

Crown Ethers with Azo or Azoxy Unit and Sulfur Atom(s) in 16-Membered Macrocycle

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16-membered crown ethers bearing oxygen and sulfur atom(s) and an azo or azoxy group in the macrocycle have been synthesized by reductive macrocyclization of respective dinitropodands. Behavior of the compounds as ionophores in ion-selective membrane electrodes has been studied. The structure of 16-membered azothiacycrown ether has been solved by X-ray analysis.

Key words: azothiacycrown, azoxythiacycrown, membrane electrodes, X-ray structure

Numerous synthesized crown ethers contain azo- or azoxybenzene unit as part of macrocycle [1]. Such compounds combine functionality for crown ethers and azo- or azoxybenzene; they are photo- and electroactive and form complexes with metal cations. Ion-selective membrane electrodes based on these crowns are highly selective for “hard” cations, *e.g.* sodium or potassium [1e,f,g]. Molecules possessing –N=N– or –N(O)=N– groups are prone to isomerization, thus they can be applied as molecular switches, sensors or optical memories.

In order to explore the chemistry of more metal ions it is necessary to insert donor atoms other than oxygen into the crown ether frames. Two important donor atoms are nitrogen and sulfur. The replacement of oxygen(s) for sulfur atom(s) in the macroring of crown ethers increases their susceptibility toward heavy-metal cations with simultaneous decrease of their affinity to form complexes with “hard” cations [2]. Sulfur donor atoms usually occur in sulfide form. Saturated thiacycrown ethers are soft bases and, as expected, exhibit great affinity toward metal ions classified as soft acids (Hg^{2+} , Pd^{2+} , Pt^{2+}), and some metal ions classified as borderline acids like Cu^{2+} . Previous studies of 13-membered azothia- and azoxythiacycrown ethers [3] evaluated their high sensitivity toward silver cations. Recently [4] we showed that azothiacycrown ethers form stronger complexes with soft transition metals than azoxythiacycrown ethers. Moreover, the membranes based on silver- and copper-azothiacycrown ether complexes are potentially useful for anion sensing [5].

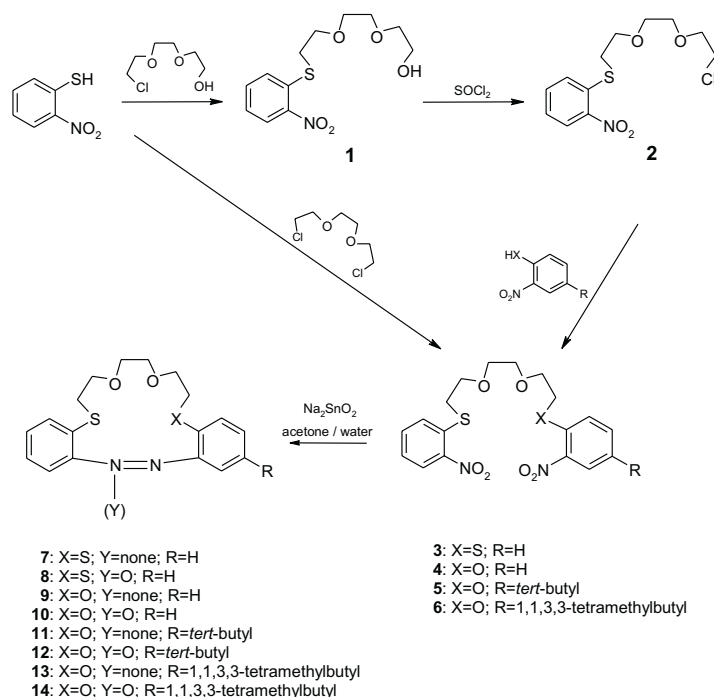
The previous successful synthesis of 13-membered thiacycrown ethers bearing azo- or azoxy group in the macrocycle [3] and their interesting properties [4,5] inspired us

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to synthesize larger analogs. The aim of this work was the synthesis of 16-membered azo- and azoxythiacrown ethers and their preliminary characterization.

RESULTS AND DISCUSSION

Synthesis. Preliminary studies showed that 16-membered azo- and azoxythiacrown ethers could be prepared in a similar way to the 13-membered analogs. The synthesis proceeds by the following route:



Dinitropodands were obtained in two ways. The symmetrical dinitrodithiacompound **3** was obtained by condensing 2-nitrothiophenol with 1,8-dichloro-3,6-dioxaoctane in dry boiling dimethylformamide in the presence of anhydrous potassium carbonate. For asymmetrical dinitropodands 2-nitrothiophenol was condensed with chloroethoxyethoxyethanol to produce alcohol **1**. It was, in turn, converted into chloro-derivative **2** with thionyl chloride in benzene and in the presence of pyridine. Chloride **2** was condensed with 2-nitrophenol or with its 4-alkyl derivatives to form asymmetric dinitropodands **4**, **5**, **6**. Both types of compounds **3–6** with one or two sulfur atoms were reduced with sodium stannite to produce 16-membered macrocyclic products and polymers. The reduction produces two sets of macrocyclic compounds: azo- and azoxythiacrown ethers **7–14**. The yield and ratio of these products depend on the structure of the starting material [6]. All isolated azocompounds were obtained as a mixture of two easily convertible isomers: *cis* and *trans*, which can be observed on

TLC chromatograms as two spots. The isomers were not separated. In the solid state compound **9** exists in *trans* form (see below).

Membrane electrodes. The properties of ion-selective membrane electrodes doped with 16-membered thiacycrown ethers with azo- or azoxy- subunits are presented in Table 1. The selectivity coefficients are related to the electrode response to potassium. The best $\log K_{K,M}^{pot}$ was found for compound **7** and Ag^+ cation (+8.3). The highest selectivity coefficients for other heavy metal cations have been observed for compound with the largest number of sulfur atoms in the macrocyclic ring. It was found that membrane doped with azocompound **7** showed higher affinity toward heavy metal ions than compounds **9**, **11** and **13**.

The alkali and alkaline earth metal ions belong to the group of most discriminated cations. The best selectivity coefficients are found for “soft” metal ions, such as Ag^+ and Hg^{2+} , according to Pearson’s Hard-Soft Acid-Base theory [7]. The response for Pb^{2+} is unexpectedly low.

Table 1. Selectivity coefficients of membrane electrodes doped with crown ethers **7**, **9**, **11** and **13** versus potassium response.

Cation	Selectivity coefficient $\log K_{K,M}^{pot}$ for			
	7	9	11	13
Na^+	-1.1	-1.7	-1.7	-1.6
Cs^+	+0.8	+0.9	-0.9	-0.2
Li^+	-1.4	-2.8	-2.7	-2.3
K^+	0.0	0.0	0.0	0.0
Ca^{2+}	-0.1	-1.9	-1.9	-1.6
Mg^{2+}	-0.5	-2.4	-2.6	-2.0
H^+	-0.7	-2.6	-1.3	-1.2
Cu^{2+}	+0.1	-1.8	-1.3	-1.1
Pb^{2+}	+1.4	-0.5	-0.6	+0.3
Ag^+	+8.3	+5.8	+4.9	+7.0
Hg^{2+}	+5.7	+1.7	+2.6	+3.9

X-ray structure of compound 9. In the structure of **9** the asymmetric part of the unit cell contains two crystallographically independent molecules labelled **a** and **b**. Figure 1 shows molecules **9a** and **9b** with displacement ellipsoids and the atomic numbering scheme. The both molecules are chemically equivalent and have similar geometric and conformational parameters (Table 2 and 3). Molecule **b** in the crystal is disordered in two orientations. The majority of the disordered atoms in these two positions overlap within resolution of the data, while two positions with approximately equal occupancies 0.539(9) and 0.461(9) could be resolved for atoms: S(1) and S(1c), O(10) and O(10c), N(13) and N(13c), and N(14) and N(14c).

The azo group in both molecules adopt the *E*-form with aromatic moieties in the *trans*-position. The dihedral angle between two aromatic residues equals 14.4(2) and

31.2(3)° for molecules **a** and **b**, respectively, and shows that this fragment in **9** is roughly planar. In the polyether chain the torsion angles around C–C bonds are *gauche*, and C–O(S) are *anti* indicating stress free conformation of polyether chain. Differently than in **9**, in the analog 13-membered azoxydithiacrown [3] two sulfur atoms tend to spread as far as possible causing an unusual sequence of *trans-trans-gauche-gauche* torsion angles in the ether chain; the aromatic residues in the dithiacrown ether are roughly perpendicular forming a dihedral angle of 86.4°.

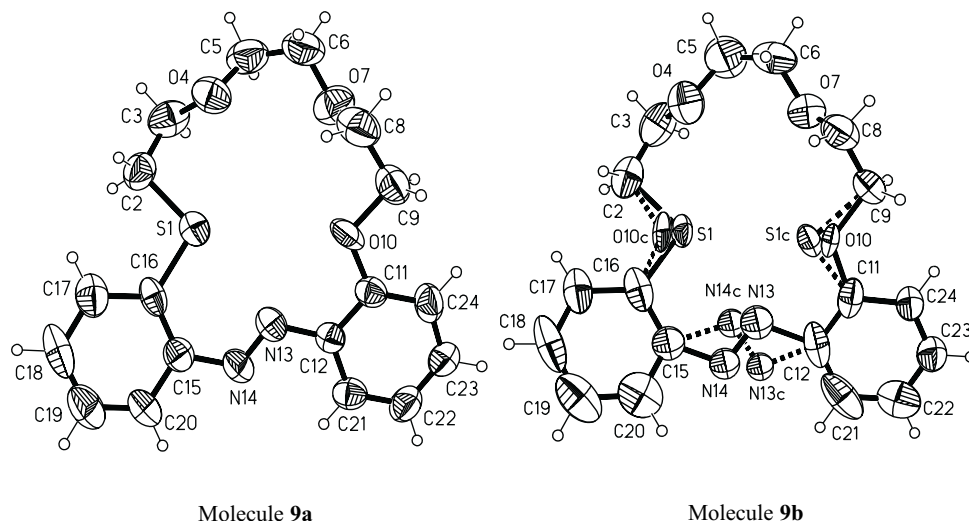


Figure 1. ORTEP plot and atomic numbering scheme for molecule **a** and **b** of compound **9**. The thermal ellipsoids have been drawn at 50% probability level. The alternative orientation of molecule **9b** has been indicated by the dashed bonds.

EXPERIMENTAL

General. All materials and solvents used for syntheses were of analytical grade. Silica gel (0.035–0.070 mm, Fluka) was used for column chromatography. ¹H NMR spectra were recorded on a Varian (200 MHz) instrument. Elemental analyses were made on a Perkin-Elmer 240C apparatus. The purity and identity of crown ethers was established by HRMS carried out on AMD-604 spectrometer or by elemental analyses. The m.p.'s are uncorrected.

Membrane electrodes and potentiometric measurements. Typical composition of membranes for ion-selective electrodes is: ionophore 10 mg, potassium tetrakis(*p*-chlorophenyl)borate 0.5 mg, poly(vinyl chloride) 50 mg and *o*-nitrophenyl-octyl ether 0.1 ml. Internal electrolyte was 1 mol·dm⁻³ potassium chloride solution. The electrodes were conditioned for two hours in 10⁻² mol·dm⁻³ KCl solution before measurements. The selectivity coefficients were determined using the separate solution method (SSM) [8] at 10⁻² mol·dm⁻³ activities of metal cations.

X-ray crystal structure analysis of (9). The deep red crystal used for the measurements was a prism of 0.2 × 0.15 × 0.15 mm. The experimental data were collected on a KUMA Diffraction KM4 diffractometer using graphite monochromated MoK α radiation. Lattice parameters were determined from least-squares refinements of 32 reflections with 9.2° ≤ 2 θ ≤ 17.4°. The ω -2 θ scan procedure was used for the data collection. The intensities of 3 standard reflections were monitored every 100 measurements and no significant

Table 2. Selected interatomic distances [\AA] and angles [$^\circ$] for compound **9**. The average value is given for the chemically equivalent bond length and angles which include the disordered atoms in the molecule **b**.

	9a	9b	9a	9b
S(1)–C(16)	1.760(6)	1.703(10)	C(12)–C(21)	1.389(8)
S(1)–C(2)	1.818(7)	1.816(9)	C(12)–N(13)	1.440(7)
C(2)–C(3)	1.485(10)	1.477(10)	N(13)–N(14)	1.223(6)
C(3)–O(4)	1.418(8)	1.383(9)	N(14)–C(15)	1.410(8)
O(4)–C(5)	1.419(8)	1.447(9)	C(15)–C(16)	1.403(8)
C(5)–C(6)	1.481(10)	1.353(11)	C(15)–C(20)	1.404(8)
C(6)–O(7)	1.436(9)	1.439(12)	C(16)–C(17)	1.391(8)
O(7)–C(8)	1.407(8)	1.396(9)	C(17)–C(18)	1.385(10)
C(8)–C(9)	1.471(10)	1.436(10)	C(18)–C(19)	1.327(11)
C(9)–O(10)	1.485(7)	1.515(14)	C(19)–C(20)	1.367(11)
O(10)–C(11)	1.419(7)	1.454(15)	C(21)–C(22)	1.373(9)
C(11)–C(12)	1.386(7)	1.353(11)	C(22)–C(23)	1.341(9)
C(11)–C(24)	1.403(9)	1.407(9)	C(23)–C(24)	1.376(9)
C(16)–S(1)–C(2)	101.9(9)	96.6(6)	C(8)–C(9)–O(10)	105.1(6)
C(3)–C(2)–S(1)	108.7(5)	103.2(6)	C(11)–O(10)–C(9)	113.7(5)
O(4)–C(3)–C(2)	109.2(6)	108.0(7)	C(12)–C(11)–O(10)	115.8(5)
C(3)–O(4)–C(5)	111.8(5)	111.7(8)	C(11)–C(12)–N(13)	115.8(5)
O(4)–C(5)–C(6)	108.2(6)	110.7(9)	N(14)–N(13)–C(12)	113.4(5)
O(7)–C(6)–C(5)	109.9(6)	110.4(11)	N(13)–N(14)–C(15)	115.0(5)
C(8)–O(7)–C(6)	115.1(6)	110.5(9)	C(16)–C(15)–N(14)	126.8(5)
O(7)–C(8)–C(9)	109.8(6)	109.5(8)	C(15)–C(16)–S(1)	121.1(4)
				116.1(8)
				124.6(10)
				126.3(8)
				103.2(9)
				109.2(11)
				106.1(11)
				142.0(8)
				111.3(6)

Table 2 (continuation)

S(1)-C(2)-C(3)-O(4)	-56.3(7)	-69.9(7)	C(9)-O(10)-C(11)-C(12)	176.7(5)	179.1(13)
C(2)-C(3)-O(4)-C(5)	166.5(6)	169.1(8)	O(10)-C(11)-C(12)-N(13)	-3.0(6)	2.6(16)
C(3)-O(4)-C(5)-C(6)	-161.3(6)	-145.5(11)	C(11)-C(12)-N(13)-N(14)	178.8(5)	-162.2(9)
O(4)-C(5)-C(6)-O(7)	69.4(8)	69.6(15)	C(12)-N(13)-N(14)-C(15)	178.4(5)	-173.3(8)
C(5)-C(6)-O(7)-C(8)	-129.3(7)	-148.0(10)	N(13)-N(14)-C(15)-C(16)	18.4(9)	9.7(14)
C(6)-O(7)-C(8)-C(9)	-177.5(6)	177.5(7)	N(14)-C(15)-C(16)-S(1)	-0.3(9)	-1.9(12)
O(7)-C(8)-C(9)-O(10)	-76.8(6)	-69.9(14)	C(15)-C(16)-S(1)-C(2)	163.2(5)	179.0(5)
C(8)-C(9)-O(10)-C(11)	178.4(5)	179.3(16)	C(16)-S(1)-C(2)-C(3)	-159.0(5)	175.7(6)

intensity variation was observed. Intensities were corrected for Lorentz and polarization effects but not for absorption.

The structure was solved by direct method and refined by full-matrix least-squares in anisotropic approximation using SHELXS-97 and SHELXL-97 programs [9]. Positions of hydrogen atoms were calculated from geometrical consideration and were refined as constrained to bonding atoms in a 'ride' mode. Crystallographic, experimental and model-refinement data are shown in Table 4.

Table 3. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) compound **9**. U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Atom	Molecule 9a				Molecule 9b			
	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	U_{eq}	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	U_{eq}
S(1)	3460(1)	1471(2)	8646(1)	61(1)	6546(8)	8455(6)	6976(5)	56(2)
S(1c)					7856(11)	8234(8)	5530(6)	68(2)
C(2)	4123(6)	106(7)	9364(4)	70(2)	5724(8)	9615(7)	7408(6)	89(2)
C(3)	5385(6)	459(8)	10005(5)	84(2)	5034(9)	10401(10)	6613(6)	115(3)
O(4)	6139(4)	883(5)	9510(3)	75(1)	5902(5)	11106(6)	6378(4)	109(2)
C(5)	7244(6)	1504(9)	10074(5)	88(2)	5337(11)	11719(14)	5508(7)	167(5)
C(6)	7749(6)	2279(9)	9493(6)	99(3)	6157(13)	11771(10)	5061(9)	176(6)
O(7)	6930(5)	3337(5)	9123(4)	88(1)	6376(8)	10516(7)	4779(4)	134(2)
C(8)	6574(7)	3488(8)	8180(5)	87(2)	7600(10)	10415(9)	4777(6)	109(3)
C(9)	5786(6)	4632(7)	7893(5)	74(2)	7814(7)	9140(7)	4532(5)	78(2)
O(10)	4534(3)	4251(5)	7905(3)	63(1)	7950(20)	8172(15)	5254(12)	73(5)
O(10c)					6580(20)	8550(20)	7281(10)	63(6)
C(11)	3636(5)	5249(6)	7668(4)	51(1)	8210(6)	6840(8)	5166(5)	75(2)
C(12)	2435(5)	4920(5)	7623(3)	45(1)	8306(7)	5942(12)	5802(5)	85(3)
N(13)	2244(4)	3597(5)	7778(3)	56(1)	8054(10)	6675(11)	6556(7)	76(4)
N(13c)					8256(9)	5692(9)	6680(7)	52(3)
N(14)	1176(5)	3358(5)	7747(3)	65(1)	8395(9)	6061(10)	7233(6)	64(3)
N(14c)					7960(10)	6745(10)	6901(8)	53(3)
C(15)	945(6)	2064(6)	7872(4)	56(2)	8129(7)	6710(8)	7916(5)	75(2)
C(16)	1845(5)	1118(5)	8258(4)	52(2)	7381(6)	7732(7)	7998(4)	75(2)
C(17)	1390(7)	-94(7)	8325(5)	79(2)	7396(8)	8029(9)	8875(5)	92(3)
C(18)	116(8)	-358(8)	8031(5)	87(2)	8119(11)	7338(14)	9588(6)	122(4)
C(19)	-719(8)	549(9)	7662(5)	91(3)	8831(8)	6331(14)	9517(7)	122(4)
C(20)	-338(6)	1769(7)	7594(4)	77(2)	8834(7)	6057(9)	8644(7)	106(3)
C(21)	1496(6)	5838(7)	7401(4)	59(2)	8579(8)	4671(13)	5629(7)	117(4)
C(22)	1743(6)	7075(7)	7234(4)	68(2)	8768(8)	4377(10)	4843(7)	108(3)
C(23)	2911(7)	7382(6)	7285(4)	67(2)	8671(7)	5270(9)	4226(5)	84(2)
C(24)	3883(6)	6520(7)	7507(4)	63(2)	8400(6)	6482(9)	4364(4)	75(2)

Syntheses of podands: 8-[(2-Nitrophenylthio)-3,6-dioxaoctanol 1. A mixture of 2-nitrothiophenol (7.75 g; 50 mmol), 2-(2-[2-chloroethoxy]ethoxy)-ethanol (7.8 ml, 54 mmol), anhydrous potassium carbonate (6.9 g) and dimethylformamide (20 ml) was refluxed for 6 h, and then diluted with water (60 ml). The product was extracted with methylene chloride (40 ml), the organic layer was washed with water (20 ml) and chromatographed on a short silica gel column using methylene chloride as eluent. The product was obtained as yellow oil; yield 13.6 g (95%). Anal. Calcd. for $\text{C}_{12}\text{H}_{17}\text{NO}_5\text{S}$: C, 50.17; H, 5.92; N, 4.88. Found: C, 50.18; H, 5.94; N, 4.90. δ_{H} (200 MHz, CDCl_3) 3.22 (2H, t, J 6.59 Hz, SCH₂), 3.58–3.82 (11H, m, OCH₂, OH), 7.21–7.26 (1H, m, ArH), 7.42–7.61 (2H, m, ArH), 8.20 (1H, dd, J 8.20, 1.34 Hz, ArH).

Table 4. Crystallographic data and structure refinement details for **9**.

Formula	C ₁₈ H ₂₀ N ₂ O ₃ S
Molecular weight	344.42
Temperature [K]	293(2)
Wavelength [Å]	0.71073
Crystal system, space group	monoclinic, <i>P2</i> ₁
Unit cell dimensions	
<i>a</i> [Å]	11.366(4)
<i>b</i> [Å]	10.493(3)
<i>c</i> [Å]	15.773(3)
β [°]	110.40(3)
Cell volume [Å ³]	1763.2(9)
Calculated density [g·cm ⁻³] for <i>Z</i> = 4	1.297
Absorption coefficient [mm ⁻¹]	0.201
<i>F</i> (000) electrons	728
θ – range for data collection [°]	1.38–25.25
Limiting indices	–12 ≤ <i>h</i> ≤ 13, –12 ≤ <i>k</i> ≤ 0, –18 ≤ <i>l</i> ≤ 0
Reflections collected/unique	3493 / 3368 [<i>R</i> (int) = 0.0219]
Completeness to θ = 25.25	99.5%
Max. and min. transmission	0.9704 and 0.9608
Refinement method	Full-matrix least-squares on <i>F</i> ²
Data/restraints/parameters	3368 / 22 / 445
Goodness-of-fit on <i>F</i> ²	0.949
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> _{<i>I</i>} = 0.0429, <i>wR</i> ² = 0.1096
<i>R</i> indices (all data)	<i>R</i> _{<i>I</i>} = 0.1389, <i>wR</i> ² = 0.1337
Largest diff. peak and hole [e·Å ⁻³]	0.332 and –0.250

8-[2-Nitrophenylthio]-3,6-dioxaoctyl chloride 2. A mixture of compound **1** (14.3 g; 50 mmol), pyridine (4 ml; 50.5 mmol) and thionyl chloride (6.7 ml; 92 mmol) was stirred and heated for 1 h at 60°C and then diluted with benzene. The solvent was evaporated and the residue was mixed with benzene (30 ml) and filtered to remove the deposited pyridine hydrochloride. The organic layer was washed with water (20 ml) and the solvent was removed. The residue was chromatographed on silica gel column using methylene chloride as eluent to give product **2** as yellow oil. Yield 12.17 g (80%). Anal. Calcd. for C₁₂H₁₆O₄ClNS: C, 47.14; H, 5.24; N, 4.58. Found: C, 47.25; H, 5.18; N, 4.49. δ_H (200 MHz, CDCl₃) 3.23 (2H, t, *J* 6.60, SCH₂), 3.65 (2H, d, *J* 5.1 Hz, ClCH₂), 3.68–3.70 (4H, m, OCH₂), 3.73–3.84 (4H, m, OCH₂), 7.20–7.32 (1H, m, ArH), 7.45–7.55 (2H, m, ArH), 8.20 (1H, dd, *J* 8.31, 1.44 Hz, ArH).

1,8-Bis[2-nitrophenylthio]-3,6-dioxaoctane 3. A mixture of 2-nitrothiophenol (3.10 g; 20 mmol), 1,8-dichloro-3,6-dioxaoctane (1.58 ml; 10 mmol), anhydrous potassium carbonate (3.9 g; 28.2 mmol) and dimethylformamide (10 ml) was refluxed for 6 h and then diluted with water. The product was isolated in a similar way as described for compound **2**. The yellow oily product **3** was crystallized from 2-propanol. Yield 7.20 g (85%), m.p. 78–80°. Anal. Calcd. for C₁₈H₂₀N₂O₆S₂: C, 50.94; H, 4.72; N, 6.60. Found: C, 50.85; H, 4.80; N, 6.34. δ_H (200 MHz, CDCl₃) 3.25 (4H, t, *J* 6.59 Hz, SCH₂), 3.67 (4H, s, OCH₂), 3.81 (4H, t, *J* 6.59 Hz, OCH₂), 7.20–7.45 (2H, m, ArH), 7.50–7.70 (4H, m, ArH), 8.25 (2H, dd, *J* 8.37, 1.12 Hz, ArH).

1-[2-Nitrophenylthio]-8-(2-nitrophenoxy)-3,6-dioxaoctane 4. A mixture of compound **2** (6.11 g, 20 mmol), *o*-nitrophenol (2.78 g; 20 mmol), anhydrous potassium carbonate (3.9 g; 28.2 mmol) and dimethylformamide (8 ml) was refluxed for 6 h and then diluted with water. The product was extracted with methylene chloride (40 ml), the solvent was evaporated and the residue was chromatographed on silica gel column using methylene chloride as an eluent. Yield 6.69 g (82%) of a brownish oil. Anal. Calcd. for C₁₈H₂₀N₂O₇S: C, 52.94; H, 4.90; N, 6.86. Found: C, 52.98; H, 4.95; N, 6.90. δ_H (200 MHz, CDCl₃) 3.25

(2H, t, J 6.60 Hz, SCH₂), 3.65–3.95 (8H, m, OCH₂), 4.26 (2H, t, J 4.86, OCH₂), 7.00–7.35 (3H, m, ArH), 7.45–7.62 (3H, m, ArH), 7.86 (1H, dd, J 8.1, 1.8 Hz, ArH), 8.18 (1H, dd, J 8.30, 1.30 Hz, ArH).

Compounds **5** and **6** were obtained analogously from compound **2** and the respective amounts of 4-*tert*-butyl-2-nitrophenol or 4-(1,1,3,3-tetramethylbutyl)-2-nitrophenol [2e].

1-[2-Nitrophenylthio]-8-(4-*tert*-butyl-2-nitrophenoxy)-3,6-dioxaoctane 5. The product was purified by chromatography using chloroform as an eluent. Yield 7.88 g (85%) of an oily yellow product. Anal. Calcd. for C₂₂H₂₈N₂O₇S: C, 56.89; H, 6.03; N, 6.03. Found: C, 56.92; H, 6.15; N, 6.12. δ_{H} (200 MHz, CDCl₃) 1.63 (9H, s, C(CH₃)₃), 3.24 (2H, t, J 6.87 Hz, SCH₂), 3.60–3.92 (8H, m, OCH₂), 4.25 (2H, t, J 4.88 Hz, OCH₂), 7.00–7.12 (1H, m, ArH), 7.20–7.35 (1H, m, ArH), 7.50–7.85 (4H, m, ArH), 8.2 (1H, dd, J 8.18, 1.47, ArH).

1-[2-Nitrophenylthio]-8-[4-(1,1,3,3-tetramethylbutyl)-2-nitrophenoxy]-3,6-dioxaoctane 6. The crude oily product was chromatographed using hexane–ethyl acetate 4:1 mixture. Yield 8.32 g (80%) of yellow oil. Anal. Calcd. for C₂₆H₃₆N₂O₇S: C, 60.00; H, 6.92; N, 5.38. Found: C, 60.12; H, 6.80; N, 5.51. δ_{H} (200 MHz, CDCl₃) 0.73 (9H, s, C(CH₃)₃), 1.36 (6H, s, C(CH₃)₂), 1.73 (2H, s, CCH₂C), 3.26 (2H, t, J 6.74 Hz, SCH₂), 3.60–4.00 (8H, m, OCH₂), 4.25 (2H, t, J 4.49 Hz, OCH₂), 7.04 (2H, d, J 8.83 Hz, ArH), 7.20–7.32 (2H, m, ArH), 7.45–7.60 (1H, m, ArH), 7.82 (1H, d, J 1.34 Hz, ArH), 8.20 (1H, dd, J 8.10, 1.20 Hz, ArH).

Syntheses of macrocyclic azo and azoxy compounds: 1,2-Azo-3,4,15,16-dibenzo-5,14-dithia-8,11-dioxacyclohexadecane 7 and azoxy 3 compound 8. A mixture consisting of compound **3** (4.24 g; 10 mmol), anhydrous stannous chloride (7.6 g), sodium hydroxide (12.2 g), acetone (35 ml) and water (30 ml) was stirred vigorously and heated to gentle boiling for 5 h. Toluene (30 ml) was added to the cooled reaction mixture and the precipitated sodium chloride was removed by filtration. The solid was washed with toluene and the filtrates were combined. The organic layer was separated, washed with water (30 ml) and the solvent was removed. The crude residue (2.6 g) was chromatographed on a silica gel column using methylene chloride. The red fraction (1 g) was rechromatographed on silica gel column using ethyl acetate: hexane mixture (1:4) as an eluent. Yield 600 mg (16.6 %) of red oil of azocrown ether **7**; δ_{H} (200 MHz, CDCl₃) 3.10–3.30 (4H, m, SCH₂), 3.50–4.00 (8H, m, OCH₂), 7.20–7.35 (4H, m, OCH₂), 7.40–7.50 (3H, m, ArH), 8.0 (1H, dd, J 7.94, 0.90 Hz, ArH); HRMS (EI): M⁺, found 360.09435. C₁₈H₂₀N₂O₂S₂ requires 360.09662.

The second orange fraction of azoxythiacrown after rechromatography afforded 800 mg (21.3 %) of orange crystals (ethanol). M.p. 106–108°; δ_{H} (200 MHz, CDCl₃) 3.15–3.30 (4H, m, SCH₂), 3.65 (4H, s, OCH₂), 3.75–3.90 (4H, m, OCH₂), 7.20–7.35 (3H, m, ArH), 7.40–7.50 (3H, m, ArH), 7.90–8.00 (1H, m, ArH), 8.10 (1H, dd, J 8.1, 1.1 Hz, ArH); HRMS (EI): M⁺, found 376.09303. C₁₈H₂₀N₂O₃S₂ requires 376.09154.

Compounds **9–14** were obtained analogously from podands **4–6**.

1,2-Azo-3,4,15,16-dibenzo-5-thia-8,11,14-trioxacyclohexadecane 9. Yield 700 mg (20.35%) of red crystals (hexane). M.p. 138–140°; δ_{H} (200 MHz, CDCl₃) 3.2 (2H, t, J 6.62 Hz, SCH₂), 3.60–4.10 (8H, m, OCH₂), 4.30–4.40 (2H, m, OCH₂), 7.00–7.10 (2H, m, ArH), 7.20–7.50 (4H, m, ArH), 7.80–8.00 (2H, m, ArH); HRMS (EI): M⁺, found 344.11951. C₁₈H₂₀N₂O₃S requires 344.11946.

1,2-Azoxy-3,4,15,16-dibenzo-5-thia-8,11,14-trioxacyclohexadecane 10. Yield 500 mg (13.8%) of orange oil. δ_{H} (200 MHz, CDCl₃) 3.15–3.30 (2H, m, SCH₂), 3.60–4.00 (8H, m, OCH₂), 4.20–4.35 (2H, m, OCH₂), 7.00–7.10 (2H, m, ArH), 7.20–7.50 (4H, m, ArH), 7.80–8.00 (1H, m, ArH), 8.10 (1H, dd, J 8.2, 1.2 Hz, ArH); HRMS (EI): M⁺, found 360.11564. C₁₈H₂₀N₂O₄S requires 360.11437.

1,2-Azo-3,4-benzo-15,16-(4-*tert*-butylbenzo)-5-thia-8,11,14-trioxacyclohexadecane 11. Yield 850 mg (21.25%) of red flakes (ethanol); m.p. 108–110°; δ_{H} (200 MHz, CDCl₃) 1.36 (9H, s, C(CH₃)₃), 3.15 (2H, t, J 6.62 Hz, SCH₂), 3.75 (4H, s, OCH₂), 3.95 (2H, m, OCH₂), 4.00–4.15 (2H, t, J 5.8 Hz, OCH₂), 4.30–4.45 (2H, m, OCH₂), 7.05 (1H, d, J 8.74 Hz, ArH), 7.30–7.50 (3H, m, ArH), 7.9–8.00 (3H, m, ArH); HRMS (EI): M⁺, found 400.18113. C₂₂H₂₈N₂O₃S requires 400.18206.

1,2-Azoxy-3,4-benzo-15,16-(4-*tert*-butylbenzo)-5-thia-8,11,14-trioxacyclohexadecane 12. Yield 300 mg (7.21%) of orange oil; δ_{H} (200 MHz, CDCl₃) 1.31 (9H, s, C(CH₃)₃), 3.15–3.20 (2H, m, SCH₂), 3.75–3.95 (6H, m, OCH₂), 4.00–4.20 (2H, m, OCH₂), 4.30–4.50 (2H, m, OCH₂), 7.05 (1H, d, J 8.74 Hz, ArH), 7.35–7.55 (3H, m, ArH), 7.90–8.00 (2H, m, ArH), 8.10 (1H, dd, J 6.2, 1.3 Hz, ArH); HRMS (EI): M⁺, found 416.17789. C₂₂H₂₈N₂O₄S requires 416.17697.

1,2-Azo-3,4-benzo-15,16-(4-tetramethylbutylbenzo)-5-thia-8,11,14-trioxacyclohexadecane 13. Yield 800 mg (17.5 %) of red crystals (hexane); m.p. 94–96°; δ_{H} (200 MHz, CDCl₃) 0.76 (9H, s, C(CH₃)₃),

1.41 (6H, s, C(CH₃)₂), 1.72 (2H, s, CCH₂C), 3.2 (2H, t, *J* 4.88 Hz, SCH₂), 3.60–3.80 (6H, m, OCH₂), 3.90 (2H, t, *J* 4.86 Hz, OCH₂), 4.25 (2H, t, *J* 5.95, 1.25 Hz, OCH₂), 7.00 (2H, d, *J* 8.7 Hz, ArH), 7.30–7.60 (4H, m, ArH), 7.84–8.00 (1H, m, ArH); HRMS (EI): M⁺, found 456.24576. C₂₆H₃₆N₂O₃S requires 456.24467.

1,2-Azoxy-3,4-benzo-15,16-(4-tetramethylbutylbenzo)-5-thia-8,11,14-trioxacyclohexadecane 14. Yield 350 mg (7.41%) of brownish oil; δ_H (200 MHz, CDCl₃) 0.76 (9H, s, C(CH₃)₃), 1.38 (6H, s, C(CH₃)₂), 1.74 (2H, s, CCH₂C), 3.25 (2H, t, *J* 4.88 Hz, SCH₂), 3.60–3.80 (6H, m, OCH₂), 3.90 (2H, t, *J* 4.86 Hz, OCH₂), 4.25 (2H, t, *J* 4.68 Hz, OCH₂), 7.00–7.15 (2H, m, ArH), 7.30–7.60 (3H, m, ArH), 7.80–8.00 (1H, m, ArH), 8.10 (1H, dd, *J* 8.18, 1.46 Hz, ArH); HRMS (EI): M⁺, found 472.23868. C₂₆H₃₆N₂O₄S requires 472.23958.

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