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New approach to the synthesis of dibenzodiazacrown ethers by ring transformation of dibenzocrown ether

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ABSTRACT

Opening of the macrocycle of 4′,4″(5″)-dinitrodibenzo-18-crown-6 ethers under the action of $MeNH_2$ or MeONa to give podands was studied. Structure of the aza podands was confirmed by X-ray diffraction. A new approach to the synthesis of previously unknown dinitrodibenzodiazacrown ethers based on one-step ring transformation of the cis isomer of dinitrodibenzo-18-crown-6 ether on treatment with aliphatic diamines was proposed.

1. Introduction

Dibenzocrown ethers are formed upon condensation of four or two non-macrocyclic compounds (so-called 2+2 or 1+1 condensations).[1] The yields of macrocycles obtained by 1+1 condensations are usually much higher than upon 2+2 condensations. However, a drawback of 1+1 condensation is a large number of process steps and, in the case of synthesis of dibenzodiazacrown ethers, one more drawback is poor accessibility of the starting compounds.[2] As regards the synthesis of functional derivatives at the benzene ring of dibenzodiazacrown ethers, the examples of such syntheses are scarce and the overall yields do not exceed 22%.[3]

Recent years have seen considerable progress in the chemistry of benzoazacrown ethers related to the development of a new strategy for their synthesis based on the stepwise ring transformation in benzocrown ethers used as synthons.[4] The routes to new dibenzodiazacrown ethers based on ring transformation in more readily accessible dibenzocrown ethers seem much more promising in this respect, although the advantages and the possibilities of this approach have not yet been discussed in the literature.

2. Results and discussion

It is known that on treatment with *O*-nucleophiles (KOH, RONa), 4′-nitrobenzocrown ethers undergo nucleophilic ring opening, while tetranitrodibenzo-18-crown-6 ether undergoes ring cleavage.[5] Previously, we studied the ring opening reaction of 4′-nitrobenzocrown ethers induced by *N*-nucleophiles (RNH_2), resulting in nitrogen-containing podands in up to 100% yields.[6] Here we studied the action of $MeNH_2$ and MeONa on compounds with two reaction sites, 4′,4″(5″)-dinitrodibenzo-18-crown-6 ethers **1a**,**b** (Scheme 1) obtained by nitration of dibenzo-18-crown-6 ether as a mixture of two isomers, which were difficult to separate.

The reaction of **1a**,**b** with $MeNH_2$ provided two aza podands **2a**,**b** corresponding to opening trans and cis isomers **1a**,**b** in 44 and 52% yields in 1: 0.6 M ratio, respectively. Upon the reaction of **1a**,**b** with MeONa, two podands **3a**,**b** were isolated in 45 and 55% yields, respectively, and in the same molar ratio (1: 0.6) as in the case of $MeNH_2$. Since this reaction is almost quantitative, it can be regarded as a promising way for estimating the quantitative composition of the products of nitration of dibenzo-18-crown-6 ether.

The aza podands **2a**,**b** were prepared as single crystals, which were studied by X-ray diffraction. These structures are shown in Fig. 1.

In the crystal, the molecules of **2a** form centrosymmetric dimers through bifurcate H-bonding between the terminal OH group of

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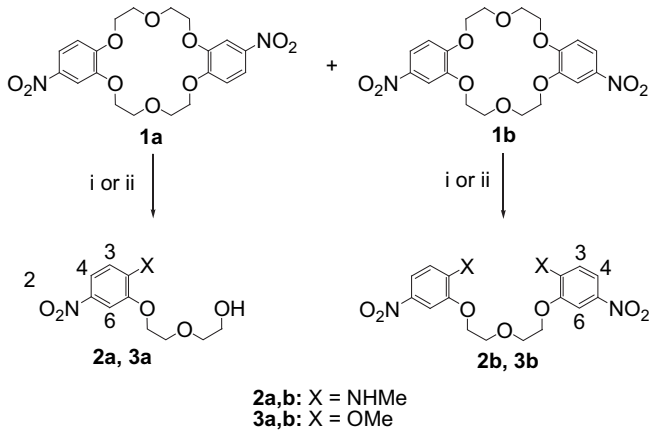


Scheme 1. Synthesis of podands **2** and **3**. Reagents and conditions: (i) $MeNH_2$, sealed tube, 100 °C, 9 days (**2a**: 44%; **2b**: 52% yield); (ii) MeONa/MeOH, reflux, 60 h (**3a**: 45%; **3b**: 55% yield).

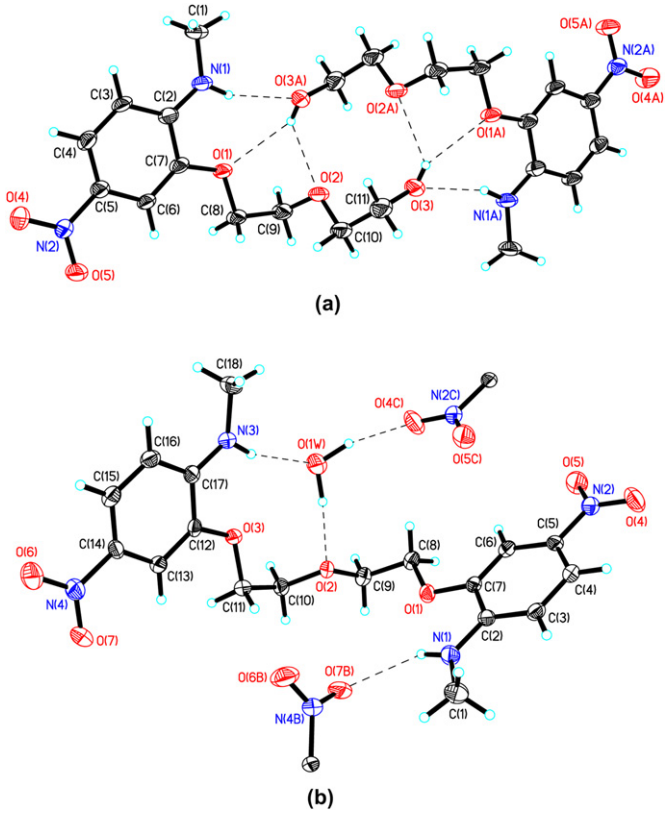


Fig. 1. Structure of (a) **2a** and (b) **2b**·H_2O. Thermal anisotropic ellipsoids are drawn at the 40% probability level. The additional letters 'A', 'B', and 'C' indicate that atoms are related through the (1−*x*, 1−*y*, −*z*), (*x*, 0.5−*y*, 0.5+*z*), and (2−*x*, −*y*, 1−*z*) symmetry operations, respectively. Hydrogen bonds are drawn with dash lines.

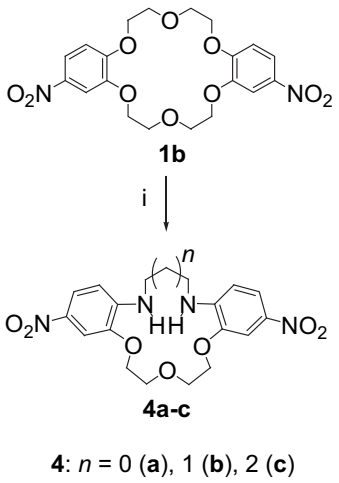
one molecule and the ether O atoms of the other molecule. The distances O(3)—H···O(1A) and O(3)—H···O(2A) are equal to 2.48 (8) and 2.26 (8) Å and the angles at the H atom are 129 (7) and 124 (7)°, respectively. The NH and OH groups of the molecules also participate in hydrogen bonding: the distance N(1)—H···O(3A) is 2.07(8) Å and the angle at the H atom is 154(7)°.

A solvation water molecule was found in the unit cell of **2b**. This $H_2O(1W)$ molecule forms hydrogen bonds with the ether atom O(2) of the basic podand molecule and with the oxygen atom of $N(2)O_2$ group of the neighboring **2b** molecule, which is connected with the basic molecule by the symmetry center. The N(3)H and N(1)H groups form hydrogen bonds with the water molecule and the N(4) O_2 group of another neighboring **2b** molecule, respectively. The parameters of the hydrogen bonds are as follows: the distances O(1W)—H···O(2), O(1W)—H···O(4C), N(3)—H···O(1W), and N(1)—H···O(7B) are equal to 1.85(3), 1.93(3), 2.03(2), and 2.32(3) Å and the angles at the H atoms are 175(3), 160(5), 161(2), and 145(2)°, respectively. Thus, the molecules of **2b** form two-dimensional layers in the lattice owing to the above-mentioned hydrogen bonds with each other and the solvate water molecules.

The common feature of compounds **2a**,**b** is an effective conjugation of the lone electron pairs of the nitrogen atoms of the NHMe groups with the benzene rings. Indeed, the methyl groups lie almost in the benzene planes, i.e., the C—N—C_{Ar}—C_{Ar} torsion angles are close to 0 or 180°, which corresponds to conjugation.

Considering the obtained results on the synthesis of podands **2a**,**b**, we suggested that the use of aliphatic diamines as di-*N*-nucleophiles may furnish previously unknown 5′,5″-dinitrodibenzodiazacrown ethers **4a**—**c**. Probably, **4a**—**c** could also be synthesized via an alternative route, namely, by the reaction of podand **3b** with alkanediamines. The former route to dibenzodiazacrown ethers appears more attractive because it comprises only one step.

Indeed, on treatment with aliphatic diamines with different lengths of the polymethylene chain with heating, the cis isomer of crown ether **1b** underwent ring transformation to give dibenzodiazacrown ethers **4a**—**c** (Scheme 2).

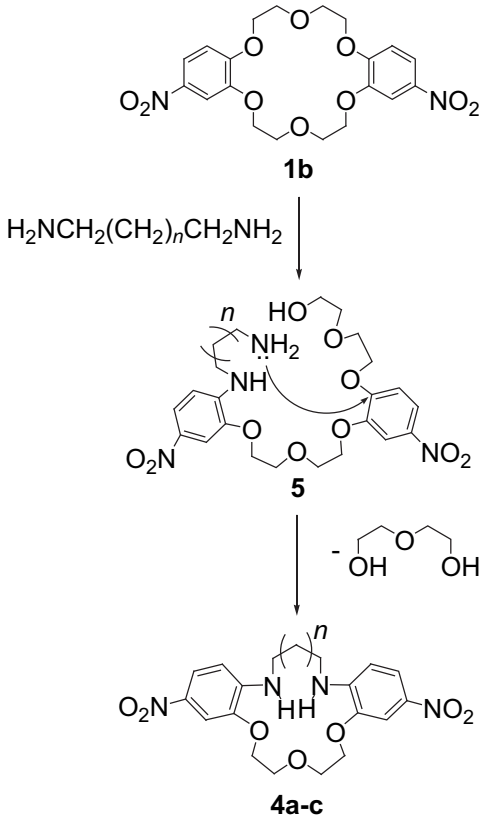


Scheme 2. Synthesis of diazacrown ethers **4a**—**c**. Reagents and conditions: (i) $H_2NCH_2(CH_2)_nCH_2NH_2$, sealed tube, 130 °C, 9 days (**4a**: 18%; **4b**: 31%; **4c**: 19% yield).

Using reactions with 1,3-propanediamine as an example, we carried out a number of experiments aimed at optimizing the conditions of ring transformation. The variation of the solvent (EtOH, MeOH, DMSO or their mixture) demonstrated that EtOH was the best choice for this reaction. At an equal molar ratio of crown ether **1b** (an isomer mixture **1a**,**b** was used) and $H_2N(CH_2)_3NH_2$, the reaction did not lead to noticeable results even after 17 days at 100 °C, probably, due to low solubility of **1a**,**b** in EtOH. By increasing the amount of diamine and raising the temperature of the reaction mixture to 130 °C, we were able to increase the yield of the target product from traces to 31%.

The reaction of **1b** with ethanediamine and butanediamine under the selected optimal conditions affords previously unknown diazacrown ethers **4a** and **4c** in 18 and 19% yields, respectively. That is, the reaction in question is common to **1b** and diamines with different length of the polymethylene chain.

We believe that the ring transformation follows the mechanism shown in Scheme 3. In the first step, the alkanediamine nitrogen atom probably attacks the carbon atom of the benzene ring located in the *para* position relative to the nitro group, resulting in opening of the

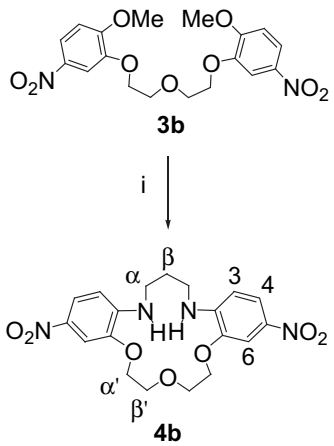


Scheme 3. Presumptive mechanism of ring transformation in crown ether **1b** to diazacrown ethers **4a**–**c**.

macroheterocycle to give podand **5**. The second step of ring transformation is intramolecular nucleophilic substitution at the second end of the dialkoxy group. This gives rise to target products—dinitrodibenzodiazacrown ethers **4a**–**c** and diethylene glycol.

In the preparation of diazacrown ether **4b** by the alternative route, namely, by the reaction of dimethoxypodand **3b** with 1,3-propanediamine (Scheme 4) under conditions similar to the conditions of synthesis of diazacrown ethers **4a**–**c** from crown ethers **1a**,**b**, the yield of **4b** was only 5%, which demonstrates the advantages of the one-step route to the target compounds starting from readily accessible mixture of dibenzo-18-crown-6-ether nitration products.

The structures of all obtained compounds were established by UV–vis spectrometry, ^{1}H and ^{13}C NMR spectroscopy (including COSY and NOESY spectra) and confirmed by mass spectrometry and



Scheme 4. Synthesis of diazacrown ether **4b**. Reagents and conditions: (i) $H_2N(CH_2)_3NH_2$, sealed tube, 130 °C, 9 days (5% yield).

elemental analysis. The UV–vis spectra of aza podands **2a**,**b** and diazacrown ethers **4a**–**c** reveal an intense long-wavelength absorption band with a maximum at 398–403 nm, which is the typical absorption of *para*-nitroanilines.[7] The NOESY spectra of dibenzodiazacrown ether **4b** (Fig. 2; atom numbering differing from the IUPAC rules is given in Scheme 4) exhibit intense cross-peaks between the 3-H protons and the methylene protons of the CH_2N groups and no coupling between the 3-H protons and NH protons. This attests to a high degree of conjugation of the nitrogen atoms with the benzene rings and to the fact the protons of the NH groups point inside the macroheterocycle, probably, being hydrogen-bonded with its oxygen atoms. The similar geometry about MeNHAr fragments is found in structures of crystalline aza podands **2a**,**b** (see Fig. 1).

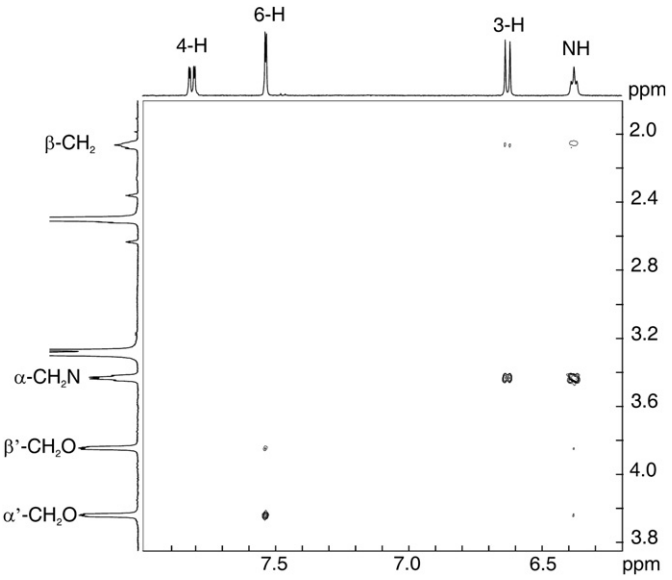


Fig. 2. Fragment of the NOESY spectrum of diazacrown ether **4b** (DMSO-d_6, 30 °C).

Our preliminary ^{1}H NMR titration studies on complex formation properties of diazacrown ether **4b** demonstrated that this ligand binds F^- ions (as tetrabutylammonium salt) in MeCN-d_3 and DMSO-d_6 solutions ($\log K_{1(\mathbf{4b}):1(F)}$ and $\log K_{1(\mathbf{4b}):2(F)}$ are 2.8±0.2 and 2.3±0.2, and 2.1±0.2 and 1.9±0.2 [M^{-1}], respectively, at 25 °C) and does not bind Na^+, Ca^{2+}, Ba^{2+}, and ClO_4^- ions in these conditions. This fact enables one to consider the diazacrown ethers of such type as promising complexing agents for fluoride anions.

We believe that *N*,*N*′-dialkyl derivatives of diazacrown ethers **4a**–**c** might be effective ligands for Group I and II metal cations, as it was shown for related *N*-alkyl(nitrobenzo)azacrown ethers.[4c,e]

3. Conclusions

Thus, we proposed a new approach to the synthesis of previously unknown nitro derivatives of dibenzodiazacrown ethers from the readily accessible mixture of 4′,4″(5″)-dinitrodibenzo-18-crown-6 ethers and aliphatic diamines. The reaction we found is the first example of one-step ring transformation of crown ethers to azacrown ethers. This approach opens up the way for the synthesis of new promising groups of complexing agents and metal ion extractants.

4. Experimental section

4.1. General

Melting points were determined with a MEL-Temp II apparatus in a capillary and are uncorrected. 1D ^{1}H and ^{13}C NMR spectra were

recorded on a Bruker DRX-500 instrument (500.13 and 125.76 MHz, respectively) as solutions in $CDCl_3$ or DMSO-d_6 using the solvent as an internal reference (δ_H 7.27 and 2.50, δ_C 77.00 and 39.43, respectively); 2D homonuclear $^1H-^1H$ COSY and NOESY spectra and heteronuclear $^1H-^{13}C$ COSY spectra were used to assign the proton and carbon signals. Absorption spectra were recorded on a Shimadzu UV-3101PC spectrophotometer in the range of 200–550 nm, $C_{\mathbf{2-4}}$=2 10^{-5} M, 1-cm quartz cell, room temperature with an increment of 1 nm. IR spectra in KBr pellets were recorded on Bruker IFS-113V spectrophotometer. Mass spectra were measured with a Varian MAT-311A instrument and high resolution mass spectra were recorded with Finnigan MAT-212 instrument (perfluoroparaffin as a standard) with direct inlet of the sample into the ionization zone; the energy of ionizing electrons was 70 and 60 eV, respectively. Elemental analyses were performed at the Microanalytical Laboratory of the A.N. Nesmeyanov Institute of Organoelement Compounds (Moscow, Russian Federation). The course of the reactions was monitored by TLC on Merck DC-Kieselgel 60 F_{254} plates. Column chromatography was performed with Merck Kieselgel 60 (0.063–0.100 mm). 4′,4″(5″)-Dinitrodibenzo-18-crown-6 ethers **1a**,**b** were prepared according to known procedure.[8]

4.2. Synthesis of podands 2a,b

A mixture of crown ethers **1a**,**b** (225 mg, 0.5 mmol) and a 35% solution of $MeNH_2$ in dry EtOH (5 mL) was heated at 100 °C (a water bath) for 9 days in a sealed tube, the tube being shaken every 10 h after cooling to ~20 °C. After tube opening, the solvent was evaporated in vacuo, and the residue was extracted with hot EtOAc and filtered to give 7 mg (0.016 mmol) of EtOAc-insoluble trans isomer **1a**, mp 245–248 °C (Ref. 9: mp 245–248 °C). The filtrate was evaporated and the residue was purified by column chromatography on silica gel using EtOAc as the eluent. The podands **2a**,**b** were isolated as crystalline powders. Yield **2a**: 108 mg (44%). Yield **2b**: 103 mg (52%).

*4.2.1. Podand **2a**.* Compound **2a** was isolated as orange crystals; [found C, 51.43; H, 6.20; N, 10.49. $C_{11}H_{16}N_2O_5$ requires C, 51.56; H, 6.29; N, 10.93%]; mp 114–116 °C; R_f 0.23 (EtOAc); UV–vis (MeCN) λ_{max} 398 nm (ϵ 14,100 L mol^{-1} cm^{-1}); ν_{max} (KBr) 3453, 3343 (N–H, O–H), 1482 (NO_2) cm^{-1}; δ_H ($CDCl_3$) 2.17 (1H, br s, OH), 2.96 (3H, d, *J* 4.6 Hz, MeN), 3.67 (2H, m, CH_2O), 3.79 (2H, m, CH_2O), 3.90 (2H, m, C*H*$_2$$CH_2OAr$), 4.24 (2H, m, C*H*$_2$OAr), 5.30 (1H, br s, NH), 6.49 (1H, d, *J* 8.9 Hz, 3-H), 7.66 (1H, d, *J* 2.3 Hz, 6-H), 7.94 (1H, dd, *J* 8.9, 2.3 Hz, 4-H); δ_C ($CDCl_3$) 29.55 (MeN), 61.61 (CH_2O), 68.32 (*C*H_2OAr), 69.26 (*C*$H_2$$CH_2OAr$), 72.47 ($CH_2O$), 106.34 (3-C, 6-C), 120.41 (4-C), 136.63 (5-C), 144.10 (1-C), 145.64 (2-C); *m*/*z* 256 (100, M^+), 168 (94), 167 (42), 150 (45), 148 (57), 138 (22), 122 (20), 121 (45), 93 (34), 78 (46).

*4.2.2. Podand **2b**.* Compound **2b** was isolated as light yellow crystals; [found C, 53.47; H, 5.47; N, 13.93. $C_{18}H_{22}N_4O_7$ requires C, 53.20; H, 5.46; N, 13.79%]; mp 161–163 °C; R_f 0.65 (EtOAc); UV–vis (MeCN) λ_{max} 398 nm (ϵ 33,100 L mol^{-1} cm^{-1}); ν_{max} (KBr) 3438, 3424 (N–H), 1488 (NO_2) cm^{-1}; δ_H ($CDCl_3$) 2.92 (6H, d, *J* 5.3 Hz, 2MeN), 3.95 (4H, m, 2C*H*$_2$$CH_2OAr$), 4.28 (4H, m, 2C*H*$_2$OAr), 5.18 (2H, br q, 2NH), 6.48 (2H, d, *J* 8.9 Hz, 2 3-H), 7.68 (2H, d, *J* 2.3 Hz, 2 6-H), 7.94 (2H, dd, *J* 8.9, 2.3 Hz, 2 4-H); δ_C ($CDCl_3$) 29.61 (2MeN), 68.42 (2*C*H_2OAr), 69.49 (2*C*$H_2$$CH_2OAr$), 106.47 (2 3-C), 106.53 (2 6-C), 120.49 (2 4-C), 136.81 (2 5-C), 144.05 (2 1-C), 145.57 (2 2-C); *m*/*z* 406 (45, M^+), 312 (64), 167 (100), 148 (69), 135 (58), 134 (86), 121 (65), 93 (58), 90 (50), 79 (47), 78 (83).

4.3. Synthesis of podands 3a,b

An alcohol solution of MeONa, prepared by dissolving Na (1.15 g, 50 mmol) in dry MeOH (50 mL), was added dropwise at room temperature to a stirred mixture of crown ethers **1a**,**b** (450 mg, 1 mmol) and dry MeOH (10 mL). The reaction mixture was stirred at reflux for 60 h, cooled, and concentrated in vacuo, and the residue was diluted with water and extracted with EtOAc. The extract was concentrated in vacuo. The residue was purified by column chromatography on silica gel using elution with benzene and then with a benzene/EtOAc (1:1) solvent system. The podands **3a**,**b** were isolated as crystalline powders. Yield **3a**: 233 mg (45%). Yield **3b**: 226 mg (55%).

*4.3.1. Podand **3a**.* Compound **3a** was isolated as dark yellow crystals; [found C, 51.49; H, 5.90; N, 5.44. $C_{11}H_{15}NO_6$ requires C, 51.36; H, 5.88; N, 5.45%]; mp 80–81 °C; R_f 0.33 (EtOAc); UV–vis (MeCN) λ_{max} 341 nm (ϵ 5700 L mol^{-1} cm^{-1}); ν_{max} (KBr) 3329, 3244 (O–H), 1501 (NO_2) cm^{-1}; δ_H ($CDCl_3$) 2.30 (1H, br s, OH), 3.69 (2H, m, CH_2O), 3.77 (2H, m, CH_2O), 3.95 (2H, m, C*H*$_2$$CH_2OAr$), 3.96 (3H, s, MeO), 4.27 (2H, m, C*H*$_2$OAr), 6.92 (1H, d, *J* 8.6 Hz, 3-H), 7.81 (1H, d, *J* 2.4 Hz, 6-H), 7.92 (1H, dd, *J* 8.6, 2.4 Hz, 4-H); δ_C ($CDCl_3$) 56.55 (MeO), 61.93 (CH_2O), 69.13 and 69.43 (*C*$H_2$$CH_2OAr$), 72.85 ($CH_2O$), 108.55 and 110.37 (3-C, 6-C), 118.37 (4-C), 141.56 (5-C), 148.27 and 155.12 (1-C, 2-C); *m*/*z* 257 (54, M^+), 169 (100), 123 (33), 94 (33), 89 (57), 79 (55), 76 (38), 65 (30), 63 (30), 59 (31).

*4.3.2. Podand **3b**.* Compound **3b** was isolated as light yellow crystals; [found C, 50.23, H, 4.70, N, 6.30. $C_{18}H_{20}N_2O_9\cdot H_2O$ requires C, 50.70; H, 5.20; N, 6.57%]; 188–190 °C; R_f 0.78 (EtOAc); UV–vis (MeCN) λ_{max} 339 nm (ϵ 12,400 L mol^{-1} cm^{-1}); ν_{max} (KBr) 1511, 1501 (NO_2) cm^{-1}; δ_H ($CDCl_3$) 3.85 (6H, s, 2MeO), 3.93 (4H, m, 2C*H*$_2$$CH_2OAr$), 4.20 (4H, m, 2C*H*$_2$OAr), 6.80 (2H, d, *J* 8.7 Hz, 2 3-H), 7.70 (2H, d, *J* 2.3 Hz, 2 6-H), 7.81 (2H, dd, *J* 8.7, 2.3 Hz, 2 4-H); δ_C ($CDCl_3$) 55.91 (2MeO), 69.08 and 69.76 (2*C*H_2*C*H_2OAr), 108.49 and 110.19 (2 3-C, 2 6-C), 118.10 (2 4-C), 140.00 (2 5-C), 148.13 and 155.01 (2 1-C, 2 2-C); *m*/*z* 408 (87, M^+), 196 (84), 151 (78), 150 (65), 124 (53), 122 (70), 109 (51), 106 (59), 89 (91), 79 (100).

4.4. Synthesis of dibenzodiazacrown ethers 4a-c from dibenzo-18-crown-6 ethers 1a,b (general procedure)

A mixture of crown ethers **1a**,**b** (360 mg, 0.8 mmol) and a 5% solution of alkanediamine (16 mmol) in dry EtOH was heated at 130 °C (an oil bath) for 9 days in a sealed tube. After tube opening, the solvent was evaporated in vacuo. Water (100 mL) and concentrated HCl (dropwise, to pH 3) were added to the residue. An aqueous solution was extracted with EtOAc, and the extract was concentrated in vacuo. The residue was purified by column chromatography on silica gel using EtOAc as the eluent. The compounds **4a**–**c** were isolated as light yellow crystalline powders.

*4.4.1. Compound **4a**.* Compound **4a** was isolated in yield 29 mg (18% based on *cis* isomer **1b**); mp 256–257 °C; R_f 0.70 (EtOAc); UV–vis (MeCN) λ_{max} 402 nm (ϵ 24,400 L mol^{-1} cm^{-1}); ν_{max} (KBr) 3395, 3385 (N–H), 1504 (NO_2) cm^{-1}; δ_H ($CDCl_3$) 3.59 (4H, m, 2CH_2N), 3.85 (4H, m, 2CH_2O), 4.32 (4H, m, 2C*H*$_2$OAr), 5.44 (2H, br s, 2NH), 6.60 (2H, d, *J* 8.9 Hz, 2 3-H), 7.66 (2H, d, *J* 2.0 Hz, 2 6-H), 7.93 (2H, dd, *J* 8.9, 2.0 Hz, 2 4-H); δ_C (DMSO-d_6) 40.03 (2CH_2N), 69.11 and 69.77 (2CH_2*C*H_2OAr), 106.93 and 107.84 (2 3-C, 2 6-C), 120.42 (2 4-C), 136.45 (2 5-C), 145.41 (2 1-C, 2 2-C); *m*/*z* 404 (36, M^+), 387 (27), 386 (100), 193 (37), 165 (28), 147 (29), 146 (91), 135 (36), 119 (34), 77 (43). HRMS: M^+, found 404.1333. $C_{18}H_{20}N_4O_7$ requires 404.1332.

*4.4.2. Compound **4b**.* Compound **4b** was isolated in yield 51 mg (31% based on *cis* isomer **1b**); mp 246–247 °C; R_f 0.54 (EtOAc); UV–vis (MeCN) λ_{max} 401 nm (ϵ 20,800 L mol^{-1} cm^{-1}); ν_{max} (KBr) 3417, 3383 (N–H), 1497 (NO_2) cm^{-1}; δ_H ($CDCl_3$) 2.17 (2H, m, C*H*$_2$$CH_2N$), 3.49 (4H, m, 2$CH_2N$), 3.90 (4H, m, 2$CH_2O$), 4.30 (4H, m, 2C*H*$_2$OAr), 5.50 (2H, br s, 2NH), 6.56 (2H, d, *J* 8.9 Hz, 2 3-H), 7.64 (2H,

d, *J* 2.2 Hz, 2 6-H), 7.93 (2H, dd, *J* 8.9, 2.2 Hz, 2 4-H); δ_C (DMSO-d_6) 26.29 (CH_2CH_2N), 43.91 ($2CH_2N$), 67.11 ($2CH_2OAr$), 67.57 ($2CH_2CH_2OAr$), 104.74 (2 6-C), 106.71 (2 3-C), 119.69 (2 4-C), 135.62 (2 5-C), 144.04 (2 1-C), 144.79 (2 2-C); *m*/*z* 418 (100, M^+), 374 (53), 193 (55), 165 (80), 147 (81), 79 (56), 78 (76), 77 (49), 65 (75), 58 (84). HRMS: M^+, found 418.1487. $C_{19}H_{22}N_4O_7$ requires 418.1488.

4.4.3. Compound **4c**. Compound **4c** was isolated in yield 32 mg (19% based on cis isomer **1b**); [found C, 55.77; H, 5.94; N, 12.60. $C_{20}H_{24}N_4O_7$ requires C, 55.55; H, 5.59; N, 12.96%]; mp 206–208 °C; R_f 0.75 (EtOAc); UV–vis (MeCN) λ_{max} 403 nm (ϵ 35,300 L mol^{-1} cm^{-1}); ν_{max} (KBr) 3417 (br, N–H), 1498 (NO_2) cm^{-1}; δ_H ($CDCl_3$) 1.86 (4H, m, 2CH_2CH$_2$N), 3.32 (4H, m, 2CH_2N), 3.95 (4H, m, 2CH_2CH$_2$OAr), 4.29 (4H, m, 2CH_2OAr), 5.01 (2H, br t, 2NH), 6.52 (2H, d, *J* 8.9 Hz, 2 3-H), 7.65 (2H, d, *J* 2.2 Hz, 2 6-H), 7.93 (2H, dd, *J* 8.9, 2.2 Hz, 2 4-H); δ_C (DMSO-d_6) 25.62 ($2CH_2CH_2N$), 40.34 ($2CH_2N$), 67.80 and 68.42 ($2CH_2CH_2OAr$), 105.35 and 106.66 (2 3-C, 2 6-C), 119.89 (2 4-C), 135.14 (2 5-C), 143.76 and 145.13 (2 1-C, 2 2-C); *m*/*z* 432 (100, M^+), 415 (28), 165 (44), 161 (41), 146 (50), 123 (36), 119 (32), 78 (27), 77 (39), 65 (42).

Table 1
Crystallographic data and structure refinement details for **2a** and **2b**·H_2O

Parameter	**2a**	**2b**·H_2O
Empirical formula	$C_{11}H_{16}N_2O_5$	$C_{18}H_{24}N_4O_8$
Formula weight	256.26	424.41
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$
Unit cell: dimensions (Å), (°)	a=13.830 (13), b=13.313 (12), c=6.731 (6) β=103.519 (16)	a=4.850 (2), b=31.974 (12), c=13.156 (5) β=100.540 (6)
Volume (Å^3)	1204.8 (19)	2005.7 (14)
Z, D_{calcd} [Mg/m^3]	4, 1.413	4, 1.406
μ [mm^{-1}]	0.112	0.112
F(000)	544	896
Crystal size (mm^3)	0.40×0.20×0.05	0.40×0.06×0.02
θ Range (°)	1.53–30.11	0.64–30.33
Index ranges	$-18\le h\le 17$, $-18\le k\le 18$, $-9\le l\le 9$	$-6\le h\le 6$, $-44\le k\le 44$, $-18\le l\le 18$
Reflections collected	9700	19,818
Independent reflections	3213 [R(int)=0.0955]	5744 [R(int)=0.0963]
Reflections with $I>2\sigma(I)$	1517	2902
Goodness-of-fit on F^2	1.054	0.961
Final R indices [$I>2\sigma(I)$]	R_1=0.1118, wR_2=0.2869	R_1=0.0608, wR_2=0.1078
R indices (all data)	R_1=0.1978, wR_2=0.3490	R_1=0.1453, wR_2=0.1324
Largest diff. peak and hole (e Å^{-3})	0.440 and −0.432	0.280 and −0.295

4.5. Synthesis of dibenzodiazacrown ether 4b from podand 3b

A mixture of **3b** (82 mg, 0.2 mmol) and a 5% solution of 1,3-propanediamine (4 mmol) in dry EtOH was heated at 130 °C (an oil bath) for 9 days in a sealed tube. After tube opening, the solvent was evaporated in vacuo. Water (20 mL) and concentrated HCl (dropwise, to pH 3) were added to the residue. An aqueous solution was extracted with EtOAc, and the extract was concentrated in vacuo. The residue was purified by column chromatography on silica gel using EtOAc as the eluent. Yield **4b**: 4 mg (5%); mp 246–247 °C.

4.6. X-ray diffraction study

All the crystals were grown using a slow evaporation of a solution of compound **2a**,**b** in a water–MeCN mixture (~2:1, v/v) at ambient temperature. The single crystals were coated with perfluorinated oil and mounted on a Bruker SMART-CCD diffractometer (graphite monochromatized Mo Kα radiation (λ=0.71073 Å), ω scan mode) under a stream of cooled nitrogen (T=173 (2) K). The sets of experimental reflections were measured and the structures were solved by direct methods and refined by the full matrix least-squares against F^2 with anisotropic thermal parameters for all non-hydrogen atoms. The hydrogen atoms were fixed at calculated positions at carbon atoms and then refined using a riding model. The hydrogen atoms of NH and OH groups of aza podands **2a**,**b** and the hydrogen atoms of solvation water molecule in structure **2b**·H_2O were located from the difference Fourier maps and refined isotropically (SADI command was applied). All the calculations were performed using the SHELXTL-Plus software.[10] The crystal parameters and structure refinement details are given in Table 1. Crystallographic data (excluding structure factors) for the structures have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-809265 (**2a**) and -809266 (**2b**·H_2O). Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 (0)1223 336033 or e-mail: deposit@ccdc.cam.ac.uk).

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