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Cation sensing by diphenyl-azobenzocrowns

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ABSTRACT

Metal cations complexation and proton binding by 13- and 16-membered diphenyl-azobenzocrowns and diphenyl-hydroxyazobenzocrowns were studied in acetonitrile using spectroscopic methods: UV–vis spectroscopy, spectrofluorimetry, and ^{1}H NMR spectroscopy. Phenyl moieties in benzene rings were found to affect binding strength alkali and alkaline earth metal cations and hydrogen ion, and affect tautomeric equilibrium of hydroxyazobenzocrowns. X-ray structure of 13-membered diphenyl-hydroxyazobenzocrown was solved showing the existence of this compound in quinone-hydrazone form in a solid state. The suitability of diphenyl-azobenzocrowns for potentiometric metal cation determination using miniature, planar, all-solid-state type electrodes was also tested.

1. Introduction

Azobenzene moiety, well known since more than 100 years (*trans* azobenzene was first described in 1834), due to its photo and redox activity, is still one of the most common chromophore inserted as a part of more sophisticated chemical structures [1]. Well known phenomena for substituted azobenzenes bearing hydroxy group in *para* position to azo moiety (but also amino-azocompounds) is azophenol – quinone-hydrazone tautomerism [2]. Because of different optical and physical properties of tautomers these systems are interesting objects of studies not only from academic but also practical point of view [3]. A curious group of azocompounds are crown ethers – azobenzocrowns – in which 2,2′-substituted azobenzene residue is an inherent part of a macrocycle. The simplest 13- and 16-membered azobenzocrowns **A** and **B** are shown in Fig. 1 [4]. Within more than 20 years, a numerous derivatives of azobenzocrowns of different size of macrocycle and diverse type of substituents in benzene rings were prepared and studied as e.g.: ionophores in membrane ion-selective electrodes (ISEs), components of electroactive and photoactive monolayers and chromoionophores [5]. 13- and 16-membered azobenzocrowns **1** and **2** were previously used as ionophores in classic membrane ion selective electrodes and furthermore compound **1** in ChemFETs (Chemically Modified Field Effect Transistors) [6,7]. Lipophilic compounds **1** and **2** are good ionophores for membrane ion selective electrodes. Typically for this class of compounds is sodium or potassium selectivity of sensors depending on the size of the macrocyclic cavity of ionophore. Recently, a considerable technological development in manufacturing of potentiometric sensors has been made. Nowadays, one of the trend is the preparation of miniature ion-selective sensors *all-solid-state* type [8]. Such sensors can be successfully used for the construction of integrated analytical platforms e.g. for clinical or environmental analysis [9]. But it is worth to note that not every ionophore suitable for classic ISEs works well in miniature, planar *all-solid-state* type electrodes. For example, compounds **A** and **B** are for this purpose insufficiently lipophilic. More lipophilic azobenzocrowns with hydrocarbon residues in *para* position to ether linkage were not studied as ionophores in membrane *all-solid-state* type electrodes up to now.

Azobenzene itself is hardly fluorescent [10] but there are some cases when fluorescence of azocompounds is measurable. There are several examples of fluorescent azocompounds functionalized with fluorophores, sterically hindered azocompounds and others [11]. In our previous papers we demonstrated that protonated forms of azobenzocrowns are fluorescent [12a] and the functionalization of macrocyclic azocompounds can lead to fluorescent metal cation probes [13]. Hydroxyazocompounds, for which the tautomeric equilibrium with the quinone-hydrazone form is stabilized by intramolecular hydrogen bond, are another example of fluorescent azocompounds [14]. Among other, the fluorescence of phenylazonaphthols was studied by Fischer [15] and Antonov

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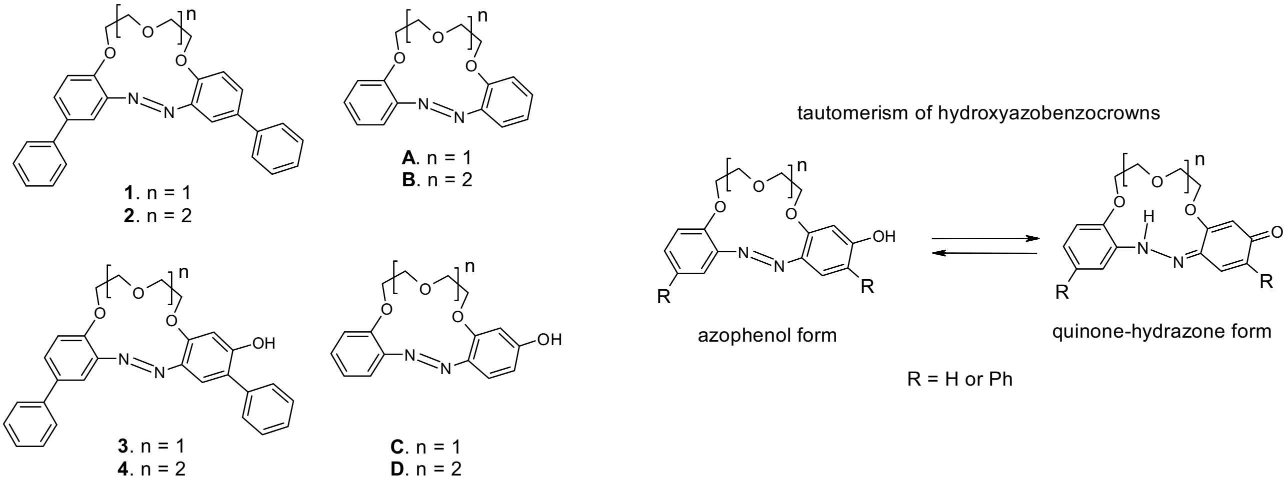

Fig. 1. Azobenzocrowns **1–4** studied in this work, reference compounds **A–D** and tautomersim of hydroxyazobenzocrowns.

[16], and phenylazopyrazolones were investigated by Polansky [17].

It was shown that the quinone-hydrazone form of hydroxyazocompounds is responsible for fluorescence. In this regard, macrocyclic hydroxyazobenzocrowns can be considered as analogs of aromatic hydroxyazocompounds.

Our last interest in azobenzocrowns chemistry is focused on hydroxyazobenzocrowns and studies of the relationship between tautomeric equilibrium and ion binding properties [6f,12].

Here, we present new results on binding and ionophoric properties of 13- and 16-membered diphenyl-azobenzocrowns **1–4** (Fig. 1). Synthetic procedures for studied compounds were elaborated and described earlier by us [6c,7,12b]. The crystal structure of quinone-hydrazone form of **3** is also presented.

2. Results and discussion

2.1. Diphenyl-azobenzocrowns 1 and 2 – metal cations complexation in solution and ionophoric properties in all-solid state electrodes

Azobenzocrown ethers form complexes with alkali and alkaline earth metal cations [4,6d–f,12]. Binding strength and selectivity of this process is dependent not only on macrocycle size but also on the type of substituents present in azocrown benzene rings. Relatively large and rigid phenyl rings in *para* position in relation to polyether linkage in azobenzocrowns **1–4** structure should also affect their ion affinity. Chromogenic character of azobenzocrowns allows the use of simple UV–vis spectroscopy to study ion-crown interaction. This method was used as the first for comparative binding studies of **1–4** and reference macrocycles **A–D**.

13-Membered azobenzocrowns selectively bind lithium cation among alkali metal cations in acetonitrile solution [4,6d]. Larger, 16-membered crowns form complexes both with alkali and alkaline earth metal ions [4c]. Previously [6d–f] it was shown, that the stability constant values of 1:1 metal cation complexes of azobenzocrowns and the observed spectral shift of the complex band depend on the presence and nature of functional groups in benzene rings.

As it could be predicted the selective lithium complexation in acetonitrile was also found for 13-membered diphenyl-azobenzocrown ether **1**. Spectral changes observed upon titration of azobenzocrown **1** solution with lithium perchlorate in acetonitrile (Fig. 2) are comparable in trend (i.e. increase of intensity without a spectral shift) to changes observed for parent azobenzocrown **A** [4b]. Stability constant value of lithium complex logK 2.8 ± 0.1 is significantly lower for diphenyl derivative than for unsubstituted macrocycle **A** (logK 4.1) [4]. The presence of sodium and potassium salts did not affect absorption spectra at all.

Comparison of stability constants (logK) for metal cation complexes of 16-membered crowns **2** and **B** (Fig. 3) shows no relevant difference in binding strength of lithium and sodium cations. However, opposite to crown **B** no spectral changes were found for **2** in the presence of potassium perchlorate. Interesting and different than for **B** is the trend of stability constant values for alkaline earth metal cations complexes. For diphenyl derivative **2** the increase of stability constant values is in agreement with the increase of ion diameter: the smallest value of stablility constant was found for magnesium and the largest for barium complex. Binding strength for **2** is almost in reverse order to **B** complexes [4].

The above studies show pronounced differences in binding strength of metal cation by non-functionalized crowns **A** and **B** and their analogs with phenyl rings **1** and **2**. The presence of phenyl substituents affecting the size and shape of the molecular cavity (steric hindrance) can be an explanation of this. The selectivity and strength of host-guest interactions strongly depend on the environment, i.e. the solvent. The ionophoric properties of azobenzocrowns are different in polar acetonitrile and in ISEs where analytical signal is generated upon contact of the ionophore

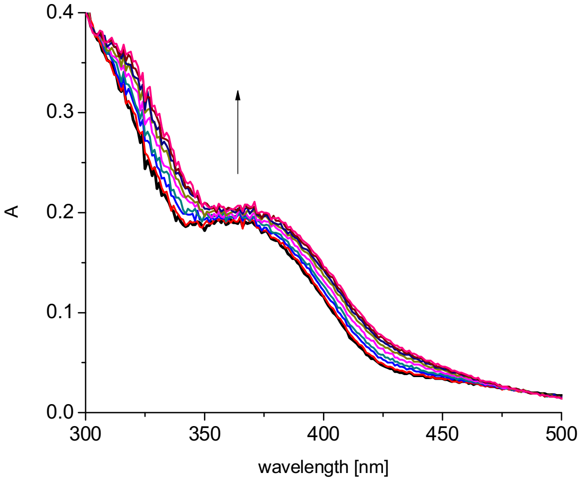

Fig. 2. Changes in UV–vis spectrum of **1** (4.2×10^{-5} M) upon titration with lithium perchlorate ($0–1.0 \times 10^{-3}$ M) in acetonitrile.