on a Perkin-Elmer Model 577 spectrometer. Mass-spectra were recorded on a Varian MAT-311A instrument. UV spectra were taken in MeOH on a Beckman DU-7 spectrophotometer. ^{1}H NMR spectra were recorded at 300 MHz and ^{13}C NMR spectra at 75 MHz on a Bruker AM-300 instrument. Chemical shifts were measured relative to internal reference TMS (^{13}C and ^{1}H). All separations were carried out under flash chromatography condition on silica gel. Analytical thin layer chromatography (TLC) was conducted on precoated silica gel plates (Silufol F_{254}).

*General Procedure for Reaction of 3-Amino-4-nitrofurazan (**3**) with 1,2-Dioles*

To solution of **3** (2.6 g, 20 mmol) and 1,2-diole (10 mmol) in DMCO (20 ml) was added K_2CO_3 (1.8 g, 13 mmol). The resulting suspension was stirred 6–10 h at 75–80°C. TLC indicated complete reaction. The reaction was cooled. After addition of water (100 ml), the resulting solid was collected by filtration. The residue was dissolved in acetonitrile and precipitated by water. Recrystallization from propanol-2 gave white fine crystals of **4**. The filtrate was extracted with ethyl acetate (3 × 30 ml). The combined extracts were concentrated by distilling off solvent. The residue was a mixture of compounds **4** and **5**. The products were separated by crystallization from propanol-2.

1,2-Di(3-aminofurazan-4-oxy) ethane (**4a**) was obtained as a white solid (1.91 g, 84%). mp 206–207°C. ^{1}H NMR ([D$_6$]DMSO): δ = 4.64m (CH_2), 6.15bs (NH_2). ^{13}C NMR ([D$_6$]DMSO): δ = 69.9 (CH_2), 148.7 (C—N), 152.7 (C—O). MS (EI), *m/z*: 228 [M^+], 198 [M^+ − NO]. IR: 3467, 3348, 2960, 1647, 1585, 1320, 1065, 1010, 910 cm^{-1}. $C_6H_8N_6O_4$ (228.17): Calcd C 31.58, H 3.53, N 36.83; Found C 31.96, H 3.88, N 36.51.

Byproduct 3-amino-4-(2-hydroxyethoxy)furazan (**5a**) was obtained as an oil (0.44 g, 15%). ^{1}H NMR (CD_3OD): δ = 3.91m ($C\underline{H}_2OH$), 4.38m (CH_2O), 5.6bs (NH_2). ^{13}C NMR (CD_3OD): δ = 60.6 ($C\underline{H}_2OH$), 74.3 (CH_2O), 149.8 (C—N), 158.8 (C—O). MS (EI), *m/z*: 145 [M^+]. IR: 3390, 3345, 3220, 2950, 1645, 1575, 1455, 1320, 1250, 1080, 1030, 1007, 910, 850 cm^{-1}. $C_4H_7N_3O_3$ (145.12): Calcd C 33.11, H 4.86, N 28.96; Found C 33.86, H 5.34, N 28.28.

1,2-Di(3-aminofurazan-4-oxy) propane (**4b**) was obtained as a white solid (1.65 g, 68%). mp 188–189°C. ^{1}H NMR ([D$_6$]acetone): δ = 1.46d (CH_3), 5.09t (CH), 4.45–4.6m (CH_2), 6.07s, 6.13s (NH_2). ^{13}C NMR ([D$_6$]acetone): δ = 17.8 (CH_3), 73.3 (CH_2), 77.2 (CH), 148.9, 149.3 (C—N), 157.1, 157.9 (C—O). MS (EI), *m/z*: 242 [M^+]. IR: 3480, 3450, 3340, 3290, 3005, 2947, 1654, 1580, 1480, 1340, 1090, 1020, 855 cm^{-1}. $C_7H_{10}N_6O_4$ (242.19): Calcd C 34.71, H 4.16, N 34.70; Found C 35.02, H 4.32, N 34.60.

Byproduct 3-amino-4-(2-hydroxypropoxy-1)-furazan (**5b**) was obtained as an oil (0.8 g, 25%). ^{1}H NMR ([D$_6$]acetone): δ = 1.21d (CH_3), 4.1–4.2m (CH_2), 4.22–4.26m (CH), 4.4bs (OH), 5.50bs (NH_2). ^{13}C NMR ([D$_6$]acetone): δ = 19.4 (CH_3), 65.8 (CH), 77.7 (CH_2), 149.6 (C—N), 158.8 (C—O). MS (EI), *m/z*: 159 [M^+]. IR: 3420, 3340, 2975, 1645, 1590, 1375, 1240, 1085, 1005, 970 cm^{-1}. $C_5H_9N_3O_3$ (159.14): Calcd C 37.74, H 5.70, N 26.40; Found C 37.98, H 6.00, N 26.12.

2,3-Di(3-aminofurazan-4-oxy) butane (**4c**): 1.15 g (45%). mp 189–191°C. ^{1}H NMR ([D$_6$]DMSO): δ = 1.42d (CH_3), 4.9m (CH), 6.03s (NH_2). ^{13}C NMR ([D$_6$]DMSO): δ = 14.7 (CH_3), 79.9 (CH), 149.4 (C—N), 157.2 (C—O). MS (EI), *m/z*: 256 [M^+]. IR: 3460, 3345, 3280, 2992, 1644, 1572, 1320, 1095, 1050, cm^{-1}. $C_8H_{12}N_6O_4$ (256.22): Calcd C 37.50, H 4.72, N 32.80; Found C 37.61, H 4.88, N 32.75.

Byproduct 3-amino-4-(2-hydroxybutoxy-3)-furazan (**5c**) was obtained as an oil (1.07 g, 31%). ^{1}H NMR ([D$_6$]acetone): δ = 1.18d ($C\underline{H}_3CHOH$), 1.35d ($C\underline{H}_3CHO$), 3.39m ($C\underline{H}OH$), 4.54m (CHO), 5.51bs (NH_2). ^{13}C NMR ([D$_6$]acetone): δ = 15.3 ($\underline{C}H_3CHOH$), 19.8 ($\underline{C}H_3CHO$), 69.7 (CHOH), 84.0 (CHO), 150.0 (C—N), 152.8 (C—O). MS (EI), *m/z*: 173 [M^+]. IR: 3475, 3380, 3345, 3206, 2990, 1644, 1580, 1570, 1316, 1205, 1108, 1035, 1008, 980, 830 cm^{-1}.

$C_6H_{11}N_3O_3$ (173.17): Calcd C 41.62, H 6.40, N 24.27; Found C 41.93, H 6.58, N 23.96.

1,2-Di(3-aminofurazan-4-oxy) cyclohexane (**4d**): 0.85 g (30%). mp 182–183°C. ^{1}H NMR ([D_6]DMSO): δ = 1.3–1.7bm (CH_2), 1.75, 2.3bm ($C\underline{H}_2CH$), 4.75bm (CH), 6.02bs (NH_2). ^{13}C NMR ([D_6]DMSO): δ = 22.0 (CH_2), 27.9 (CH_2CH), 91.3 (CH), 149.0 (C—N), 156.7 (C—O). MS (EI), *m/z*: 282 [M^+]. IR: 3455, 3335, 2970, 1650, 1585, 1340, 1315, 1270, 1100, 1010, 960 cm^{-1}. $C_{10}H_{14}N_6O_4$ (282.26): Calcd C 42.55, H 5.00, N 29.77; Found C 42.66, H 5.08, N 29.71.

Byproduct 3-amino-4-(2-hydroxycyclohexanoxy-1)furazan (**5d**) was obtained as white solid (2.03 g, 51%). mp 101–102°C. ^{1}H NMR (CD_3OD): δ = 1.0–1.5, 1.7, 2.0, 2.3bm ($C\underline{H}_2$), 3.67m ($C\underline{H}OH$), 4.80m (CHO), 4.7 (NH_2 + OH + H_2O). ^{13}C NMR (CD_3OD): δ = 23.7, 23.8, 29.2, 33.0 (CH_2), 79.0 (CHOH), 86.8 (CHO), 149.5 (C—N), 157.6 (C—O). MS (EI), *m/z*: 199 [M^+]. IR: 3490, 3460, 3345, 2955, 1690, 1650, 1565, 1525, 1375, 1205, 1110, 1050, 830 cm^{-1}. $C_8H_{13}N_3O_3$ (199.21): Calcd C 48.23, H 6.58, N 21.09; Found C 48.78, H 6.79, N 20.87.

Oxidative Cyclization of **4a**

General Procedure for Construction of Macrocycles. A suspension of diamine **4a** (1.14 g, 5 mmol) and DBI (5.74 g, 20 mmol) in CH_2Cl_2 (20 ml) was stirred vigorously for 0.5 h. The precipitate (cyanuric acid) was collected by filtration. The filtrate was evaporated in vacuo, a crude mixture of compounds **6a** and **7a** was obtained. The products were separated by silica gel flash chromatography using CH_2Cl_2/hexane (4:1) as eluent.

The first fraction, compound **6a** (0.26 g, 23%) was obtained as orange crystals. mp 118–120°C (chloroform). MS (EI), *m/z*: 224 [M^+], 194 [M^+ − NO], 178, 155, 126, 112. IR: 2924, 1580, 1532, 1488, 1456, 1416, 1392, 1284, 1228, 1048, 1032, 972 cm^{-1}. $C_6H_4N_6O_4$ (224.14): Calcd C 32.15, H 1.80, N 37.50; Found C 32.21, H 1.94, N 37.44.

The second fraction, isomer **7a′** (0.16 g, 14.6%). mp 219–220°C. MS (EI), *m/z*: 448 [M^+], 390 [M^+ − NO − N_2], 363, 278, 225, 166. IR: 2960, 1580, 1496, 1440, 1356, 1284, 1260, 1028, 896 cm^{-1}. $C_{12}H_8N_{12}O_8$ (448.27): Calcd C 32.15, H 1.80, N 37.50; Found C 32.19, H 1.88, N 37.34.

The third fraction, isomer **7a″** (0.23 g, 20.5%). mp 263–265°C. MS (EI), *m/z*: 448 [M^+]. IR: 2960, 2928, 1580, 1496, 1452, 1436, 1356, 1300, 1280, 1256, 1236, 1060, 1024, 912, 892, 880, 868, 852 cm^{-1}. $C_{12}H_8N_{12}O_8$(448.27): Calcd C 32.15, H 1.80, N 37.50; Found C 32.22, H 1.83, N 37.41.

The fourth fraction, isomer **7a‴** (0.03 g, 2.9%). mp 185–186°C. MS (EI), *m/z*: 448 [M^+]. IR: 2960, 1580, 1496, 1450, 1356, 1310, 1282, 1260, 1056, 910 cm^{-1}. $C_{12}H_8N_{12}O_8$ (448.27): Calcd C 32.15, H 1.80, N 37.50; Found C 32.24, H 1.85, N 37.48.

Oxidative Cyclization of **4b**

Following the general procedure and starting from diamine **4b** (1.21 g, 5 mmol), a mixture of compounds **6b** and **7b** was obtained. Chromatography (same as above) gave the following.

The first fraction, orange oil **6b** (0.11 g, 9%). MS (EI), *m/z*: 238 [M^+], 180 [M^+ − NO − N_2], 169, 150, 113, 97, 83. IR: 2958, 2922, 1580, 1488, 1448, 1416, 1388, 1290, 1226, 1052, 1040, 982 cm^{-1}. $C_7H_6N_6O_4$ (238.16): Calcd C 35.30, H 2.54, N 35.29; Found C 35.35, H 2.59, N 35.31.

The second fraction, isomer **7b′** (0.36 g, 30.6%). mp 253–255°C. MS (EI), *m/z*: 476 [M^+], 418 [M^+ − NO − N_2], 391, 292, 279, 219, 180. IR: 3000, 1565, 1490, 1450, 1355, 1280, 1250, 1115, 1045, 982, 928 cm^{-1}. $C_{14}H_{12}N_{12}O_8$ (476.32): Calcd C 35.30, H 2.54, N 35.29; Found C 35.33, H 2.57, N 35.25.

The third fraction, isomer **7b″** (0.14 g, 12.2%). mp 195–197°C. MS (EI), *m/z*: 476 [M^+], 418 [M^+ − NO − N_2], 219, 205, 192. IR: 2988, 2935, 1568, 1488, 1448, 1412, 1384, 1356, 1346, 1328, 1292, 1252, 1164, 1040, 1016, 984, 926, 884 cm^{-1}. $C_{14}H_{12}N_{12}O_8$ (476.32): Calcd C 35.30, H 2.54, N 35.29; Found C 35.38, H 2.57, N 35.24.

The fourth fraction, isomer **7b‴** (0.06 g, 6.1%). mp 149–150°C. MS (EI), *m/z*: 476 [M^+], 418 [M^+ − NO − N_2]. $C_{14}H_{12}N_{12}O_8$ (476.32): Calcd C 35.30, H 2.54, N 35.29; Found C 35.34, H 2.56, N 35.26.

Oxidative Cyclization of **4c**

Following the general procedure and starting from diamine **4c** (1.28 g, 5 mmol), a mixture of compounds **6c** and **7c** was obtained. Chromatography (same as above) gave the following:

The first fraction, macrocycle **6c** (0.006 g, 0.5%). mp 118–120°C Calcd for $C_8H_8N_6O_4$ (252.19): MS *m/z* 252 [M^+], 237 [M^+ − CH_3], 223, 219, 210, 205, 194, 183, 167, 164, 154, 152, 140. IR: 2992, 2958, 2924, 1570, 1532, 1454, 1412, 1392, 1290, 1255, 1228, 1050, 1040, 982, 924 cm^{-1}.

The second fraction, isomer **7c′** (0.14 g, 11%). mp 259–260°C. MS (EI), *m/z*: 504 [M^+], 445, 365, 305, 256, 253, 234, 222, 219, 199, 194, 164, 152, 139. IR: 3000, 2930, 1570, 1495, 1450, 1350, 1250, 1045, 1020, 935 cm^{-1}. $C_{16}H_{16}N_{12}O_8$ (504.38): Calcd C 38.10, H 3.20, N 33.32; Found C 38.15, H 3.25, N 33.34.

The third fraction, isomer **7″** (0.1 g, 8%). mp 263–265°C. MS (EI), *m/z*: 504 [M^+], 474 [$M^+ - NO$], 444 [$M^+ - NO - 2CH_3$], 419, 401, 392, 386, 372, 365, 306, 256, 253, 234, 222, 219, 199, 194, 183. $C_{16}H_{16}N_{12}O_8$ (504.38): Calcd C 38.10, H 3.20, N 33.32; Found C 38.18, H 3.24, N 33.25.

The fourth fraction, isomer **7c‴** (0.33g, 26%). mp 249–250°C. MS (EI), *m/z*: 504 [M^+]. IR: 2990, 2958, 1570, 1488, 1450, 1356, 1348, 1330, 1292, 1254, 1165, 1038, 1016, 985, 930 cm^{-1}. $C_{16}H_{16}N_{12}O_8$ (504.38): Calcd C 38.10, H 3.20, N 33.32; Found C 38.11, H 3.25, N 33.30.

The fifth fraction, isomer **7c^{IV}** (0.07g, 6%). mp 240–242°C. MS (EI), *m/z*: 504 [M^+]. $C_{16}H_{16}N_{12}O_8$ (504.38): Calcd C 38.10, H 3.20, N 33.32; Found C 38.14, H 3.26, N 33.34.

Oxidative Cyclization of **4d**

Similarly, starting from diamine **4d** (1.41 g, 5 mmol), a mixture of isomeric macrocycles **7b** was obtained. Chromatography (same as above) gave the following:

The first fraction, isomer **7d′** (0.24 g, 17%). mp 258–260°C. MS (EI), *m/z*: 556 [M^+], 526 [$M^+ - NO$], 498 [$M^+ - NO - N_2$], 456, 241, 217, 185. IR: 2950, 2870, 1585, 1495, 1280, 1045, 1000 cm^{-1}. $C_{20}H_{20}N_{12}O_8$ (556.45): Calcd C 43.17, H 3.62, N 30.21; Found C 43.20, H 3.66, N 30.15.

The second fraction, isomer **7d″** (0.43 g, 31%). mp 92–95°C. MS (EI), *m/z*: 556 [M^+], 498, 391, 359, 292, 279, 241. IR: 2940, 2868, 1584, 1504, 1448, 1352, 1280, 1140, 1036, 928, 896 cm^{-1}. $C_{20}H_{20}N_{12}O_8$ (556.45): Calcd C 43.17, H 3.62, N 30.21; Found C 43.18, H 3.65, N 30.19.

The third fraction, isomer **7d‴** (0.28 g, 20%). mp 224–225°C. MS (EI), *m/z*: 498 [$M^+ - NO - N_2$], 279, 241. IR: 2928, 1580, 1496, 1448, 1364, 1344, 1292, 1272, 1152, 1108, 1040, 1020, 932, 892 cm^{-1}. $C_{20}H_{20}N_{12}O_8$ (556.45): Calcd C 43.17, H 3.62, N 30.21; Found C 43.19, H 3.69, N 30.17.

X-Ray Crystallography

Single-crystal X-ray diffraction experiments were carried out with an Enraf-Nonius CAD-4 diffractometer (**7c**) and a SMART 1000 CCD area detector mounted on a 3-circle diffractometer (**12** and **6a**), using graphite monochromated Mo-K_α radiation (λ = 0.71073 Å). Crystal data and experimental details are listed in Table 4.

The structures were solved by direct methods and refined by full-matrix least squares against F^2 of all data, using SHELXTL software [55]. Non-H atoms were refined in anisotropic approximation and H atoms in isotropic one, except for disordered groups, which were refined in isotropic approximation. Atomic coordinates, thermal parameters, and bond lengths and angles for compounds **6a, 7c**, and **12** have been deposited at the Cambridge Crystallographic Data Centre as supplementary publication numbers 222151–222154.

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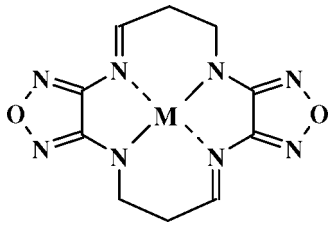
[37] Recently we reported the metal ion template cyclization to synthesis of stable complexes (M = Cu, Co, Ni), which can be defined by formula:



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[39] Our initial communication [25] described the reaction of bis(aminofurazanylic) ether of diethylene glicol with DBI; intramolecular product was main (63%).

[40] In contrast, *E* and *Z*-isomers of azobenzene crowns may be easily assigned by ^{1}H NMR [13].

[41] In an earlier paper [42], the term "trans/cis position" refers to the position of furazan rings relative one to the other, the term "configuration" to *Z*, *E* geometry of furazan rings relative to N=N bond, and the term "conformation" to geometry around the single bonds.

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[48] It seems that in this case we have encountered a specific impact of the furazan ring that is a strong electron acceptor. In ^{1}H and ^{13}C NMR spectra all signals are broadened what makes detailed research impossible (for an example, see Sheremetev, A. B., Mantseva, E. V., Dmitriev, D. D., Izv AN, Ser Khim 2001, (12), 2366–2367; Russ Chem Bull (Engl. Transl.) 2001, 50, 2479–2480). At lower temperatures solubility drops drastically thereby hampering low-temperature examinations.

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