

## The effect of Benzo Substitution on Complexation of Diaza 18-crown-6 ethers Derivatives with NaClO<sub>4</sub>

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### Abstract

The complexation of the crown ethers with Na<sup>+</sup> ion was studied. <sup>1</sup>H-NMR chemical shifts are discussed in terms of structural modification as well as also binding studies with UV-vis spectra were included.

### Introduction

Crown ethers, first introduced in 1967 by Pedersen [1, 2] are macrocyclic polyethers which are able to form stable and selective complexes with alkali, alkaline-earth metal, and primary ammonium cations. The aza-crowns have important uses as synthetic receptors in molecular recognition processes [3] and, in some cases, anion complexation properties that are similar to those in certain biological system [4–6].

The most promising studies in this field have been reported for cyclohexano crown ethers [7–10]. The molecular and conformational dynamics of such macrocycles play an essential role in a cationic and molecular recognition; in particular the interactions of the cations influence the molecular internal motions. Therefore the effect of a cation on the motion of the binding sites of a host molecule should be a measure of interactions [11]. Different methods have been used in order to investigate the interaction of alkali and alkaline-earth cations with macrocyclic ionophores [12]. We previously described the synthesis of diaza crown-6 ether derivatives [13]. Gokel [14] reported the importance of arene sidearms on complexation of crown ether. And also Gokel and co workers used lariat ether receptor systems to obtain clear evidence for cation- $\pi$  interactions between Na<sup>+</sup> or K<sup>+</sup> and benzene, phenol and indole [15–17]. Here we choose three macrocycles that have increasing amount of arene units to investigate the effect of benzo substitution on complexation of diaza 18-crown-6 ethers derivatives (1–3, Scheme-1) with sodium.

### Result and discussion

#### UV-vis

Uv-vis spectroscopy is a convenient and widely used method for the study of binding phenomena. When the receptor (or substrate) absorbs light at different wavelengths in free and complexed states, the differences in ultraviolet spectrophotometry may suffice for estimation of molecular recognition. In the UV spectroscopic titration experiments, addition of varying concentration of guest molecule resulted in gradual increase or decrease of characteristic absorptions of the host molecules. The typical UV spectral changes upon the addition of NaClO<sub>4</sub> to **3**, **1** and **2** are shown in Figure 1, Figure 3 and Figure 5 respectively.

The association constant of supramolecular system formed were calculated according to the modified Benesi–Hildebrand equation, Equation (1), [18] where [H]<sub>o</sub> and [G]<sub>o</sub> refer to the total concentration of crown ether and NaClO<sub>4</sub> respectively,  $\Delta\epsilon$  is the change in molar extinction coefficient between the free and complexed crown ether and  $\Delta A$  denotes the absorption changes of crown ether on addition of NaClO<sub>4</sub>.

$$[H]_o[G]_o/\Delta A = 1/K_a\Delta\epsilon + [G]_o/\Delta\epsilon \quad (1)$$

The determined binding constants ( $K_a$ ) for **1**, **2** and **3** were ca. 17000 mol dm<sup>-3</sup>, 2200 mol dm<sup>-3</sup> and 5000 mol dm<sup>-3</sup>, respectively. The UV-vis studies indicate that the benzo substitution on macrocycle have a pronounced effect on cavity size. From the obtained results we conclude that the cavity of **1** is much more convenient for Na<sup>+</sup> than the cavity of **3**. Replacement

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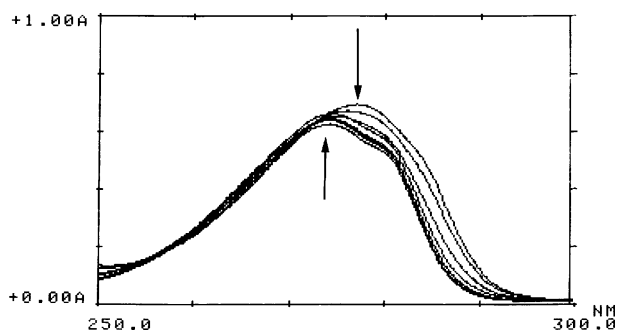


Figure 1. UV-vis spectra of **3** ( $2.5 \times 10^{-4}$ ) in the presence of  $\text{NaClO}_4$  ( $5 \times 10^{-5}$ – $2 \times 10^{-3}$ ).

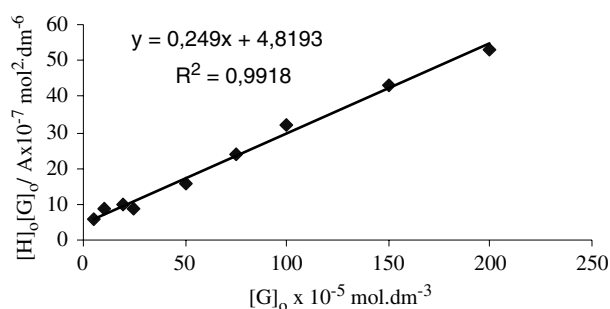


Figure 2. Typical plot of  $[\text{H}]_0[\text{G}]_0/\Delta A$  versus  $[\text{G}]_0$  for the host-guest complexation of **3** and  $\text{NaClO}_4$  in ( $\text{CH}_3\text{CN}$ ).

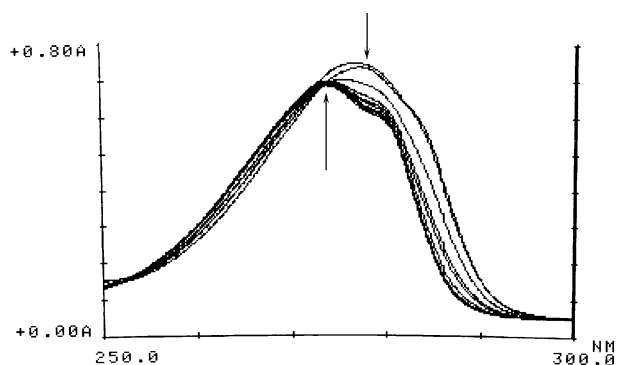


Figure 3. UV-vis spectra of **1** ( $1, 25 \times 10^{-4}$ ) in the presence of  $\text{NaClO}_4$  ( $5 \times 10^{-5}$ – $2 \times 10^{-3}$ ).

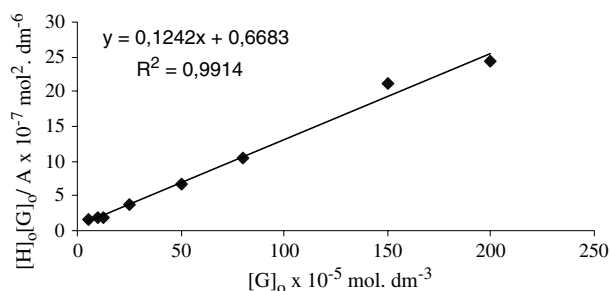


Figure 4. Typical plot of  $[\text{H}]_0[\text{G}]_0/\Delta A$  versus  $[\text{G}]_0$  for the host-guest complexation of **1** and  $\text{NaClO}_4$  in ( $\text{CH}_3\text{CN}$ ).

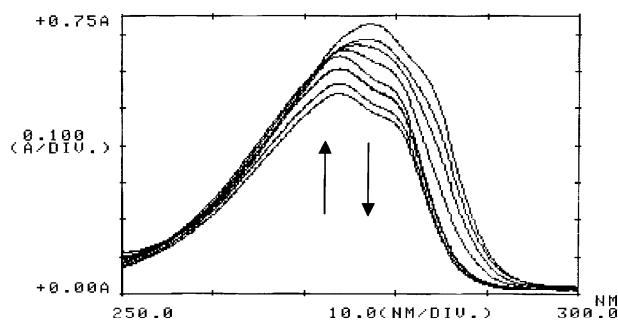


Figure 5. UV-vis spectra of **2** ( $1, 25 \times 10^{-4}$ ) in the presence of  $\text{NaClO}_4$  ( $2 \times 10^{-5}$ – $2 \times 10^{-3}$ ).

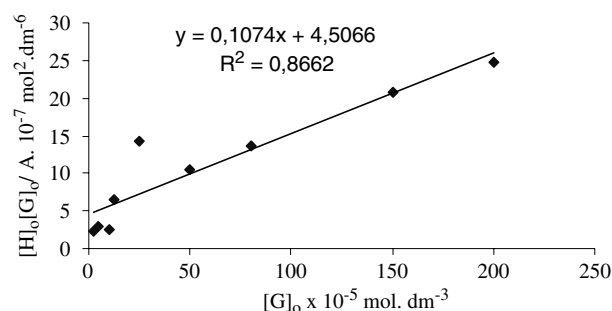
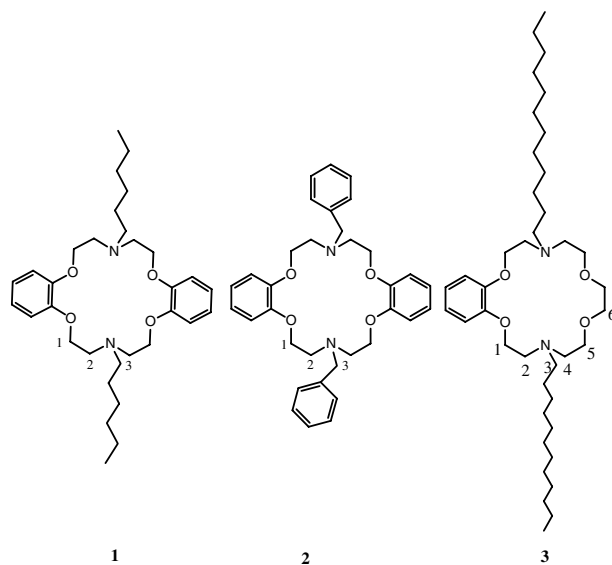


Figure 6. Typical plot of  $[\text{H}]_0[\text{G}]_0/\Delta A$  versus  $[\text{G}]_0$  for the host-guest complexation of **2** and  $\text{NaClO}_4$  in ( $\text{CH}_3\text{CN}$ ).

of aliphatic oxygen atoms in **3** by aromatic oxygen atoms decreases the size the cavity so that  $\text{Na}^+$  ion can fit in the cavity much better than in the case of **3**. The behaviour of macrocycle **2** deserves a special treatment. The dibenzo substitution on diaza crown ether, due to steric hindrance of the arene units on the ring and  $\pi$ - $\pi$  interaction between aromatic moieties on the ring and aromatic moieties on the side chains may diminishes the cavity. Hence complex formation of macrocycle **2** with  $\text{Na}^+$  was hindered as result the binding constant of **2** towards  $\text{Na}^+$  was reasonable small when compared **1** and **3**.

#### $^1\text{H}$ NMR spectra

The  $^1\text{H}$  NMR spectra of the compounds were recorded in  $\text{CD}_3\text{CN}$  as free crown ethers as well as with increasing amounts of  $\text{NaClO}_4$ . The corresponding chemical shifts are given in Table 1. The aliphatic protons of the macrocyclic ring are well separated from the benzene resonances and they also appear as well resolved signals. The methylenic protons H-1 in **3** are shifted to lower field (4.13 ppm) with respect to H-5 (3.55 ppm) and H-6 (3.51 ppm) protons [19, 20] due to the anisotropy effect of the benzene ring. The alkali metal salt, when added to  $\text{CD}_3\text{CN}$  solutions of the crown ethers, causes a low-field shift in the resonances of almost all of the protons, whereas  $-\text{NCH}_2-$  protons resonances move to high-field. Several effects could be responsible for the low field shifts of the proton resonances:



Scheme 1.

Table 1.  $^1\text{H}$  chemical shifts of macrocyclic protons (H-1–H-6) at  $\text{NaClO}_4$  concentrations (in  $\text{CD}_3\text{CN}$ )

Free Crown	H-1	H-2	H-3	H-4	H-5	H-6
Free Crown 1						
$\delta(\text{ppm})$	3.99	3.20	2.53	–	–	–
$\Delta\delta(\text{ppm})$ [ $\text{NaClO}_4$ ]/ [Crown]:1:1	0.16	–0.23	0.05	–	–	–
Free Crown 2						
$\delta(\text{ppm})$	4.00	3.23	3.73	H-4	H-5	H-6
$\Delta\delta(\text{ppm})$ [ $\text{NaClO}_4$ ]/ [Crown]:1:1	0.19	–0.25	–0.01	–	–	–
Free Crown 3						
$\delta(\text{ppm})$	4.13	3.01	2.47	2.86	3.55	3.51

1. the electric field effect of the alkali metal cation when complexed within the cavity of the crown ethers [21–23];
2. charge density variations at the carbon atoms, adjacent to the studied protons, owing to an increased electron attraction of the ring oxygen and nitrogen atoms as a result of the cation complexation (this type of effect has been found to control the binding strength of crown ethers quantitatively via inductive effects [24] and mesomerism [25]),
3. conformational skeletal variations during the complexation,
4. medium effect.

Taking into account the results of UV–vis and  $^1\text{H}$  NMR studies, the following conclusions can be drawn: Arene substitution on macro ring has profound effect on cavity size. The structure of the side arm also has effect on complexation of crown ether. And finally, the macro-ring- side arm cooperativity play an important role in complexation.

## Experimental

NMR spectra were recorded on a BRUKER DPX-400 High Performance Digital FT–NMR spectrometer. The concentrations of crown ethers were kept constant with an increasing concentration of the added  $\text{NaClO}_4$  at 25 °C.

The abilities of crown ethers to coordinate to  $\text{Na}^+$  were investigated using UV spectroscopic titration [27]. The UV–vis spectra were measured at 25 °C with a Shimadzu 160 UV spectrometer. The maximum wavelengths are 277, 277 and 276.8 nm for **1**, **2** and **3** respectively. A solution of  $\text{CH}_3\text{CN}$  (HPLC grade) was used as the solvent. The concentrations of the crown ethers are  $1.25 \times 10^{-4}$ – $2.5 \times 10^{-4}$  M with an increasing concentration of the added  $\text{NaClO}_4$ .

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