First representatives of macrocyclic poly(diazene oxide furazans): 3,4:7,8:11,12:15,16-tetrafurazano-1,2,5,6,9,10,13,14-octaazacyclohexadeca-1,3,5,7,9,11,13,15-octaene 1,9- and 1,10-dioxides; 1,5,9,13-tetraoxide and its crystal structure

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Macrocyclic poly(diazene oxide furazans) have been synthesised for the first time: the tetraoxide was prepared by the oxidation of diazene fragments in the tetradiazenofurazan macrocycle, and the dioxides were synthesised by the intramolecular and intermolecular oxidative cyclisation of structures already containing diazene oxide fragments. The structure of the tetraoxide derivative has been established by X-ray diffraction analysis.

Previously, we have reported[1–4] on the preparation of macrocycles consisting only of diazenofurazan fragments. In this work, we have studied two approaches to the synthesis of similar macrocyclic systems that incorporate diazene oxide groups.

One of the approaches involves oxidation of the diazene fragments in previously obtained macrocyclic systems using oxidising mixtures based on H_2O_2 (30%, 85%) or $(NH_4)_2S_2O_8$ in the presence of concentrated H_2SO_4 or oleum (10%, 30%, 60%). According to the other approach, the desired macrocycles are obtained by forming diazene bridges by the oxidative cyclisation of diamines already containing N=N(O) fragments.

The first approach was studied using the tetradiazenofurazan macrocycle **1** as an example, and the second method was investigated in relation to 4,4′-diamino-3,3′-azoxyfurazan **2** and bis[4-aminofurazanyl-3-azoxy]azofurazan **3**[†] (Schemes 1 and 2).

Since compound **1** incorporates four diazene groups, its oxidation can lead, in principle, to several species differing either in the number of diazene oxide groups or (if the numbers of these groups are the same) in the position of the *N*-oxide oxygen atoms with respect to the same furazan rings (whether it is distal or proximal) and in their spatial arrangement with respect to the macrocycle (directed inwards or outwards).

It has been shown[5] that oxidation of the macrocycle containing two diazenodifurazanyl fragments by Caro's acid in oleum results in the conversion of both diazene groups into diazene oxide groups, an equimolar mixture of isomeric bis(diazene oxides) being formed.

We have found that when the macrocycle **1** is oxidised by the above oxidising systems, the prevailing reaction pathway leads to the tetraoxide **4** under most of the conditions studied.[‡]

The structure of the macrocycle **4** was determined based on combined data from elemental analysis, IR, ^{13}C NMR, ^{14}N

[†] The diamine **3** was kindly provided by V. O. Kulagina Ph.D. (N. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences).

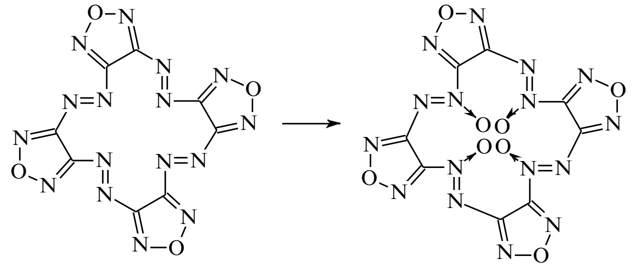
[‡] Compound **4** precipitated from the reaction mixture or was settled out with ice water. Compound **5** was isolated by subjecting to column chromatography (silica gel L 100/250, C_6H_6 as an eluent) the mixture of compounds precipitated with water from the mother liquor remaining after isolation of the macrocycle **4**. The macrocycles **6** and **7** were separated by column chromatography (silica gel L 40/100, a 1 : 1 : 1 $CHCl_3$–CH_2Cl_2–hexane mixture as the eluent).

For **4**: mp 234–235 °C (MeOH); yield 60–72%; R_f 0.6 (eluent C_6H_6); IR (KBr), ν/cm^{-1}: 1560, 1500, 1470, 1410, 1350, 1170, 1120, 1040, 930, 910, 765, 755, 735, 725; ^{13}C NMR ([$^2H_6$]acetone) δ 150.13 (C–N=NO), 155.93 (C–NO=N); ^{14}N NMR ([$^2H_6$]acetone) δ −83.19 (N→O); MS *m/z*: 448 [M$^+$], 432 [M$^+$ − O], 416 [M$^+$ − 2(O)], 400 [M$^+$ − 3(O)], 364 [M$^+$ − C_2N_2O − O].

For **5**: mp 50 °C; yield 5%; R_f 0.34 (eluent C_6H_6); IR (KBr), ν/cm^{-1}: 1575, 1515, 1360, 1190, 1050, 950, 910, 895; MS *m/z*: 432 [M$^+$], 416 [M$^+$ − O].

For **6**: mp 144–145 °C (C_6H_6); yield 59–92%; R_f 0.47 (hexane–CH_2Cl_2 1 : 1); IR (KBr), ν/cm^{-1}: 1560, 1510, 1330, 1235, 1180, 1040, 940, 920, 890, 740, 720; ^{13}C NMR (CD_3CN) δ 150.1, 154.6, 157.8, 159.7; ^{14}N NMR ([$^2H_6$]acetone) δ −65.3 (N→O); MS *m/z*: 416 [M$^+$], 400 [M$^+$ − O], 386 [M$^+$ − NO], 276.

For **7**: mp 105–106 °C (C_6H_6); yield 30%; R_f 0.30 (hexane–CH_2Cl_2 1 : 1); IR (KBr), ν/cm^{-1}: 1550, 1510, 1330, 1250, 1170, 1040, 940, 890, 770; ^{13}C NMR (CD_3CN) δ 148.0, 148.1, 157.6, 157.8, 157.9, 159.8, 159.9, 160.3; ^{14}N NMR ([$^2H_6$]acetone) δ −67.0 (N→O); MS *m/z*: 416 [M$^+$], 400 [M$^+$ − O], 370 [M$^+$ − O − NO], 348, 304.



Scheme 1 *Reagents and conditions*: H_2O_2, oleum (conc. H_2SO_4); oleum, $[(NH_4)_2S_2O_8]$, 10–15 °C.

NMR, mass spectra§ and X-ray diffraction analysis.¶ The ^{13}C NMR spectrum exhibits only two signals corresponding to the carbon atoms of the furazan rings, which attests to the same alternation of the *N*-oxide groups. This is also indicated by the ^{14}N NMR spectrum, which exhibits one signal due to the nitrogen atom in the *N*-oxide fragment. The X-ray diffraction data confirmed this assumption (Figure 1).

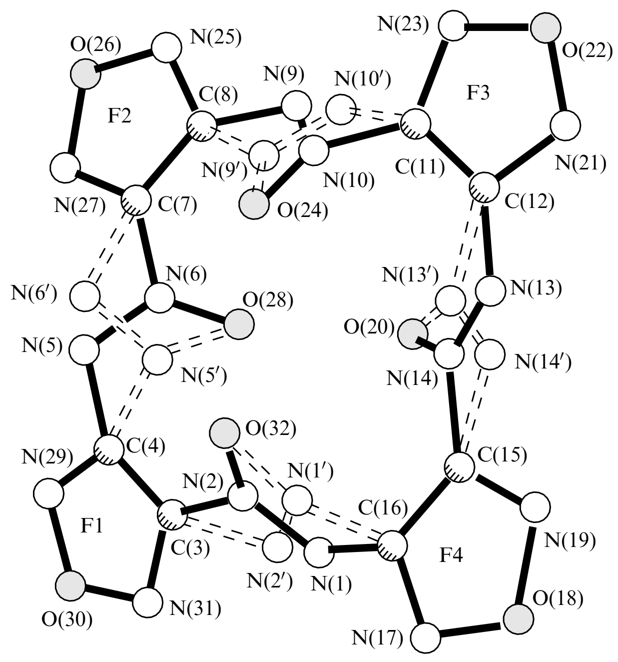
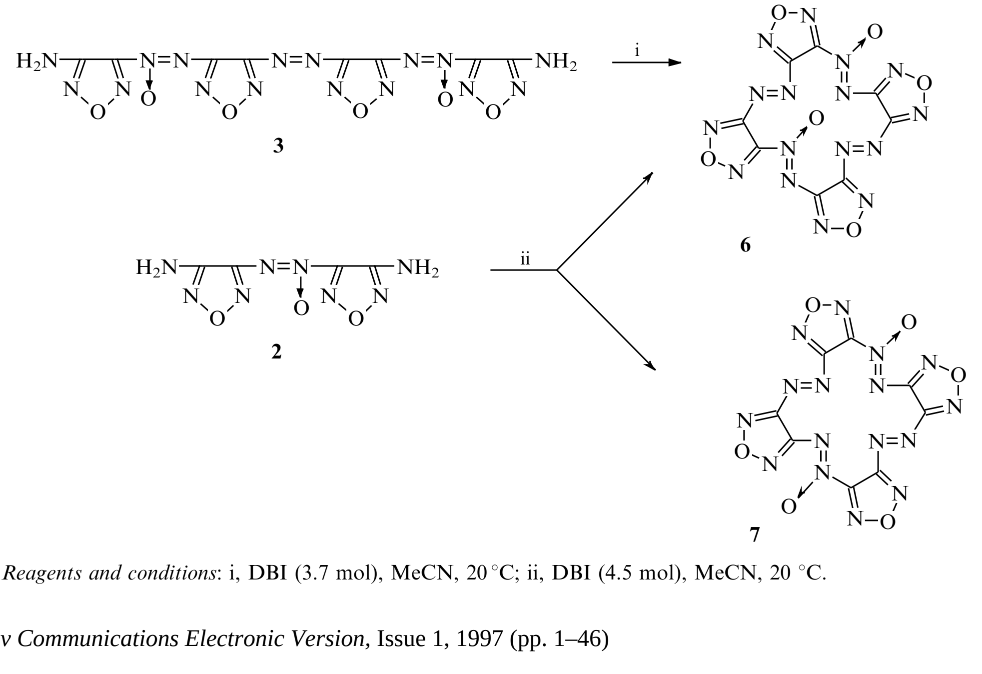


Figure 1 Molecular structure of **4**.

The tetraoxide molecule consists of planar furazan rings joined by strictly alternating diazene oxide bridges. The macrocycle is nonplanar: the furazan rings are rotated with respect to one another through angles of 11.7, 6.7, 10.1 and 13.9° (plane F1-F2, F2-F3, F3-F4 and F1-F4, respectively), and the azo bond in each diazene oxide furazan fragment occurs in the ˜sc-ap and ˜sp-ap orientation with respect to the nearest C=N bond of the furazan ring (Table 1). The oppositely positioned oxygen atoms are arranged in pairs above and below the plane of the picture and are directed inside the macrocycle. The distances between the O(20)···O(28), O(20)···O(24) and O(24)···O(28) atoms, equal to 2.763(7), 2.853(8) and 2.877(6) A, respectively, are somewhat shorter than the sum of the van der Waals radii (3.04 A)[7] (Figure 1, Table 1).

Apart from compound **4**, one more compound, namely compound **5**, was isolated in low yield (5%) from the products of the oxidation of **1**. Based on the mass spectra, the structure of a four-unit macrocycle consisting of one diazenofurazan and three diazene oxide furazan units was assigned to this product.



Scheme 2 *Reagents and conditions*: i, DBI (3.7 mol), MeCN, 20 °C; ii, DBI (4.5 mol), MeCN, 20 °C.

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§ The elemental analysis data for the compounds **4**, **6** and **7** correspond to the calculated data. NMR spectra were obtained on a Bruker AM-300 instrument. IR spectra were measured on a UR-20 spectrometer and mass spectra were recorded on a Varian MAT CH6 instrument. The TLC of the reaction products was performed on Silufol UV-254 plates.

¶ *Crystallographic data for* **4**: $C_8H_{16}O_8$, $M = 448.2$, monoclinic, space group *Pc*, $a = 9.662(2)$, $b = 13.989(3)$, $c = 5.729(1)$, $\beta = 96.69(3)$, $V = 769.1(3)\,A^3$, $d_{calc} = 1.936$ g cm^{-3}, $Z = 2.2160$ independent reflections with $I \geqslant 2\sigma(I)$ measured at 183 K on a Siemens P3/PC diffractometer (λMoK$\alpha = 0.71069$ A, graphite monochromator, $\theta/2\theta$-scanning, $2\theta \leqslant 54°$).

The structure **4** was solved by direct methods and refined by a full-matrix least-squares method in anisotropic [for the N(1′), N(2′), N(5′), N(6′), N(9′), N(10′), N(13′) and N(14′) atoms] and isotropic approximations. The nitrogen atoms of the diazene oxide groups are disordered over two positions [N(1), N(2), N(5), N(6), N(9), N(10), N(13), N(14) with site occupation factors equal to 0.8 and N(1′), N(2′), N(5′), N(6′), N(9′), N(10′), N(13′), N(14′) equal to 0.2]. The final discrepancy factors were $R = 0.0504$, $R_w = 0.0496$. All calculations were performed on an IBM-PC/AT using the SHELXTL PLUS programs.[8] Full lists of bond angles, bond lengths, atomic coordinates and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). For details, see ‘Notice to Authors’, *Mendeleev Commun.*, 1997, issue 1. Any request to the CCDC for data should quote be full literature citation and the reference number 1135/12.

Table 1 Torsion angles in diazenoxidofurazan fragments of **4**.

Fragment	Angle/°
N(1)–N(2)–C(3)–N(31)	43.4
N(2)–N(1)–C(16)–N(17)	−131.4
N(13)–N(14)–C(15)–N(19)	−31.4
N(14)–N(13)–C(12)–N(21)	−146.6
N(9)–N(10)–C(11)–N(23)	42.8
N(10)–N(9)–C(8)–N(25)	136.5
N(5)–N(6)–C(7)–N(27)	−30.9
N(6)–N(5)–C(4)–N(29)	−143.3

To synthesize macrocyclic systems with an *a fortiori* known sequence of oxygen atoms in the diazene oxide groups, oxidation of the diamines **2** and **3** through the action of dibromoisocyanurate (DBI) was studied. Previously we successfully used this reagent for macrocyclocondensation of several diamines of the furazan series.[2,3,5,6] We found that the diamine **3** undergoes intramolecular oxidative cyclisation to give 3,4:7,8:11,12:15,16-tetrafurazano-1,2,5,6,9,10,13,14-octaazacyclohexadeca-1,3,5,7,9,11,13,15-octaene 1,10-dioxide **6**, whereas in the case of the diamine **2**, intermolecular cyclocondensation occurs yielding two isomeric compounds, namely, the dioxide **6** (as the major product) and 3,4:7,8:11,12:15,16-tetrafurazano-1,2,5,6,9,10,13,14-octaazacyclohexadeca-1,3,5,7,9,11,13,15-octaene 1,9-dioxide **7** (Scheme 2).

The structures of the compounds **6** and **7** were determined based on the combined elemental analysis data, IR, ^{13}C NMR, ^{14}N NMR and mass spectra.[§]

The arrangement of the *N*-oxide atoms in the compound **6** is unambiguously determined by the positions of these atoms in the initial diamine **3**. Thus, the second isomer obtained by the oxidation of **2** has the structure of **7**.

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