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Azo and azoxythiacrown ethers: synthesis and properties

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ABSTRACT

A series of 16- and 18-membered azo- and azoxythiacrown ethers have been synthesized by reductive macrocyclization of the respective bis(nitrophenoxy)oxaalkanes. The aromatic residues located in the polyether region of the molecule were introduced to macrocyclic skeletons and their affinities toward different groups of metal cations in ion-selective electrodes were described. X-ray structures for one dinitropodand and one azoxybenzothiacrown exhibiting strong π–π and π–H interactions have been found.

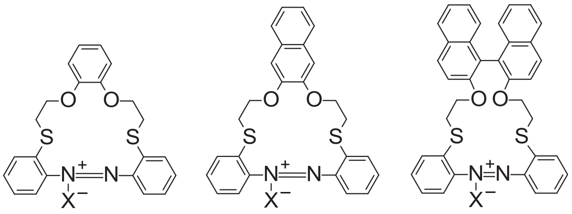
1. Introduction

Since the discovery of crown ethers, many of these compounds have been synthesized and documented in the literature. The structures of crown ethers determine their binding properties, such as binding selectivity and strength toward a wide range of metal ions, nonmetal ions, and neutral molecules. Thanks to their remarkable binding properties, the study of crown ethers has largely contributed to the development of host–guest chemistry. In such molecules, the number of oxygen atoms in the crown can be varied to alter the physical and chemical properties of the molecular structure. Replacement of oxygen atoms by sulfur in azo- and azoxycrown ethers leads to new products with different properties, especially in the area of cation selectivity. According to Pearson's theory,[1] sulfur atoms cause an increase in the affinity of macrocyclic ionophores toward 'soft' metal cations and a decrease in the affinity for the formation of complexes with 'hard' cations. This theory has previously been elaborated by us through studies of cation responsive sulfur containing 13- and 16-membered crown ethers.[2–5] Valuable results that we obtained from these previous successful syntheses, together with previously reported oxygen containing analogues of 13- and 16-membered thiacrown ethers[6] inspired us to synthesize more rigid molecules with enhanced lipophilicity. The new parts forming the macrocyclic skeletons are aromatic residues located in the polyether region of the molecule. In this way, the presence of flexible dioxyethylene chains and rigid aromatic residues alter the flexibility of the structure of investigated compounds and hence their complexation properties.

2. Results and discussion

2.1. Synthesis

The 16- and 18-membered azo- and azoxythiacrown ethers were prepared by multistep reactions (Scheme 1).



4-a: (X: none) **5-a:** (X: O)
4-b: (X: none) **5-b:** (X: O)
4-c: (X: none) **5-c:** (X: O)

Scheme 1. Azo and azoxybenzothiacrown ethers.

The first step was the alkylation of catechol, 2,3-dihydroxynaphthalene or 2,2′-dihydroxy-1,1′-bisnaphthalene with 2-chloroethanol to obtain disubstituted diols (Scheme 2). In the next step the obtained diols were converted into chlorides via reaction with thionyl chloride in the presence of pyridine.

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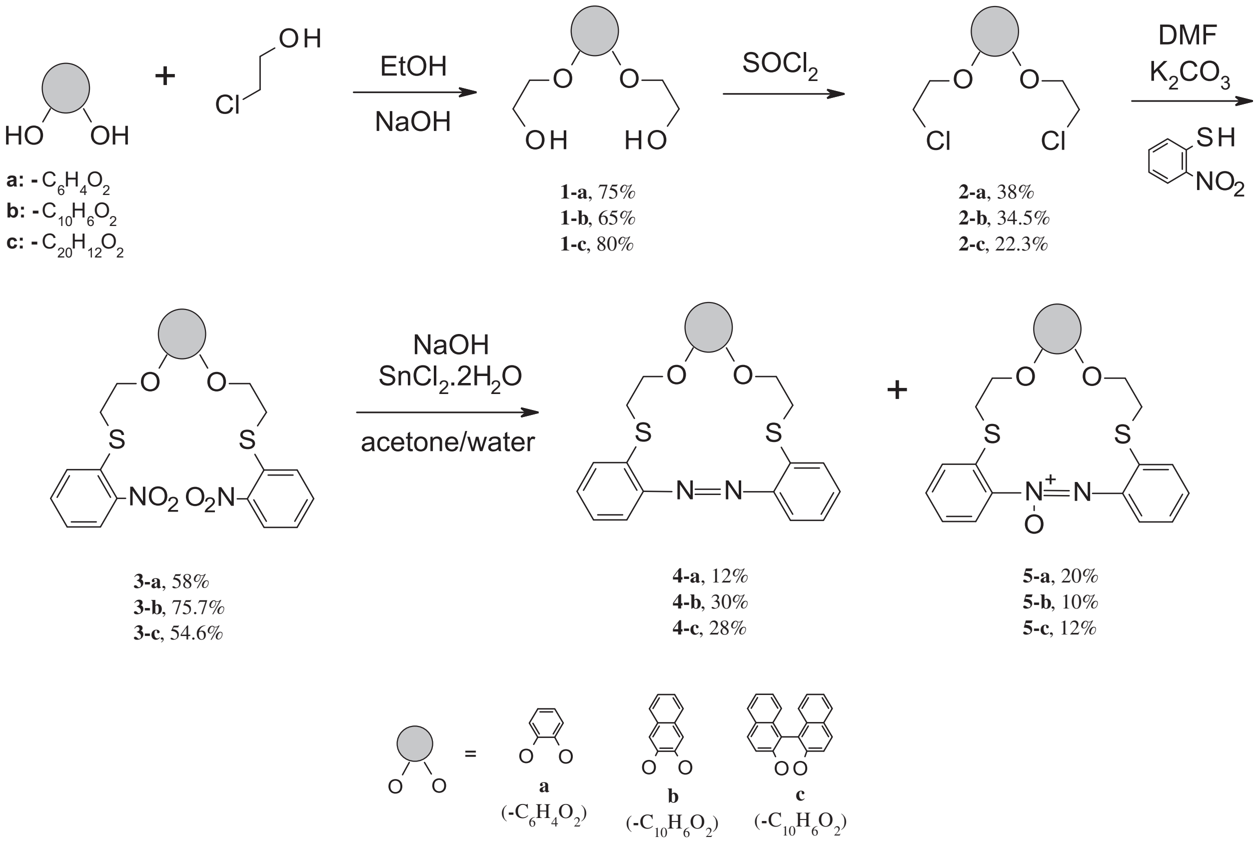
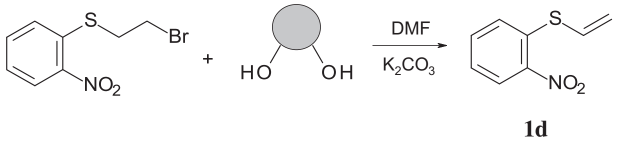


Scheme 2. General synthesis route for azo- and azoxythiacrown ethers.

Dinitropodands were obtained by condensing 2-nitrothiophenol with the respective aromatic dichloride in warm DMF in the presence of anhydrous potassium carbonate.

Then dinitro compounds **3-a**,**b**,**c** were subjected to reaction with sodium stannite (generated in situ from NAOH and $SnCl_2 \cdot 2H_2O$) to yield macrocyclic products. After these processes two main products were obtained: azo- and azoxy macrocycles (Scheme 1).

As shown, this procedure is composed of several stages. Such a synthetic route was chosen despite a much simpler way, which was previously used for the preparation of analogous oxygen compounds.[7] In this method, the condensation step of 2-(2-nitrophenyl)ethyl bromide/chloride with an aromatic diol (2,3-dihydroxynaphthalene, catechol or 1,1′-binaphthyl-2,2′-diol) gave respective dinitro compounds with good yield. The same reaction route was applied for the synthesis of analogous sulfur compounds (**4-a**,**b**,**c** and **5-a**,**b**,**c**) with same aromatic diols. However, the resulting reaction mixture mainly contained a yellow product, which after analyses was identified as vinyl sulfide **1d** (Scheme 3). Changing the solvent did not give better results.



Scheme 3. Formation of vinyl sulfide product.

The presence of the vinyl sulfide was confirmed by NMR spectroscopy (please see the Experimental section). The synthesis of analogous compounds was previously reported by Kuad et al. and dehydrohalogenation reactions of alkyl halides took place under similar conditions.[8] Correspondingly, it can be concluded that replacement of sodium hydroxide by potassium carbonate in the synthesis procedure demonstrated by us also causes the formation of sulfur ylides and does not yield the desired products.

2.2. Potentiometric studies

Because of the observed progress in minimization of the sensor size, we decided to use all the synthesized compounds as ionophores in miniature potentiometric sensors. The membranes of similar composition to those used for classic ISE were poured onto graphite screen-printed electrodes. The characteristics of these electrodes and the selectivity coefficient values determined in the earlier described manner[4,9] were collected in Table 1 and shown in Fig. 2. All of the synthesized azo- and azoxybenzothiacrown ethers were applied to ion-selective membrane electrodes as ion carriers. Their selectivity toward Na^+, K^+, Mg^{2+}, Ca^{2+}, Cu^{2+}, Pb^{2+}, Zn^{2+}, Hg^{2+}, Ni^{2+} and Ag^+ were demonstrated. Potentiometric selectivity coefficients $K_{I,J}^{pot}$ were determined by the separate solution method

Table 1
Experimental selectivity coefficients $\log K_{Pb,X}^{pot}$

	4-a	5-a	4-b	5-b	4-c	5-c
Cu^{2+}	−0.292	−0.635	1.609	1.504	−1.074	−1.037
K^+	−1.388	−1.141	−0.021	−0.494	−1.288	−1.649
Na^+	−5.628	−8.650	−2.665	−2.690	−8.450	−4.650
Ag^+	10.982	6.217	12.232	6.020	5.979	8.951
Hg^{2+}	4.330	4.025	7.775	—	5.560	6.039
Ni^{2+}	—	−7.330	−4.259	—	−7.151	−8.670
Zn^{2+}	−6.212	−9.382	—	−7.594	−9.654	—
Ca^{2+}	−5.395	−8.261	—	−6.583	−8.404	—
Mg^{2+}	−1.599	−1.507	5.003	−0.334	—	—