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New macrocyclic ligands. X-Ray study of three macrocycles involving azofurazan subunit

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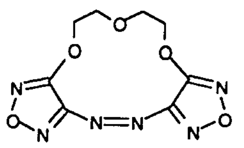
The first X-Ray crystallographic analysis of conformationally immobilized polyfurazan macrocycles, involving both a furazan ring and an azo-group has been carried out. The configurational and conformational features observed in the crystal have been analysed; all results show that the intramolecular non-bonded interactions influence the observed conformation.

There have been many attempts to understand the manner by which small molecules bind to macromolecules and how this binding can result in specific activity. The specificity of interactions between oxygen and nitrogen atoms of O, N-containing molecules on organic and biological systems is observed; these molecules consist of a series of alternating positively and negatively charged atoms. Organic π-donors based on furazan (**F**) have been studied intensively for many years. The motif of alternating positive and negative charged atoms produces push-pull forces essential for their conformation.

Due to strong π-donor activity it appeared very attractive to incorporate **F** into macrocycles with the aim of creating molecular associations in which the polyfurazan π-system can interact with guest species such as ions, neutral molecules or electron acceptors. Recently we published the crystal structure analysis of the nine linear furazan derivatives.[1] Among them are molecules containing furazan rings linked by -O- or/and -N = N- bridges. Macrocycles consisting of the same subunits have been synthesized in the Institute of Organic Chemistry, Moscow.[2] We herein report the crystal structure determination of three such macrocycles, **1–3**, and the discussion of their conformational features. Macrocycle **1** consists of crown ether and azodifurazan subunits, while macrocycles **2** and **3** are composed of azo-difurazan and azo- and oxo-difurazan skeletons, respectively. (Scheme 1).

As already mentioned in a previous paper,[1] the polyfurazan compounds can exist as a number of configurational and/or conformational isomers which are characterised by *trans*/*cis* position of furazan rings, *Z*/*E* term and by using Klyne-Prelog[3] definitions. Therefore in this article, the term 'position' will refer to the position of furazan rings relative one to the other, the term 'configuration' to *Z*,*E* geometry of furazan ring relative to N = N bond, and the term 'conformation' to geometry around the single bonds.



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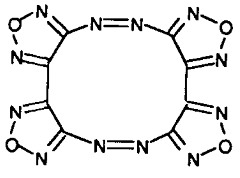

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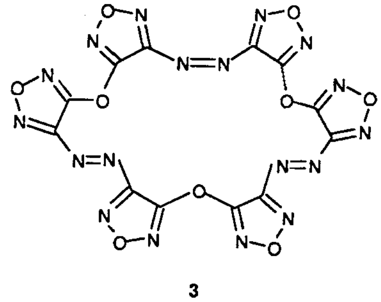

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Macrocycles **1–3** are thus very interesting objects for a structural study, and X-Ray analysis is the only method able to establish unambiguously their structure.

RESULTS AND DISCUSSION

Figures 1–3 show the structure of compounds **1**, **2** and **3**. The atomic coordinates are reported in Tables 1, 2 and 3, respectively. Tables of bond distances and angles are available as supplementary material from L.C.

Macrocycle **1** is roughly coplanar with the largest derivations from planarity for C(5) and C(7) atoms −0.8 and +0.5 Å, respectively, and adopts an irregular structure. The furazan rings have *cis*-position. In structure **2**, the molecule crystallizes with two independent molecules having a similar conformation (Fig 4). In both molecules, according to Gutsche labelling[4] for

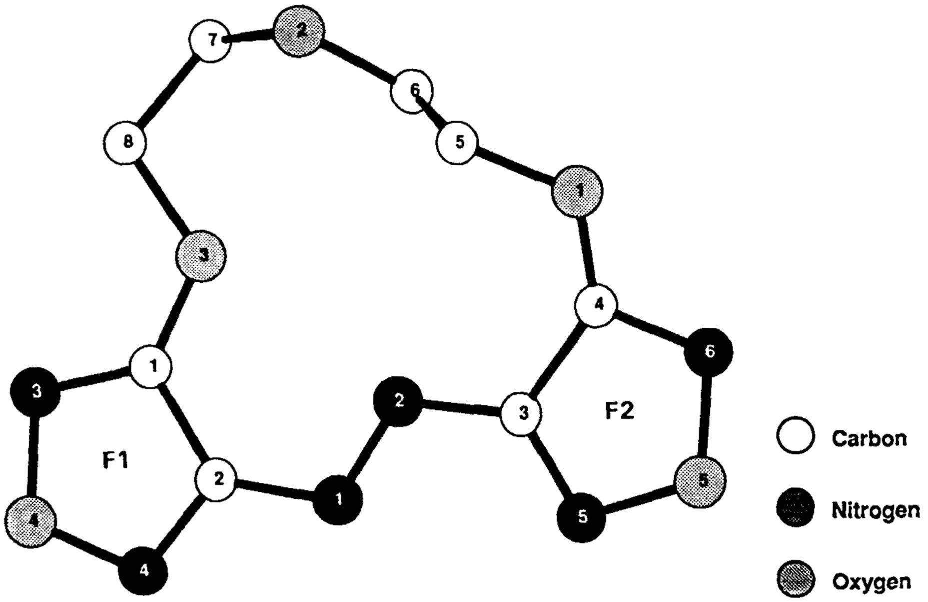

Figure 1 Molecular structure of compound **1** showing the crystallographic numbering scheme. H-atoms are omitted.

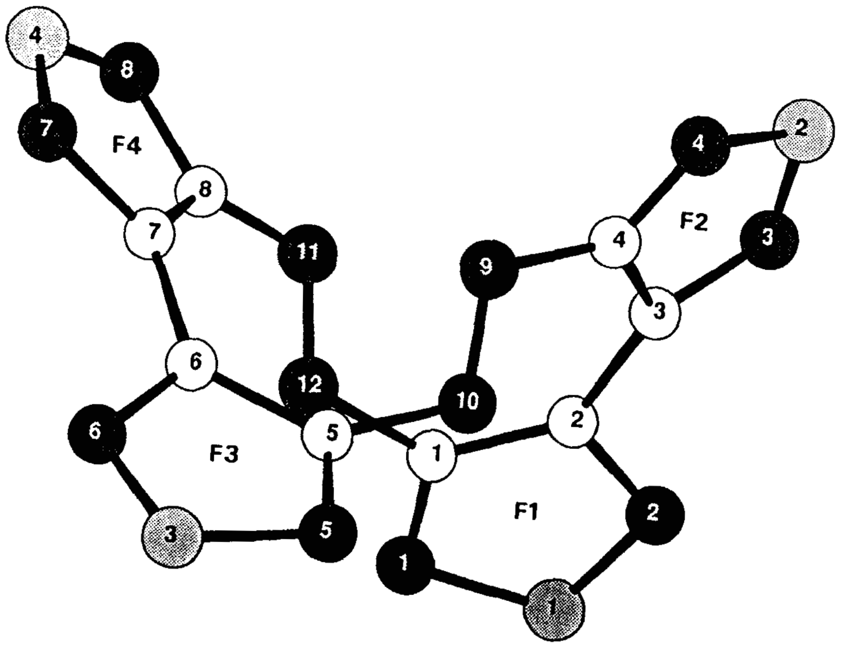

Figure 2 Molecular structure of compound **2** showing the crystallographic numbering scheme.

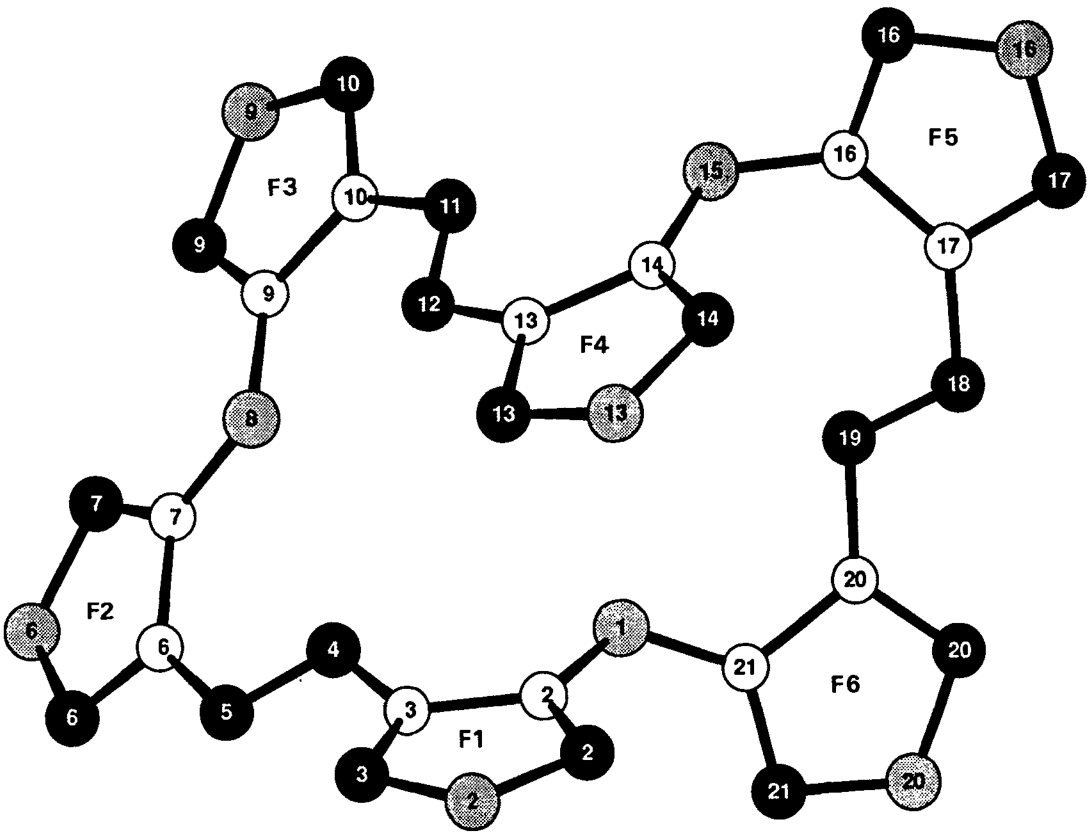

Figure 3 Molecular structure of compound 3 showing the crystallographic numbering scheme.

Table 1 Atomic co-ordinates (x10^4) for structure **1**

Atom	*X*	*Y*	*Z*	*B* (Å^2)
O(1)	7737(5)	2842(7)	3948(4)	6.9(2)
O(2)	5503(5)	1403(7)	4778(4)	5.4(2)
O(3)	4737(4)	1340(6)	3158(4)	4.6(1)
O(4)	4031(5)	227(6)	1225(4)	6.2(2)
O(5)	8611(5)	3977(6)	2090(5)	6.7(2)
N(1)	6148(5)	1924(7)	1642(4)	4.2(2)
N(2)	6417(5)	2262(6)	2352(4)	3.7(2)
N(3)	3845(6)	314(7)	2093(5)	5.3(2)
N(4)	4881(6)	837(7)	985(5)	5.4(2)
N(5)	7775(6)	3414(7)	1739(5)	5.1(2)
N(6)	8676(6)	3795(8)	2969(6)	6.3(2)
C(1)	4589(6)	976(7)	2363(6)	4.1(2)
C(2)	5233(7)	1294(8)	1670(5)	3.8(2)
C(3)	7340(6)	2903(7)	2383(5)	3.9(2)
C(4)	7879(6)	3132(8)	3185(7)	5.0(2)
C(5)	7051(8)	1870(9)	4175(6)	5.3(3)
C(6)	6072(5)	2390(9)	4457(6)	5.4(2)
C(7)	4459(8)	1477(9)	4614(5)	5.2(2)
C(8)	4174(7)	769(9)	3858(6)	5.1(2)

the cyclic tetramer, a 1,3-alternate shape is realized corresponding to the so-called 'propeller' structure. It is an almost perfect C_2 propeller. The 12-membered macrocycle exhibits a 'boat-shape'. Going from the tetramer to the hexamer the conformation of the macrocycle becomes less symmetrical (Fig 3). The 21-membered macrocycle has a flattened saddle shape; the cavity is stretched in one direction with distance O(8)...N(19) 6.287 Å, and is compressed in the orthogonal direction with minimum distance 3.574 Å. All six furazan rings are oriented towards the interior of the cavity: four of them are in the large dimension of the saddle, and two in the orthogonal direction.

In the three structures there are a number of non-bonded distances that are shorter than the accepted van der Waals contacts (Table 4).

Inside of macroring **1** short non-bonded distances N(2)...O(3) 2.759, O(3)...C(6) 2.955 and N(2)...C(5) 3.049 Å of 1...5 type, and O(2)...O(3) 2.769 and N(2)...C(1) 2.804 Å of 1...4 type are observed. On the external edge of the macrocycle, short distances N(1)...N(5) 2.714 and N(3)...C(8) 2.885 Å of 1...4 type are observed.

In structure **2** the cross-ring diagonal distances between 'opposite' nitrogen atoms range from 2.879 to 2.932 Å, the average being 2.898 Å. The cross-ring parallel distances between nitrogen atoms of azo-group show small but significant differences from mentioned distances and range from 3.030 to 3.209 Å

Table 2 Atomic co-ordinates (× 10^4) for two independent molecules in structure **2**

Atom	*X*	*Y*	*Z*	*B* (Å^2)
O(1a)	8424(8)	2527(8)	3099(4)	4.7(2)
O(2a)	5899(8)	−653(8)	4409(4)	4.5(2)
O(3a)	13355(8)	−1927(8)	4479(4)	5.0(2)
O(4a)	9706(9)	−4861(8)	3020(5)	5.2(2)
N(1a)	9158(8)	1422(8)	2909(4)	2.8(2)
N(2a)	7685(9)	2089(9)	3482(4)	3.8(2)
N(3a)	6157(8)	308(9)	4028(4)	3.3(2)
N(4a)	7130(10)	−1420(10)	4602(5)	6.3(3)
N(5a)	12262(7)	−1102(9)	4616(4)	3.5(2)
N(6a)	12799(9)	−2710(10)	4052(5)	4.9(3)
N(7a)	10750(10)	−4578(9)	3450(5)	3.9(2)
N(8a)	8873(8)	−3854(7)	2868(4)	2.5(2)
N(9a)	9139(9)	−1642(8)	4345(4)	3.2(2)
N(10a)	10093(9)	−893(8)	4402(5)	3.6(2)
N(11a)	8686(8)	−1643(8)	3107(4)	2.6(2)
N(12a)	945(9)	−754(9)	3168(4)	3.1(2)
C(1a)	8840(10)	490(10)	3218(5)	3.0(2)*
C(2a)	7980(10)	830(10)	3544(5)	2.4(2)*
C(3a)	7390(10)	150(10)	3964(5)	2.5(2)*
C(4a)	7970(10)	−1030(10)	4362(5)	2.7(2)*
C(5a)	11307(8)	−1497(8)	4322(4)	2.5(2)*
C(6a)	11515(9)	−2500(10)	3964(5)	2.4(2)*
C(7a)	10540(10)	−3250(10)	3532(5)	2.8(2)*
C(8a)	9330(10)	−2840(10)	3160(5)	3.6(2)*
O(1b)	8461(6)	−5637(8)	4422(3)	3.9(2)
O(2b)	4606(8)	−2627(7)	3028(4)	3.6(2)
O(3b)	3392(8)	−10027(7)	3086(3)	3.6(2)
O(4b)	1123(7)	−6890(8)	4471(4)	4.9(2)
N(1b)	7644(6)	−6336(8)	4601(4)	3.1(2)
N(2b)	7821(9)	−4699(8)	3994(4)	3.4(2)
N(3b)	5708(9)	−3036(9)	3428(5)	3.9(2)
N(4b)	3727(9)	−3690(10)	2862(5)	5.0(3)
N(5b)	4064(9)	−9092(8)	2900(5)	4.0(2)
N(6b)	2741(9)	−9610(9)	3495(4)	3.6(2)
N(7b)	1310(10)	−7760(10)	4079(5)	4.8(2)
N(8b)	2143(6)	−6097(8)	4607(4)	3.6(2)
N(9b)	3690(9)	−5837(9)	3125(5)	4.0(2)
N(10b)	4478(8)	−6822(9)	3128(4)	3.2(2)
N(11b)	4293(8)	−5870(9)	4383(4)	3.2(2)
N(12b)	5199(9)	−6637(9)	4366(4)	4.3(2)
C(1b)	634(10)	−5950(10)	4351(6)	3.2(3)*
C(2b)	658(10)	−4890(10)	3934(5)	2.0(2)*
C(3b)	561(10)	−4220(10)	3519(5)	2.9(2)*
C(4b)	4348(9)	−4625(9)	3149(4)	2.2(2)*
C(5b)	3845(9)	−7980(10)	3165(4)	2.4(2)*
C(6b)	297(10)	−8410(10)	3567(5)	3.4(2)*
C(7b)	247(10)	−7520(10)	3986(5)	3.0(2)*
C(8b)	301(10)	−6560(10)	4280(5)	3.2(2)*

Starred atoms were refined with isotropic thermal parameters.

Table 3 Atomic co-ordinates (× 10^4) structure **3**

Atom	*X*	*Y*	*Z*	*B* (Å^2)
O(1)	8545(2)	−1096(6)	7767(2)	3.68(9)
O(2)	8232(2)	−6490(6)	7583(3)	4.9(1)
O(6)	5771(2)	266(9)	4442(2)	5.7(1)
O(8)	6116(2)	1076(6)	6345(2)	4.0(1)
O(9)	5214(3)	5751(7)	6604(3)	6.1(1)
O(13)	7700(2)	−2827(6)	9199(2)	3.9(1)
O(15)	7524(2)	2567(7)	9469(2)	3.7(1)
O(16)	8694(2)	4654(7)	11093(2)	4.1(1)
O(20)	10535(2)	−160(7)	8288(2)	3.62(9)
N(2)	8676(3)	−4792(8)	7954(3)	3.6(1)
N(3)	7623(3)	−5820(8)	6975(3)	4.3(1)
N(4)	7189(2)	−2262(8)	6509(2)	3.1(1)
N(5)	6869(2)	−2969(8)	5863(3)	3.7(1)
N(6)	6197(3)	−1560(10)	4703(3)	5.1(1)
N(7)	5682(3)	1580(10)	5038(3)	4.8(1)
N(9)	5378(3)	4249(8)	6106(3)	5.2(1)
N(10)	5564(3)	5242(9)	7349(3)	5.4(1)
N(11)	6381(2)	2512(8)	7995(3)	3.5(1)
N(12)	6550(3)	616(8)	7898(3)	3.5(1)
N(13)	7189(3)	−2361(8)	8518(3)	3.5(1)
N(14)	7892(3)	−1023(7)	9661(3)	3.6(1)
N(16)	7962(3)	4029(8)	10631(3)	3.7(1)
N(17)	9294(3)	4108(8)	10789(3)	3.8(1)
N(18)	9465(2)	2404(8)	9744(3)	3.4(1)
N(19)	9089(2)	1590(7)	9139(2)	2.7(1)
N(20)	10342(3)	973(7)	8848(3)	3.4(1)
N(21)	9881(3)	−1152(7)	7812(2)	3.4(1)
C(2)	8335(3)	−3149(9)	7585(3)	2.9(1)*
C(3)	7699(3)	−3748(9)	6976(3)	2.9(1)*
C(6)	6381(3	−1370(10)	5428(3)	3.4(1)*
C(7)	6.55(3)	530(10)	5626(3)	2.9(1)
C(9)	5810(3)	2840(10)	6557(3)	3.3(1)*
C(10)	5923(3)	3450(10)	7313(3)	3.5(1)*
C(13)	7046(3)	−323(9)	8550(3)	2.7(1)*
C(14)	7485(3)	493(9)	9246(3)	3.0(1)*
C(16)	8135(3)	3165(9)	10067(3)	2.8(1)*
C(17)	8960(3)	3185(9)	10153(3)	3.0(1)*
C(20)	9581(3)	727(9)	8718(3)	2.5(1)*
C(21)	9312(3)	−582(9)	8084(3)	2.7(1)*

Starred atoms were refined with isotropic thermal parameters.

with average value 3.142 Å. Also, inside the macrocycle the short distances N ... C 1 ... 4 type range from 2.881 to 3.024 Å. The average for two molecules N ... N distance between neighbouring nitrogen atoms of difurazan units is 2.903 Å.

In **3** there is only one cross-ring short distance, N(13) ... C(2) 3.031 Å, and three short contacts of the 1 ... 5 type O(8) ... N(4) 2.805, O(8) ... N(12) 2.777 (inside the macroring) and N(7) ... N(9) 2.764 Å (outside the macroring) are observed.

The above-mentioned decreasing molecular symmetry is shown by the weakening of the through-space interactions as compared with ones in the tetramer. Two short distances N ... N (N(3) ... N(5) 2.774 and N(18) ... N(20) 2.706 Å) and as well some N ... C distances in the range from 2.844 to 3.031 Å of 1 ... 4 type are oserved.

All these macrocycles involve the same subunit, -F-N = N-F-, one in **1**, two in **2** and three in **3**.

In the previously reported structures of the linear polymers, Me-F-N = N-F-Me and Me-F-O-F-N = N-F-O-F-Me have the same fragment azodifurazan

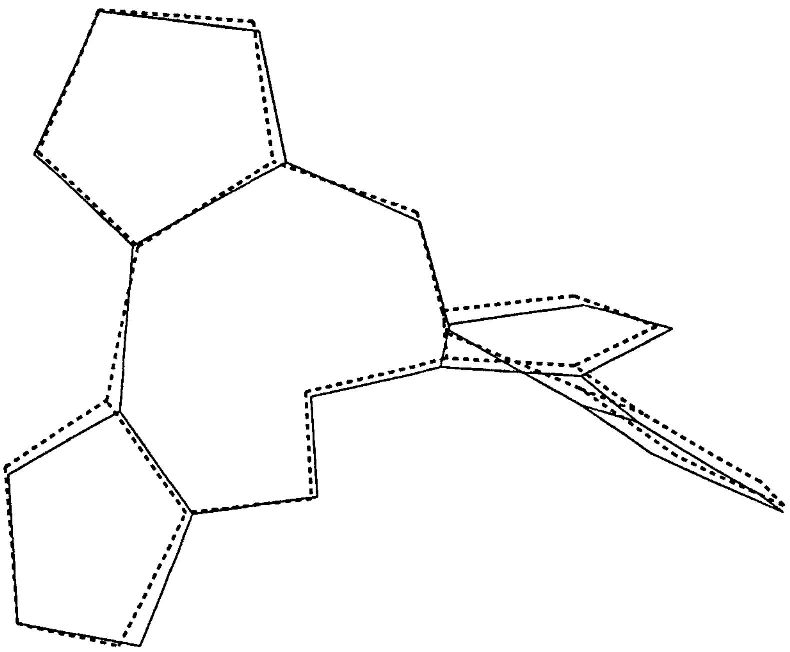

Figure 4 Superposition of two crystallographically independent molecules of 2.

Table 4 Summary of intramolecular non-bonded contacts with distances less than 3.2 Å for the structures 1–3

structure 1			*structure* 3	
O(1) -N(2)	3.146		O(1) -N(4)	2.938
O(2) -O(3)	2.769		-N(19)	2.976
O(3) -N(2)	2.759		-N(13)	3.172
-C(6)	2.955		O(8) -N(12)	2.778
-N(1)	3.116		-N(4)	2.779
N(1) -N(5)	2.714		-N(11)	3.090
-O(3)	3.116		-N(5)	3.100
N(2) -C(1)	2.804		O(15)-N(11)	2.915
-C(5)	3.049		-N(19)	3.045
-O(1)	3.146		-N(12)	3.187
N(3) -C(8)	2.885		N(2) -N(21)	3.174
			N(3) -N(5)	2.774
structure 2			N(4) -C(7)	2.836
	a	*b*	*N*(7) -*N*(9)	2.749
N(2) -*N*(3)	2.880	2.850	-C(9)	2.868
N(6) -N(7)	2.967	2.916	N(9) -C(7)	2.896
N(9) -N(11)	2.890	2.932	N(11)-C(14)	2.887
-C(6)	2.899	2.980	N(12)-C(9)	2.844
-N(12)	3.029	3.141	N(13)-C(2)	3.031
-C(8)	3.103	3.069	-N(19)	3.027
-C(7)	3.110	3.130	N(18)-N(20)	2.706
N(10)-N(12)	2.879	2.893	N(19)-C(16)	2.887
-C(3)	3.024	2.968	-C(14)	2.969
-N(11)	3.209	3.190	N(21)-C(2)	2.931
N(11)-C(2)	2.881	2.942	C(14)-C(17)	3.183

which is planar and has a *trans*-position, *E*-configuration and *ap-ap* conformation.1 However, in macrocycle **1** the *cis*-form of the azodifurazan moiety with *E*, *ap-sp* conformation is observed (Table 5). In **2**, both azodifurazan fragments of each independent molecule are *E*, *trans* with *ac-ac* conformation. As for macrocycle **3**, it contains two azodifurazan subunits in *cis* and one in *trans*-form.

In macrocycle **1** this fragment exhibits significant distortion from coplanarity (**F**1/**F**2: 17.3°). This not too large value comes from torsion about the N(2)-C(3) bond of **F**1 relative to the coplanar azofurazan **F**2 moiety.

The two -O-CH_2-CH_2-O- subunits of the crown ether fragment in molecule **1** are clearly different. The chain comes as close as possible to the azodifurazan system and this causes deviation of the O-C-C-O and C-C-O-C torsion angles from the normal 60, 120 and 180° value in crown ethers.[5] It follows that the conformation of the 13-membered ring is *ap*, +*ac*, +*ac*, −*sc*,*ap*,*ap*,*sp*,*ap*, −*sp*, −*ac* going from atom O(1) counter clockwise.

In both *trans*-azodifurazan fragments of **2**, the furazan rings are rotated around C-N bonds and are practically perpendicular. These building-blocks are linked one to another, forming a symmetrical molecule in which both difurazan units, F1-F2 and F3-F4, have *cis*-position and their **F** rings are rotated around their common link (mean value of dihedral angles, 38.3°).

As mentioned above, in structure **3** two azodifurazan fragments, (**F**1-N = N-**F**2 and **F**5-N = N-**F**6), have the *cis*-position of furazan rings with *E*-configuration and *sc-ap* and *ap-sp* conformation, respectively. In one of them, **F**5-N = N-**F**6, the extremely small torsion angle around the N-C bonds (**F**5/**F**6, 8.7) leads to a nearly

Table 5 Selected torsion angles (°) for structures **1–3**

1		
C(5)-O(1)-C(4)-C(3)	16.6	
C(4)-O(1)-C(5)-C(6)	−100.6	
C(7)-O(2)-C(6)-C(5)	−143.9	
C(6)-O(2)-C(7)-C(8)	96.7	
C(8)-O(3)-C(1)-C(2)	−166.9	
C(1)-O(3)-C(8)-C(7)	−174.7	
C(2)-N(1)-N(2)-C(3)	179.7	
N(2)-N(1)-C(2)-C(1)	−1.0	
N(1)-N(2)-C(3)-C(4)	−166.2	
O(1)-C(5)-C(6)-O(2)	−171.9	
O(2)-C(7)-C(8)-O(3'	−61.9	
3	*a*	*b*
C(4)-N(9)-N(10)-C(5)	−173.4	173.6
N(10)-N(9)-C(4)-N(4)	−138.5	143.2
N(10)-N(9)-C(4)-C(3)	54.2	−45.3
N(9)-N(10)-C(5)-N(5)	−144.0	143.4
N(9)-N(10)-C(5)-C(6)	33.9	−48.5
C(8)-N(11)-N(12)-C(1)	−168.6	168.4
N(12)-N(11)-C(8)-N(8)	−144.1	142.7
N(12)-N(11)-C(8)-C(7)	35.8	−34.4
N(11)-N(12)-C(1)-N(1)	−132.9	145.9
N(11)-N(12)-C(1)-C(2)	47.3	−54.6
N(2)-C(2)-C(3)-N(3)	42.5	−42.4
N(2)-C(2)-C(3)-C(4)	−147.6	141.7
C(1)-C(2)-C(3)-N(3)	−142.9	140.5
C(1)-C(2)-C(3)-C(4)	27.1	−35.4
N(6)-C(6)-C(7)-N(7)	36.9	−34.4
N(6)-C(6)-C(7)-C(8)	−144.0	143.6
C(5)-C(6)-C(7)-N(7)	−144.1	146.3
C(5)-C(6)-C(7)-C(8)	34.9	−35.7
3		
C(21)-O(1)-C(2)-N(2)	33.3	
N(11)-N(12)-C(13)-N(13)	173.6	
C(21)-O(1)-C(2)-C(3)	−148.5	
N(11)-N(12)-C(13)-C(14)	−11.5	
C(2)-O(1)-C(21)-N(21)	51.1	
C(2)-O(1)-C(21)-C(20)	−132.8	
C(9)-O(8)-C(7)-N(7)	−1.6	
C(9)-O(8)-C(7)-C(6)	−179.3	
C(7)-O(8)-C(9)-N(9)	3.3	
C(7)-O(8)-C(9)-C(10)	−176.0	
C(10)-N(11)-N(12)-C(13)	176.2	
C(17)-N(18)-N(19)-C(20)	−178.4	
N(19)-N(18)-C(17)-C(16)	4.5	
N(19)-N(18)-C(17)-N(17)	−178.7	
N(18)-N(19)-C(20)-N(20)	−10.3	
N(18)-N(19)-C(20)-C(21)	168.8	
C(16)-O(15)-C(14)-C(13)	−162.2	
C(16)-O(15)-C(14)-N(14)-	14.9	
C(14)-O(15)-C(16)-N(16)	−123.2	
C(14)-O(15)-C(16)-C(17)	63.7	
C(3)-N(4)-N(5)-C(6)	−178.8	
N(5)-N(4)-C(3)-N(3)	−33.3	
N(5)-N(4)-C(3)-C(2)	154.6	
N(4)-N(5)-C(6)-N(6)	159.6	
N(4)-N(5)-C(6)-C(7)	−17.9	

coplanar geometry of this fragment. The other *cis*-azodifurazan, F1-N = N-F2, is not planar, the furazan rings making a dihedral angle F1/F2 47.8°.

The configuration of the *trans*-azodifurazan subunit F3-N = N-F4 is *Z* with *ap-ap* conformation as it was observed in the previously reported linear polymers, but the furazan rings are twisted around N-C bonds (dihedral angle F3/F4, 27.2°).

These three azodifurazan subunits are linked in the macroring by an oxo-bridge, forming three oxodifurazan subunits: F1-O-F6, F2-O-F3 and F4-O-F5. The first and second units are in *cis*-, and the third one is in the *trans*-position.

In the linear polymers,[1] the same fragments exist, CN-F-O-F-CN and Me-F-O-F-N = N-F-O-F-Me: in both molecules, -F-O-F- subunit is in the *cis*-position with *sp-sp* conformation with dihedral angle between the F rings of 24 and 12.7°, respectively.

In structure **3** the conformation between the two *cis*-oxodifurazan subunits is different: thus, in F2-O-F3, it is *sp-sp*, and in F1-O-F6 *sc-sc*. The conformation of the *trans*-oxodifurazan subunit is *sp-ac*. The values of dihedral angles between furazan rings belonging to these fragments are: F2/F3, 2°; F4/F5, 67.5°; and F1/F6, 72.8°.

These results indicate the various conformations of those macrocycles. We may summarize the general features from this structural investigation:

- In all studied polyfurazans, both *cis*- and *trans*-azodifurazan fragments have *E*-configurations;
- The furazan rings rotate about the exocyclic bonds and this rotation is not limited, so that each subunit, F-F, F-O-F and F-N = N-F, gives rise to a wide variety of dihedral angles between the F rings (values ranging from 0° to 90°);
- In planar or nearly planar azodifurazan fragments the observed *cis*-position is stabilized by a pair of through-space interactions: O ... N (1 ... 5 type) and N ... N (1 ... 4 type); as to the *trans*-position, this is due to pair of identical through-space interactions O(C) ... N of 1 ... 5 type.

Within the experimental error, the bond lengths and angles of furazan rings agree generally well with those found in other difurazan derivatives. Intermolecular contacts in **1–3** are at normal van der Waals separations.

In conclusion, these three macrocycles belong to an original family of molecular receptors. The best candidate for the encapsulation of a metal ion or an organic guest is macrocycle **3**. Its cup-shape and the flexibility of its skeleton are very favourable for the accommodation of a guest in the cavity (Fig 5).

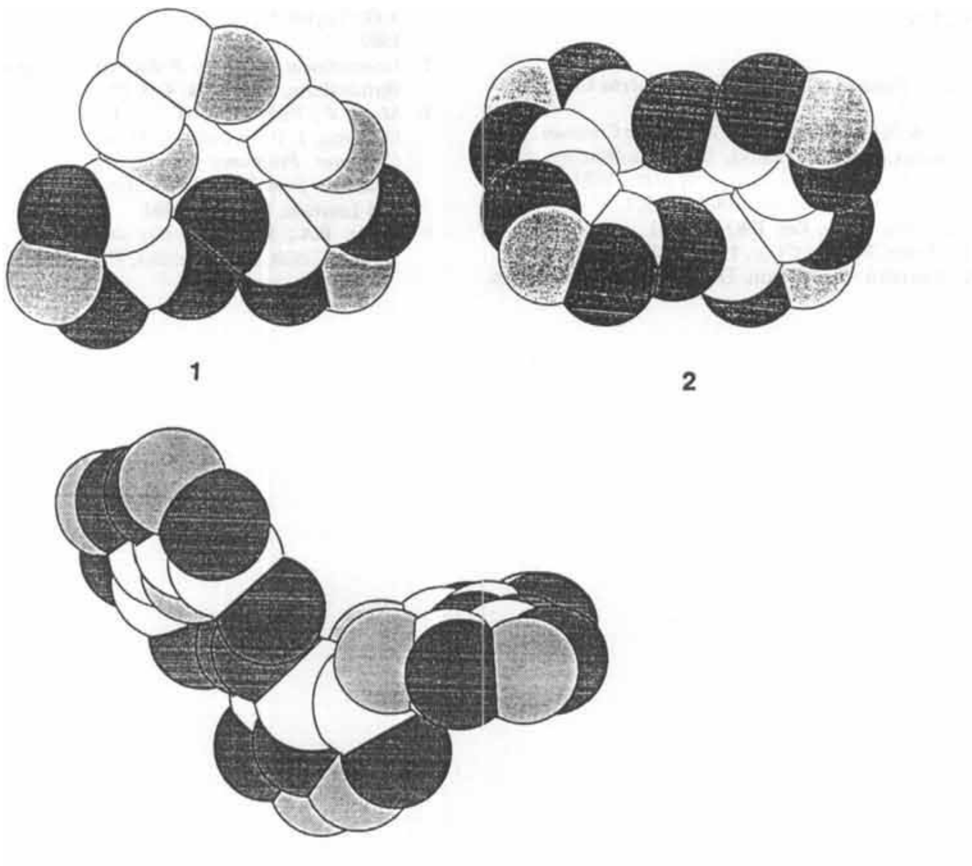

Figure 5 Space-filling models of the macrocycles **1–3**.

EXPERIMENTAL SECTION

Crystal Data **1**: $C_8H_8N_6O_5$, mol wt = 268.19, orthorhombic, Pbca, a = 13.216(4), b = 11.067(4), c = 15.906(4) Å, V = 2326.4 Å^3, Z = 8, d_{calc} = 1.531 g.cm^{-3}, R = 0.055 for 735 reflections with $I > 3\ \sigma(I)$.

2: $C_8N_{12}O_4$, mol wt = 328.17, nonoclinic, $P2_1/c$, a = 10.207(3), b = 10.210(3), c = 23.844(9) Å, β = 102.22(3)°, V = 2428.62 Å^3, Z = 8, two independent molecules in the asymmetric unit, d_{calc} = 1.795 g.cm^{-3}, R = 0.096 for 1726 reflections with $I > 3\ \sigma(I)$.

3: $C_{12}N_{18}O_9$, mol wt = 540.25, monoclinic, $P2_1/c$, a = 17.619(4), b = 6.264(11), c = 18.476(5) Å, β = 105.74(2)°, V = 1962.59 Å^3, Z = 4, d_{calc} = 1.828 g.cm^{-3}, R = 0.034 for 1149 reflections with $I > 3\ \sigma(I)$. All X-ray diffraction data were collected at room temperature on a ENRAF-NONIUS CAD4 diffractometer with graphite monochromated MoK_α-radiation (λ = 0.71073 Å) with the $\omega/2\theta$-scan technique. Lattice constants were determined by least-squares fitting of the setting angles of 25 reflections in the range $10 < \theta < 14°$. Intensities of three standard reflections were measured every 2 h and did not show significant variations for any of the three compounds investigated. All intensities were collected in the range $1.5 \langle \theta \langle 30°$ and corrected for Lorenz and polarization effects but absorbtion was ignored. Scattering factors were taken from ref.[7] Structures were solved by using MULTAN82.[8] All calculations were accomplished by the SDP system of programs.[9] All structures were refined by full-matrix least-squares. Refinement was anisotropic for all non-H atoms of molecule **1**, structure **2** was refined isotropically. In **3** refinement was anisotropic for N and O atoms and isotropic for c atoms. All H atoms in **1** were inserted in calculated positions and their contributions were included in structure factor-calculation.

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