Pergamon

Tetrahedron 55 (1999) 8433–8442

TETRAHEDRON

Crown Ethers with an Azo or Azoxy Unit and Sulfur Atom(s) in a 13-Membered Macrocycle

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Received 5 November 1998; revised 27 April 1999; accepted 13 May 1999

Abstract: 13-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 dinitropodands. The structure of a 13-membered azoxydithiacrown ether has been studied by X-ray analysis. Preliminary studies of these compounds as ion carriers in ion-selective membrane electrodes is reported. © 1999 Elsevier Science Ltd. All rights reserved.

INTRODUCTION

Renewed interest in azobenzene derivatives can be related to their application in molecular switches, optical memories and image storage devices.[1] Numerous synthesized compounds contain the azobenzene unit as part of the macrocycle in crown ethers.[2] Such compounds combine functionalities for crown ether and azobenzene; they are photo- and electroactive and form complexes with lithium, sodium and potassium cations. Ion-selective membrane electrodes based on azocrown ethers are highly sodium or potassium selective[2e,f,g]. Replacement of oxygen(s) by sulfur atom(s) in azo- or azoxycrown ethers leads to new macrocycles. Compounds known to date have sulfur atoms bonded to azobenzene residues through methylene groups in *p*- or *m*-position;[3] in these compounds rotation of azo groups is hindered. A new type of azo- or azoxythiacrown ether in which vicinal oxygen or sulfur atoms and azo- or azoxy groups constitute one macrocyclic unit are an attractive target for synthesis. Close location of the electron-donating sites forced by macrocyclic structure of these compounds should cause strong cooperation in complexation ability. Size exclusion effects, typical for crown ethers, could also be expected.[4] Sulfur atoms possess high affinity towards heavy and transition metal ions; one could expect increased affinity of azo- and azoxythiacrowns towards these cations. Azo- or azoxythiacrown ethers applied as ion carriers should improve selectivity and

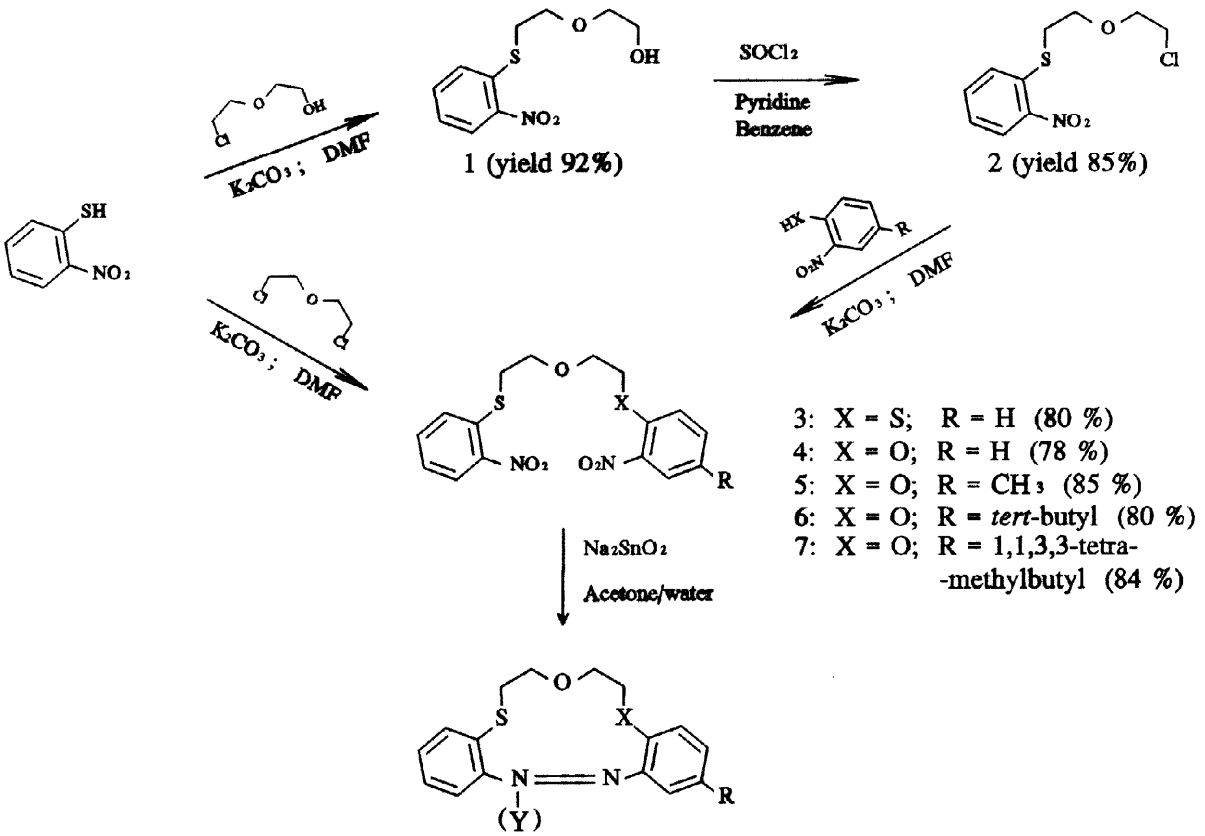
PII: S0040-4020(99)00430-5

sensitivity of the respective ion-selective membrane electrodes.

RESULTS AND DISCUSSION

Synthesis

The synthesis of 13-membered azo- and azoxythiacrown ethers proceeds by the following route:



3: X = S; R = H (80 %)
4: X = O; R = H (78 %)
5: X = O; R = CH_3 (85 %)
6: X = O; R = *tert*-butyl (80 %)
7: X = O; R = 1,1,3,3-tetra-methylbutyl (84 %)

8: X = S; Y = O; R = H (30 %)
9: X = O; Y = none; R = H (16 %)
10: X = O; Y = O; R = H (22 %)
11: X = O; Y = none; R = CH_3 (7.6 %)
12: X = O; Y = O; R = CH_3 (20 %)
13: X = O; Y = none; R = *tert*-butyl (4.2 %)
14: X = O; Y = O; R = *tert*-butyl (5.4 %)
15: X = O; Y = none: R = 1,1,3,3-tetra-methylbutyl (25 %)
16: X = O; Y = O; R = 1,1,3,3-tetra-methylbutyl (7.5 %)

2-nitrothiophenol was condensed with 2,2'-dichlorodiethyl ether in dry dimethylformamide in the presence of anhydrous potassium carbonate to form podand **3**. 2-Nitrothiophenol condensed as above with chloroethoxyethanol produces alcohol **1**. It was, in turn, converted into compound **2** with thionyl chloride in benzene and in the presence of pyridine. Chloride **2** was condensed with 2-nitrophenol or its 4-alkyl derivatives to form dinitropodands **4-7**. Compounds **3-7** were reduced with sodium stannite to produce 13-membered macrocyclic products (Scheme) with moderate yields.

The final reduction product of compound **3** is 13-membered azoxydithiacrown ether **8**. Reduction of

the monothiapodands **4-7** produces two sets of compounds: the azothiacrown ethers **9**, **11**, **13**, **15** and azoxythiacrown ethers **10**, **12**, **14** and **16**.

Reduction of nitrocompounds with stannites was originally applied for the synthesis of azoxy compounds.[5] The same reducing agent applied to (bis-nitrophenoxy)alkanes, oxaanalogues of compounds **3-7** (Scheme), produces azo and azoxy compounds. The ratio of these products depend on the structure of the starting material and on the template effect.[2e,2g,6-8]

The =N(O)- group of azoxythiacrown ethers obtained from compounds **4-7** is in a vicinal position with respect to the sulfur atom (compounds **10**, **12**, **14**, **16**). Location of this group in relation to the sulfur atom was established by comparison of ^{1}H NMR spectra for azoxythiacrown ethers with spectra of the respective oxygen analogues.[2] Isomeric azoxythiacompounds were not isolated from reaction mixtures. Compounds **10**, **12**, **14** and **16** adopt *Z* geometry with the phenyl residues occupying *trans* positions around the -N(O)=N- group. This was deduced from comparison of their NMR spectra with spectra of azoxydithiacrown ether **8**, the geometry of which is known from X-ray studies.

The $Z \rightleftarrows E$ isomerization of azothiacrown ethers is fast. Chromatography (TLC) always shows two spots corresponding to the *Z* and *E* isomers. ^{1}H NMR signals for *trans* isomers were selected from spectra of stereoisomers with >80% content of *trans* isomer.

In UV-VIS spectra the azocompounds showed two characteristic absorption bands at 216.5 and 460 nm; for compound **9** the respective ϵ_{max} values are 23580 and 2146 $M^{-1}cm^{-1}$ (see ref.[9]). For compound **15** ϵ values are 24008 and 1502. For the azoxycompound **8** λ_{max} = 216.5 nm, ϵ = 19380.

Membrane electrodes

The properties of ion-selective membrane electrodes doped with 13-membered thiacrown ethers with azo or azoxy subunits are presented in Figure 1. The selectivity coefficients are related to electrode response for cesium. All electrodes show high silver affinity. The best (SSM[10]) selectivity coefficient $\log K^{pot}_{Cs,Ag}$ equals 8.3 for compound **(8)** in accordance with the largest number of sulfur atoms in the macrocycle. Affinities for silver exceed those for lead and cadmium. Electrodes doped with compound **(10)** do not significantly distinguish different cations with the exception of silver. The high affinity of the title thiacrowns towards heavy metal cations as compared to sodium selective 13-membered azo- and azoxycrown ethers,[2e] could be related to the more

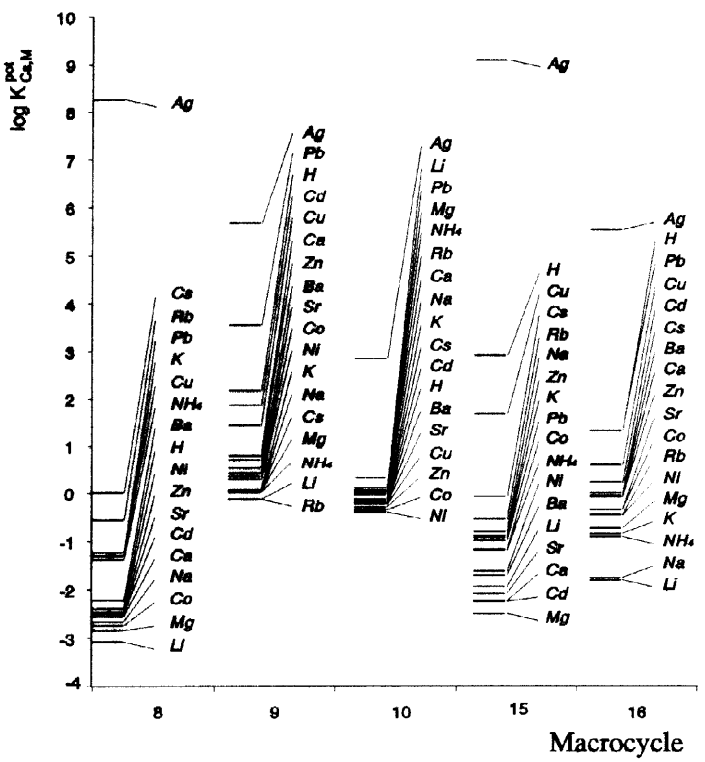


Figure 1. $\text{Log}K^{pot}_{Cs,M}$ values of membrane electrodes.

'soft' character of the sulfur atom and to the differences in size of oxygen and sulfur atoms, leading to differences in conformation of thiacrown ethers and their oxygen analogues.

X-Ray structure of compound 8

The X-ray structure of compound 8 with displacement ellipsoids and the atomic numbering scheme is shown in Figure 2. Selected bond distances and valence and torsion angles are listed in Table 1 and 2.

The azoxy group in the molecule adopts the *Z*-form with aromatic moieties in the *trans*-position. The molecule is non planar and can be described by mutual arrangement of four flat fragments. The aromatic residues are roughly perpendicular forming a dihedral angle of 86.4°. The mean plane of the azoxy group bisects this angle and forms dihedral angles of 33.4° and 60.5° with the planes of aromatic residues at N(10) and N(11), respectively. Another flat fragment is formed by a chain consisting of S(1), C(2), C(3), O(4) and C(5) atoms. These atoms lie in the mean plane with rms deviation of fitted atoms of 0.044 Å. The dihedral

Table 1. Selected interatomic distances (Å)

Bond	Distance	Bond	Distance	Bond	Distance
S(1)-C(13)	1.772(4)	O(4)-C(5)	1.404(7)	C(2)-C(3)	1.499(8)
S(1)-C(2)	1.783(6)	N(10)-C(9)	1.456(5)	C(5)-C(6)	1.561(9)
S(7)-C(8)	1.783(4)	O(10)-N(10)	1.263(4)	C(8)-C(9)	1.404(6)
S(7)-C(6)	1.820(6)	N(10)-N(11)	1.269(4)	C(12)-C(13)	1.405(6)
O(4)-C(3)	1.434(7)	N(11)-C(12)	1.426(5)		

Table 2. Selected valence and torsion angles (°)

System	Angle	System	Angle	System	Angle
C(13)-S(1)-C(2)	109.8(2)	C(3)-C(2)-S(1)	113.2(4)	C(21)-C(9)-N(10)	119.8(4)
C(8)-S(7)-C(6)	102.2(3)	O(4)-C(3)-C(2)	105.9(5)	C(8)-C(9)-N(10)	117.8(4)
C(5)-O(4)-C(3)	116.2(5)	O(4)-C(5)-C(6)	109.5(5)	C(17)-C(12)-N(11)	124.4(4)
O(10)-N(10)-N(11)	128.1(4)	C(5)-C(6)-S(7)	109.2(4)	C(13)-C(12)-N(11)	116.3(4)
O(10)-N(10)-C(9)	116.3(3)	C(18)-C(8)-S(7)	122.7(3)	C(14)-C(13)-C(12)	118.6(4)
N(11)-N(10)-C(9)	115.6(3)	C(9)-C(8)-S(7)	120.7(3)	C(14)-C(13)-S(1)	113.9(3)
N(10)-N(11)-C(12)	118.5(3)	C(21)-C(9)-C(8)	122.3(4)	C(12)-C(13)-S(1)	127.4(3)
C(13)-S(1)-C(2)-C(3)	-59.8(0.5)	O(4)-C(5)-C(6)-S(7)	-66.0(0.7)	C(8)-C(9)-N(10)-N(11)	119.7(0.4)
S(1)-C(2)-C(3)-O(4)	175.3(0.3)	C(5)-C(6)-S(7)-C(8)	103.1(0.4)	C(9)-N(10)-N(11)-C(12)	-176.9(0.3)
C(2)-C(3)-O(4)-C(5)	-173.9(0.5)	C(6)-S(7)-C(8)-C(9)	-130.2(0.4)	N(10)-N(11)-C(12)-C(13)	148.7(0.4)
C(3)-O(4)-C(5)-C(6)	126.0(0.6)	S(7)-C(8)-C(9)-N(10)	-1.6(0.5)	N(11)-C(12)-C(13)-S(1)	0.6(0.5)
				C(12)-C(13)-S(1)-C(2)	-34.2(0.4)

angle between the last mean plane and the aromatic ring C(12), C(13), C(14), C(15) and C(17) equals 74.4°. The geometric features of the azoxy group, (Table 2), agree with those previously reported.[6-8,11] The differences in N-C bond lengths [N(10)-C(9) = 1.456 and N(11)-C(12) = 1.423 Å, respectively] correspond to a different degree of π-conjugation of the -N(O)=N- group with the neighboring aromatic moieties. A

close S(7)...O(10) intramolecular contact (= 2.949 Å) was found in the molecule (for nature of this effect see ref.[12]). A short C(2)...N(11) intramolecular distance (2.936 Å) was also found in the molecule. It can be considered as a CH...N interaction (H...N distance equals 2.34 Å; C...H...N angle equals 117.2°).

The sulfur atoms tend to be as far as possible causing an unusual sequence of *trans-trans-gauche-gauche* (beginning from S(1)-C(2) bond) torsion angles in the ether chain. The corner[13] fragment is at C(6) atom, resulting close S(7)...O(4) intramolecular contact (= 3.146 Å).

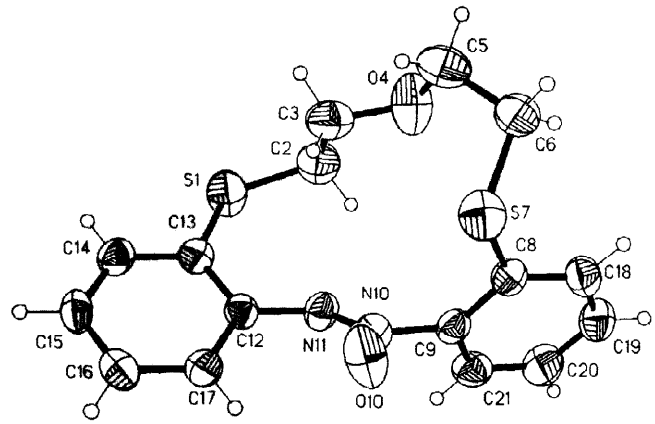


Figure 2. Displacement ellipsoid plot and atomic numbering scheme for compound **8**.

EXPERIMENTAL

General

All materials and solvents used for syntheses were of analytical reagent grade. Silica gel (0.035-0.070 mm, Fluka) was used for column chromatography. ^{1}H NMR spectra were recorded on a Varian (200 MHz) instrument. IR spectra were recorded on Specord M80 apparatus. The purity and identity of crown ethers was established by high resolution mass spectra carried out on a AMD-604 spectrometer or by elemental analyses. The m.p. are uncorrected.

Membrane electrodes and potentiometric measurements

Preparation of membranes for ion-selective electrodes was described earlier in detail.[2e] Typical composition of membranes 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 potassium chloride solution. The electrodes were soaked in 10^{-2} mol·dm^{-3} KCl solution before measurements. The selectivity coefficients were determined using the separate solution method (SSM)[10] at 10^{-2} mol·dm^{-3} activities of metal cations.

X-Ray Crystal Structure analysis of (**8**)

A single crystal of azoxydithiacrown ether (**8**) was obtained by crystallization from ethyl acetate - hexane solution. Yellowish prisms, crystal dimensions 0.40 x 0.15 x 0.1 mm; μ(Mo-$K\alpha$) 0.342 mm^{-1} $C_{16}H_{16}N_2O_2S_2$, M 332.43, triclinic, a = 9.943(5), b = 9.964(4), c = 8.613(3) Å, α = 79.39(3), β = 95.37(3), γ = 73.92(3)°, V 796.4(6) Å^3 The unit cell dimensions were obtained by least squares fit of 25 centered reflections in the range of 10.8° ≤ θ ≤ 21.3°, λ = 0.71069 Å), space group P$\bar{1}$, Z 2, D_x 1.386 g·cm^{-3}. The data were collected at 293 K on a DAR-UMB computer controlled diffractometer, ω-$\omega/2\theta$ scan

mode, graphite-monochromated Mo-K_α radiation; 1509 reflections were collected at θ range 2.16 to 27.48°; 1451 independent reflections [R(int) = 0.0106]. The structure was solved by the direct method using SHELXS-86[14] and refined in anisotropic approximation by full matrix least squares using SHELXL-93 program.[15] Positions of hydrogen atoms were calculated from geometrical considerations and were refined as constrained to bonding atoms in a 'ride' mode. The individual isotropic temperature factors were applied for them. Final $R1$ indices $R1$= 0.0428; $wR2$ = 0.1070 for 1444 reflections with $I > 2\sigma(I)$. The weight scheme {$w = 1/[\sigma(F)^2 + (0.0576P)^2+1.01P]$, where $P = [\max(F_o^2,0) + 2F_c^2]/3$, was applied during refinement.

SYNTHESES OF PODANDS

2-{2-[2-Nitrophenyl(thio)]ethoxy}ethanol (1)

A mixture of 2-nitrothiophenol (7.75 g; 50 mmol), 2-chloroethoxyethanol (5.70 cm^3; 54 mmol), anhydrous potassium carbonate (6.9 g) and dimethylformamide (20 cm^3) was refluxed for 6 h, and then diluted with water (60 cm^3). The product was extracted with methylene chloride (40 cm^3), washed with water (20 cm^3) and chromatographed on a short silica gel column using methylene chloride as eluent. Yellow oil, yield 11.2 g (92%). [Found: C, 49.6; H, 5.3; N, 5.8. $C_{10}H_{13}NO_4S$ requires C, 49.37; H, 5.39; N, 5.76%]; ν_{max}(nujol) 3600-3200(br), 1570, 1520, 1340, 1300, 1110, 1040, 730 cm^{-1}; δ_H (200 MHz, $CDCl_3$) 8.20 (1 H, dd, J 8.3, 1.4 Hz, ArH), 7.24-7.62 (3 H, m, ArH); 3.60-3.83 (7 H, m, OCH_2, OH); 3.24 (2 H, t, J 6.6 Hz, SCH_2).

2-[2-Nitrophenyl(thio)ethoxy]ethyl chloride (2)

A mixture of [2-nitrophenyl(thio)]ethoxyethanol (1) (12.2 g; 50 mmol), pyridine (4 cm^3; 50.5 mmol) and thionyl chloride (6.7 cm^3) was stirred and refluxed for 1 h at 60° and then diluted with benzene. The solvent was evaporated. The residue was mixed with benzene (30 cm^3) and filtered to remove the solid pyridine hydrochloride. The organic layer was washed with water (20 cm^3) and the solvent was removed. The residue was chromatographed on a silica gel column using methylene chloride as eluent to give **2** as an yellow oil. Yield 11.2 g (85%). [Found: C, 45.9; H, 4.6; N, 5.5. $C_{10}H_{12}NO_3ClS$ requires C, 45.87; H, 4.57; N, 5.35%]; ν_{max}(nujol) 1510, 1340, 1300, 1120, 1040, 730 cm^{-1}; δ_H (200 MHz, $CDCl_3$) 8.20 (1 H, dd, J 8.3, 1.3 Hz, ArH); 7.48-7.64 (2 H, m, ArH); 7.24-7.34 (1 H, m, ArH); 3.74-3.86 (4 H, m, OCH_2); 3.66 (2 H, d, J 5.0 Hz, $ClCH_2$); 3.24 (2 H, t, J 6.6 Hz, SCH_2).

1.5-Bis[2-Nitrophenyl(thio)]-3-oxapentane (3)

A mixture of 2-nitrothiophenol (3.10 g; 20 mmol), 2,2'-dichlorodiethyl ether (1.3 cm^3; 10 mmol), anhydrous potassium carbonate (3.9 g; 28.2 mmol) and dimethylformamide (8 cm^3) was refluxed for 6 h and then diluted with water. The product was isolated in a similar manner as given for compound **2**. The oily compound **3** was covered with a small amount of 2-propanol and left for few day for crystallization. Yield 3.0 g (80%), m.p. 130-132°. [Found: C, 50.5; H, 4.2; N, 7.4. $C_{16}H_{16}N_2O_5S_2$ requires C, 50.51; H, 4.24; N, 7.36%]; ν_{max}(nujol) 1600, 1570, 1510, 1330, 1110, 740 cm^{-1}; δ_H (200 MHz, $CDCl_3$) 8.20 (2 H, dd, J 8.2, 1.5 Hz, ArH), 7.46-7.63 (4 H, m, ArH), 7.23-7.33 (2 H, m, ArH), 3.80 (4 H, t, J 6.5 Hz, OCH_2), 3.21 (4 H, t, J 6.5 Hz, SCH_2).

1-[2-Nitrophenyl(thio)]-5-(2-nitrophenoxy)-3-oxapentane (4)

A mixture of compound **2** (5.23 g; 20 mmol), 2-nitrophenol (2.78 g; 20 mmol), anhydrous potassium carbonate (3.9 g; 28.2 mmol) and dimethylformamide (8 cm^3) was boiled for 6 h and then diluted with water. The product was extracted with methylene chloride (30 cm^3), the solvent was evaporated and the residue chromatographed on silica gel column using methylene chloride as an eluent. Yield 5.68 g (78%) of yellow oil. [Found: C, 52.6; H, 4.4; N, 7.7. $C_{16}H_{16}N_2O_6S$ requires C, 52.74; H, 4.43; N, 7.69%]; ν_{max}(nujol) 1530, 1500, 1340, 1250, 1170, 1110, 720 cm^{-1}; δ_H (200 MHz, $CDCl_3$) 8.18 (1 H, dd, *J* 8.3, 1.3 Hz, ArH), 7.84 (1 H, dd, *J* 8.1, 1.8 Hz, ArH), 7.46-7.62 (3 H, m, ArH), 7.0-7.4 (3H, m, ArH), 4.22-4.30 (2 H, m, $ArOCH_2$), 3.83-3.96 (4 H, m, OCH_2), 2.90-3.40 (2 H, m, SCH_2).

Analogously were obtained compounds (**5**) - (**7**) from compound **2** and the respective amounts of 4-methyl-2-nitrophenol, 4-*tert*-butyl-2-nitrophenol,[2e] or 4-(1,1,3,3-tetramethylbutyl)-2-nitrophenol.[2e]

1-[2-Nitrophenyl(thio)]-5-(4-methyl-2-nitrophenoxy)-3-oxapentane (5)

The product (**5**) crystallized upon addition of ethanol. Yield 85% of yellowish crystals; m.p. 56-58°C. [Found: C, 53.8; H, 4.7; N, 7.38. $C_{17}H_{18}N_2O_6S$ requires C, 53.96; H, 4.79; N, 4.40%]; ν_{max}(nujol) 1450, 1250, 1170, 1110, 720 cm^{-1}; δ_H (200 MHz, $CDCl_3$) 8.20 (1 H, dd, *J* 8.3, 1.2 Hz, ArH), 7.48-7.70 (3 H, m, ArH), 7.20-7.38 (2 H, m, ArH), 7.0 (1 H, d, *J* 8.6 Hz, ArH), 4.20-4.30 (2 H, m, $ArOCH_2$), 3.85-4.0 (4 H, m, OCH_2), 3.20-3.30 (2 H, m, SCH_2), 2.40 (3 H, s, CH_3).

1-[2-Nitrophenyl(thio)]-5-(4-*tert*-butyl-2-nitrophenoxy)-3-oxapentane (6)

The crude oily product was purified by chromatography using a hexane : ethyl acetate (4:1) mixture. Yield 80% of an oily yellowish product. [Found: C, 57.1; H, 5.7; N, 6.7. $C_{20}H_{24}N_2O_6S$ requires C, 57.13; H, 5.75; N, 6.66%]; ν_{max}(film) 3090, 2980, 1610, 1570, 1540, 1520, 1360, 1270, 1130, 1100, 1050, 830, 740 cm^{-1}; δ_H (200 MHz, $CDCl_3$) 8.20 (1 H, dd, *J* 8.3, 1.4 Hz, ArH), 7.20-7.36 (4 H, m, ArH), 7.0 (2 H, d, *J* 8.5 Hz, ArH), 4.15-4.35 (2 H, m, $ArOCH_2$), 3.70-4.0 (4 H, m, OCH_2), 3.20-3.30 (2 H, m, SCH_2), 1.35 (9 H, s, CH_3).

1-[2-Nitrophenyl(thio)]-5-[4-(1,1,3,3-tetramethylbutyl)-2-nitrophenoxy]-3-oxapentane (7)

The crude product was chromatographed using hexane - ethyl acetate mixture. Yield 84% of an yellowish oil. [Found: C, 59.9; H, 6.7; N, 5.9. $C_{24}H_{32}N_2O_6S$ requires C, 60.48; H, 6.77; N, 5.88%]; ν_{max}(film) 3090, 2970, 1620, 1570, 1540, 1460, 1360, 1300, 1270, 1120, 1050, 740 cm^{-1}; δ_H (200 MHz, $CDCl_3$) 8.20 (1 H, dd, *J* 8.1, 1.2 Hz, ArH), 7.82-7.84 (1 H, d, *J* 2.4 Hz, ArH), 7.48-7.60 (2 H, m, ArH), 7.20-7.34 (2 H, m, ArH), 7.0 (1 H, d, *J* 8.7 Hz, ArH), 4.17-4.40 (2 H, m, $ArOCH_2$), 3.70-4.00 (4 H, m, OCH_2) 3.25 (2 H, t, *J* 6.6 Hz, SCH_2), 1.74 (2 H, s, CCH_2C), 1.40 (6 H, s, $C(CH_3)_2$), 0.80 (9 H, s, $C(CH_3)_3$).

SYNTHESES OF MACROCYCLIC AZO AND AZOXY COMPOUNDS

1,2-Azoxy-3,4,12,13-dibenzo-5,11-dithia-8-oxacyclotridecane (8)

A mixture of compound (**3**) (3.8 g; 10 mmol), anhydrous stannous chloride (7.6 g), sodium hydroxide (12.2 g), acetone (35 cm^3) and water (30 cm^3) was stirred vigorously and heated to gentle boiling for 5 h.

Toluene (30 cm^3) was added to the cooled reaction mixture and the precipitated sodium chloride was removed by filtration. The solid was washed with toluene; the filtrates were combined, the organic layer was separated, washed with water (30 cm^3) and the solvent was removed. The crude product (3 g) was chromatographed on a silica gel column using methylene chloride to remove polymers. The yellow fraction (1.8 g) was rechromatographed on silica gel column using ethyl acetate : hexane mixture (1 : 4) as eluent. The yellowish macrocyclic product crystallized from the eluate after partial removal of solvent. Yield 1 g (30 %) of azoxycrown ether (**8**); m.p. 124-126°. ν_{max} (nujol) 1460, 1100, 1050, 750, 720 cm^{-1}; δ_H (200 MHz, $CDCl_3$) 7.95 (1 H, dd, *J* 8.0 Hz, 1.5 Hz, ArH), 7.25-7.70 (7 H, m, ArH), 3.55-3.78 (4 H, m, OCH_2), 3.02-3.23 (4 H, m, SCH_2); UV-VIS, λ_{max} = 216.5 nm (ϵ_{max} = 19380); HRMS (EI): M^+, found 332.06358. $C_{16}H_{16}N_2O_2S_2$ requires 332.06532.

1,2-Azo-3,4,12,13-dibenzo-5-thia-8,11-dioxacyclotridecane (9) and azoxy compound (10)

A mixture of compound (**4**) (3.5 g; 10 mmol), stannous chloride (8.2 g) and sodium hydroxide (13 g), acetone (50 cm^3) and water (40 cm^3) was stirred vigorously and boiled gently for 5 h. The mixture was diluted with toluene (30 cm^3). The precipitate was removed and the organic layer evaporated. The product (2.2 g) was dissolved in a small amount of methylene chloride and chromatographed on a silica gel column with an ethyl acetate : hexane (1 : 4) mixture as an eluent. The first red fraction was evaporated and crystallized from hexane to afford 500 mg (16%) of azocrown ether (**9**) red crystals. The second orange fraction after crystallization from methanol afforded 700 mg (22%) of azoxy crown ether (**10**) orange crystals.
Azocrown ether (**9**) m.p. 103-105°. ν_{max} (film) 3060, 2930, 1600, 1490, 1455, 1280, 1250, 1125, 1055, 975, 925, 745 cm^{-1}; δ_H (200 MHz, $CDCl_3$) 7.79 (1 H, dd, *J* 7.7, 1.8 Hz, ArH), 7.63-7.70 (2 H, m, ArH), 7.33-7.43 (3 H, m, ArH), 6.99-7.22 (2 H, m, ArH), 4.14-4.20 (2 H, m, $ArOCH_2$), 3.82-3.94 (4 H, m, OCH_2), 3.37 (2 H, d, *J* 6.9 Hz, SCH_2); UV-VIS, λ_{max} = 216.5 nm (ϵ = 23580); λ_{max} = 460 nm (ϵ_{max} = 2146); HRMS (EI): M^+, found 300.09625. $C_{16}H_{16}N_2O_2S$ requires 300.09325.
Azoxycrown ether (**10**) m.p. 138-140°. ν_{max} (film) 1600, 1460, 1290, 1140, 1100, 1050, 930, 760 cm^{-1}; δ_H (200 MHz, $CDCl_3$) 8.10 (1 H, dd, *J* 8.1, 1.4 Hz, ArH), 7.66-7.73 (2 H, m, ArH), 7.24-7.50 (3 H, m, ArH), 7.05-7.14 (2 H, m, ArH), 4.18-4.24 (2 H, m, $ArOCH_2CH_2O$), 3.86-3.92 (2 H, m, SCH_2CH_2O), 3.75 (2 H, t, *J* 6.4 Hz, $ArOCH_2$), 3.13 (2 H, t, *J* 6.2 Hz, SCH_2); HRMS (EI): M^+, found 316.08300. $C_{16}H_{16}N_2O_3S$ requires 316.08816.

Compounds **11** - **16** were obtained analogously from podands **5** - **7**

1,2-Azo-3,4-benzo-12,13-(4-methylbenzo)-5-thia-8,11-dioxacyclotridecane (11)

Yield 240 mg (7.6%) of red crystals (ethanol). M.p. 130-132°. ν_{max}(nujol) 1490, 1290, 1250, 1140, 1050, 750, 730 cm^{-1}; δ_H (200 MHz, $CDCl_3$) 7.10-7.70 (6 H, m, ArH), 6.80-6.90 (1 H, m, ArH), 4.00-4.20 (2 H, m, $ArOCH_2$), 3.75-3.90 (4 H, m, OCH_2), 3.30 (2 H, t, *J* 6.9 Hz, SCH_2), 2.35 (3 H, s, CH_3); HRMS (EI): M^+, found 314.11438. $C_{17}H_{18}N_2O_2S$ requires 314.10890.

1,2-Azoxy-3,4-benzo-12,13-(4-methylbenzo)-5-thia-8,11-dioxacyclotridecane (12)

Yield 660 mg (20%) of pale yellow crystals (from 2-propanol). M.p. 63-65°. ν_{max}(film) 2940, 2860, 1500, 1460, 1340, 1270, 1120, 750 cm^{-1}; δ_H (200 MHz, $CDCl_3$) 8.17 (1 H, dd, *J* 8.3, 1.5 Hz, ArH), 7.20-7.70 (5 H, m, ArH), 6.99 (1 H, d, *J* 8.5 Hz, ArH), 4.22 (2 H, t, *J* 3.9 Hz, $ArOCH_2$), 3.80-3.95 (4 H, m,

$SCH_2C\underline{H}_2$ and $OC\underline{H}_2$), 3.20 (2 H, t, *J* 6.2 Hz, $SC\underline{H}_2$), 2.35 (3 H, s, $C\underline{H}_3$); HRMS (EI):, found 330.10101. $C_{17}H_{18}N_2O_3S$ requires 330.10381.

1,2-Azo-3,4-benzo-12,13-(4-*tert*-butylbenzo)-5-thia-8,11-dioxacyclotridecane (13)
Yield 150 mg (4.2%) of a red crown; m.p. 118-120° (2-propanol). ν_{max}(film) 2970, 1500, 1460, 1360, 1270, 1140, 1060, 760, 740 cm^{-1}; δ_H (200 MHz, $CDCl_3$) 7.84 (1 H, d, *J* 2.6 Hz, Ar$\underline{H}$), 7.62-7.69 (2 H, m, Ar$\underline{H}$), 7.33-7.44 (3 H, m, Ar$\underline{H}$), 6.95 (1 H, d, *J* 8.6 Hz, Ar$\underline{H}$), 4.10-4.20 (2 H, m, $ArOC\underline{H}_2$), 3.83-3.94 (4 H, m, $OC\underline{H}_2$), 3.38 (2 H, t, *J* 6.8 Hz, $SC\underline{H}_2$), 1.40 (9 H, s, $C(C\underline{H}_3)_3$); HRMS (EI): M^+, found 356.15336. $C_{20}H_{24}N_2O_2S$ requires 356.15585.

1,2-Azoxy-3,4-benzo-12,13-(4-*tert*-butylbenzo)-5-thia-8,11-dioxacyclotridecane (14)
Yield 200 mg (5.4%) of a pale orange oily azoxycrown ether. ν_{max}(film) 2970, 1620, 1580, 1500, 1460, 1290, 1140, 1100, 750 cm^{-1}; δ_H (200 MHz, $CDCl_3$) 8.16 (1 H, dd, *J* 8.1, 1.4 Hz, Ar$\underline{H}$), 7.62-7.66 (1 H, m, Ar$\underline{H}$), 6.90-7.50 (3 H, m, Ar$\underline{H}$), 6.30-6.80 (2 H, m, Ar$\underline{H}$), 4.41-4.20 (2 H, m, $ArOC\underline{H}_2$), 3.84-3.90 (2H, m, $OC\underline{H}_2$), 3.65 (2 H, t, *J* 6.4 Hz, OCH_2), 3.12 (2 H, t, *J* 6.3 Hz, $SC\underline{H}_2$), 1.35 (9 H, s, $C(C\underline{H}_3)_3$); HRMS (EI):M^+, found 372.14529. $C_{20}H_{24}N_2O_3S$ requires 372.15076.

1,2-Azo-3,4-benzo-12,13-(4-tetramethylbutylbenzo)-5-thia-8,11-dioxacyclotridecane (15)
Yield 1 g (25%) of red oily azocrown ether. ν_{max}(film) 2980, 1500, 1460, 1270, 1120, 760, 740 cm^{-1}; δ_H (200 MHz, $CDCl_3$) 7.84 (1 H, d, *J* 2.6 Hz, Ar$\underline{H}$), 7.6-7.7 (2 H, m, Ar$\underline{H}$), 7.30-7.40 (3 H, m, Ar$\underline{H}$), 6.92 (1 H, d, *J* 8.7, Ar$\underline{H}$), 4.10-4.16 (2 H, m, $ArOC\underline{H}_2$), 3.82-3.92 (4 H, m, $OC\underline{H}_2$), 3.38 (2 H, t, *J* 6.8 Hz, $SC\underline{H}_2$), 1.80 (2 H, s, $CC\underline{H}_2C$), 1.42 (6 H, s, $C(C\underline{H}_3)_2$), 0.79 (9 H, s, *J* 9.7 Hz, $C(C\underline{H}_3)_3$); HRMS (EI):M^+, found 412.21820. $C_{24}H_{32}N_2O_2S$ requires 412.21845.

1,2-Azoxy-3,4-benzo-12,13-(4-tetramethylbutylbenzo)-5-thia-8,11-dioxacyclotridecane (16)
Yield 324 mg (7.5%) of a pale orange azoxycrown ether. ν_{max}(film) 2970, 1500, 1460, 1300, 1270, 1130, 1100, 750 cm^{-1}; δ_H (200 MHz, $CDCl_3$) 8.10 (1 H, dd, *J* 8.1, 1.5 Hz, Ar$\underline{H}$), 7.65-7.75 (3 H, m, Ar$\underline{H}$), 7.20-7.40 (3 H, m, Ar$\underline{H}$), 4.15 (2 H, t, *J* 3.9 Hz, $ArOC\underline{H}_2$), 3.85-3.94 (2 H, m, $C\underline{H}_2O$), 3.73 (2 H, t, *J* 6.2 Hz, $OC\underline{H}_2$), 3.15 (2 H, t, *J* 6.2 Hz, $SC\underline{H}_2$), 1.75 (2 H, s, $CC\underline{H}_2C$), 1.35 (6 H, s, $C(C\underline{H}_3)_2$), 0.78 (9 H, s, $C(C\underline{H}_3)_3$); UV-VIS, λ_{max} = 216.5 and 460 nm; ϵ_{max} = 24008 and 1502, respectively; HRMS (EI) M^+, found 428.20958. $C_{24}H_{32}N_2O_3S$ requires 428.21336.

Supplementary Material Available

Crystallographic data, atomic parameters for non-hydrogen atoms, their anisotropic displacement parameters, atomic and thermal parameters for hydrogen atoms, bond distances, valence and torsion angles in the structure (6 pages) and listing of observed and calculated structure factors (3 pages) have been deposited at the Cambridge Crystallographic Data Centre, Lensfield Road, Cambridge, CB2 IEW, UK.

Acknowledgement

Financial support of this work from the Technical University of Gdańsk, Grant No. DS013478/003 is kindly acknowledged. The Authors are indebted to Dr E. Luboch for valuable discussion.

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