New Macrocyclic Systems – Tetrafurazano[3,4-*c*:3,4-*e*:3,4-*i*:3,4-*k*]-1,2,7,8-tetraazacyclododeca-1,3,5,7,9,11-hexane and Hexafurazano-[3,4-*c*:3,4-*e*:3,4-*i*:3,4-*k*:3,4-*o*:3,4-*r*]-1,2,7,8,13,14-hexaazacyclooctadeca-1,3,5,7,9,11,13,15,17-nonane by Oxidative Macrocyclization of Diaminodifurazanyl

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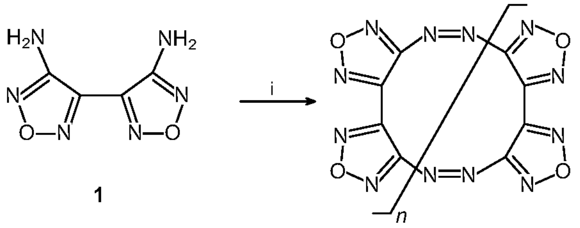
The title compounds have been synthesised by interaction of diaminodifurazanyl with dibromoisocyanurate (DBI) and it was shown that the diazene fragment in such structures is capable of being oxidized into a diazene oxide fragment.

Macrocyclic conjugated systems involving nitrogen heterocycles are well known. Thus, natural macrocyclic compounds – porphyrins and corrins – are the components of many enzymes and coenzymes. Metallophthalocyanines are widely used in the production of organic dyes and by-products. An expansion of the chemistry of such systems with the inclusion of different heterocycles in a macrocycle may be of potential importance for the development of organic as well as coordination, analytical and biological chemistry.

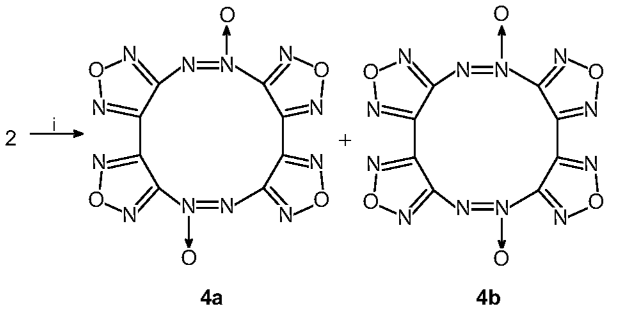
Recently,[1,2] macrocycles similar to crown-ethers, involving the furazan ring, have been synthesised. In this paper the synthesis of new types of conjugated macrocyclic compounds **2** and **3** is reported. Compounds **2** and **3** contain two and three subunits, the difurazanyldiazene fragment, respectively. The synthesis of these compounds was carried out by intermolecular oxidative macrocyclization of diaminodifurazanyl[3] using DBI in an organic solvent (Scheme 1). Both compounds formed simultaneously with similar yields. The formation of macrocycles with more than three subunits is possible in this reaction according to ^{13}C NMR data for the third fraction, which was isolated in a small yield by preparative chromatography of the reaction mixture. In this ^{13}C NMR spectrum there are resonance signals due to carbon atoms in the same region as for **2** and **3**.



1

2 *n* = 2
3 *n* = 3

Scheme 1 *Reagents and conditions:* i, DBI (4 mol), MeCN, 20 °C, 48 h.



4a **4b**

Scheme 2 *Reagents and conditions:* i, H_2O_2 (85%) 16.5 mol, oleum (20%) 40 mol, 10 °C → 80 °C, 30 min, 80 °C, 30 min.

Among various chemical transformations of the synthesised macrocycles, the possibility of oxidation of the diazene fragment in **2** into the diazene oxide fragment was tested. For this transformation to proceed was found to require quite severe conditions (Karo's acid in 20% oleum). This is apparently connected with the reducing electronic density of the diazene fragment because of the strong electron-withdrawing effect of the furazan rings. Both diazene groups in **2** are subjected to oxidation, resulting in a mixture of isomeric diazene oxide derivatives **4a,b** in the ratio 1:1 (Scheme 2). Attempts at their separation were unsuccessful.

In all experiments the reaction mixture was poured into water. Compounds **2** and **3** were isolated by preparative column chromatography on silica gel (benzene–hexane, 1:5). A mixture of compounds **4a,b** was purified by preparative TLC on silica gel (CH_2Cl_2–CCl_4, 1:1, three times, R_f 0.38). All compounds obtained have satisfactory elemental analysis data and their structure has been confirmed by spectroscopic data (IR, UV, NMR and mass spectrometry).[†] For compound **2**, X-ray structural analysis has also been performed.[4]

References

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[†] Spectroscopic data: ^{13}C NMR (75.47 MHz), standard TMS,^{14}N NMR (21.6 MHz), internal standard $MeNO_2$, δ/ppm ([$^2H_6$]acetone); IR (KBr) ν/cm^{-1}; UV λ_{max}/nm (MeOH), mass, *m*/*z*.

2, yield 32.5%, m.p. 220 °C (CH_2Cl_2), $\rho_{X\text{-ray}} = 1.795$ g cm^{-3}, IR: 860, 915, 930, 1000, 1030, 1110, 1230, 1270, 1370, 1400, 1500. UV: 227, 370. ^{13}C NMR: 138.82 (C–*C*–C), 163.24 (C–*C*–N=). Mass: 328 [M^+], 270 [$M^+ - NO - N_2$], 232 [$M^+ - NO - N_2 -$(C–C–N)], 202 [$M^+ -$ 2NO $- N_2 -$(C–C–N)].

3, yield 28%, m.p. 300 °C (precipitated with hexane from CH_2Cl_2). IR: 915, 1000, 1040, 1100, 1230, 1370, 1400, 1450. ^{13}C NMR: 138.28 (C–*C*–C), 163.28 (C–*C*–N=). Mass: 492 [M^+], 434 [$M^+ - NO - N_2$], 300 [$M^+ - NO - N_2 - 2$(C–C–N)].

4a,b, yield 60%, m.p. 137–140 °C (CCl_4). IR: 890, 910, 920, 1000, 1030, 1060, 1180, 1260, 1300, 1360, 1415, 1440, 1480, 1500, 1510, 1550. UV: 222, 270. ^{13}C NMR: 138.77, 139.69, 140.52, 140.72, 153.87, 153.98, 159.74 [ex.s. C–N(O)=]. ^{14}N NMR: –66.66, –64.41. Mass: 360 [M^+], 330 [M^+–NO], 300 [M^+–2NO].