Synthesis of 3,4:7,8:11,12-trifurazano-1,2,5,6,9,10-hexaazacyclododeca-1,3,5,7,9,11-hexaene-1,5,9-trioxide

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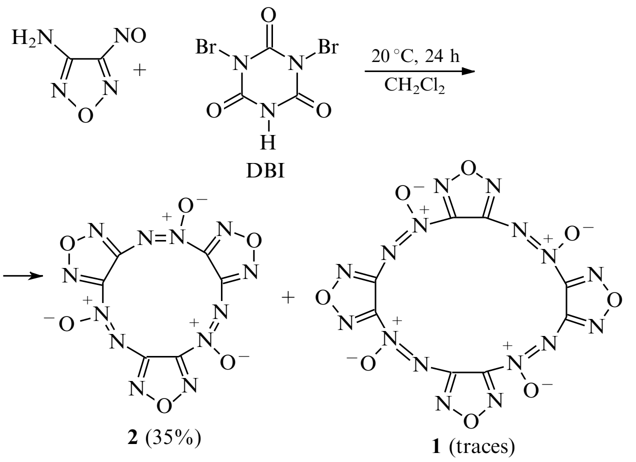
The title compound has been synthesized for the first time from a reaction of 3-amino-4-nitrosofurazan with dibromoisocyanurate.

Oxidation of 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 by Karo's acid affords 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-1,5,9,11-tetraoxide **1**.[1] Taking into account the known ability of nitroso compounds to react with amino compounds in the presence of dibromoisocyanurate (DBI) to give diazene oxides[2–6] one would expect that similar macrocycles might be synthesized from reactions of DBI with 3-amino-4-nitrosofurazan.[†]

We have shown that the principal product of this reaction was 3,4:7,8:11,12-trifurazano-1,2,5,6,9,10-hexaazacyclododeca-1,3,5,7,9,11-hexaene-1,5,9-trioxide **2**. The yield of compound **2** in the solvents studied (CH_2Cl_2, $CHCl_3$, dichloroethane, MeCN) at temperatures 0–30 °C did not exceed 35%. Traces of tetraoxide **1**, as well as a complex mixture of polymeric products, were also recorded in the reaction mixture by TLC and MS.[‡]

The structure of compound **2** has been established by IR, ^{1}H and ^{13}C NMR spectroscopy and mass spectrometry. The IR spectrum of **2** contains characteristic diazene oxide group absorptions (1520 cm^{-1})[2–6] and furazan heterocycle signals (1560 cm^{-1}). ^{1}H and ^{14}N NMR spectra of the compound have two carbon signals and one narrow nitrogen signal that suggests a symmetrical location of oxygen atoms in the macrocycle **2**. The chemical shifts of the ^{13}C and ^{14}N signals in **2** are similar to those reported for the tetraoxide **1** (150.1, 155.9, −83.2 ppm).[1] The molecular mass (M^+ 336) and elemental composition of compound **2** are consistent with the proposed structure.



Scheme 1

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[†] 3-Amino-4-nitrosofurazan was obtained by the procedure of T. S. Novikova, T. M. Mel'nikova and A. B. Sheremetev (this Institute), unpublished data.

[‡] *Experimental procedure*. To a vigorous stirred suspension of DBI (22.00 g, 77 mmol) in CH_2Cl_2 (100 ml) was added during 3 h at 20 °C a solution of 3-amino-4-nitrosofurazan (3.00 g, 26 mmol) in the same solvent (100 ml). The reaction mixture was stirred for 24 h at 20 °C, and the resulting precipitate filtered off and washed with CH_2Cl_2 (2×30 ml). The combined organic extracts were evaporated under reduced pressure and the residue was recrystallized three times from benzene to give 1.03 g (35%) of **2**, mp 187–188 °C. IR ν/cm^{-1} (KBr): 1140, 1340, 1460, 1490, 1520, 1560; ^{13}C NMR (75 MHz, [$^2H_6$]acetone) δ 149.2, 158.4; ^{14}N NMR (21.7 MHz, [$^2H_6$]acetone) δ 68.9 (CH_3NO_2 was used as an external standard); MS m/z 336 (M^+); Found (%): C, 21.54; H, 49.90. $C_6H_{12}N_6$. Calc. (%): C, 21.42; N, 50.00.