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Synthesis and properties of azobenzocrown ethers with π-electron donor, or π-electron donor and π-electron acceptor group(s) on benzene ring(s)

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Abstract—New azobenzocrown ethers of differentiated size and with substituted benzene residues have been synthesized. These crown ethers possess π-electron donor, or π-electron donor–π-electron acceptor pair of functional group(s) in benzene ring(s) in the *para* position to azo-grouping. Their metal ion complexation abilities in solution were studied using UV–vis spectrophotometry. The X-ray structure of a 19-membered crown ether with 4-dimethylamino-4′-nitroazobenzene fragment has been solved.

1. Introduction

Crown ethers possessing an azo group as a part of the macrocycle are interesting metal complexing reagents preserving properties typical for azo metallochromic reagents.[1] The arrangement of lone electron pairs and the diameter of the macrocyclic cavity additionally discriminates between complexed species according to their size. Moreover, the presence of benzene rings allows almost unlimited modifications of these compounds to obtain new chromo- or fluoroionophores. Azobenzocrown ethers bearing 2,2′-linked azobenzene were prepared by Williamson ether synthesis using 2,2′-dihydroxyazobenzene.[2,3] Another route leading to the discussed crown ethers consists in using 2,2′-difluoroazobenzene; this method also enables the preparation of aza and thia analogs.[4] Alternatively, azobenzocrown ethers were obtained by stannite reduction followed by macrocyclization of the respective bis(2-nitrophenoxy)-oxaalkanes.[5] The last procedure was used in the synthesis of numerous azobenzocrown ethers, and derivatives substituted mainly with alkyl groups in aromatic rings.[6,7]

The behaviour of lipophilic azobenzocrown ethers as ionophores in ion selective membrane electrodes (ISME's)[6,7] and chemically sensitive field effect transistors (ChemFET's)[8] was studied. As found for non-cyclic azobenzene derivatives, amphiphilic azobenzocrown ethers form stable Langmuir monolayers[6,9] capable of $E \rightleftarrows Z$ isomerization.

The complexation properties of azobenzocrown ethers with alkali and alkaline earth metal salts were investigated spectrophotometrically in acetonitrile solution.[3,10,11] 13- and 16-membered chromoionophoric azobenzocrown ethers with a hydroxyl or dimethylamino group in aromatic ring, in the *para* position to the azo group, were investigated among others.[11]

For *para* or *ortho* hydroxyazobenzenes the tautomerization to quinone–hydrazone form is known to occur.[12] The physical properties of azo dyes (e.g., colour) are closely related to this tautomerism. The phenylazophenol ⇄ quinone–phenylhydrazone tautomerization also proceeds in the case of macrocyclic azophenol chromoionophores, cf.[13]

It was stated that compound **1** (Fig. 1) dissolved in, for example, chloroform, acetonitrile or methanol exists in the quinone–hydrazone form; in dimethyl sulfoxide this form predominates.[11] The structure of the quinone–hydrazone form of crown ether **1** (**1-QH**) was solved by X-ray crystallographic analysis.[14] Compound **2** (Fig. 1) in chloroform and in acetonitrile exists, like **1**, in the quinone–hydrazone form but in dimethyl sulfoxide only the

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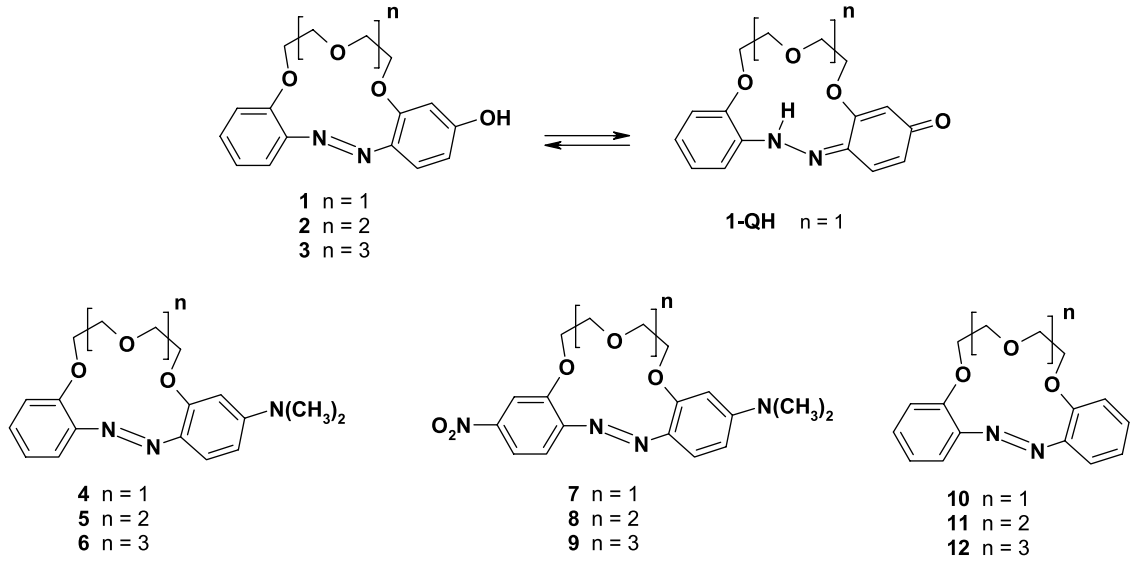


Figure 1. Structures of investigated azobenzocrown ethers.

azophenol form was observed. Cation complexation by compounds **1** and **2** affects the tautomeric equilibrium.[11]

The presence of the dimethylamino substituent (*para* to the azo group) in azobenzocrowns **4** and **5** (Fig. 1) made the absorption maxima well pronounced compared to the spectra of parent compounds **10** and **11**.[11] In the case of compounds **4** and **5** complexation of lithium ions in acetonitrile is clearly evident from spectrophotometric studies due to adequate spectral band separation (60 nm) of crown ether and its complex.

This paper describes the synthesis and properties of new 19-membered azobenzocrown ethers containing hydroxyl or dimethylamino group in *para* position to azo group.

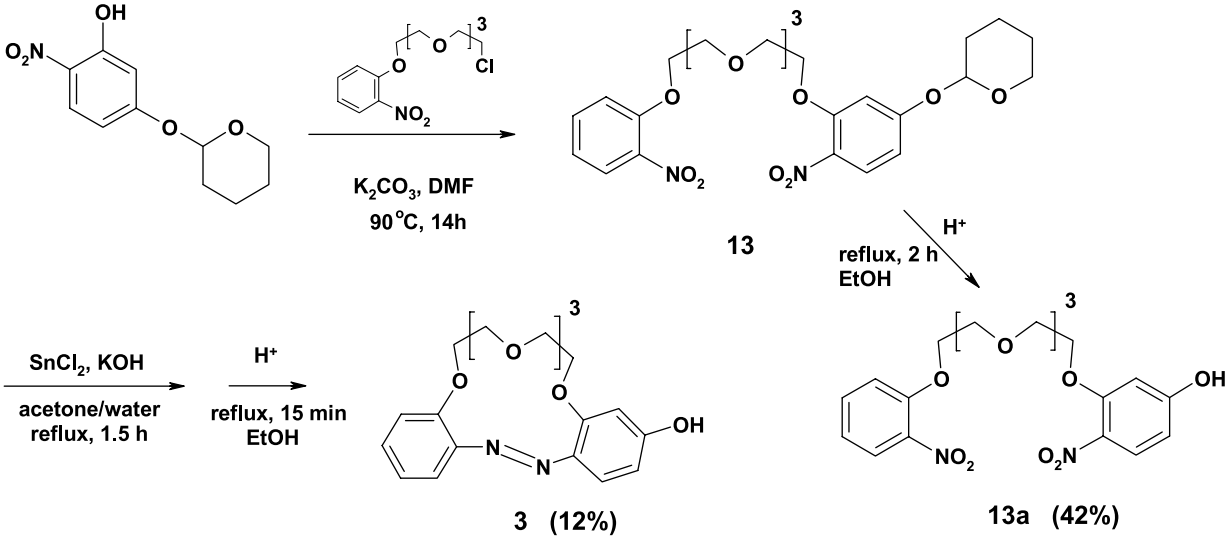
The synthesis of new 13-, 16- and 19-membered crowns bearing two different electron donating/accepting groups (dimethylamino and nitro) in the azobenzene fragment was also elaborated. For the synthesized compounds, spectral properties and metal ion complexation studies were carried out. Their complexation properties were compared to properties of unsubstituted azobenzocrown ethers **10**–**12**.[3,10]

2. Results and discussion

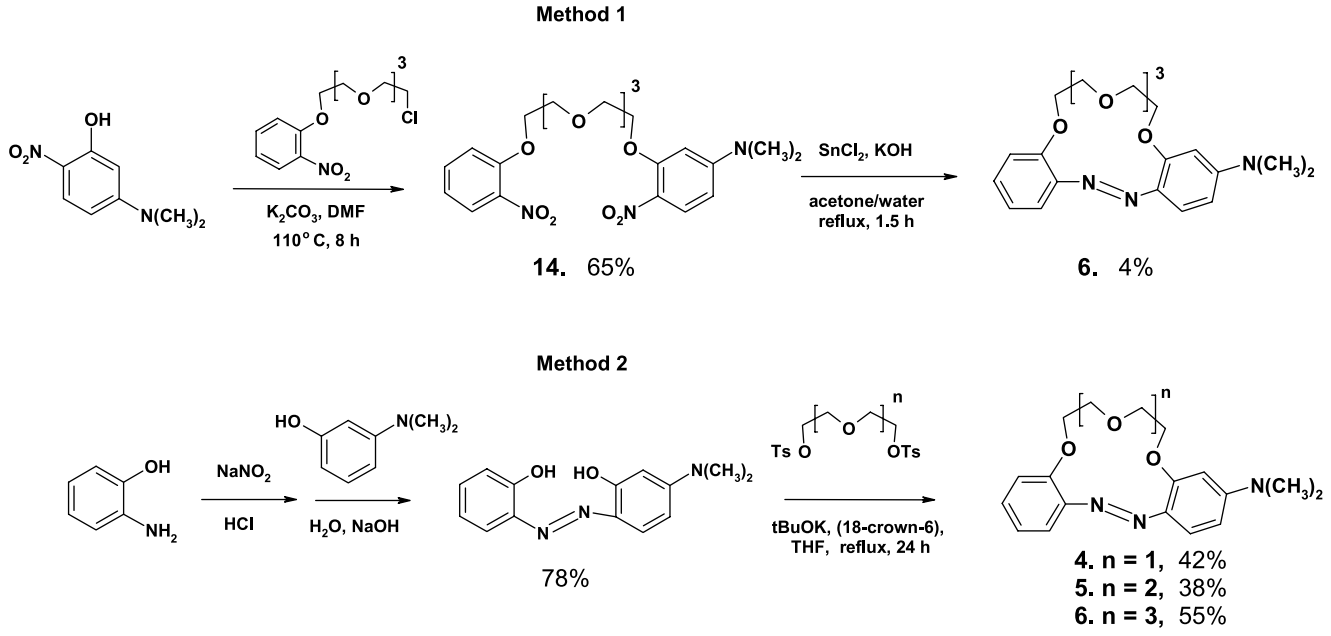
2.1. Synthesis

The synthesis of compounds **3**, **4**–**6** and **7**–**9** is presented in Schemes 1–3. The 19-membered hydroxyazobenzocrown ether **3** was obtained by stannite reduction of dinitropodand **13** (Scheme 1) in a way similar to the method described earlier for azobenzocrown ethers of smaller size.[11] It is worth noting that Williamson synthesis of this compound starting from 4-protected 2,2′,4 -trihydroxyazobenzene resulted in lower yield (around 1%) of **3**.

Tautomeric equilibria for 19-membered azobenzocrown ether with a hydroxyl group were successfully investigated



Scheme 1. Synthesis of 19-membered azobenzocrown ether **3**.



Scheme 2. Synthesis of azobenzocrown ethers **4**–**6**.

using ^{1}H NMR spectroscopy and compared with data for smaller analogs. It was found that the equilibrium depends on the size of the macrocycle. 13-Membered compound **1** exists in quinone–hydrazone form, which is stabilized by a strong intramolecular hydrogen bond.[14] 19-Membered compound **3** exclusively exists in the azophenol form in DMSO and chloroform, whereas in acetonitrile this form is present in no less than 75%.

Compound **6** was obtained by two routes. The first synthesis was performed analogously to the previously described method,[11] which consists of reductive macrocyclization of the appropriate dinitropodand **14** (yield 4%, Scheme 2, method 1). The second synthetic procedure involved diazocoupling of 2-hydroxybenzenediazonium salt with 3-dimethylaminophenol. The obtained 4-dimethylamino-2,2′-dihydroxyazobenzene, upon reaction with 1,13-ditosyl-1,4,7,10,13-pentaoxatridecane produced macrocyclic azo compound **6** (Scheme 2, method 2) with much better yield (55%). This method was also used for the efficient synthesis of compounds **4** and **5** with yields of 42 and 38%, respectively.

Azobenzocrowns **7**–**9** were obtained by reacting 4-dimethylamino-4′-nitro-2,2′-dihydroxyazobenzene with the appropriate ditosylates (Scheme 3, $n=1$–3).

It was found that compounds **7**–**9**, contrary to the parent azobenzocrown ethers, in solution and in the solid state, only exist in *E* form. Single crystal X-ray diffraction study of **9**·2H$_2$O confirmed the *E* geometry of the azo unit with aromatic moieties in the *trans*-positions and proved the existence of a molecular diaqua-complex (Fig. 2).

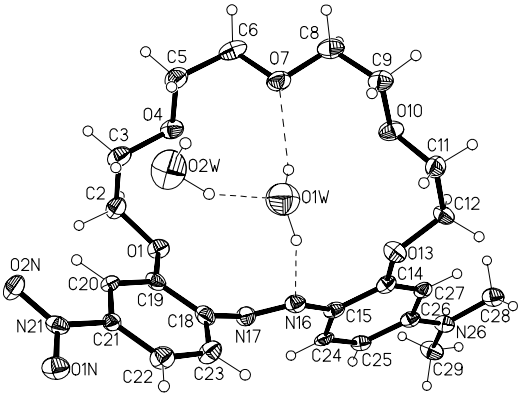
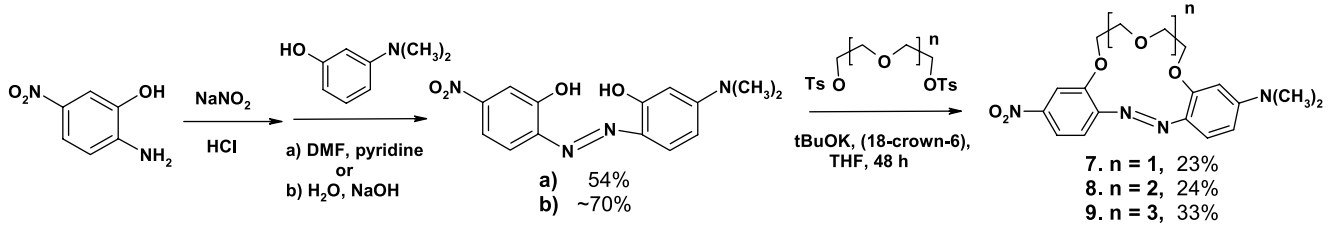


Figure 2. Molecular structure of **9**·2H$_2$O with the atom labeling scheme; ellipsoids are drawn at 50% probability level.

The heteroatoms of macrocyclic unit deviate from their mean plane in the range of −0.255(2)–0.217(2) Å. The flat nitrobenzene and dimethylaminobenzene moieties are located at opposite sides of the plane. The dihedral angle between these two aromatic systems equals 79.4(2)°. The torsion angles around C15–N16 and N17–C18 bonds equal



Scheme 3. Synthesis of azobenzocrown ethers **7**–**9**.

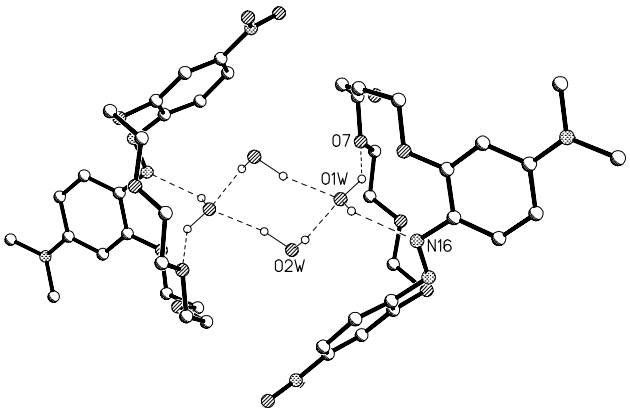


Figure 3. Hydrogen bonded centrosymmetric dimer in the structure of **9**·2H_2O. Hydrogen atoms of crown ethers are omitted for clarity.

164.0(4) and 125.7(4)°, respectively. These differences indicate various degree of π-conjugation of the azo-group with the adjacent aromatic rings and agree well with the corresponding bond lengths of C15–N16 [1.417(6) Å] and N17–C18 [1.431(6) Å]. In the polyether chain the torsion angles around C–C bonds are *gauche* and equal 62.4(5), −73.7(5), 67.8(5) and −72.1° clockwise starting from the C2–C3 bond. The majority of C–O bonds adopt an *anti* conformation and their deviations from 180° are less than 20° except for the torsion angle C19–O1–C2–C3, which is *gauche* and equals 71.4°. The sequence of two *gauche* torsion angles at C2 atom forms the corner fragment.[15]

To the best of our knowledge, this is the first structurally characterized example of water molecule coordination by crown ethers with azobenzene subunit in the macrocycle, although water complexation by Pedersen type macrocycles[16] is an ordinary and well established phenomenon.[17] One water molecule is located 1.723(5) Å above the macrocycle mean plane, and donates protons to form O1w–H···O7 and O1w–H···N16 hydrogen bonds. Two other water molecules bridge neighbouring aqua complexes via O2w–H···O1w hydrogen bonds and result in formation of a centrosymmetric H-bonded dimer. In this dimer, two crown ether molecules encapsulate a tetrameric water cluster (Fig. 3, Table 1).

Table 1. Hydrogen bonds in the structure of **9**·2H_2O (Å and °)[a]

D–H···A	*d* (D–H)	*d* (H···A)	*d* (D···A)	Angle (D–H···A)
O1w–H1w1···O7	1.01(2)	2.10(6)	2.923(6)	137(7)
O1w–H2w1···N16	1.00(2)	2.31(7)	3.157(6)	142(8)
O2w–H1w2···O1w#1	1.05(2)	1.87(3)	2.904(7)	166(6)
O2w–H2w2···O1w	1.08(2)	1.97(4)	2.967(7)	153(6)

[a] Symmetry transformations used to generate equivalent atoms: #1 $-x, -y+2, -z+1$.

In turn, the dimers associate to form chains along the [0 −1 1] direction of crystal due to π-stacked assembly of centrosymmetrically related dimethylaminobenzene moieties. The centroid–centroid distance and the interplanar separations between the corresponding aromatic rings in the stack are 3.908 and 3.530 Å, respectively. No distinct π–π stacking interactions were found for the nitrobenzene aromatic moiety (Fig. 4).

2.2. Spectroscopy and complexation behaviour

The UV–vis spectroscopic properties of investigated and parent compounds (Fig. 1) are collected in Table 2.

The general solvatochromic effect for the above dimethylaminocrown ethers was studied for 19-membered crown ether **6** as an example. UV–vis spectra of **6** in methylene chloride, acetonitrile, acetone, methanol and DMSO were recorded. Characteristic absorption bands and molar absorptivity coefficients in different solvents are collected in Table 3. In all cases noticeable bathochromic shifts of absorption bands at about 390 nm were observed comparing to spectra in acetonitrile. The most significant intensity changes were found for methylene chloride and DMSO; hyper- or hypochromic effects were observed for these solvents, respectively, (Fig. 5).

As expected, the presence of π-electron donor, or π-electron donor and π-electron acceptor groups attached to benzene ring(s) of azobenzocrown ether causes a red shift of the absorption maximum.

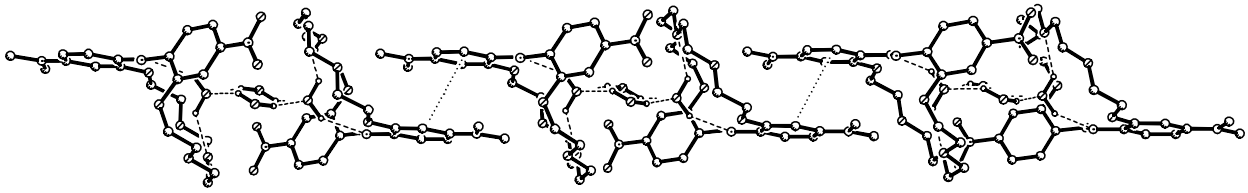


Figure. 4. Hydrogen bonds and π–π stacking interactions linking crown ether and water molecules into chain laying in the [0 −1 1] direction of crystal. Only hydrogen atoms involved in H-bonds are shown.

Table 2. Characteristic absorption bands and molar absorptivity coefficients for azobenzocrown ethers in acetonitrile

Crown ether	λ_{max} (nm)	ε_{max}	Crown ether	λ_{max} (nm)	ε_{max}
1[11]	434	2.31×10^4	**7**	459	1.90×10^4
2[11]	431	2.05×10^4	**8**	463	1.90×10^4
3	342, 434	1.70×10^4, 1.60×10^4	**9**	287, 485	8.30×10^3, 1.70×10^4
4[11]	403	7.70×10^3	**10**(*trans*)	347, 456	1.10×10^4, 5.04×10^2
5[11]	400	1.78×10^4	**11**(*trans*)[10]	351, 461	9.40×10^3, 9.80×10^2
6	380, 455	1.30×10^4, 8.10×10^3	**12**(*trans*)[10]	337, 439	7.88×10^3, 2.83×10^3

Table 3. Characteristic absorption bands and molar absorptivity coefficients for azobenzocrown ether **6** in different solvents

Solvent	λ_{max} (nm)	ε_{max}	Solvent	λ_{max} (nm)	ε_{max}
Methylene chloride	394, ~460	2.40×10^4, 1.20×10^4	Acetone	393, ~460	1.40×10^4, 6.50×10^3
Methanol	389, ~460	1.70×10^4, 1.20×10^4	Dimethyl sulfoxide	392, ~460	7.00×10^3, 4.60×10^3

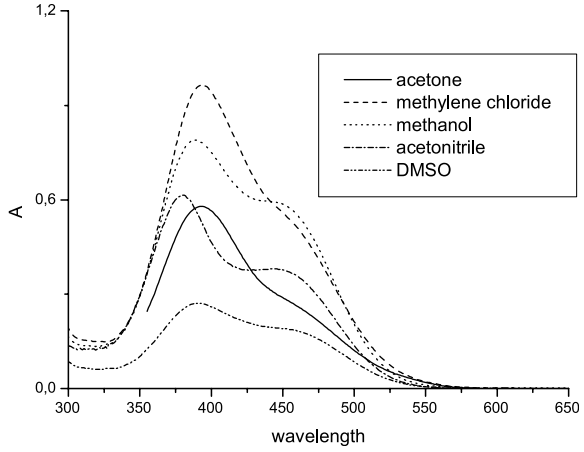


Figure 5. Absorption spectra of compound **6** ($c=4.1\times10^{-5}$ mol dm^{-3}) in different solvents.

Furthermore, the absorption maxima for substituted crown ethers are well pronounced compared with the spectra of the parent unsubstituted crown ethers. A significant effect of the presence of dimethylamino-, or dimethylamino- and nitro-group(s) in benzene rings for compounds **4**–**6** and **7**–**9** is that the $E\rightarrow Z$ isomerization in different solvents under usual conditions is not observed. Absorption spectra of 13-membered crown ethers **10**, **4** and **7** in acetonitrile are presented in Figure 6.

Complexation of alkali and alkaline earth metal ions by macrocycles was investigated by UV–vis spectroscopy in organic solvents. Studies of metal cation complexation performed for 19-membered hydroxyazobenzocrown ether **3** were combined with studies of azophenol⇄quinone–hydrazone equilibration. It was found that the azophenol form is stabilized by complexation of metal cations. In ^{1}H NMR spectra recorded in acetonitrile well pronounced signals for only the azophenol form are observed in the presence of barium, strontium and calcium salts. UV–vis absorption spectra registered in acetonitrile show a decrease of band intensity at 430 nm followed by an increase of the band at 350 nm (typical for the azo form) upon titration with the above metal perchlorates. The respective changes for interaction with strontium perchlorate are exemplified in Figure 7.

The results of spectrophotometric titration did not allow full characterization of the equilibria that occur in the system with compound **3**. It was only stated that beside complex formation tautomeric equilibrium takes place.

For 19-membered azobenzocrown ether with dimethylamino group (compound **6**) selective complex formation was found with the magnesium cation among alkali and alkaline earth metal cations in acetonitrile solution. The complexation was manifested by characteristic colour change from orange to pink. The spectral changes accompanying complex formation are presented in Figure 8.

Other studied cations do not cause such distinct colour changes. Comparison of spectral changes of compound **6** in the presence of potassium, strontium and magnesium perchlorate with evident selectivity for magnesium is shown in Figure 9.

Complexation studies for compound **6** were also carried out in methanol. In this case, no significant spectral changes enabling determination of binding constants were found in the presence of lithium, sodium, potassium and magnesium salts. As could be expected the values of stability constants in methanol are smaller than in acetonitrile. However, in both solvents the largest value of stability constant was found for barium complex (Table 4).

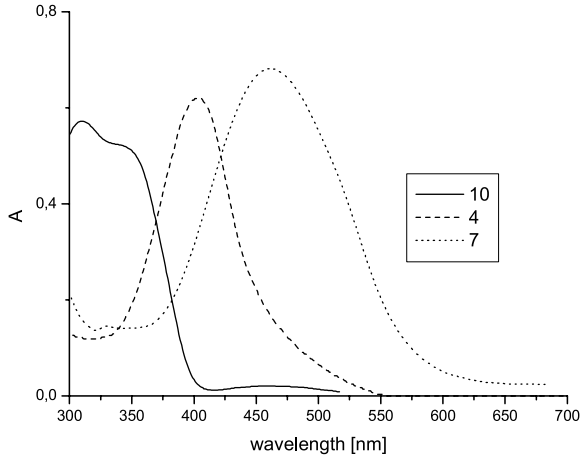


Figure 6. Absorption spectra of azobenzocrown ethers: **10**, **4** and **7** ($c=7.0\times10^{-5}$ mol dm^{-3}) in acetonitrile.

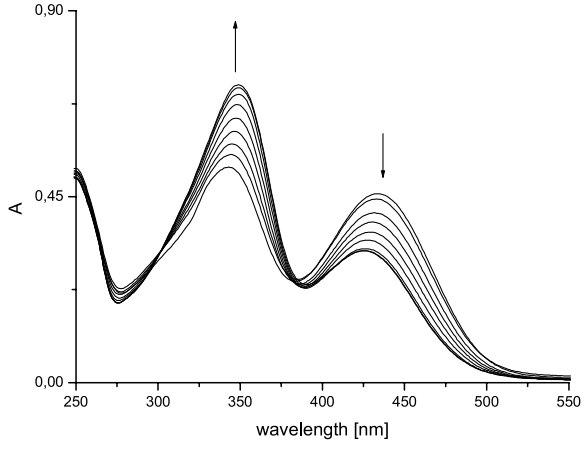


Figure 7. Changes of absorption spectra upon titration of compound **3** ($c=3.0\times10^{-5}$ mol dm^{-3}) with strontium perchlorate (0–4.4×10^{-5} mol dm^{-3}) in acetonitrile.

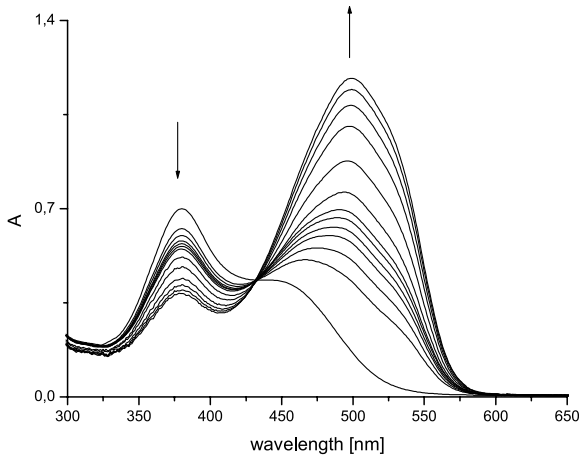


Figure 8. Spectral changes of compound **6** ($c=5.7\times10^{-5}$ mol dm^{-3}) upon titration with magnesium perchlorate (0–1.9×10^{-3} mol dm^{-3}) in acetonitrile.

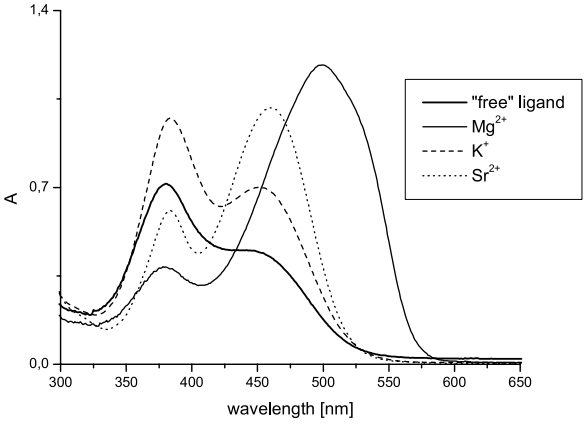


Figure 9. Absorption spectra of compound **6** and its complexes. 'Free' ligand ($c=5.7\times10^{-5}$ mol dm^{-3}) and limiting spectra in the presence of: potassium ($c=2.6\times10^{-3}$ mol dm^{-3}); strontium ($c=4.4\times10^{-5}$ mol dm^{-3}); and magnesium ($c=1.9\times10^{-3}$ mol dm^{-3}) perchlorates in acetonitrile.

Investigations of metal ion complexation were performed also for new type of synthesized compounds containing two different functional groups on the benzene rings (compounds **7–9**). It was found that the crown ethers complex alkali and alkaline earth metal cations and that the selectivity depends on the cavity size. 13-Membered azobenzocrown **7** forms complexes with most of the investigated metal cations. Only the presence of potassium salt causes small changes in the absorption spectra preclude determination of stability constant, similarly to other 13-membered azobenzocrowns. For the sodium complex of compound **7** the calculated stability constant is a little smaller than for sodium complex of compound **4**, whereas for unsubstituted compound **10**, changes in the absorption spectra made determination of stability constant impossible. Generally, the values of the stability constants are higher for alkaline earth metal cation complexes than for lithium and sodium. Changes in the absorption spectra of compound **7** in the presence of alkaline earth metal cations perchlorates are presented in Figure 10. Changes upon titration of above crown ether with lithium perchlorate are shown in Figure 11. The respective values of stability constants for compounds **7–9** and shifts of absorption bands are collected in Table 5.

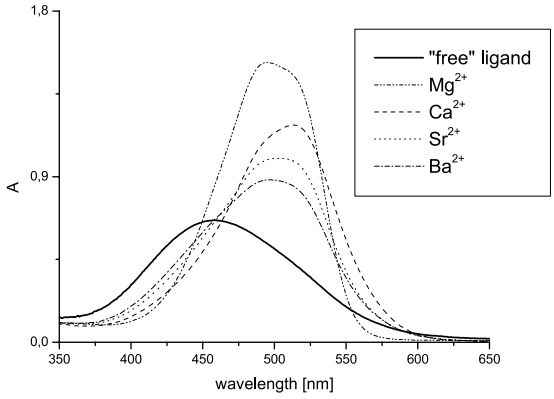


Figure 10. Absorption spectra of compound **7** and its complexes. 'Free' ligand ($c=3.5\times10^{-5}$ mol dm^{-3}); and limiting spectra in the presence of: magnesium ($c=2.2\times10^{-4}$ mol dm^{-3}); calcium ($c=4.5\times10^{-4}$ mol dm^{-3}); strontium ($c=4.1\times10^{-4}$ mol dm^{-3}); and barium ($c=3.9\times10^{-4}$ mol dm^{-3}) perchlorates in acetonitrile.

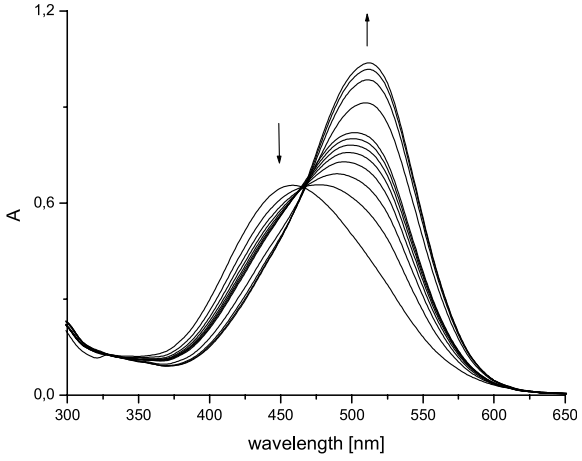


Figure 11. Changes of absorption spectra upon titration of compound **7** ($c=3.5\times10^{-5}$ mol dm^{-3}) with lithium perchlorate (0–4.1×10^{-3} mol dm^{-3}) in acetonitrile.

Table 4. Stability constants of 1:1 complexes of compound **6** with metal perchlorates in acetonitrile and methanol

Solvent	Log K_{Me} ($\Delta\lambda$ (nm))						
	Li	Na	K	Mg	Ca	Sr	Ba
Acetonitrile	2.7[a]	3.4[a]	4.3[b]	4.2 (46)	5.1[a]	5.4[a]	6.7[a]
Methanol	—	—	—	—	2.7[a]	3.5[a]	4.3[a]

[a] Increase of intensity for band at 442 nm.
[b] Increase of intensity for bands at 380 and 442 nm.

Table 5. Stability constants of 1:1 complexes of compounds **7–9** with metal perchlorates in acetonitrile

Compound	Log K_{Me} ($\Delta\lambda$ (nm))						
	Li	Na	K	Mg	Ca	Sr	Ba
7	3.1 (51)	1.8 (28)	—	4.3 (37)	4.5 (56)	3.6 (45)	3.8 (39)
8	4.3 (37)	3.7 (37)	3.2 (27)	5.0 (35)	5.3 (55)	5.4 (55)	5.1 (37)
9	2.1[a]	2.9[a]	2.8[a]	2.5[a]	6.2[a]	5.7[a]	5.6[a]

[a] Increase of intensity for band at ~480 nm.

3. Conclusions

New approaches to the synthesis of functionalized azobenzocrown ethers were presented. In most cases these unsymmetrical compounds were obtained with more than satisfactory yield (even over 55%). For the synthesized compounds, in particular for compounds **7–9**, no detectable $E \rightleftarrows Z$ isomerization under ordinary conditions was found. This presents an advantage of the synthesized macrocycles because it simplifies UV–vis and NMR spectra and limits the number of species during complexation. Selective magnesium cation complexation was found for 19-membered dimethylaminoazobenzocrown ether **6**. Compared with the parent, non-functionalized azobenzocrown ethers, for the studied compounds beneficial influence of the presence of functional groups on changes in absorption spectra upon metal cation complexation was observed.

4. Experimental

4.1. General

All solvents were of analytical reagent grade. Tetrahydrofuran was distilled from $LiAlH_4$ and stored over molecular sieves. For spectrophotometric measurements HPLC grade solvents were used. The reagents from Aldrich were used without further purification. Silica gel 60 (63–200 μm) was used for column chromatography (Merck). ^{1}H NMR and ^{13}C NMR spectra were recorded on Varian instrument at 500 and 125 MHz, respectively. Chemical shifts are reported as δ values in ppm in relation to TMS. IR spectra were recorded on Mattson Genesis II instrument. UV–vis spectra were recorded on a UNICAM UV 300 apparatus. Mass spectrometry was conducted on an AMD-604 apparatus (70 eV, EI method). Melting points (mp) are uncorrected.

4.2. Synthesis

4.2.1. Synthesis of azobenzocrown ether with peripheral hydroxyl group (compound 3).

4.2.1.1. 1-Chloro-11-(2-nitrophenoxy)-3,6,9-trioxaundecane. A mixture of 2-nitro-phenol (3.8 g, 25 mmol), anhydrous potassium carbonate (5 g), 1,11-dichloro-3,6,9-trioxaundecane (17.33 g, 75 mmol) and dimethylformamide (10 mL) was heated for 20 h at 95 °C. The cooled reaction mixture was diluted with water and extracted with chloroform. The desired product was isolated by column chromatography using hexane/methylene chloride 5:1 mixture as an eluent. Yield 3.2 g (38%) of oily product. ^{1}H NMR ($CDCl_3$): δ 3.63 (t, J=6.1 Hz, 2H), 3.65–3.69 (m, 6H), 3.73–3.77 (m, 4H), 3.91 (t, J=4.9 Hz, 2H), 4.27 (t, J=4.9 Hz, 2H), 7.04 (dt, J_1=7.6 Hz, J_2=1.5 Hz, 1H), 7.11 (d, J=8.8 Hz, 1H), 7.50–7.54 (m, 1H), 7.83 (dd, J_1=8.3 Hz, J_2=1.6 Hz, 1H).

4.2.1.2. Podand 13. A mixture of 2-nitro-5-tetrahydropyranyloxyphenol[11] (3 g, 12.5 mmol), anhydrous potassium carbonate (4 g), 1-chloro-11-(2-nitrophenoxy)-3,6,9-trioxaundecane (3.9 g, 11.7 mmol) and dimethylformamide (12 mL) was heated for 14 h at 90 °C. The cooled reaction mixture was diluted with water and extracted with chloroform. The desired product was isolated by column chromatography using methylene chloride as an eluent. A crude product **13** was obtained of insufficient purity. Therefore, the product was fully characterized after removing tetrahydropyranyl protecting group. To the crude product in ethanol (20 mL), catalytic amount of *p*-toluenesulfonic acid was added and the mixture was refluxed for 2 h. After solvent evaporation, the residue was chromatographed using methylene chloride at the beginning and methylene chloride/acetone 10:1 v/v mixture at the end. Yield 2.63 g (42%) of product **13a** as a pale yellow oil. ^{1}H NMR ($CDCl_3$): δ 3.66–3.72 (m, 4H), 3.72–3.76 (m, 2H), 3.81–3.85 (m, 4H), 3.93 (t, J=4.4 Hz, 2H), 4.19–4.24 (m, 4H), 6.40 (dd, J_1=8.8 Hz, J_2=2.4 Hz, 1H), 6.68 (d, J=2.4 Hz, 1H), 7.01–7.05 (m, 2H), 7.50 (dt, J_1=7.8 Hz, J_2=1.7 Hz, 1H), 7.80–7.84 (m, 2H). IR (film): ν_{max} 3167, 3113, 2925, 2878, 1607, 1584, 1518, 1487, 1453, 1352, 1304, 1275, 1197, 1126, 1093, 1046, 949, 851, 747 cm^{-1}. HRMS *m*/*z*: calcd for $C_{20}H_{24}O_{10}N_2$: 452.1431; found: 452.1436.

4.2.1.3. Azobenzocrown ether 3. To a vigorously stirred suspension of podand **13** (0.72 g, 1.3 mmol) stannous chloride dihydrate (1.47 g, 6.43 mmol), potassium hydroxide (2.5 g), and acetone (9 mL) water (8 mL) was added dropwise. When the exothermic reaction ceased, the mixture was heated to 55 °C for 1.5 h. After this time chloroform was added, the organic layer was separated, washed with water and evaporated to dryness. The residue was chromatographed on a column. The orange fraction containing azocrown was hydrolyzed in ethanol in the presence of catalytic amount of *p*-toluenesulfonic acid for 15 min. The solvent was removed and the residue was rechromatographed. Azobenzocrown ether **3** was eluted with methylene chloride/acetone 4:1 mixture. An oily orange-red crown ether (0.062 g, 12%) was obtained. ^{1}H NMR (*d*-acetonitrile), signals characteristic for azo form, selected from spectrum of mixture of tautomeric forms: δ 3.42–3.54 (m, 8H), 3.70–3.77 (m, 4H), 4.23–4.34 (m, 4H), 6.50 (d, J=8.3 Hz, 1H), 6.64 (s, 1H), 6.93–7.15 (m, 4H), 7.35–7.42 (m, 1H). Some selected signals of quinone–hydrazone form: 5.91 (s); 6.22 (d, J=7.8 Hz); 11.78 (s); ratio 3:1 azophenol:quinone–hydrazone. ^{1}H NMR (*d*-acetonitrile + strontium perchlorate): δ 3.78–3.81 (m, 4H), 3.85–3.90 (m, 4H), 3.97 (d, J=4 Hz, 2H), 4.03 (d, J=4.4 Hz, 2H), 4.42–4.47 (m, 4H), 6.77 (dd, J_1=8.8 Hz, J_2=2.4 Hz, 1H), 6.82

(d, $J=2$ Hz, 1H), 7.24 (t, $J=7.6$ Hz, 1H), 7.32 (d, $J=8.3$ Hz, 1H), 7.50–7.55 (2H, m), 7.70 (d, $J=8.8$ Hz, 1H), 8.34 (br s, 1H). ^{13}C NMR (*d*-acetonitrile + strontium perchlorate): δ 69.43, 69.56, 69.74, 70.22, 70.47, 70.49, 70.89, 70.92, 103.01, 111.33, 114.94, 124.02, 124.79, 131.56, 133.00, 137.61, 163.92, 151.08, 151.49, 162.73. IR (film): ν_{max} 3303, 2924, 1622, 1601, 1518, 1488, 1447, 1308, 1263, 1240, 1182, 1108, 1047, 946, 854, 753 cm^{-1}. HRMS *m/z*: calcd for $C_{20}H_{24}O_6N_2$: 388.1634; found: 388.1639.

4.2.2. Synthesis of azobenzocrown ethers with peripheral dimethylamino group (compounds 4–6). *Method A*. According to this method, compound **6** was obtained, as described above for compounds **4** and **5**,[11] using 1-chloro-11-(2-nitrophenoxy)-3,6,9-trioxaundecane.

4.2.2.1. Podand 14. A mixture of 5-dimethylamino-2-nitro-phenol[11] (1.46 g, 8 mmol), 1-chloro-11-(2-nitrophenoxy)-3,6,9-trioxaundecane (2.7 g, 8.2 mmol), potassium carbonate (2.2 g) and dimethylformamide (10 mL) was stirred and heated at 110 °C for 8 h. Then water was added and the product was extracted with methylene chloride. The evaporated extract was chromatographed using methylene chloride as an eluent. Compound **14** (2.5 g, 65%) was obtained as a yellow oil. ^{1}H NMR ($CDCl_3$): δ 3.1 (s, 6H), 3.67–3.72 (m, 4H), 3.74–3.83 (m, 4H), 3.90–3.98 (m, 4H), 4.24–4.29 (m, 4H), 6.21 (s, 1H), 6.29 (dd, $J_1=9.3$ Hz, $J_2=2.4$ Hz, 1H), 7.03 (t, $J=7.8$ Hz, 1H), 7.12 (d, $J=8.3$ Hz, 1H), 7.52 (t, $J=7.8$ Hz, 1H), 7.83 (dd, $J_1=8.3$ Hz, $J_2=1.5$ Hz, 1H), 8.01 (d, $J=9.3$ Hz, 1H). IR (film): ν_{max} 2875, 1607, 1572, 1524, 1491, 1349, 1300, 1252, 1130, 1096, 1046, 947, 928, 852, 810, 747 cm^{-1}. HRMS *m/z*: calcd for $C_{22}H_{29}O_9N_3$: 479.1904; found: 479.1913.

4.2.2.2. Azobenzocrown ether 6. To vigorously stirred mixture of podand **14** (1.29 g, 2.7 mmol) in acetone (10 mL), stannous chloride dihydrate (2.5 g, 11 mmol) and potassium hydroxide (4.76 g) water (9 mL) was added and the mixture was gently boiled for 1.5 h. Isolation was carried out as described.[11] The desired product was eluted from chromatographic column as the last using methanol as an eluent. Compound **6**, crystallized from acetone/hexane mixture, was obtained (44 mg, 4%) as a fire-brick solid. Mp 105–107 °C. ^{1}H NMR (*d*-acetone): δ 3.10 (s, 6H), 3.38–3.44 (m, 4H), 3.48–3.52 (t, $J=4.6$ Hz, 2H), 3.54–3.58 (t, $J=4.40$ Hz, 2H), 3.78–3.82 (t, $J=4.6$ Hz, 2H), 3.83–3.86 (t, $J=4.6$ Hz, 2H), 4.28–4.32 (t, $J=4.8$ Hz, 2H), 4.34–4.38 (m, 2H), 6.41–6.46 (m, 2H), 7.02 (t, $J=7.6$ Hz, 1H), 7.15 (d, $J=7.8$ Hz, 1H), 7.30 (t, $J=7.8$ Hz, 2H), 7.55 (d, $J=8.3$ Hz, 1H). ^{13}C NMR (*d*-acetone): δ 39.76, 69.55, 69.58, 69.87, 70.12, 70.69, 70.71, 70.74, 70.78, 98.29, 105.06, 116.03, 119.97, 121.24, 129.31, 135.63, 146.08, 153.86, 154.00, 157.52. IR (film): ν_{max} 2923, 2874, 1608, 1516, 1485, 1446, 1363, 1279, 1243, 1107, 1048, 950, 810, 753 cm^{-1}. HRMS *m/z*: calcd for $C_{22}H_{29}O_5N_3$: 415.2107; found: 415.2091.

Method B

4.2.2.3. 4-Dimethylamino-2,2′-dihydroxyazobenzene. A suspension of 2-amino-phenol (0.44 g, 4 mmol) in water (10 mL) was cooled and acidified with concd hydrochloric acid (1 mL). The solution was diazotized with sodium nitrite (0.28 g in 2 mL cold water). Then the reaction mixture was kept at 5 °C for 15 min.

The obtained diazonium salt was added dropwise to an ice-cold solution of 3-dimethylamino-phenol (0.55 g, 4 mmol) and NaOH (0.4 g) in water (10 mL). The reaction mixture was stirred at 10 °C for 1 h. The mixture was then cooled and made slightly acidic with 0.1 M hydrochloric acid. The precipitated solid was separated and washed with water. The solid was in turn suspended in a small amount of acetone, cooled and filtered. The crude, solid 4-dimethylamino-2,2′-dihydroxyazobenzene (0.8 g, 78%) was used for macrocycle synthesis. Analytical sample was obtained by purifying crude product on column chromatography using methylene chloride/acetone 30:1 mixture as an eluent. Crystallization from propan-2-ol gave the title compound as a red-brown solid. Mp 235–237 °C. ^{1}H NMR (*d*-DMSO): δ 3.06 (s, 6H), 6.05 (d, $J=2.9$ Hz, 1H); 6.50 (dd, $J_1=9.2$ Hz, $J_2=2.4$ Hz, 1H); 6.92 (dt, $J_1=7.6$ Hz, $J_2=1$ Hz, 1H); 6.98 (dd, $J_1=8.3$ Hz, $J_2=1.2$ Hz, 1H); 7.19 (dt, $J_1=7.6$ Hz, $J_2=1.5$ Hz, 1H); 7.52 (d, $J=9.2$ Hz, 1H); 7.67 (dd, $J=8.3$, 1.5 Hz, 1H); 10.95 (s, 1H); 13.88 (s, 1H). The NOESY spectrum confirms the position of the dimethylamino group in benzene ring. IR (nujol): ν_{max} 1631, 1535, 1328, 1255, 1238, 1213, 1147, 795, 750 cm^{-1}. UV–vis (acetonitrile): $\lambda_1=264$ nm, $\varepsilon_1=2.56\times10^3$; $\lambda_2=287$ nm, $\varepsilon_2=2.161\times10^3$; $\lambda_3=470$ nm, $\varepsilon_3=1.50\times10^4$. MS *m/z*: calcd for $C_{14}H_{15}O_2N_3$: 257; found: 257. HRMS *m/z*: calcd for $C_{14}H_{15}O_2N_3$: 257.1164; found: 257.1169.

4.2.2.4. Azobenzocrown ethers 4–6. To 4-dimethylamino-2,2′-dihydroxyazobenzene (0.52 g, 2 mmol) potassium *tert*-butoxide (0.78 g, 7 mmol) in dry THF (50 mL) was added. The mixture was stirred for 0.5 h at room temperature and then (in case of compounds **4** and **5**) 18-crown-6 (10 mg) was added. After that, the appropriate ditosyl derivative[18] (2.2 mmol) in THF (50 mL) was added dropwise over 1 h. The reaction mixture was heated at 70 °C for 24 h. The solid was removed by filtration and washed with THF until colorless filtrate was obtained. The filtrate was evaporated under reduced pressure, the residue was dissolved in methylene chloride and chromatographed on column using methylene chloride, acetone/methanol mixtures and finally pure methanol as eluents. The fractions containing the azobenzocrown ether were evaporated, the red residue was dissolved in methylene chloride, filtered and the filtrate was evaporated to dryness. Crystallization from acetone/hexane mixture or propan-2-ol gave desired compounds identical with those obtained by method A or described earlier.[11]

By this method were obtained: compound **4** as a dark red solid, yield 42%, mp 121–123 °C; compound **5** as a fire-brick solid, yield 38%, mp 113–116 °C; compound **6** as a dark red solid, yield 55%, mp 105–107 °C.

4.2.3. Synthesis of azobenzocrown ethers 7–9.

4.2.3.1. 4-Dimethylamino-4′-nitro-2,2′-dihydroxyazobenzene. *Method A*. To a suspension of 2-amino-5-nitrophenol (1.23 g, 8 mmol) in water (10 mL) concd HCl (2 mL) was added. The mixture was diazotized with $NaNO_2$ (0.56 g) dissolved in water (4 mL). The precipitated, wet solid was collected (caution!), suspended in a mixture of

DMF (10 mL) and pyridine (4 mL), stirred and cooled in an ice-water bath. To this mixture solution of 3-dimethylamino-phenol (1.1 g, 8 mmol) in DMF (10 mL) was added. The reaction mixture was stirred for 3 h at 5 °C, 3 h at room temperature and diluted with cold water (30 mL). The solid was collected and dried (2 g). Afterwards the solid was triturated with acetone (10 mL), filtered and the solid washed with cold acetone. The crude solid product (1.32 g, 54%) was used in the synthesis of azobenzocrown ethers. An analytical sample was obtained by column chromatography using THF as an eluent. The eluate was evaporated and the product was precipitated with propan-2-ol.

The residual acetone filtrate contains mainly isomeric compound—2-dimetylamino-4′-nitro-2′,4-dihydroxyazobenzene (about 30% in the main reaction product), which was also isolated (purification: column chromatography with a methylene chloride/acetone 30:1 mixture) and characterized by spectroscopic methods.

4-Dimethylamino-4′-nitro-2,2′-dihydroxyazobenzene. Black solid, mp 275 °C (dec). ^{1}H NMR (*d*-DMSO): δ 3.14 (s, 6H), 5.82 (d, $J=2.4$ Hz, 1H), 6.71 (dd, $J_1=9.6$ Hz, $J_2=2.5$ Hz, 1H), 7.30 (d, $J=9.6$ Hz, 1H), 7.75 (s, 1H), 7.80 (s, 2H), 11.28 (s, 1H), 14.6 (br s, 1H). IR (nujol): ν_{max} 1633, 1602, 1535, 1504, 1320, 1259, 1240, 1271, 1150, 1074, 929, 870, 816, 791, 745 cm^{-1}. (UV–vis (acetonitrile): $\lambda_1=292$ nm, $\varepsilon_1=2.89\times10^2$; $\lambda_2=518$ nm, $\varepsilon_2=2.21\times10^3$. HRMS *m/z*: calcd for $C_{14}H_{14}O_4N_4$: 302.1015; found: 302.1013.

2-Dimethylamino-4′-nitro-2′,4-dihydroxyazobenzene. Black solid, mp 164–165 °C. ^{1}H NMR (*d*-DMSO): δ 3.08 (s, 6H), 6.34 (dd, $J_1=9.2$ Hz, $J_2=2.1$ Hz, 1H), 6.39 (d, $J=2.1$ Hz, 1H), 7.67 (d, $J=8.6$ Hz, 1H), 7.75–7.80 (m, 2H), 7.87 (d, $J=8.8$ Hz, 1H), 10.36 (s, 1H), 11.18 (s, 1H). The NOE spectrum confirms position of dimethylamino group in benzene ring. IR (nujol): ν_{max} 3301, 1607, 1566, 1511, 1339, 1304, 1257, 1178, 1123, 1074, 985, 856, 740 cm^{-1}. UV–vis (acetonitrile): $\lambda_1\sim280$ nm, $\varepsilon_1=9.88\times10^2$; $\lambda_2=385$ nm, $\varepsilon_2=1.20\times10^3$; $\lambda_3=499$ nm, $\varepsilon_3=1.43\times10^3$. MS *m/z*: calcd for $C_{14}H_{14}O_4N_4$: 302; found: 302.

Method B. Solution A: to a suspension of 5-nitro-2-amino-phenol (1.23 g, 8 mmol) in water (20 mL) concd HCl (2 mL) was added. The mixture was diazotized with $NaNO_2$ (0.56 g) dissolved in water (4 mL) for 15 min at $\sim$3 °C.

Solution B: 3-dimethylamino-phenol (1.1 g, 8 mmol) and NaOH (0.8 g) were dissolved in cold water (20 mL).

Both solutions were added dropwise to ice-cold water (60 mL) over 15 min with the same molar rate. The mixture was kept at 5 °C at the beginning and at 15 °C at the end for 3 h. The reaction mixture was cooled and 0.1 M HCl (50 mL) was added. The precipitate (2.2 g, 91%), containing 4-dimethylamino-4′-nitro-2,2′-dihydroxyazobenzene and 2-dimethylamino-4′-nitro-2′,4-dihydroxyazobenzene in 4:1 ratio, was separated, washed with water and dried at room temperature. The mixture of isomers was separated as described above in method A.

4.2.3.2. Azobenzocrown ethers 7–9. To 4-dimethylamino-4′-nitro-2,2′-dihydroxyazobenzene 0.3 g (1 mmol) potassium *tert*-butoxide (0.39 g, 3.5 mmol) in dry THF (30 mL) was added. The mixture was stirred at room temperature for 0.5 h, then heated to 40 °C. 5 mg 18-crown-6 was added and next the appropriate ditosyl derivative (1 mmol) in THF (30 mL) was added dropwise over 3 h. The synthesis was continued at gentle boiling for 48 h. The solid was separated and washed with THF until a colorless filtrate was obtained. The filtrate was evaporated and the residue was extracted with methylene chloride. The concentrated extract was chromatographed on a column. Mixtures of methylene chloride with acetone and finally acetone were used as eluents. The crude product was rechromatographed using the same eluents. Azobenzocrown ethers were crystallized from propan-2-ol. By this method were obtained compounds **7**, **8**, **9** as black-brown solids with 23, 24 and 33% yield, respectively.

Compound 7. Mp 165–168 °C. ^{1}H NMR (*d*-acetone): δ 3.16 (s, 6H), 3.89 (t, $J=4.5$ Hz, 2H), 3.93 (t, $J=4.3$ Hz, 2H), 4.33 (t, $J=4.5$ Hz, 2H), 4.42 (t, $J=4.3$ Hz, 2H), 6.45 (d, $J=2.6$ Hz, 1H), 6.60 (dd, $J_1=9.2$ Hz, $J_2=2.7$ Hz, 1H), 7.78 (d, $J=9.3$ Hz, 1H), 7.81 (d, $J=8.8$ Hz, 1H), 7.97 (d, $J=2.3$ Hz, 1H), 8.02 (dd, $J_1=8.8$ Hz, $J_2=2.3$ Hz, 1H). ^{13}C NMR ($CDCl_3$ and one drop of CD_3OD): δ 40.49, 69.57, 70.02, 70.99, 71.36, 100.34, 106.89, 113.22, 117.97, 123.86, 125.54, 135.92, 147.10, 149.50, 152.38, 154.59, 157.44. IR (nujol): ν_{max} 1610, 1542, 1509, 1327, 1256, 1211, 1172, 1136, 1108, 1080, 1046, 955, 922, 892, 828, 807, 723 cm^{-1}. HRMS *m/z*: calcd for $C_{18}H_{20}N_4O_5$: 372.1434; found: 372.1431.

Compound 8. Mp 168–170 °C. ^{1}H NMR (*d*-acetone): δ 3.17 (s, 6H), 3.69–3.73 (m, 4H), 3.93–3.67 (m, 4H), 4.29 (t, $J=4.5$ Hz, 2H), 4.38 (t, $J=4.5$ Hz, 2H), 6.40 (d, $J=2.4$ Hz, 1H), 6.54 (dd, $J_1=9.2$ Hz, $J_2=2.5$ Hz, 1H), 7.64 (d, $J=8.6$ Hz, 1H), 7.79 (d, $J=9.3$ Hz, 1H), 7.94 (dd, $J_1=8.6$ Hz, $J_2=2.5$ Hz, 1H), 7.96 (d, $J=2$ Hz, 1H). ^{13}C NMR ($CDCl_3$): δ 40.56, 68.98, 69.17, 69.46, 70.22, 70.48, 96.39, 105.28, 108.90, 116.75, 121.22, 131.07, 147.37, 148.60, 153.12, 154.28, 155.15. IR (nujol): ν_{max} 1614, 1511, 1321, 1254, 1218, 1162, 1136, 1084, 964, 861, 809, 730 cm^{-1}. HRMS *m/z*: calcd for $C_{20}H_{24}N_4O_6$: 416.1696; found: 416.1688.

Compound 9. Mp 133–135 °C. ^{1}H NMR (*d*-acetone): δ 3.15 (s, 6H), 3.37–3.43 (m, 4H), 3.49 (t, $J=4.6$ Hz, 2H), 3.58 (t, $J=4.6$ Hz, 2H), 3.82–3.87 (m, 4H), 4.37 (t, $J=4.6$ Hz, 2H), 4.45 (t, $J=4.6$ Hz, 2H), 6.42 (d, $J=2.4$ Hz, 1H), 6.49 (dd, $J_1=8.7$ Hz, $J_2=2.4$ Hz, 1H), 7.40 (d, $J=8.3$ Hz, 1H), 7.64 (d, $J=9.3$ Hz, 1H), 7.92 (dd, $J_1=8.7$ Hz, $J_2=2.4$ Hz, 1H), 7.96 (d, $J=2$ Hz, 1H). NOE spectrum confirmed the position of substitution of the benzene rings. ^{13}C NMR (*d*-acetone): δ 39.75, 69.44, 69.48, 69.81, 70.60, 70.61, 70.67, 70.74, 70.85, 97.43, 105.28, 110.93, 116.82, 119.84, 122.21, 135.61, 147.51, 150.62, 153.88, 155.05, 158.44. IR (nujol): ν_{max} 1609, 1544, 1512, 1328, 1245, 1226, 1138, 1083, 1028, 979, 876, 866, 807, 728 cm^{-1}. HRMS *m/z*: calcd for $C_{22}H_{28}N_4O_7$ 460.1958; found: 460.1950.

4.3. X-ray structure determination

Crystallographic data for $\mathbf{9}\cdot2H_2O$ were collected at 100 K on a Bruker SMART-APEX diffractometer using Mo K_α radiation ($\lambda=0.7107$ Å) equipped with CCD-type area

detector and an Oxford Cryosystems open flow Nitrogen gas cooling device. The data were corrected for Lorentz and polarization effects and for absorption using the SADABS program. The structure was solved using direct methods and refined by full-matrix least squares on F^2.[19] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms of water molecules were located on a difference Fourier map and refined isotropically. Other hydrogen atoms were placed in geometrically calculated positions and refined with temperature factors 1.2 and 1.5 times of those of their bonded atoms for CH_2 and CH_3 groups, respectively. Crystal data for $\mathbf{9}\cdot 2H_2O$: triclinic, space group P-1, $a=8.647(3)$, $b=12.109(4)$, $c=12.505(5)$ Å, $\alpha=85.538(7)$, $\beta=75.995(6)$, $\gamma=76.519(6)°$, $V=1235.1(8)$ Å^3, $Z=2$, $D_c=1.335$ g/m^3, $\mu=1.04$ cm^{-1}, $F(000)=528$, $\theta_{max}=25.25°$ ($-10\leq h\leq 10$, $-14\leq k\leq 8$, $-14\leq l\leq 14$), reflections collected 5167, independent reflections 4068 ($R_{int}=0.0405$), GOF on F^2 1.016. Final residuals (for 334 parameters) $R1=0.0822$, $wR2=0.1930$ for 2270 reflections with $I>2\sigma(I)$, and $R1=0.1424$, $wR2=0.2139$ for all data. Residual electron density: 0.767 and -0.493 e Å^{-3}.

Crystallographic data (excluding structure factors) for the structure in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication numbers CCDC 287144. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: +44 1223 336033; or e-mail: deposit@ccdc.cam.ac.uk].

4.4. Determination of stability constants

Stability constants for complexes were determined by spectrophotometric titration of ligand solution with the appropriate metal perchlorate solution. The stability constants were calculated with a program DynaFit.[20]

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