Synthesis of Macrocycles Incorporating Azo-bis(azofurazan) Framework

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A series of macrocycles containing four furazan rings bonded by three azo bonds **2**, **5** and **7** have been synthesized from the common precursor, 3-amino-3'-nitro(azofurazan) **3**. The macrocycles closure is a result of N=N bond formation at oxidative cyclization of corresponding bis(3-aminofurazan-4-yl) precursors. X-Ray crystal structures of macrocycles **2, 2**•AcOH, **11** and **13** are reported.

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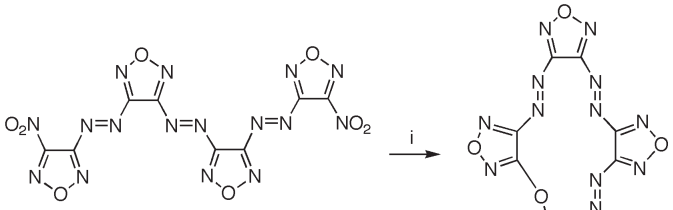
Introduction.

We have recently described some chemistry of the furazan-annulated macrocycles [1]. There is a current interest in the structural properties as well as application of these modified macrocycles. Thus, it has been shown that these compounds are useful as ingredients to explosives and rocket propellants [2,3]. At the same time, a set of azofurazans containing macrocycles exhibits interesting biological and pharmacological properties, for instance as effective inhibitors of soluble guanylate cyclase [4,5]. An example of such active compound is tetrakisfurazano[3,4-*b*:3',4'-*f*:3'',4''-*j*:3''',4'''-*n*][1,4,5,8,9,12,13]oxahexaazacyclopentadecacene (**2**). In earlier work we have reported that the zero-hydrogen chomophore compound **2** has been prepared in 95% yield by the base-promoted cyclization of highly preorganized linear dinitro precursor **1** (Scheme 1) [6].

Scheme 1 [6].



1 2

Reagents and conditions: *i*, Na_2CO_3, MeCN, reflux

Our interest in preparation of drugs containing four furazan rings bonded by three azo bonds, the azo-bis(azofurazan) framework as a subunit has prompted us to examine various methods for the preparation of such compounds. Primarily, due to high explosive properties of the dinitro compound **1** [7] as starting material, we needed an alternative precursor.

We wish to describe herein a novel and general method to produce macrocycles incorporating azo-bis(azofurazan) framework that does not involve highly dangerous starting material. The 3-(3-aminofurazan-4-azo)-4-nitrofurazan **3** [8] was chosen as a key synthetic precursor. It contains a number of features which make its useful for our purposes: (*i*) it may be handled without special precautions; (*ii*) nucleophilic aromatic substitution reactions of nitro group [9,10] at one end and a simple transformation of the amino group to the azo group [7,11] at the other one gives an opportunity to prepare of macrocycles of interest.

Results and Discussion.

Synthesis.

Our initial goal was diamino ether **4**. Difurazanyl ethers are usually prepared in good yield by reaction of the corresponding nitrofurazan with base [6,10,12-15]. In dramatic contrast to this method, no individual product(s) were obtained when nitro derivative **3** was exposed to the same reaction conditions. Thus, at treatment of **3** with Na_2CO_3 a complex product mixture was obtained and isolation of discernible products proved to be not feasible. The difficulties were associated with diazotization of amino group by nitrogen oxides generating at the transformation of nitro groups to ether bond.

We concluded therefore that reaction could likely be achieved by utilization of a protected amino precursor. We concentrated our efforts on the routes outlined in Scheme 2. Upon treatment of **3** with Vilsmeier reagent [16] in an

excess of $POCl_3$ at 50 °C for 2 h the amino group was transformed to the formamidine moiety [17], a 95% yield of compound **5** was obtained. Subsequent reaction of amidine **5** with Na_2CO_3 in acetonitrile at 80 °C for 8 h afforded the corresponding difurazanyl ether **6** in 48% yield. Changing the base to K_2CO_3 improved the yield to 85% and reduced the reaction time by one half. Deprotection of compound **6** using a 12% HCl solution produced diamine **4** in 90% yield. Finally, macrocycle closure was achieved *via* N=N bond formation at oxidative cyclization of the diamine **6** with dibromoisocyanurate (DBI). The oxidation of **6**, containing the ether bridging unit defines the flexibility and leads to two isomers of the macrocycle **2**. Alternative coupling product, the known inner salt **7** [10], were not observed. The isomers, orange **2'** and yellow **2"**, were obtained in a ratio of 2:1 and showed the same molecular ion in MS and elemental composition but different melting points, UV spectra, and TLC spots. Orange isomer **2'** corresponded in all respects to the compound described earlier [6]. The X-ray structures of **2'** and its AcOH solvate, **2'**•AcOH, were determined (Figure 1-3, Table 1). All of our attempts to prepare a single crystal of **2"** suitable for X-ray investigation failed. Structural difference **2'** and **2"** could not be made by the ^{13}C NMR.

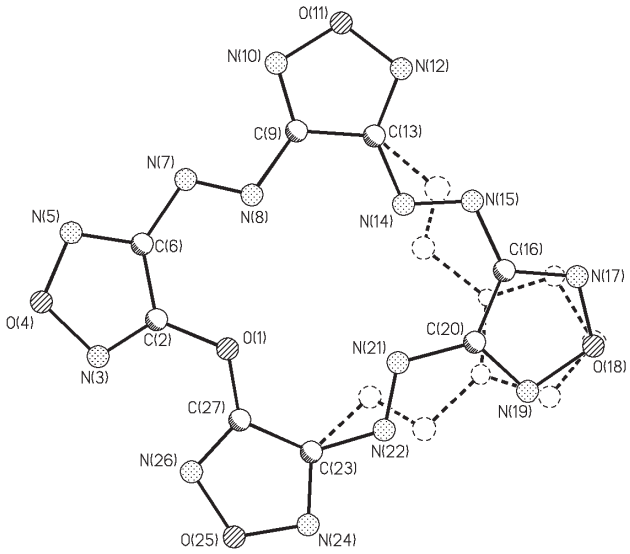
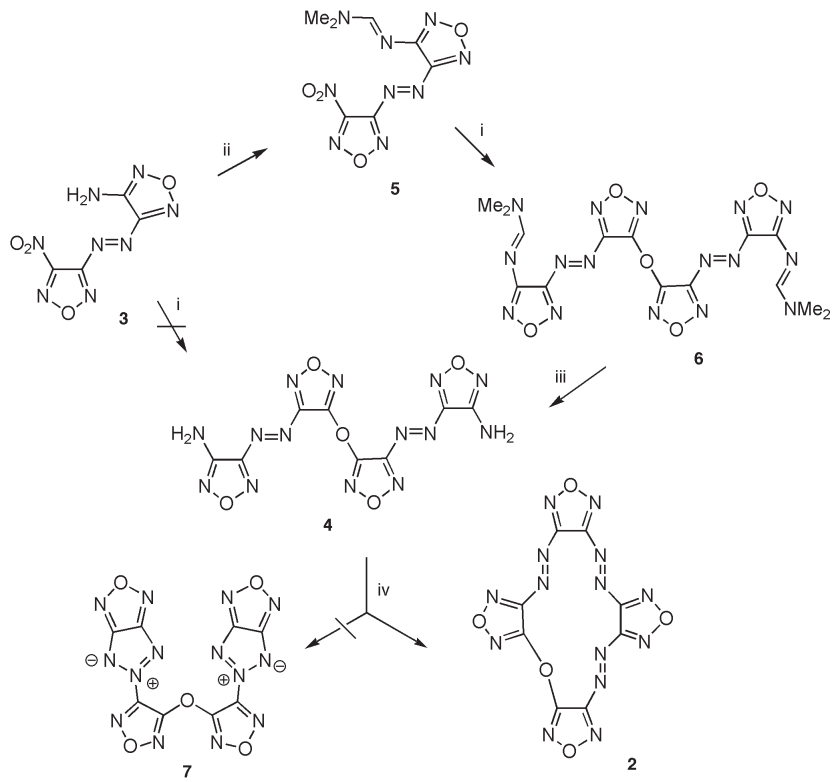


Figure 1. General view of molecule **2'**. The second positions of disordered part or the molecule is outlined with dashed lines.

A similar isomerism has been observed for macrocycles incorporating two azofurazan moieties bonded by flexible

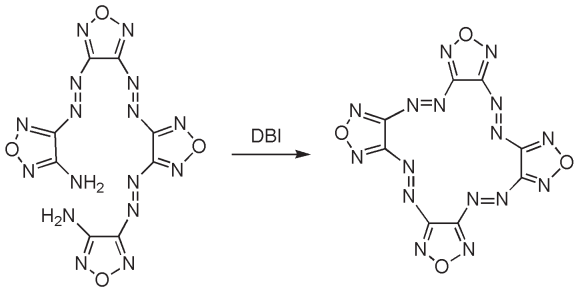
Scheme 2



Reagents and conditions: *i*, K_2CO_3, MeCN, 80 °C; *ii*, $POCl_3$, DMFA; *iii*, HCl/H_2O; *iv*, DBI

spacers [1]. In contrast, a closely related macrocycle **9** has been recently prepared as a single isomer at similar oxidation of more highly preorganized diamine **8** (Scheme 3) [18].

Scheme 3 [18]



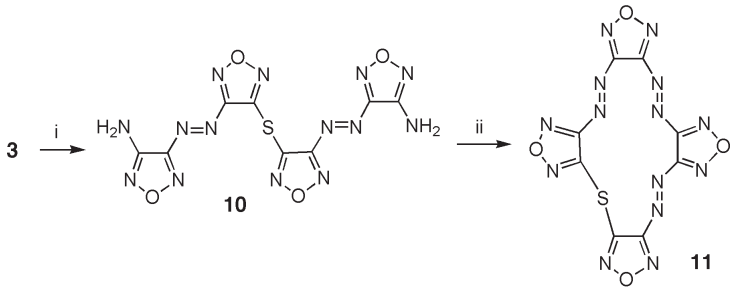
8 **9**

Nitro compound **3**, when treated with sodium sulfide in acetonitrile at 0 °C, produced the diamino thioether **10** in 54% yield, as shown in Scheme 4. Interestedly, a similar reaction in ethanol as the solvent failed to gave any of the desired thio compound giving instead 3-amino-3'-ethoxyazofurazan [10] as the major product. Treatment of **10** with DBI produced the single thiomacrocycle **11**, analogous to above observation. The macrocycle **11** was isolated by chromatographic purification in 37 % yield. The structure of **11** was proved by X-ray diffraction analysis (Figure 4, Table 1).

The furazan carbons attached to S-bridge are more shielded by *ca.* 20 ppm in the ^{13}C NMR specter relative to their *O*-bridged counterpart. The ^{13}C chemical shift of the other furazan carbon atoms also differs significantly in *O*- and *S*-bridged macrocycles **2** and **11**, respectively (see, experimental section).

We were interested in studying the effect of the length of the bridging unit on macrocycle properties.

Scheme 4



Reagents and conditions: *i*, $Na_2S\bullet 9H_2O$, MeCN, 80 °C; *ii*, DBI

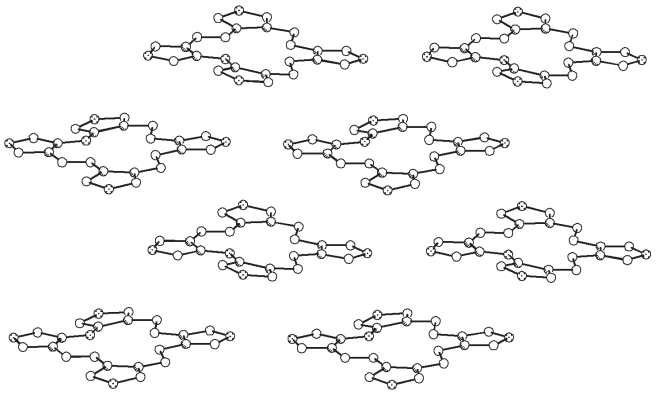


Figure 2. The arrangement of molecules **2'** in the wall.

Extension of the chemistry for synthesis macrocycle **13** incorporating more long flexible spacers was also investigated. Linear diamine **12** was synthesized from the same starting material **3** and ethyleneglycol using the procedure developed by us [1,10], on the nucleophilic displacement reaction. As outlined in Scheme 5, treatment of the diamine **12** with DBI is accomplished by azo-bond formation.

Two major products, the 18- and 36-membered macrocycles **13** (23%) and **14** (2.5%), were separated in the reaction, although some other compounds were present as suggested by TLC and HPLC, however they were formed in a quantity too small to be isolated on a scale suitable for spectral study.

The intra- **13** and intermolecular **14** coupling products are readily distinguishable only from their mass spectra. The molecular ion peak was observed in both cases. The ^1H NMR spectra as **13** and **14** each show a single methylene resonance at *ca.* 5 ppm (see, experimental section).

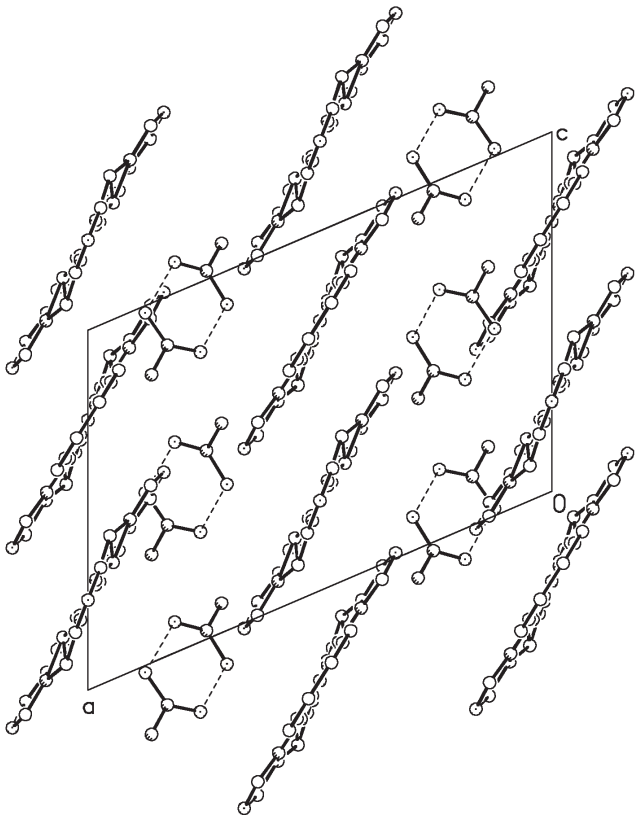


Figure 3. The crystal packing of **2'**•AcOH. The projection on the plane (0 1 0).

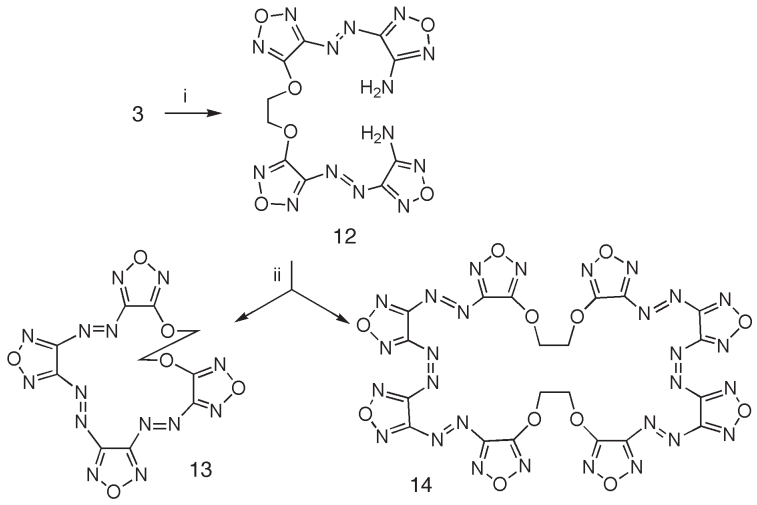
The structure of macrocycle **13** was proven by X-ray analysis (Figure 5, Table 1).

Crystallography.

X-Ray diffraction analysis has revealed that molecules **2'** and **11** are flattened unlike **13** which has a saddle-like conformation (Figures 1-3). It is noteworthy that in all crystal structures studied (**2'**, **2'**•AcOH, **11** and **13**) at least one of the three azo-groups is disordered. In molecules **2'** and **13** the occupancies of alternative positions are 0.5/0.5, while in structure **11** the occupancies are 0.75/0.25. In molecules **11** and **13** these groups are N(14)=N(15) and N(15)=N(16), respectively. Thus, molecule **11** possesses the local C_s symmetry, and molecule **13** has local C_2-symmetry. In the crystal of **2'** two azo-groups N(14)=N(15) and N(21)=N(22) connected *via* furazan ring are also disordered. In the crystal of **2'**•AcOH two azo-groups and one furazan ring are disordered. The crystallographic disorder of the azo-group has been detected very often for different organic molecules, and the study of its nature was a subject of the paper [19].

Molecular geometry of two furazan rings in **11** and **13** which are not disordered is rather similar. It is obviously from the bond lengths, that there is a conjugation in the chain *azo-group–furazan ring–donor atom* (atom S for molecule **11**, and atom O for molecule **13**). On the contrary, in the crystal of **2'** the furazan ring does not participate in conjugation with atom O(1): bond lengths C(2)-C(6) (1.403(7)Å) and C(2)=N(3) (1.261(6)Å) are shorter than corresponding values for **11** and **13** (the lengths of the C-C bonds are in the interval 1.429-1.441Å, the C=N bond varies in the range 1.290-1.303Å). The bond length of C(2)-O(1) 1.393(5)Å in **2'** also demonstrates the absence of conjugation. This value is longer than the similar bond O(1)-C(27) 1.314(6)Å in the same molecule, and two C-O bonds in molecule **13** (O(2)-

Scheme 5



Reagents and conditions: *i*, glycol, K_2CO_3, DMSO, 80 °C; *ii*, DBI

Table 1

Crystal and data reduction parameters for compounds **2, 2•AcOH**, **13** and **11**.

	2	**2•AcOH**	**13**	**11**
Formula	$C_8N_{14}O_5$	$C_8N_{14}O_5$•4($C_2O_2H_4$)	$C_{10}H_4N_{14}O_6$	$C_8N_{14}O_4S$
Molecular mass	372.22	612.43	416.27	388.28
T [K]	110	110	110	298
Crystal system	Orthorhombic	Monoclinic	Orthorhombic	Monoclinic
Space group	$P2_12_12_1$	C2/c	Aba2	$P2_1/c$
a [Å]	10.188(1)	16.209(2)	a = 25.549(3)	9.486(4)
b [Å]	10.624(1)	14.974(1)	b = 20.022(3)	b = 12.167(5)
c [Å]	12.277(1)	11.555(1)	c = 6.333(1)	c = 12.059(6)
β [°]		113.165(2)		95.07(4)
V [Å ^{3}]	1328.9(3)	2578.5(4)	3239.4(7)	1386(1)
Z	4	4	8	4
μ(Mo-K_α) [mm^{-1}]	0.159	0.138	0.145	0.297
D_x [g cm^{-3}]	1.860	1.578	1.707	1.860
	Diffractometer		SMART CCD 1000K	Siemens P3/PC
λ, Å	0.71073			
Scan method		Phi and omega scans		θ/2θ
$2\theta_{max}$ [°]	54	54	50	50
Crystal size [mm]	0.3 x 0.1 x 0.1	0.5 x 0.2 x 0.2	0.8 x 0.2 x 0.2	0.3 x 0.2 x 0.2
Reflections measured	7324	8384	9440	2619
Unique reflections	2864	2834	2810	2456
R_{int}	0.0338	0.0294	0.0468	0.0247
Reflections with $I\_2\sigma(I)$	1715	1624	2201	1784
Refined variables	235	281	285	242
$R[F^2\_2\sigma(F^2)]$	0.0712	0.0534	0.0381	0.0493
Goodness-of-fit	0.942	0.950	0.966	1.007
$wR(F^2)$, all data	0.1943	0.1532	0.0928	0.1296

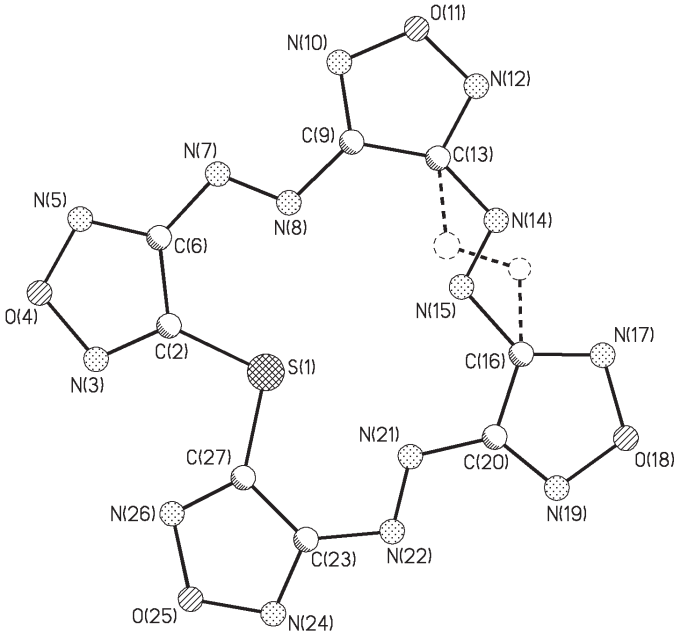


Figure 4. General view of molecule **11**. The second positions of disordered part of the molecule is outlined with dashed lines.

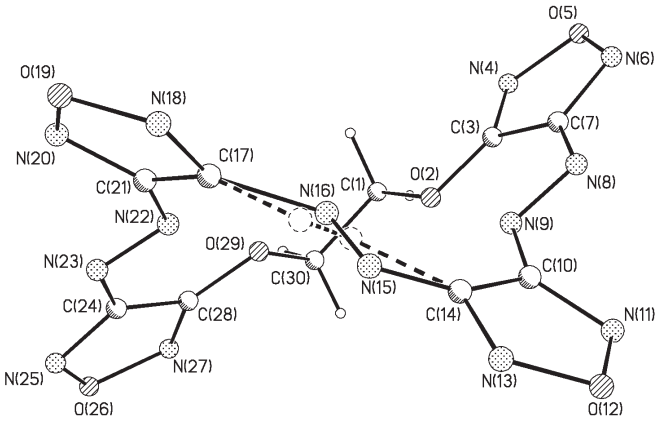


Figure 5. General view of molecule **13**. The second positions of disordered part of the molecule is outlined with dashed lines.

C(3) 1.319(3)Å, O(29)-C(28) 1.318(3)Å. More detailed analysis of the molecular geometry of the compounds studied is hardly possible because of crystal disorder.

In the crystal molecules **2'** are arranged in parquet layers parallel to (0 0 1) plane. The shortest distance O(11)…O(25) between furazan rings from two neighbouring layers is equal to 2.936(5)Å. The neighbour parallel molecules form walls parallel to (1 0 0) plane) (Figure 2). The shortest distances between molecules in these walls correspond to the Wan-der-Vaals contacts. The similar walls are found in the crystal structure of **2'**•AcOH. However in this case these walls are separated by dimers of the acetic acid (Figure 3).

The parameters of H-bonds in dimers of AcOH are O(1S)…O(3S) 2.611(3)Å, O(4S)…O(2S) 2.652(3)Å, H(1S)…O(3S) 1.51(3)Å, H(4S)…O(2S) 1.57(4)Å, O(1S)-H(1S)O-(3S) 165(4)°, O(4S)-H(4S)-O(2S) 178(3)°.

In the crystal packing of **11** there are also parquet layers, parallel (1 0 0), but in this case molecules form sandwich herringbone motif of the centrosymmetric pairs of **11**. The distance between planes of molecules in a pair is equal to 3.68Å. There are no shortened contacts in these pairs.

The crystal packing of **13** differs from others because of nonplanarity of the molecule. The crystal packing consists of the columns directed along the [0 0 1] direction (Figure 6). The distance between parallel furazan rings is 3.16Å, the intermolecular distance between atoms C(28) is equal to 3.185(3)Å. We may suggest that there is a staking in these columns between conjugation systems of furazan rings and oxygen atom of neighbour molecules in the column.

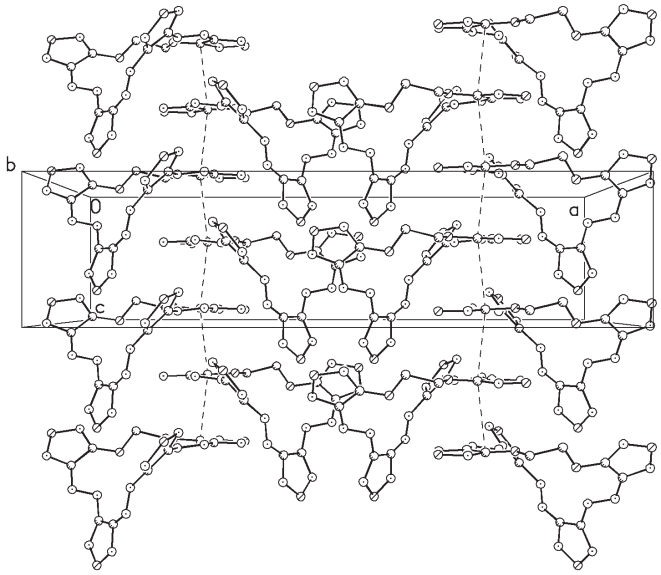


Figure 6. The crystal packing of **13**. The projection on the plane (0 1 0). The shortest contacts within the column C(28)…C(28) are shown by dashed line.

EXPERIMENTAL

Melting points were determined on Gallenkamp melting point apparatus and they are not corrected. 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 spectra at 75 MHz on a Bruker AM-300 instrument. Chemical shifts for both ^{1}H NMR and ^{13}C NMR are referred to chemical shifts for solvent (for DMSO-d_6 it is 2.50 ppm and 39.51 ppm for proton and carbon NMR, respectively). 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}).

Formamidine **5**.

To a solution of 3-(3-aminofurazan-4-azo)-4-nitrofurazan **3** (0.5 g, 2.21 mmol) in $POCl_3$ (5 mL) was added dropwise dimethylformamide (0.3 mL, 4.42 mmol). The reaction mixture was stirred at 40 °C for 2 h. The cooled mixture was poured into ice-water and a yellow solid precipitated. The solid was washed with water to afford 0.62 g (98%) of the product, a red orange solid. An analytical sample was recrystallized from $CHCl_3$: mp 141-142C°; ms: (*m/z*) 281 [M^+], 235 [M^+ - NO_2]; ^{1}H nmr (acetone-d_6/$CDCl_3$): δ 3.1 (s, 3H), 3.2 (s, 3H), 8.24 (s, 1H); ^{13}C nmr (acetone-d_6/$CDCl_3$): δ 40.9 (Me), 153.9 (C-NO_2), 158.2, 157.6, 158.9 (CH), 159.8; ^{14}N nmr (acetone-d_6/$CDCl_3$): δ -36.15 (NO_2).

Anal. Calcd. for $C_7H_7N_9O_4$ (281.19): C 29.90, H 2.51, N 44.83. Found C 29.94, H 2.55, N 44.82.

Ether **6**.

A mixture of compound **5** (0.5 g, 1.78 mmol) and K_2CO_3 (0.5 g, 3.56 mmol) in CH_3CN (5 mL) was heated while stirring at 80 °C. After 3-4 h TLC monitoring confirmed that the starting material had completely been consumed. The reaction was deluted with water (50 mL) and extracted with CH_2Cl_2 (3×25 mL). Washing the organic layer with brine (15 mL), drying ($MgSO_4$), and removal of solvent afforded the crude ether (85%) as a yellow orange solid; mp 159-162 °C. Purification was accomplished by recrystallization from hot benzene to give the product as red orange crystals: mp 173-174 °C; ms: (*m/z*) 486 [M^+]; ^{1}H nmr (acetone-d_6): δ 3.04 (s, 3H), 3.18 (s, 3H), 8.22 (s, 1H); ^{13}C nmr (acetone-d_6): δ 41.0 (Me), 156.0, 156.6, 156.9, 159.4 (CH), 160.1 (C-O).

Anal. Calcd. for $C_{14}H_{14}N_{16}O_5$ (486.37): C 34.57, H 2.90, N 46.08. Found C 34.59, H 2.95, N 46.02.

Diamine **4**.

Ether **6** (0.4 g, mmol) was added in one portion to a solution of 36% hydrochloric acid (5 mL) in water (15 mL) at 30 °C. Stirring at this temperature was maintained for 24 h during which time complete deprotection occurred. The solid was collected by filtration, washed with water until neutral to litmus and dried at room temperature. Crystallization from DMFA yielded the product as yellow powder (0.28 g, 90%): mp 191-192°C; ms: (*m/z*) 376 (M^+), 349 (M^+ - NO), 292, 280, 230, 196; ^{1}H nmr (DMSO-d_6/CD_3OD): δ 4.35 (NH_2); ^{13}C nmr (DMSO-d_6/CD_3OD): δ 150.6 (C-NH_2), 156.7, 159.2, 164.9 (C-O); ir: 3480, 3330, 1630, 1570, 1490, 1280, 1040, 780 cm^{-1}.

Anal. Calcd. for $C_8H_4N_{14}O_5$ (376.21): C, 25.54; H, 1.07; N, 52.12. Found: C, 25.56; H, 1.08; N, 52.08.

Macrocycle **2**.

A slurry of **4** (0.3 g, 0.79 mmol) and DBI (1 g, 3.4 mmol) in CH_3CN (10 mL) was stirred vigorously for 4 h. The reaction was deluted with a mixture of CH_2Cl_2 (50 mL) and CCl_4 (20 mL), and the precipitate (cyanuric acid) was collected by filtration. The filtrate was evaporated *in vacuo*, a crude mixture of isomeric compounds **2'** and **2"** was obtained. These products were separated by silica gel flash chromatography using $CHCl_3$ as eluent.

The *first fraction*, compound **2'** (0.16 g, 55%) was obtained as red brawn crystals: mp 235-236 °C (ref. [6] 235-236 °C, mixed mp 235-236 °C); R_f = 0.8 (in $CHCl_3$); UV (ethanol): λ_{max} = 222 nm (ε = 14500), 258 nm (ε = 13650), 435 nm (ε = 197). On the basis of mp, IR, NMR and TLC, the substance corresponded in all respects with the compound described in ref. [6].

The *second fraction* gave isomer **2"** (0.07 g, 24%): mp 253-254 °C; R_f = 0.7 (in $CHCl_3$); UV (ethanol): λ_{max} = 262 nm (ε = 22500), 432 nm (ε = 330); ms: (*m/z*) 372 (M^+), 256 (M^+ - 2NO - $2N_2$), 248; **ir**: 1580, 1500, 1220, 1190, 1010, 600 cm^{-1}; ^{13}C nmr (DMSO-d_6): δ 155.5, 155.8, 158.4, 159.5 (C-O).

Anal. Calcd. for $C_8N_{14}O_5$ (372.18): C, 25.82; N, 52.69. Found: C, 25.85; N, 52.63.

Thio Ether **10**.

Sodium sulfide hydrate (1.5 g, mmol) was added to a stirring solution of 3-(3-aminofurazan-4-azo)-4-nitrofurazan **3** (1 g, 4.42 mmol) in CH_3CN (20 mL) at 0 °C. The suspension was stirred at 0 °C for 2 h and then poured into ice/water (50 mL); the yellow brown solid was collected and dried. The residue was purified *via* column chromatography on silica gel by eluting with $CHCl_3$/hexane (3/1). Pure **10** (0.43 g, 54%) was thereby obtained as a yellow powder: mp 210-211 °C; R_f = 0.5 (in $CHCl_3$:hexane - 3:1); ^1H nmr (acetone-d_6): δ 6.51 (NH_2); ^{13}C nmr (acetone-d_6): δ 142.8 (C-S) 150.3, 156.9, 163.3; ir: 3450, 3310, 1630, 1490, 1375, 1145, 1040, 970, 765, 687 cm^{-1}.

Anal. Calcd. for $C_8H_4N_{14}O_4S_1$ (392.27): C, 24.50; H, 1.03; N, 49.99; S, 8.17. Found: C, 24.54; H, 1.02; N, 49.92; S, 8.13.

Macrocycle **11**.

The treatment of diamine **10** (0.3 g, 0.76 mmol) with DBI (0.88 g, 3.07 mmol) by the above procedure to **2** gave product **11**, a red yellow solid (0.11 g, 37%). An analytical sample was recrystallized from $CHCl_3$: mp 209-210°C; ir: 1550, 1500, 1492, 1273, 1240, 1035, 600 cm^{-1}; ms: (*m/z*) 388 (M^+); ^{13}C nmr (acetone-d_6): δ 143.2 (C-S) 157.7, 162.5, 164.9.

Anal. Calcd. for $C_8H_4N_{14}O_4S_1$ (388.24): C, 24.75; N, 50.51; S, 8.26. Found: C, 24.74; N, 50.49; S, 8.24.

Diamine **12**.

To solution of 3-(3-aminofurazan-4-azo)-4-nitrofurazan **3** (2.26 g, 10 mmol) and ethyleneglycol (0.31 g, 5 mmol) in CH_3CN (10 mL) was added K_2CO_3 (1.38 g, 10 mmol). The resulting suspension was stirred 3 h at room temperature. After addition of water (25 mL), the resulting solid was collected by filtration. The residue was dissolved in acetonitrile and precipitated by water. Recrystallization from 2-propanol gave light-yellow crystals **12** (1.05 g, 25%); mp 177-178 °C; ^1H nmr (DMSO-d_6): δ 4.89 (s, 4H, CH_2), 6.74 (s, 4H, NH_2); ^{13}C nmr (DMSO-d_6): δ 70.9 (CH_2), 149.3, 154.8, 156.0, 158.5; ir: 3450, 3250, 1620, 1580, 1500, 1420, 1350, 1280, 1040, 1000 cm^{-1}.

Anal. Calcd. for $C_{10}H_8N_{14}O_6$ (420.26): C, 28.58; H, 1.92; N, 46.66. Found: C, 28.60; H, 1.93; N, 46.57.

Macrocycles **13** and **14**.

Prepared as for compound **2** using diamine **1 2** (0.2 g, 0.48 mmol) and DBI (0.55 g, 1.9 mmol). The products were separated by silica gel flash chromatography using CH_2Cl_2 as eluent.

The *first fraction*, compound **13** (0.046 g, 23%) was obtained as orange crystals: mp 218-220 °C (chloroform); ms: (*m/z*) 416 (M^+), 358 (M^+ - NO - C_2H_4), 331, 246, 150; ^1H nmr (acetone-d_6): δ 4.94 (s, CH_2); ^{13}C nmr (acetone-d_6) δ 70.7 (CH_2), 156.8, 158.4, 159.3, 161.4.

Anal. Calcd. for $C_{10}H_4N_{14}O_6$ (416.23): C, 28.86; H, 0.97; N, 47.11. Found: C, 28.89; H, 1.00; N, 47.04.

The *second fraction* gave isomer **14** (0.005 g, 2.5%): mp 274-278°C; ^1H nmr (DMSO-d_6): δ 5.07 (s, CH_2); ms: (*m/z*) 832 (M^+), 802 (M^+ - NO), 772 (M^+ - 2NO), 744 (M^+ - 2NO - C_2H_4), 714 (M^+ - 3NO - C_2H_4). Calcd for $C_{20}H_8N_{28}O_{12}$ (832.46).

X-ray Analysis.

Orange crystals of compound **2**, **11**, and **13** grown by slow evaporation from a chloroform solution at room temperature. The solvate **2**•AcOH was obtained by rapid crystallization from acetic acid. The parameters of the single-crystal X-ray diffraction experiments and reduction parameters for compounds **2, 2**·AcOH, **13** and **11** are presented in Table 1.The structures were solved by direct method and refined by full-matrix least squares against F^2 using SHELXTL software [20]. Non-hydrogen atoms were refined in anisotropic approximation. All hydrogen atoms were located in the difference Fourier maps and refined in isotropic approximation. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 235742 – 235745. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax:(internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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