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Synthesis and electrode properties of 19-membered azo- and azoxycrown ethers. Structure of dibenzo-19-azocrown-7

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Abstract—19-Membered azo- and azoxycrown ethers have been synthesized by reductive macrocyclization of respective bis-(nitrophenoxy)oxaalkanes. The behavior of these compounds as ionophores in ion-selective membrane electrodes has been studied. The structure of the 19-membered dibenzoazocrown ether has been determined.

1. Introduction

The chromogenic system of azo dyes consists of a chain of conjugated double bonds and azo group(s). An azo group inserted into conjugated system causes a strong increase of color intensity. Additionally azo compounds can exist in two isomeric forms (*Z* and *E*) that make the system even more interesting for physicochemical study especially if the azo group forms part of a macrocyclic system.

So far, three procedures for azocrown ether synthesis have been described. The first consists of alkylation of 2,2′-hydroxyazobenzene.[1] The second method utilizes reduction of bis(2-nitrophenoxy)-oxaalkanes with sodium or potassium stannite whereupon the azo bond is formed.[2] This procedure allowed two main macrocyclic products to be obtained with azo or azoxy groupings. According to this reductive macrocyclization method, 10-, 13-, and 16-membered azo and azoxycrown ethers have been synthesized.[3–5] Finally, the third procedure consists of nucleophilic substitution of difluoroazobenzene with alcoholates, thiolates or diamines.[6]

Preliminary studies have shown that 19-membered azo- and azoxycrown ethers could be prepared by reductive macrocyclization in a similar way to the 13- and 16-membered analogs.

The aim of this work was preparation of 19-membered azocrown ethers, identification of their stereoisomers, and presentation of their properties in ion-selective membrane electrodes.

2. Results and discussion

2.1. Synthesis

The presented synthesis of 19-membered azo- and azoxycrown ethers is a two-step reaction. 1,11-Bis(2-nitrophenoxy)-3,6,9-trioxaundecanes were obtained by reaction of 2-nitrophenol or its derivatives with 1,11-dichloro-3,6,9-trioxaundecane in dry dimethylformamide in the presence of anhydrous potassium carbonate (compounds **1–3**) (Scheme 1).

In the next step, nitroderivatives **1–3** were reduced in water–acetone with sodium or potassium stannite to produce 19-membered azo- and azoxycrown ethers. A remarkable sodium template effect for azo compound formation was noticed only in the case of reduction of compound **1**. If sodium hydroxide was used instead of potassium hydroxide the yield of compound **4** increased almost twice. The yield of macrocyclic products was lower than in the case of 13- and 16-membered compounds and more polymeric products were formed. In addition, the separation of *Z* and *E* isomers of 19-membered substituted azocrown ethers was troublesome because of rapid isomerization; in some cases, their geometry was ascribed considering significant differences in ^{1}H NMR spectra. Surprisingly, compound **4** in the solid state and in solutions in chloroform, methanol and acetone solution existed only in *E* form.

Keywords: Azocrown; Azoxycrown ethers; Ion-selective membrane; Thallium(I) selectivity.
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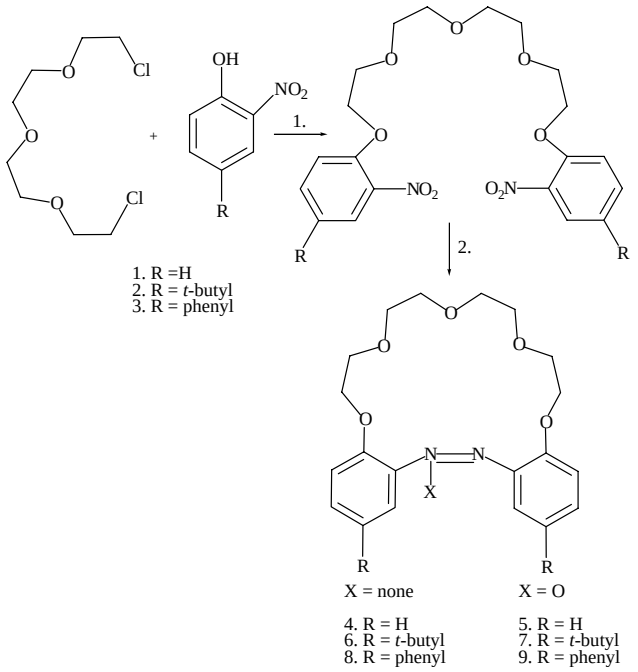

Scheme 1. Synthesis of 19-membered azo and azoxycrown ethers; (1) K_2CO_3, DMF, 120 °C; (2) NaOH or KOH, $SnCl_2$, water/acetone.

2.2. Membrane electrodes

The most frequently studied property of azo- and azoxycrown ethers is their behavior in ion-selective membrane electrodes. 13-Membered azocrown ethers are selective toward sodium cations[7] while 16-membered compounds are potassium selective[8] in membrane electrodes. We expected that 19-membered derivatives should be selective to larger cations. In a preliminary experiments the ion-selective membrane electrodes doped with 19-membered azo- and azoxycrown ethers were selective for the thallium(I) cation (Fig. 1).

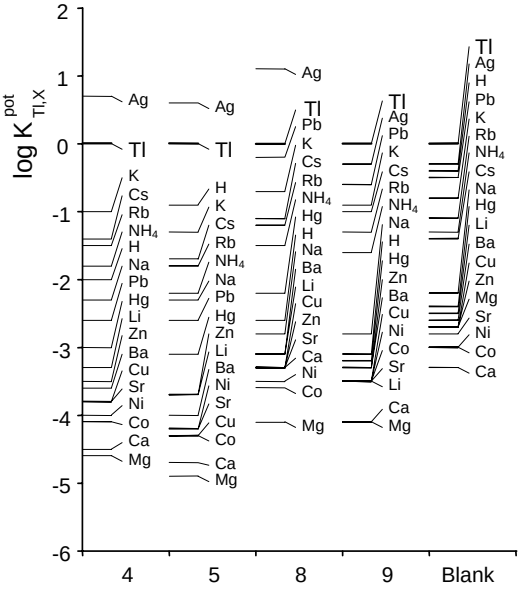

Figure 1. Diagram of log $K^{pot}_{Tl/X}$ values of ion-selective membrane electrode doped with azo- or azoxycrown ethers **4**, **5**, **8**, or **9** compared to blank electrode.

Compared to this cation, only the electrode response to Ag(I) was higher for ionophores **4**, **5**, and **8**. Furthermore, electrodes based on compounds **4** and **5** showed high thallium selectivity in the presence of many transition and heavy metal cations like Pb(II), Hg(II), Zn(II) and Ni(II), and alkali earth cations.

Thallium salts are extremely toxic. Thallium is obtained as a side product in sulfuric acid manufacture and during lead decontamination. Thallium can be delivered into human body from contaminated air, water or food. Thallium replaces potassium cations, thus causing deactivation of some enzymes. Therefore, thallium distribution has to be under strict control; the ion-selective membrane electrodes based on 19-membered azo- and azoxycrown ethers appeared as potentially useful for that purpose.

2.3. X-Ray structure

X-ray study reveals that in the crystal structure of **4** the asymmetric part of unit cell contains two crystallographically independent molecules labeled **A** and **B**, Figure 2. Both molecules are chemically equivalent and adopt *E* geometry with aromatic moieties in *trans*-positions around the –N═N– bond, but differ essentially in the conformation of their polyether chains.

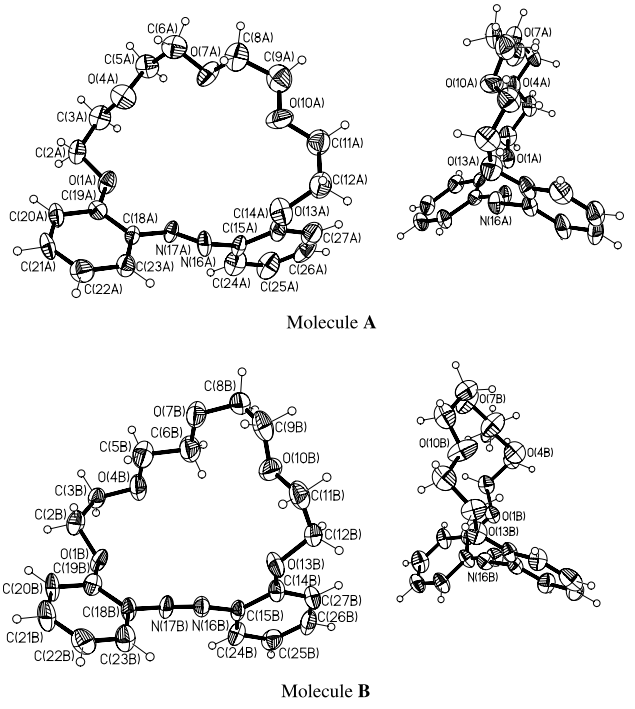

Figure 2. Top and side view of molecules **A** and **B** in the structure of **4** with atom numbering scheme.

The torsion angles around the C–C bonds in the polyethylene chain of **A** are *gauche*, and *anti* around C–O bonds, except C(11A)–C(12A)–O(13A)–C(14A)=74.5°, which is *gauche*, Table 1, and the conformation of the polyoxyethylene chain units may be described as: $a, a, -g, a, a, g, a, a, -g, a, a, g, g, a$, starting at the O(1A)–C(19A) bond. The sequence of two *gauche* torsion angles form corner fragment[9] at C(12A) atom

Table 1. Selected valence and torsion angles (°) for **4** and selected bond lengths for **4**

Angle	Molecule **A**	Molecule **B**	Angle	Molecule **A**	Molecule **B**
O(1)–C(2)–C(3)–O(4)	−67.9(8)	−58.5(9)	C(6)–O(7)–C(8)–C(9)	−161.2(8)	−85.8(11)
C(2)–C(3)–O(4)–C(5)	176.2(7)	−77.0(9)	O(7)–C(8)–C(9)–O(10)	−77.3(10)	72.2(11)
C(3)–O(4)–C(5)–C(6)	−175.6(7)	173.2(8)	C(8)–C(9)–O(10)–C(11)	170.4(7)	172.9(7)
O(4)–C(5)–C(6)–O(7)	74.6(8)	179.1(8)	C(9)–O(10)–C(11)–C(12)	172.1(8)	−164.2(7)
C(5)–C(6)–O(7)–C(8)	−177.0(7)	−177.1(8)	O(10)–C(11)–C(12)–O(13)	59.1(9)	−74.0(8)
C(11)–C(12)–O(13)–C(14)	74.5(10)	156.6(7)	N(16)–N(17)–C(18)–C(19)	160.0(7)	140.8(7)
C(12)–O(13)–C(14)–C(15)	−167.6(7)	−165.1(6)	N(17)–C(18)–C(19)–O(1)	−8.7(9)	−3.2(11)
O(13)–C(14)–C(15)–N(16)	−0.5(11)	−7.9(10)	C(18)–C(19)–O(1)–C(2)	−166.7(6)	−149.5(7)
C(14)–C(15)–N(16)–N(17)	137.1(7)	150.9(7)	C(19)–O(1)–C(2)–C(3)	153.9(6)	161.1(6)
C(15)–N(16)–N(17)–C(18)	170.7(6)	171.6(7)			
Bond	Molecule **A**	Molecule **B**	Bond	Molecule **A**	Molecule **B**
O(1)–C(19)	1.362(8)	1.357(9)	C(5)–O(4)–C(3)	113.7(6)	113.6(6)
O(1)–C(2)	1.437(9)	1.421(8)	O(4)–C(5)–C(6)	108.3(7)	108.6(7)
C(2)–C(3)	1.496(10)	1.483(10)	O(7)–C(6)–C(5)	111.9(8)	108.4(8)
C(3)–O(4)	1.397(9)	1.424(8)	C(6)–O(7)–C(8)	113.5(7)	115.3(7)
O(4)–C(5)	1.394(8)	1.389(10)	O(7)–C(8)–C(9)	112.3(8)	115.0(8)
C(5)–C(6)	1.471(10)	1.521(10)	O(10)–C(9)–C(8)	112.7(9)	113.1(8)
C(6)–O(7)	1.402(9)	1.350(10)	C(9)–O(10)–C(11)	112.6(8)	116.0(8)
O(7)–C(8)	1.403(9)	1.400(8)	O(10)–C(11)–C(12)	109.7(8)	107.1(7)
C(8)–C(9)	1.462(11)	1.449(11)	C(11)–C(12)–O(13)	111.7(7)	108.6(7)
C(9)–O(10)	1.332(10)	1.352(11)	C(14)–O(13)–C(12)	120.4(7)	116.0(6)
O(10)–C(11)	1.416(10)	1.457(10)	O(13)–C(14)–C(27)	124.0(9)	124.3(7)
C(11)–C(12)	1.442(11)	1.474(11)	O(13)–C(14)–C(15)	117.1(7)	116.4(7)
C(12)–O(13)	1.459(10)	1.441(8)	C(27)–C(14)–C(15)	118.8(9)	119.3(8)
O(13)–C(14)	1.366(10)	1.334(9)	C(24)–C(15)–C(14)	120.7(8)	120.6(7)
C(14)–C(27)	1.386(10)	1.375(10)	C(24)–C(15)–N(16)	123.3(8)	123.1(7)
C(14)–C(15)	1.400(11)	1.417(10)	C(14)–C(15)–N(16)	115.9(7)	115.9(8)
C(15)–C(24)	1.385(10)	1.359(10)	C(25)–C(24)–C(15)	119.7(9)	120.3(8)
C(15)–N(16)	1.416(9)	1.431(9)	C(24)–C(25)–C(26)	118.9(9)	118.2(8)
C(24)–C(25)	1.384(11)	1.396(10)	C(27)–C(26)–C(25)	121.9(9)	122.7(8)
C(25)–C(26)	1.385(12)	1.377(11)	C(26)–C(27)–C(14)	119.9(10)	118.9(8)
C(26)–C(27)	1.362(12)	1.376(11)	N(17)–N(16)–C(15)	113.3(6)	113.8(6)
N(16)–N(17)	1.236(7)	1.257(7)	N(16)–N(17)–C(18)	114.7(6)	112.3(6)
N(17)–C(18)	1.426(8)	1.425(9)	C(23)–C(18)–C(19)	119.1(7)	119.8(7)
C(18)–C(23)	1.393(9)	1.370(10)	C(23)–C(18)–N(17)	123.7(7)	122.4(6)
C(18)–C(19)	1.404(10)	1.401(9)	C(19)–C(18)–N(17)	117.0(7)	117.6(7)
C(19)–C(20)	1.373(9)	1.381(10)	O(1)–C(19)–C(20)	123.3(8)	123.7(7)
C(20)–C(21)	1.398(10)	1.370(11)	O(1)–C(19)–C(18)	116.8(7)	116.6(7)
C(21)–C(22)	1.333(11)	1.371(11)	C(20)–C(19)–C(18)	119.9(7)	119.7(8)
C(22)–C(23)	1.374(10)	1.387(10)	C(19)–C(20)–C(21)	119.1(8)	119.6(8)
C(19)–O(1)–C(2)	118.6(6)	117.5(6)	C(22)–C(21)–C(20)	121.0(8)	121.2(8)
O(1)–C(2)–C(3)	107.6(7)	108.5(6)	C(21)–C(22)–C(23)	121.2(8)	119.5(9)
O(4)–C(3)–C(2)	108.4(7)	115.0(6)	C(22)–C(23)–C(18)	119.5(8)	120.1(8)

of macrocycle **A**. In macrocycle **B** one of the torsion angles around C–C bond (O(4B)–C(5B)–C(6B)–O(7B)=179.1°) is *anti* creating sequence of three *anti* torsion angles in the polyether chain, which is unusual for azo-macrocycles. The conformation of the polyether chain starting from O(1B)–C(19B) is: *a*, *a*, −*g*, −*g*, *a*, *a*, *a*, −*g*, *g*, *a*, *a*, −*g*, *a*, *a*. The series of torsion angles points to the presence of two corner fragments in macrocycle **B**, at atoms C(3B) and C(8B). Torsion angles around N16–N17 and bond lengths equal 170.7(6) and 171.6(7)°, and 1.236(7) and 1.257(7) Å, respectively, for molecules **A** and **B** and had of common values, Table 1.

The heteroatoms of the macrocycle **A** cavity are roughly coplanar and deviate from their mean plane in the range −0.200(4) – 0.229(4) Å. In the case of macrocycle **B**, the cavity is non-planar and the heteroatoms deviate from the mean plane in the range from −0.761(5) to 0.480(4) Å. The benzene residues are located at different sides of the mean plane in both molecules. Despite conformational differences between the polyether chains, the dihedral angles between aromatic residues in molecules **A** and **B** adopt very similar values of 71.1(2) and 77.9(2)°, respectively. These angles essentially exceed the corresponding dihedral angles found in the relative small sized 10-membered[10] and 13-membered,[11] or bigger 21-membered[12] trans-isomers of azobenzocrown ethers bearing 2,2′-linked azobenzene moiety, where they are in the range of 0–40°. Interestingly, in the closest by size 20-membered azoazoxycrown[13] the dihedral angles between benzene residues of azo- and azoxybenzene moieties equal 73.5 and 76.4°, and agree well with the values reported here for the 19-membered azomacrocycle.

3. Experimental

All materials and solvents used for synthesis were of analytical reagent grade. Silica gel 60 (Merck) was used for column chromatography. Preparative TLC glass plates covered with Silica gel 60 F_{254} (Merck) were used for final separation of crown ethers. ^{1}H NMR spectra, all in $CDCl_3$, were taken on Varian instruments at 200 MHz and/or 500 MHz. In the case of *Z* or *E* isomers of azocrown ethers, the spectra were recorded immediately after

dissolution of crystals or oil. IR and mass spectra were recorded on AMD-604 and Genesis II (Mattson) apparatus, respectively. Additionally, purity and identity of macrocyclic compounds was established by elemental analysis taken on an EAGER 200 apparatus. The mp were uncorrected. 4-*t*-Butyl-2-nitrophenol and 4-phenyl-2-nitrophenol were obtained according to literature data.[9]

3.1. Membrane electrodes and potentiometric measurements

The preparation of membranes for ion-selective electrodes was described earlier in detail.[9] The standard composition of membranes was: ionophore 10 mg, potassium tetrakis-(4-chlorophenyl)borate 0.5 mg, poly(vinyl chloride) 50 mg, and 2-nitrophenyl octyl ether 0.1 mL.

3.2. X-Ray crystal structure determination

A single crystal of azocrown **4** was obtained by crystallization from hexane. The data were collected at room temperature on KUMA diffractometer using graphite-monochromated Mo $K\alpha$ radiation and were corrected for Lorentz and polarization effects. The structure was solved using direct methods and refined by full-matrix least squares on F^2.[14] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in geometrically calculated positions and refined using temperature factors 1.2 times those of their bonded carbon atoms. Crystal data for **4**: $C_{20}H_{24}N_2O_5$, $M_r=372.41$, monoclinic, $P2_1/n$, $a=14.976(3)$ Å, $b=14.024(3)$ Å, $c=18.577(4)$ Å, $\beta=97.71(3)°$, $V=3866(1)$ Å^3, $Z=8$, $D_c=1.280$ g/cm^3, $\mu=0.92$ cm^{-1}, $F(000)=1584$, $\theta_{max}=25.56°$($-18\le h\le 17$, $0\le k\le 17$, $0\le l\le 21$), reflections collected 7435, independent reflections 7203 ($R_{int}=0.0566$), goodness-of-fit on F^2 $S=1.068$. Final residuals (for 488 parameters) $R1=0.0633$, $wR2=0.1805$ for 2657 reflections with $I>2\sigma(I)$, and $R1=0.1724$, $wR2=0.2164$ for all data. Residual electron density: 0.432 and -0.244 eÅ^{-3}.

3.3. Syntheses.

3.3.1. 1,11-Bis(2-nitrophenoxy)-3,6,9-trioxaundecane (1). A mixture of 2-nitrophenol (6.9 g, 50 mmol), 1,11-dichloro-3,6,9-trioxaundecane (5.8 g, 25 mmol), anhydrous potassium carbonate (6.9 g, 50 mmol) and dimethylformamide (15 mL) was heated at 120 °C for 8 h. The mixture was poured into water and the product was extracted with chloroform. After evaporation of solvent, the residue was purified by gradient column chromatography using petroleum ether/chloroform solvent system. Yield of the pure oily product was 14.8 g (68%). Calculated for $C_{20}H_{24}N_2O_9$: [M+H peak] $m/z=437.1560$. Found: 437.1562. Anal. Calcd C 55.04, H 5.50, N 6.42. Found C 55.0, H 5.48, N 6.41; δ_H ($CDCl_3$, 200 MHz): 3.58–3.63 (4H, m); 3.67–3.71 (4H, m); 3.82–3.88 (4H, m); 4.18–4.23 (4H, m); 6.92–7.09 (4H, m); 7.42–7.51 (2H, m); 7.74 (2H, dd, $J_1=1.7$ Hz, $J_2=8.1$ Hz); Mass Spec (MeOH, ES+) *m/z* expected: 436.15. Found: 437.16 (M+H); IR (film) 2870, 1604, 1520, 1349, 1280, 1130, 936, 849, 746 (cm^{-1}).

3.3.2. 1,11-Bis(4-*tert*-butyl-2-nitrophenoxy)-3,6,9-trioxaundecane (2). Obtained analogously to **1** using: 4-*tert*-butyl-2-nitrophenol[9] (9.8 g, 50 mmol), 1,11-dichloro-3,6,9-trioxaundecane (5.8 g, 25 mmol), anhydrous potassium carbonate (6.9 g, 50 mmol) and dimethylformamide (15 mL). Yield of pure oily product was 16.5 g (60%). Calculated for $C_{28}H_{41}N_2O_9$: [M+H peak] $m/z=549.2812$. Found: 549.2810. Anal. Calcd C 61.31, H 7.30, N 5.11. Found C 61.28, H 7.31, N 5.10; δ_H ($CDCl_3$, 200 MHz): 1.31 (18H, s); 3.64–3.69 (4H, m); 3.73–3.78 (4H, m); 3.89 (4H, t, $J=4.6$ Hz); 4.24 (4H, t, $J=5.1$ Hz); 7.04 (2H, d, $J=8.8$ Hz); 7.52 (2H, dd, $J_1=4.8$ Hz, $J_2=8.8$ Hz); 7.82 (2H, d, $J=2.5$ Hz). Mass Spec (MeOH, ES+) *m/z* expected: 548.27. Found: 549.28 (M+H); IR (film) 2778, 1606, 1542, 1353, 1278, 1133, 1043, 938, 851, 746, 668 (cm^{-1}).

3.3.3. 1,11-Bis(4-phenyl-2-nitrophenoxy)-3,6,9-trioxaundecane (3). Obtained analogously to **1** using: 4-phenyl-2-nitrophenol[9] (10.8 g, 50 mmol), 1,11-dichloro-3,6,9-trioxaundecane (5.8 g, 25 mmol), anhydrous potassium carbonate (6.9 g, 50 mmol) and dimethylformamide (15 mL). Crude compound **3** was purified by column chromatography using chloroform as an eluent. Yield after crystallization from 2-propanol was 17.6 g (60%). Mp 80–82 °C, yellow crystals. Calculated for $C_{32}H_{33}N_2O_9$: [M+H peak] $m/z=589.2186$. Found: 549.2188. Anal. Calcd C 65.31, H 5.61, N 4.76. Found C 65.29, H 5.62, N 4.75; δ_H ($CDCl_3$, 200 MHz): 3.67–3.72 (4H, m); 3.76–3.81 (4H, m); 3.91–3.96 (4H, m); 4.28–4.33 (4H, m); 7.17 (2H, d, $J=8.7$ Hz); 7.36–7.56 (10H, m); 7.71 (2H, dd, $J_1=2.4$ Hz, $J_2=8.7$ Hz); 8.05 (2H, d, $J=2.3$ Hz). Mass Spec (MeOH, ES+) *m/z* expected: 588.21. Found: 589.22 (M+H); IR (film) 2783, 1607, 1524, 1356, 1279, 1132, 1044, 940, 850, 746, 664 (cm^{-1}).

3.3.4. Bis(benzo)-19-azocrown-7 (4) and bis(benzo)-19-azoxycrown-7 (5). *In the presence of potassium hydroxide*. Water (12 mL) was added dropwise to a vigorously stirred mixture of dinitroderivative **1** (1.3 g, 3 mmol), stannous chloride dihydrate (2.9 g, 13 mmol), potassium hydroxide (5.6 g) and acetone (15 mL). The mixture was additionally vigorously stirred at 50 °C for 5 h. Then the cooled mixture was diluted with water (10 mL) and extracted with chloroform (3×50 mL). The organic layer was dried over anhydrous $MgSO_4$ and the solvent was evaporated under reduced pressure. The crude product was preliminarily chromatographed on a short silica gel column using methylene chloride at the beginning and then methylene chloride–acetone mixture (10/1) as eluents to remove polymers and diacetone alcohol. The eluate was evaporated and the residue was extracted with hot heptane to isolate a mixture of compounds **4** and **5** that finally were separated by preparative thin-layer chromatography. The azocrown ether was crystallized from heptane to obtain *E* isomer (56 mg, 5%), mp 114–116 °C. The azoxycrown ether was obtained as yellowish oil (112 mg, 10%).

In the presence of sodium hydroxide. The synthesis was performed analogously using an equivalent amount of sodium hydroxide. After the reaction was completed, the mixture was cooled and the precipitated sodium chloride was filtered off and washed with toluene (2×25 mL). The combined organic layers were dried over $MgSO_4$ and the solvents were evaporated under reduced pressure. After separation of the crown ethers as above, the azocrown ether was crystallized from heptane to afford *E* isomer

(200 mg, 18%), mp 116 °C. The azoxycrown ether was obtained as yellowish oil (104 mg, 9%).

Azocrown **4**. Calculated for $C_{20}H_{25}N_2O_5$: [M+H peak] m/z=373.1763. Found: 373.1764. Anal. Calcd C 64.50, H 6.50, N 7.52. Found C 64.56, H 6.44, N 7.44; Mass Spec (MeOH, ES+) m/z expected: 372.17. Found: 373.18 (M+H); isomer *E*: δ_H ($CDCl_3$, 500 MHz): 3.45–3.47 (4H, m); 3.59–3.61 (4H, m); 4.40 (4H, t, J=4.4 Hz); 4.37 (4H, t, J=4.4 Hz); 7.02 (2H, d, J=7.8 Hz); 7.33 (2H, dd, J_1=1.5 Hz, J_2=7.8 Hz); 7.39 (2H, dt, J_1=1.5 Hz, J_2=7.32 Hz). IR (film), ν_{max} (cm^{-1}) 2924, 2872, 1589, 1482, 1452, 1285, 1242, 1124, 1046, 938, 753.

Azoxycrown **5**. Calculated for $C_{20}H_{25}N_2O_6$: [M+H peak] m/z=389.1713. Found: 389.1712. Anal. calcd C 61.84, H 6.23, N 7.21. Found C 61.90, H 6.23, N 7.18; δ_H ($CDCl_3$, 500 MHz): 3.59–3.62 (4H, m); 3.64–3.69 (4H, m); 3.90–3.93 (4H, m); 4.27–4.31 (4H, m); 7.04 (3H, m); 7.11 (1H, d, J=8.3 Hz); 7.32 (1H, dt, J_1=1.5 Hz, J_2=7.8 Hz); 7.42 (1H, dt, J_1=1.5 Hz, J_2=8.8 Hz); 7.63 (1H, dd, J_1=1.5 Hz, J_2=8.3 Hz); 8.05 (1H, dd, J_1=1.5 Hz, J_2=8.3 Hz); Mass Spec (MeOH, ES+) m/z expected: 388.16. Found: 389.17 (M+H); IR (film) 2957, 2917, 2874, 1600, 1521, 1486, 1453, 1351, 1261, 1107, 1056, 940, 850, 801,745, 672 (cm^{-1}).

3.3.5. Bis(4-*tert*-butylbenzo)-19-azocrown-7 (6) and bis(4-*tert*-butylbenzo)-19-azoxycrown-7 (7). Water (10 mL) was added drop by drop to vigorously stirred mixture of dinitroderivative **2** (1.1 g, 2 mmol), stannous chloride dihydrate (1.95 g, 8 mmol), sodium hydroxide (2.4 g) and acetone (8 mL). The mixture was additionally stirred at 65 °C for 4.5 h. The products were separated analogously to **4** and **5**, and finally purified by preparative thin-layer chromatography using chloroform as mobile phase. The azocrown ether crystallized in 'mass' as a mixture of isomers, 77 mg (8%), mp 128–129 °C. The azoxycrown ether was obtained as yellowish oil 100 mg (10%).

Azocrown **6**. Calculated for $C_{28}H_{41}N_2O_5$: [M+H peak] m/z=485.3015. Found: 485.3013. Anal. calcd C 69.40, H 8.32, N 5.78. Found C 68.95, H 8.27, N 5.74.

Azocrown **6**, isomer *Z*: δ_H ($CDCl_3$, 500 MHz): 1.15 (18H, s); 3.70–3.74 (8H, m); 3.86 (4H, t, J=4.9 Hz); 3.98 (4H, t, J=4.9 Hz); 6.80 (2H, d, J=8.8 Hz); 6.90 (2H, d, J=2.4 Hz); 7.15 (2H, dd, J_1=2.4 Hz, J_2=8.3 Hz).

Azocrown **6**, isomer *E*: δ_H ($CDCl_3$, 500 MHz): 1.35 (18H, m); 3.50–3.52 (4H, m); 3.62–3.64 (4H, m) 3.89 (4H, t, J=4.4 Hz); 4.33 (4H, t, J=4.4 Hz); 7.01 (2H, d, J=8.8 Hz); 7.40 (2H, dd, J_1=2.4 Hz, J_2=8.3 Hz); 7.42 (2H, d, J=2.4 Hz). The signals ascribed to this form were selected from spectrum of a mixture of isomers (around 75% *E*, and 25% *Z*). Mass Spec (MeOH, ES+) m/z expected: 484.29. Found: 485.30 (M+H); IR (mixture of isomers) (film), 2960, 2870, 1601, 1497, 1461, 1395, 1360, 1260, 1134, 1053, 992, 938, 894, 815, 755 (cm^{-1}).

Azoxycrown **7**. Calculated for $C_{28}H_{41}N_2O_6$: [M+H peak] m/z=501.2965. Found: 501.2967. Anal. calcd C 67.18, H 8.05, N 5.60. Found C 67.00, H 7.99, N 5.56; δ_H ($CDCl_3$, 500 MHz): 1.34 (9H, s); 1.36 (9H, s); 3.62–3.65 (4H, m); 3.67–3.69 (4H, m); 3.90–3.93 (4H, m); 4.26–4.29 (4H, m); 7.00 (1H, d, J=8.8 Hz); 7.04 (1H, d, J=8.8 Hz); 7.34 (1H, dd, J_1=2.4 Hz, J_2=8.8 Hz); 7.43 (1H, dd, J_1=2.4 Hz, J_2=8.3 Hz); 7.66 (1H, d, J=2.4 Hz); 8.03 (1H, d, J=2.4 Hz). Mass Spec (MeOH, ES+) m/z expected: 500.29. Found: 501.30 (M+H); IR (film) 2965, 2872, 1731, 1605, 1504, 1457, 1359, 1265, 1134, 942, 896, 819, 753 (cm^{-1}).

3.3.6. Bis(4-phenylbenzo)-19-azocrown-7 (6) and bis(4-phenylbenzo)-19-azoxycrown-7 (7). Water (8 mL) was dropwise added to a vigorously stirred mixture of dinitroderivative **3** (1.2 g, 2 mmol), stannous chloride dehydrate (1.95 g, 8 mmol), sodium hydroxide (2.4 g) and acetone (8 mL). The mixture was stirred at 55 °C additionally for 4 h. After work-up as above the azocrown ether was obtained as red oil, 83 mg (8%), mp 128–129 °C. The azoxycrown ether was obtained as yellowish oil (162 mg, 15%).

Azocrown **8**. Calculated for $C_{32}H_{33}N_2O_5$: [M+H peak] m/z=525.2395. Found: 529.2398. Anal. calcd C 73.28, H 6.11, N 5.34. Found C 73.01, H 8.22, N 5.70.

Azocrown **8**, isomer *Z*: δ_H ($CDCl_3$, 500 MHz): 3.73–3.75 (6H, m); 3.79–3.81 (2H, m) 3.85 (2H, t, J=4.5 Hz); 3.95 (2H, t, J=4.5 Hz); 4.19 (2H, t, J=4.5 Hz); 4.30 (2H, t, J=4.5 Hz); 6.95 (2H, d, J=8.8 Hz); 7.27 (2H, dd, J=2.2 Hz); 7.28–7.38 (10H, m); 7.67 (2H, dd, J_1=2.2 Hz, J_2=8.8 Hz); These signals ascribed to form *Z* were selected from spectrum of a mixture of isomers (around 50% *E*, and 50% *Z*).

Azocrown **8**, isomer *E*: δ_H ($CDCl_3$, 500 MHz): 3.49–3.50 (2H, m); 3.63–3.64 (2H, m); 3.71–3.73 3.85 (4H, m); 3.90–3.92 (4H, m); 4.06 (2H, t, J=4.8 Hz); 4.40 (2H, t, J=4.3 Hz); 7.11–7.15 (2H, m); 7.40–7.46 (6H, m); 7.48–7.52 (6H, m); 8.04 (2H, d, J=2.2 Hz). Signals ascribed to this form were selected from spectrum of a mixture of isomers (75% *E*, and 25% *Z*). Mass Spec (MeOH, ES+) m/z expected: 528.23. Found: 529.24 (M+H); IR (mixture of isomers) (film) 2920, 2867, 1602, 1516, 1480, 1356, 1273, 1128, 1057, 942, 828, 758, 698 (cm^{-1}).

Azoxycrown **9**. Calculated for $C_{32}H_{33}N_2O_6$: [M+H peak] m/z=541.2339. Found: 541.2335; (540.6) MS: m/e=540. Anal. calcd C 71.11, H 5.92, N 5.18. Found C 71.08, H 5.90, N 5.16; δ_H ($CDCl_3$, 500 MHz): 3.63–3.64 (4H, m); 3.69–3.71 (4H, m); 3.94–3.97 (4H, m); 4.33–4.36 (4H, m); 7.14 (1H, d, J=8.8 Hz); 7.20 (1H, d, J=8.8 Hz); 7.31–7.37 (2H, m); 7.43–7.46 (4H, m); 7.57 (1H, dd, J_1=2.4 Hz, J_2=8.8 Hz); 7.58–7.63 (4H, m); 7.66 (1H, dd, J_1=2.4 Hz, J_2=8.8 Hz); 7.91 (1H, d, J=2.0 Hz); 8.34 (1H, d, J=2.4 Hz). Mass Spec (MeOH, ES+) m/z expected: 540.23. Found: 541.23 (M+H); IR (film) 3016, 2925, 2872, 1606, 1517, 1478, 1456, 1278, 1136, 1055, 939, 890, 818, 757, 697 (cm^{-1}).

4. Supplementary data

Crystallographic data for the structure reported in this paper has been deposited with the Cambridge Crystallographic Data Centre as Supplementary Publication No. CCDC 247296. Copies of the data can be obtained free of charge from the

CCDC (12 Union Road, Cambridge CB2 1EZ, UK; Tel.: +44 1223 336 408; fax: +44 1223 336 003; e-mail:deposit@ccdc.cam.ac.uk; www:http://ccdc.cam.ac.uk).

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