organic compounds

Difurazano[3,4-b:3′,4′-f]-4,5-diaza-1,8-dioxacyclododecine and an acyclic analogue

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The novel title furazan-containing macrocycle (systematic name: 6,9,14,17-tetraoxa-2,3,5,7,16,18-hexaazatricyclo[13.3.0.- $0^{4,8}$]octadeca-4,7,15,18-tetraene), $C_8H_{10}N_6O_4$, (I), is the first macrocycle where the furazan rings are connected via a hydrazine group. In spite of the strain in the 12-membered macrocycle of (I), the geometry of the furazan fragment is the same in (I) and in its acyclic analogue 1,8-bis(5-aminofurazan-4-yloxy)-3,6-dioxaoctane, $C_{10}H_{16}N_6O_6$, (II). In both compounds, the participation of the furazan rings in intermolecular hydrogen bonding equalizes the N—O bonds within the furazan rings, in contrast with rings which do not participate in such interactions.

Comment

Furazan derivatives have potential as high-energy materials (Coburn, 1968; Beal & Brill, 2000), and it has been shown that these compounds are useful as ingredients of explosives and rocket propellants (Sheremetev et al., 1996; Batog et al., 1998). At the same time, furazan-containing macrocycles have exhibited interesting biological and pharmacological properties, for instance, as effective inhibitors of soluble guanylate cyclase (Kots et al., 1999; Sheremetev et al., 2000). Recently, we have been involved in the construction of furazan-containing macrocycles (Sheremetev, Shatunova et al., 2004; Sheremetev, Ivanova et al., 2004), in which the macrocyclic furazan fragments are linked by a rigid azo group.

In the present paper, we discuss the structure of a new 12-membered macrocycle containing two furazan rings linked by the less rigid hydrazine group, namely difurazano[3,4-b:3′,4′-f]-4,5-diaza-1,8-dioxacyclododecine, (I). We also describe the structure of 1,8-bis(3-aminofurazan-4-yloxy)-3,6-dioxaoctane, (II), which is an acyclic analogue of (I). We are interested in

the influence of steric factors caused by the macrocyclic structure of the molecule on the geometry of the furazan rings. Compound (II) is not an exact acyclic analogue of (I) because the former contains the additional O5—C7—C8—O6 fragment, but this fragment should not influence the geometry of the furazan rings, because it is remote from them.
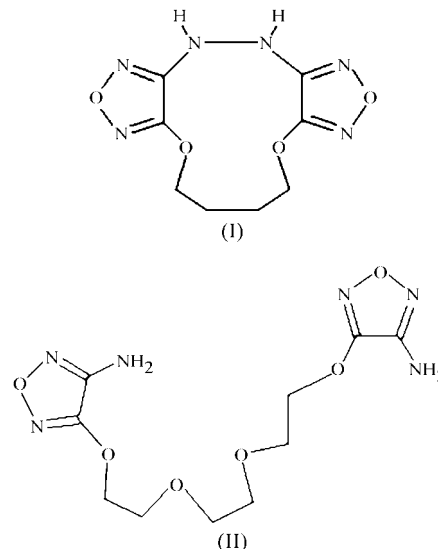
Ellipsoid plots of the molecules of (I) and (II) are presented in Figs. 1 and 2, respectively. Due to the incorporation of the hydrazine group, the molecule of (I) is non-planar, unlike previously studied macrocycles, where the furazan rings were connected via an azo group (Sheremetev, Shatunova et al., 2004; Sheremetev, Ivanova et al., 2004) or an ether O atom (Averkiev et al., 2003). The dihedral angle between the furazan rings in (I) is 99.0° (Fig. 1). The molecule of (II) is also non-planar and adopts a crimped shape (Fig. 2).

The strain in the macrocycle of (I) is evident from the increased bond angles at atoms C6, C7 and C8 [113.8 (2), 114.9 (2) and 111.8 (2)°, respectively] relative to the ideal tetrahedral angle. However, the bond angles at atoms O1 and
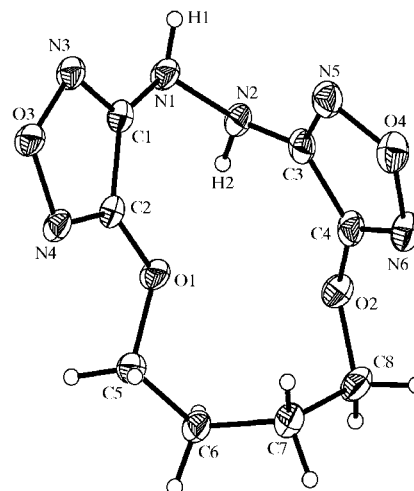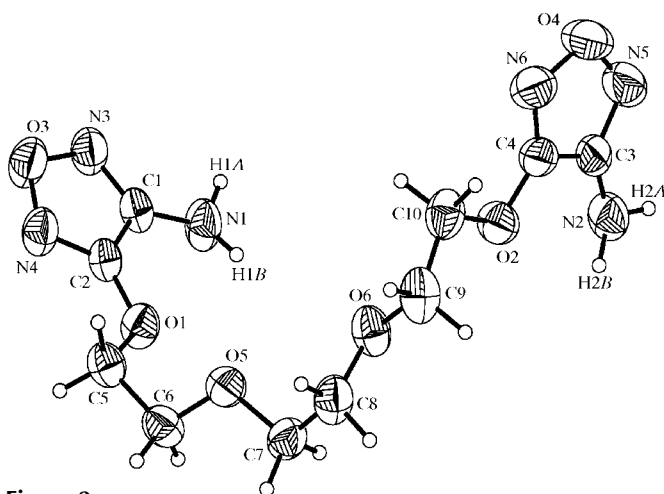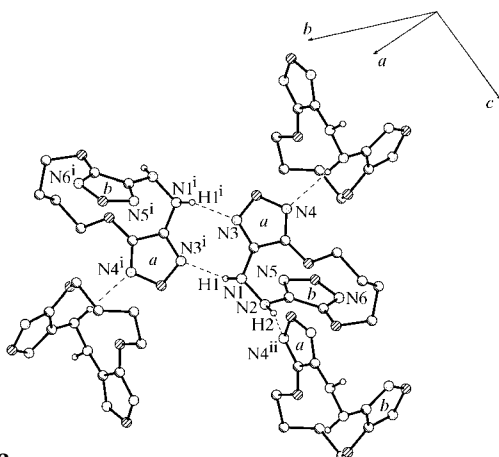

Figure 1
A general view of (I), showing the atom-numbering scheme and displacement ellipsoids drawn at the 50% probability level.

O2 are not increased in comparison with those in (II): in both compounds, these are between 115 and 116°. Perhaps the slight lengthening of the C—C bonds within the furazan rings in (I), to 1.443 (2) Å for C1—C2 and 1.437 (2) Å for C3—C4, in comparison with values of 1.429 (2) and 1.423 (3) Å for the respective analogous bonds in (II) and the standard database value of 1.428 Å (Allen *et al.*, 1987), may be explained by the strained structure of (I) (Tables 1 and 3).

In spite of possible conjugation between the lone pairs of the N atoms and the π system of the furazan rings, the configuration around atoms N1 and N2 is noticeably non-planar; the sum of the bond angles is 346 (2)° for N1 and 341 (2)° for N2 in (I), and 348 (2)° for N1 and 345 (2)° for N2 in (II). The trigonal configuration of the N atoms in (I) cannot be explained by steric interactions with neighbouring alkoxy substituents (Borbulevych *et al.*, 2002), because deviation from planarity does not affect the N1—H1A···O1 and N2—H2A···O2 intramolecular contacts (2.67 and 2.65 Å, respectively). The corresponding N—H···O distances for the

calculated planar configuration of an N atom are 2.68 and 2.67 Å, and are very close to the sum of the van der Waals radii of O and H atoms (2.65 Å; Rowland & Taylor, 1996). In (I), the non-planar coordination at N1 and N2 can be attributed in part to the cyclic structure of the molecule. In both compounds, the bond angles at the O atoms of the methoxy fragments [115.2 (2)–116.5 (2)°] are slightly wider than the average value of 112.9° found for the unconjugated C—O—C fragment in the Cambridge Structural Database (CSD, Version of April 2002; Allen, 2002).

Analysis of the furazan geometry in (I) and (II) reveals the unexpected feature that, in each compound, the geometries of the two chemically equivalent furazan rings are slightly different. It might be expected that the lengths of the N—O bonds close to the alkoxy substituents should be about 1.379–1.390 Å, as we reported previously (Averkiev *et al.*, 2003), while the lengths of the N—O bonds close to an amine or hydrazine group should be about 1.400–1.411 Å, according to our analysis of aminofurazan fragments in the CSD. However, only the C3—N5—O4—N6—C4 furazan ring in both compounds shows the expected lengths for the N—O bonds: O4—N5 is elongated to 1.410 (2) Å in (I) and 1.411 (3) Å in (II), while O4—N6 is shortened to 1.391 (3) Å in (I) and 1.393 (3) Å in (II). Meanwhile, the O3—N3 and O3—N4 bonds in both compounds are unexpectedly equal, at 1.399 (2) and 1.395 (2) Å, respectively, for (I), and 1.402 (2) Å and 1.403 (2) Å, respectively, for (II). The only explanation that we can suggest is participation of atoms N3 and N4 in both compounds in the intermolecular hydrogen bonds (see below).

Molecules of (I) are arranged in centrosymmetrical dimers linked by N1—H1···N3 hydrogen bonds. These dimers are arranged into crimped layers by another hydrogen bond, *viz.* N2—H2···N4 (Table 2 and Fig. 3). These layers are parallel to the (10$\bar{1}$) plane. Molecules of (II) are arranged in helices along the *b* direction. All molecules in a helix are translationally identical, hence each molecule composes one coil of the helix. Two intermolecular hydrogen bonds, namely N2—H2B···O5

Figure 2
A general view of (II), showing the atom-numbering scheme and displacement ellipsoids drawn at the 50% probability level.

Figure 3
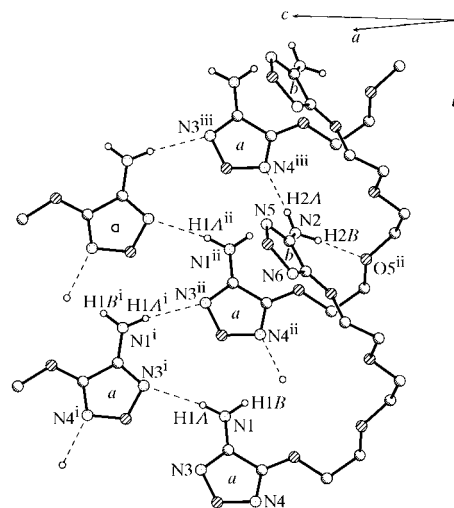The hydrogen-bonding scheme in (I); the symmetry codes are as given in Table 2.

Figure 4
The hydrogen-bonding scheme in (II); the symmetry codes are as given in Table 4.

organic compounds

and N2—H2A···N4, were found inside each helix (Table 4 and Fig. 4). Each helix is connected by N1—H1A···N3 hydrogen bonds to a neighbouring helix, symmetrically related by 2_1 screw axes. As can be seen from the pattern of hydrogen bonds, for both compounds (I) and (II), one furazan ring (C1—C2—N3—O3—N4, labelled 'a' in Figs. 3 and 4) participates in intermolecular hydrogen bonding via both N atoms, while the other furazan ring (C3—C4—N6—O4—N5, labelled 'b') does not participate in hydrogen bonding. We believe that it is because of this hydrogen bonding that the N—O bonds in the C1—C2—N3—O3—N4 ring are equal.

Experimental

Compound (I) (m.p. 333–334 K) was obtained in 40% yield according to the literature procedures of Kharitinova *et al.* (1991) and Shatunova & Sheremetev (1995). X-Ray quality crystals of (I) were grown by slow evaporation of a methanol solution at room temperature. Using the previously reported procedure of Poncio & Avogadro (1923), compound (II) (m.p. 453–454 K) was obtained in 52% yield by reduction of the N=N bond in the corresponding azomacrocycle [1,2] with phenyl hydrazine in Et$_2$O at room temperature. Separation of (II) by flash chromatography followed by recrystallization from AcOH solution afforded X-ray quality crystals.

Compound (I)

Crystal data

C$_8$H$_{10}$N$_6$O$_4$	$D_x = 1.558$ Mg m^{-3}
$M_r = 254.22$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/n$	Cell parameters from 908
$a = 8.3331$ (12) Å	reflections
$b = 14.695$ (2) Å	$\theta = 3$–29°
$c = 9.2384$ (13) Å	$\mu = 0.13$ mm^{-1}
$\beta = 106.619$ (3)°	$T = 110$ (2) K
$V = 1084.1$ (3) Å^3	Rectangular prism, colourless
$Z = 4$	$0.4 \times 0.3 \times 0.3$ mm

Data collection

Bruker SMART 1000 CCD area-detector diffractometer	2100 independent reflections
	1757 reflections with $I > 2\sigma(I)$
φ and ω scans	$R_{int} = 0.025$
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1998)	$\theta_{max} = 26.0°$
	$h = -10 \rightarrow 8$
$T_{min} = 0.882$, $T_{max} = 0.965$	$k = -16 \rightarrow 18$
4776 measured reflections	$l = -9 \rightarrow 11$

Refinement

Refinement on F^2	All H-atom parameters refined
$R[F^2 > 2\sigma(F^2)] = 0.056$	$w = 1/[\sigma^2(F_o^2) + (0.1347P)^2]$
$wR(F^2) = 0.171$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.06$	$(\Delta/\sigma)_{max} = 0.001$
2100 reflections	$\Delta\rho_{max} = 0.53$ e Å^{-3}
203 parameters	$\Delta\rho_{min} = -0.34$ e Å^{-3}

Table 1
Selected interatomic distances (Å) for (I).

O1—C2	1.330 (2)	O3—N4	1.3951 (18)
N1—C1	1.378 (2)	O3—N3	1.3991 (19)
N1—N2	1.417 (2)	C3—N5	1.301 (2)
C1—N3	1.307 (2)	C3—C4	1.437 (2)
C1—C2	1.443 (2)	O4—N6	1.391 (2)
O2—C4	1.336 (2)	O4—N5	1.410 (2)
N2—C3	1.381 (2)	C4—N6	1.296 (2)
C2—N4	1.301 (2)		

Table 2
Hydrogen-bonding geometry (Å, °) for (I).

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1···N3^i	0.83 (2)	2.18 (2)	2.974 (2)	159 (2)
N2—H2···N4^{ii}	0.87 (2)	2.21 (2)	3.066 (2)	167 (2)

Symmetry codes: (i) $1 - x, 1 - y, 1 - z$; (ii) $\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z$.

Compound (II)

Crystal data

C$_{10}$H$_{16}$N$_6$O$_6$	Mo $K\alpha$ radiation
$M_r = 316.29$	Cell parameters from 24
Monoclinic, $C2/c$	reflections
$a = 31.363$ (6) Å	$\theta = 11$–13°
$b = 6.0550$ (12) Å	$\mu = 0.12$ mm^{-1}
$c = 15.724$ (3) Å	$T = 293$ (2) K
$\beta = 98.34$ (3)°	Plate, colourless
$V = 2954.5$ (10) Å^3	$0.4 \times 0.3 \times 0.1$ mm
$Z = 8$	
$D_x = 1.422$ Mg m^{-3}	

Data collection

Enraf–Nonius CAD-4 diffractometer	$\theta_{max} = 25.5°$
	$h = 0 \rightarrow 36$
$\theta/\frac{5}{3}\theta$ scans	$k = 0 \rightarrow 7$
2742 measured reflections	$l = -19 \rightarrow 18$
2689 independent reflections	2 standard reflections
1877 reflections with $I > 2\sigma(I)$	every 98 reflections
$R_{int} = 0.032$	intensity decay: 2.5%

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0625P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.036$	$+ 0.8023P]$
$wR(F^2) = 0.109$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.00$	$(\Delta/\sigma)_{max} = 0.003$
2689 reflections	$\Delta\rho_{max} = 0.13$ e Å^{-3}
263 parameters	$\Delta\rho_{min} = -0.15$ e Å^{-3}
All H-atom parameters refined	

Table 3
Selected interatomic distances (Å) for (II).

O1—C2	1.324 (2)	O3—N3	1.402 (2)
C1—N3	1.297 (2)	O3—N4	1.403 (2)
C1—N1	1.360 (2)	C3—N5	1.296 (2)
C1—C2	1.429 (2)	C3—C4	1.423 (3)
O2—C4	1.335 (2)	O4—N6	1.393 (3)
C2—N4	1.290 (2)	O4—N5	1.411 (3)
N2—C3	1.345 (3)	C4—N6	1.295 (2)

Table 4
Hydrogen-bonding geometry (Å, °) for (II).

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1A···N3^i	0.91 (2)	2.25 (2)	3.148 (3)	169 (2)
N2—H2B···O5^{ii}	0.90 (3)	2.13 (3)	3.024 (2)	170 (2)
N2—H2A···N4^{iii}	0.83 (3)	2.44 (3)	3.196 (3)	151 (2)

Symmetry codes: (i) $\frac{1}{2} - x, y - \frac{1}{2}, \frac{5}{2} - z$; (ii) $x, y - 1, z$; (iii) $x, y - 2, z$.

In both compounds, all H atoms were refined. The C—H distances are in the range 0.95 (2)–1.01 (3) Å in (I) and in the range 0.96 (2)–1.03 (2) Å in (II).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: BM1564). Services for accessing these data are described at the back of the journal.

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