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Construction of Crown Ethers possessing an Azofurazan Subunit

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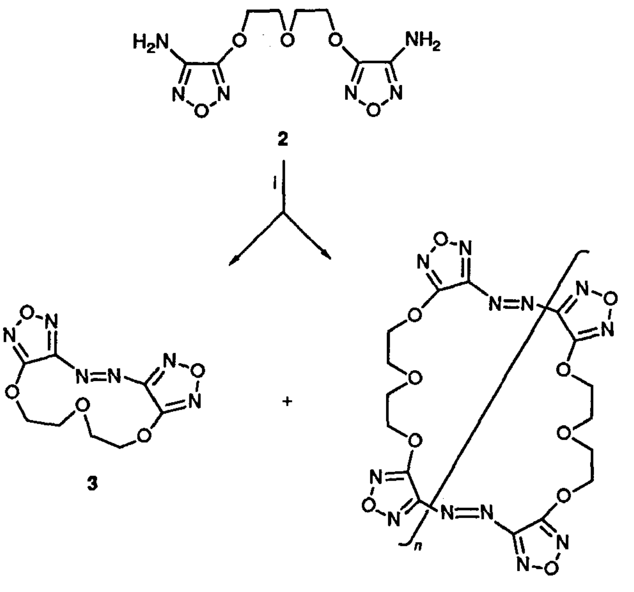
Crown ethers involving both a furazan ring and an azo group have been synthesized; the ring closure step, as a result of N═N bond formation, consisted of oxidative condensation of bis[2-(3-aminofurazanoxy)ethyl] ether by dibromoisocyanurate.

Crown ethers and related macrocycles find many applications in specific metal ion complexation, as phase-transfer reagents, general and specific catalysts, biological mimics, drugs and so on. Modification of crown ethers by insertion of various functional groups and heterocyclic subunits is the most common method of altering their properties.[1]

Previously,[2] we have reported crown ether **1**, possessing a furazan ring as the subunit (directly to the macroring[3]), that was synthesized by the usual route from 3,4-dihydroxyfurazan and 2,2′-dichlorodiethyl ether.

Here, we present a new route for the synthesis of furazano crown ethers additionally modified by an azo group. In this method the macrocycle closure is implemented *via* N═N bond formation. Thus, treatment of diamine **2** with dibromoisocyanurate (DBI)[4] in an organic solvent leads to oxidative cyclocondensation (Scheme 1) and affords the intramolecular coupling product **3**. Along with **3**, a number of macrocyclic oligomers (**4** and **5**) are formed as a result of intermolecular cyclization.[†] The use of $KMnO_4$ or NaOCl as oxidizing agents, which is usually effective for the synthesis of linear azofurazans,[5] did not afford here compounds **3**, **4** and **5**.

The presence of an azo-linkage in the macrocycles, which allows *cis–trans* isomerization, makes it possible to use this property to influence the macrocyclic cavity (for instance, under UV irradiation). Compounds **3**, **4** and **5** are thus rather interesting objects for investigation.



2

3

4; *n* = 1
5; *n* = 2

Scheme 1 *Reagents and conditions*: i, DBI, CH_2Cl_2, room temperature

The starting diamine **2** was obtained by treatment of **6** with diethylene glycol, the derivative **7** was formed as a by-product (Scheme 2). It should be noted that **7** may be regarded as the

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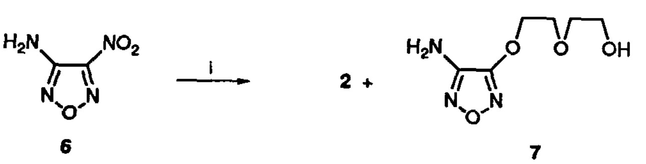
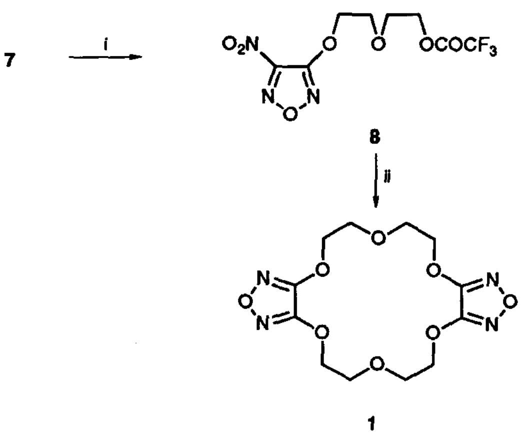
[†] Products were isolated by column chromatography on silica gel. The yields were **3** (63%), **4** (6%) and **5** (1%). Traces of higher-molecular weight oligomers were also obtained.

All new compounds exhibited satisfactory elemental analyses and high resolution mass measurement on homogeneous samples. Compound **3** m.p. 94–95°C (from CCl_4); **4** m.p. 232–234°C (from $CHCl_3$); **5** oil. All compounds gave spectroscopic data in agreement with their structures. For example, for **3**: IR (KBr) ν/cm^{-1} 2930, 1590, 1560, 1440, 1260, 1240, 1130, 1100, 1070, 1050, 1030, 1000, 960, 880; ^{13}C NMR [$(CD_3)_2CO$] δ 70.21 (C-4), 73.80 (C-3), 156.55 (C-1), 162.06 (C-2); MS *m/z* 268 [M$^+$], 238 [M$^+$ − NO], 210 [M$^+$ − NO − N_2]. The structure of compound **3** was confirmed by an X-ray structural study, which will be published elsewhere.



Scheme 2 *Reagents and conditions*: i, diethylene glycol, KOH, dimethyl sulfoxide (DMSO), room temperature



Scheme 3 *Reagents and conditions*: i, $(CF_3CO)_2O$, 95% H_2O_2, CH_2Cl_2, 10°C; ii, Na_2CO_3, MeCN, 80°C

starting material for the synthesis of crown ether **1** (Scheme 3). The overall yield is about 1%.

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