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NOVEL METHOD FOR SYNTHESIS OF 3,4:7,8:11,12:15,16-TETRAFURAZANO-1,2,5,6,9,10,13,14-OCTAAZACYCLOHEXADEKA-1,3,5,7,9,11,13,15-OCTAENE AND ITS CRYSTAL STRUCTURE

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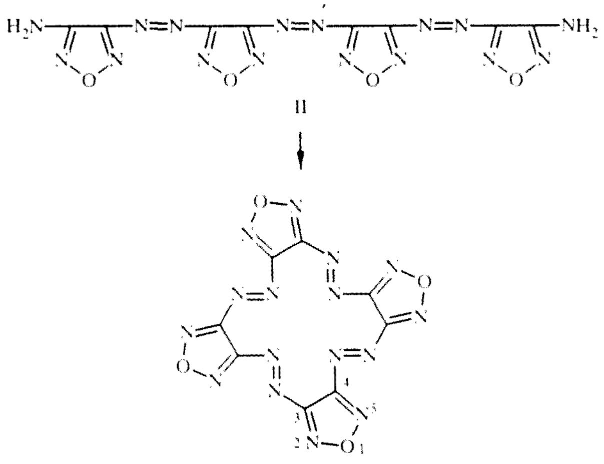
We have established the formation of a tetradiazenofurazan macrocycle as a result of intramolecular oxidative cyclization of 4,4'-bis(4-aminofurazanyl-3-azo)-3,3'-azofurazan and have studied its crystal structure.

By means of intermolecular oxidative cyclocondensation of 3,4-diaminofurazan or 4,4'-diamino-3,3'-azofurazan with treatment by a mixture of $Pb(OAc)_4$ and Bu_4NBr, for the first time we have obtained polydiazenofurazan macrocycles. The predominant compound among these contains four diazenofurazan moieties: 3,4:7,8:11,12:15,16-tetrafurazano-1,2,5,6,9,10,13,14-octaazacyclohexadeka-1,3,5,7,9,11,13,15-octaene (I) [1].

In this report, we propose a novel method for obtaining I in quantitative yield by treatment of 4,4'-bis(4-aminofurazanyl-3-azo)-3,3'-azofurazan (II)[†] with the mentioned oxidative mixture, and also dibromoisocyanurate (DBI), successfully used previously for oxidation of heterocyclic amines to azo compounds [2] and also for the formation of macrocycles from diamines [3,4].

Formation of I occurs as a result of intramolecular oxidative cyclization of II.



I

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[*] Deceased.

[†] This compound was kindly provided to us by our coworker V. O. Kulagina at the Institute of Organic Chemistry, Russian Academy of Sciences.

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TABLE 1. Bond Lengths (d, Å, σ = 0.003 Å), Bond Angles (ω, σ = 0.2°), and Torsional Angles (ω, σ = 0.3°) in Molecule I

Bond	Diazenofurazan moieties				Average value
	А	Б	В	Г	
$O_{(1)}-N_{(2)}$	1,393	1,398	1,395	1,396	1,396
$O_{(1)}-N_{(5)}$	1,371	1,360	1,374	1,365	1,368
$N_{(2)}-C_{(3)}$	1,296	1,296	1,301	1,299	1,298
$N_{(5)}-C_{(4)}$	1,306	1,307	1,309	1,307	1,307
$C_{(3)}-C_{(4)}$	1,428	1,419	1,430	1,422	1,425
$C_{(3)}-N_{(6)}$	1,413	1,421	1,417	1,420	1,418
$N_{(6)}-N_{(7)}$	1,257	1,247	1,257	1,252	1,253
$N_{(7)}-C_{(4)}$*	1,408	1,410	1,412	1,407	1,409
		Bond angle			
$N_{(2)}-O_{(1)}-N_{(5)}$	111,2	111,8	111,9	111,9	111,7
$O_{(1)}-N_{(2)}-C_{(3)}$	105,1	104,3	104,6	104,4	104,6
$O_{(1)}-N_{(5)}-C_{(4)}$	105,4	105,1	104,9	104,9	105,1
$N_{(2)}-C_{(3)}-C_{(4)}$	109,3	109,7	109,4	109,4	109,4
$N_{(2)}-C_{(3)}-N_{(6)}$	122,1	123,2	121,6	123,5	122,6
$C_{(4)}-C_{(3)}-N_{(6)}$	128,3	126,9	128,6	127,1	127,7
$N_{(5)}-C_{(4)}-C_{(3)}$	109,0	109,1	109,2	109,4	109,2
$N_{(5)}-C_{(4)}-N_{(7)}$*	118,1	117,5	118,1	117,7	117,8
$C_{(3)}-C_{(4)}-N_{(7)}$*	132,9	133,3	132,7	132,8	132,9
$C_{(3)}-N_{(6)}-N_{(7)}$	111,4	112,1	111,8	111,1	111,2
$N_{(6)}-N_{(7)}-C_{(4)}$*	111,4	110,7	111,4	111,5	111,2
		Torsional angle			
$N_{(2)}-C_{(3)}-N_{(6)}-N_{(7)}$	-54,6	55,9	-49,6	54,7	
$C_{(3)}-N_{(6)}-N_{(7)}-C_{(4)}$*	177,0	179,3	175,6	178,5	
$N_{(6)}-N_{(7)}-C_{(4)}-N_{(5)}$*	-174,8	175,4	-176,5	175,5	

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*Atom assigned to one of the diazenofurazan moieties directly connected with the considered moiety (A, B, C, or D).

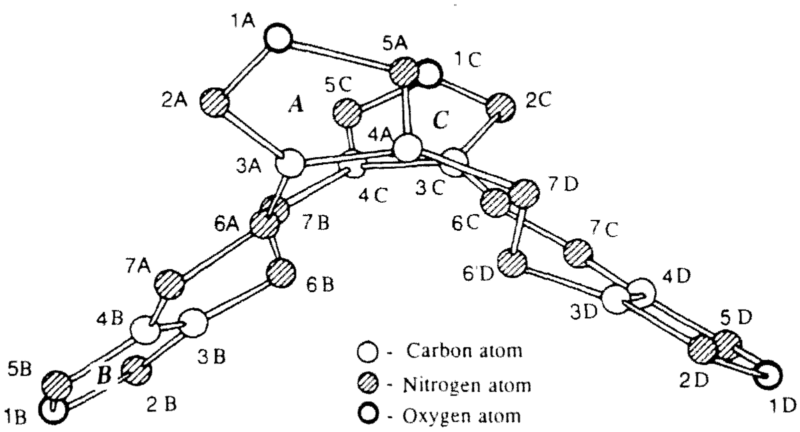

Fig. 1. Structure of Molecule I.

We have established that II successfully undergoes cyclization when treated with $Pb(OAc)_4$ and Bu_4NBr in MeCN or in C_6H_6. When II is reacted with a two-fold excess of DBI in MeCN, C_6H_6, or a 2:1 mixture of $CH_2Cl_2-EtOAc$, cyclization of II is observed only in MeCN. In other solvents under the studied conditions, the reaction does not occur and the starting compound is recovered from the reaction mixture unchanged.

With the goal of determining the spatial orientation of the furazan rings relative to the N=N bonds in I, their arrangement relative to each other, and also establishing other geometric parameters of molecule I, we carried out x-ray diffraction analysis of this compound. We should note that compound I was the first representative of macrocycles consisting only of diazenofurazan units whose crystal structure has been rigorously established. We have shown that the azo group in the 3 position of the furazan ring is almost coplanar with the furazan ring and has an *E* orientation (torsional angles C−N=N−C are equal to 175-177°) relative to its C=N bond, while the azo group in the 4 position of the furazan ring has a *Z* orientation and is rotated by 50-56° relative to the plane of the ring. The dihedral angle between the planes of the rings A and B is −104.7°; between B and D, 117.4° (see Fig. 1). The bond lengths, bond angles, and torsional angles in molecule I are presented in Table 1.

EXPERIMENTAL

The x-ray diffraction experiment was carried out on a Syntex P2$_1$ automatic four-circle diffractometer, λMoKα, at −120°C, 2353 independent reflections with $I \geq 2\sigma I$. Crystals of compound I ($C_8N_{16}O_4$) were grown from a mixture of CH_2Cl_2 and heptane (1:1) and are monoclinic, a = 25.577(8), b = 6.835(2), c = 16.376(5) Å, β = 95.41(2)°, V = 2850(2) Å^3, space group *C2/c*, Z = 8, d_{calc} = 1.80 g/cm^3, R = 0.040, R_w = 0.033.

Compound I was obtained according to the following procedures: A. A suspension of 0.1 g (0.26 mmoles) II, 0.09 g (0.28 mmoles) Bu_4NBr, and 1 g (2.26 mmoles) $Pb(OAc)_4$ in 30 ml dry C_6H_6 or MeCN was stirred at room temperature for 1 h. The residue was filtered and washed with 5 ml solvent. The mother liquor was evaporated under vacuum to dryness. I was extracted with 10 ml C_6H_6, the solution was evaporated under vacuum to dryness, again extracted with 10 ml C_6H_6, and chromatographed on a column (silica gel LS 40/100, eluent C_6H_6). Obtained: 0.095 g (97%) I. Its physicochemical characteristics correspond to the characteristics of compound I obtained in [1].

B. A suspension of 0.1 g (0.26 mmoles) II and 0.14 g (0.49 mmoles) DBI in 30 ml MeCN was stirred at room temperature for 15 min, the residue was filtered, and the mother liquor was evaporated under vacuum to dryness. I was extracted with 10 ml C_6H_6, the solution was evaporated to dryness, and the residue was dissolved in 10 ml C_6H_6. I was isolated as in method A. Obtained: 0.098 g (100%) I.

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