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Protonation of 25,27-bis(1-octyloxy)calix[4]arene-crown-6 in the 1,3-*alternate* conformation

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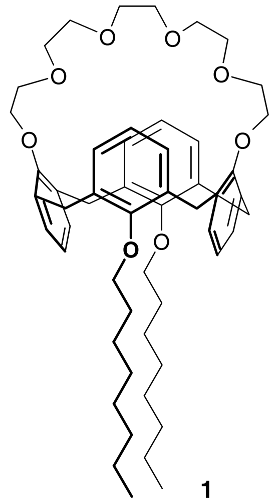
Abstract From extraction experiments in the two-phase water-nitrobenzene system and γ-activity measurements, the stability constant of protonated 1,3-*alternate*-25,27-bis(1-octyloxy)calix[4]arene-crown-6 in nitrobenzene saturated with water was determined. By using DFT calculations, the most probable structure of the 1,3-*alternate*-25,27-bis(1-octyloxy)calix[4]arene-crown-6 $\cdot$ H_3O^+ complex species was derived.

Keywords Calixarenes; Macrocycles; Protonation; DFT; Structure.

Introduction

Calixarenes are macrocyclic compounds which are not only easily available on a large scale, but also offer nearly boundless possibilities for chemical modification [1]. This makes them highly attractive as building blocks for more sophisticated and elaborate host molecules. Among the numerous 'tailor made' ligands for a large variety of metal cations, crown ether derivatives of calixarenes (calixcrowns) represent not only some of the earliest complexes [2], but also elegantly demonstrate the potential of these compounds [3]. Calixarenes find applications as selective binders and carriers, as analytical sensors, as catalysts and model structures for biomimetic studies [4].

New cesium-selective extractants from the calix[4]arene-crown-6 family have been introduced [5, 6]. The corresponding crystal structures of model complexes with cesium salts have demonstrated a significant π – interaction between the facing aromatic rings and the Cs^+ guest cation [5–7]. Besides, the calix[4]arene-crown-6 family of the mentioned compounds gives Cs^+/Na^+ separation factors exceeding 10^4 [6].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Scheme 1

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Recently, the interactions of the H_3O^+ cation with some calix[4]arenes have been investigated [8–11]. In the present work, the stability constant of protonated 25,27-bis(1-octyloxy)calix[4]arene-crown-6 in the 1,3-*alternate* conformation ($\mathbf{1}\cdot H_3O^+$) (*cf.* Scheme 1) is evaluated in water saturated nitrobenzene and its DFT calculated structure is solved.

Results and discussion

Extraction experiments

In terms of previous papers [12–14], the two-phase water-HCl/nitrobenzene-Na*DCC*-**1** (1,3-alternate-25,27-bis(1-octyloxy)calix[4]arene-crown-6) extraction system, chosen for determination of stability constant of the complex $\mathbf{1}\cdot H_3O^+$ in nitrobenzene saturated with water, can be characterized by the main chemical equilibrium (1) to which the equilibrium extraction constant (Eq. (2)) corresponds; aq and nb denote the presence of the species in the aqueous and nitrobenzene phases.

$$H_3O^+(aq) + \mathbf{1}\cdot Na^+(nb) \leftrightharpoons \mathbf{1}\cdot H_3O^+(nb) + Na^+(aq); \quad K_{ex}(H_3O^+, \mathbf{1}\cdot Na^+) \tag{1}$$

$$K_{ex}(H_3O^+, \mathbf{1}\cdot Na^+) = \frac{[\mathbf{1}\cdot H_3O^+]_{nb}[Na^+]_{aq}}{[H_3O^+]_{aq}[\mathbf{1}\cdot Na^+]_{nb}} \tag{2}$$

It is necessary to emphasize that **1** is a considerably hydrophobic ligand, practically present in the nitrobenzene phase only, where this ligand forms – with H_3O^+ and Na^+ – the relatively stable complexes $\mathbf{1}\cdot H_3O^+$ and $\mathbf{1}\cdot Na^+$.

Taking into account the conditions of electroneutrality in the organic and aqueous phases of the system under study, the mass balances of H_3O^+ and Na^+ ions at equal volumes of the nitrobenzene and aqueous phases, as well as the measured equilibrium distribution ratio of sodium, $D_{Na} = [\mathbf{1}\cdot Na^+]_{nb}/[Na^+]$, combined with Eq. (2), we get the final expression for the mentioned extraction constant (Eq. (3)); $C_{HCl}^{in,aq}$ is the initial concentration of HCl in the aqueous phase and $C_{Na\mathit{DCC}}^{in,nb}$ denotes the initial concentration of Na*DCC* in the organic phase of the system under consideration.

$$K_{ex}(H_3O^+, \mathbf{1}\cdot Na^+) = \frac{1}{D_{Na}} \frac{C_{Na\mathit{DCC}}^{in,nb}}{(1+D_{Na})C_{HCl}^{in,aq} - C_{Na\mathit{DCC}}^{in,nb}} \tag{3}$$

From the extraction experiments and γ-activity measurements by using Eq. (3), the following value of the constant K_{ex} (H_3O^+, $\mathbf{1}\cdot Na^+$) was evaluated as $\log K_{ex}(H_3O^+, \mathbf{1}\cdot Na^+) = 0.1 \pm 0.1$. Moreover, with respect to Refs. [14–16], for the exchange extraction constant $K_{ex}(H_3O^+, Na^+)$ corresponding to the equilibrium $H_3O^+(aq) + Na^+(nb) \leftrightharpoons H_3O^+(nb) + Na^+(aq)$ and for the extraction constant $K_{ex}(H_3O^+, \mathbf{1}\cdot Na^+)$ defined above, as well as for the stability constants of the complexes $\mathbf{1}\cdot Na^+$ and $\mathbf{1}\cdot H_3O^+$ in nitrobenzene saturated with water, denoted by β_{nb} ($\mathbf{1}\cdot Na^+$) and β_{nb} ($\mathbf{1}\cdot H_3O^+$), one gets Eq. (4).

$$\begin{aligned}\log \beta_{nb}(\mathbf{1}\cdot H_3O^+) = {} & \log \beta_{nb}(\mathbf{1}\cdot Na^+) \\ & + \log K_{ex}(H_3O^+, \mathbf{1}\cdot Na^+) \\ & - \log K_{ex}(H_3O^+, Na^+)\end{aligned} \tag{4}$$

Using the value $\log K_{ex}(H_3O^+, Na^+) = 0.3$ inferred from Ref. [12], the constant $\log K_{ex}(H_3O^+, \mathbf{1}\cdot Na^+)$ given above as well as $\log \beta_{nb}$ $(\mathbf{1}\cdot Na^+) = 6.5 \pm 0.1$ [17], and applying Eq. (4), we obtain the stability constant of the $\mathbf{1}\cdot H_3O^+$ complex in water saturated nitrobenzene at 25°C as $\log \beta_{nb}$

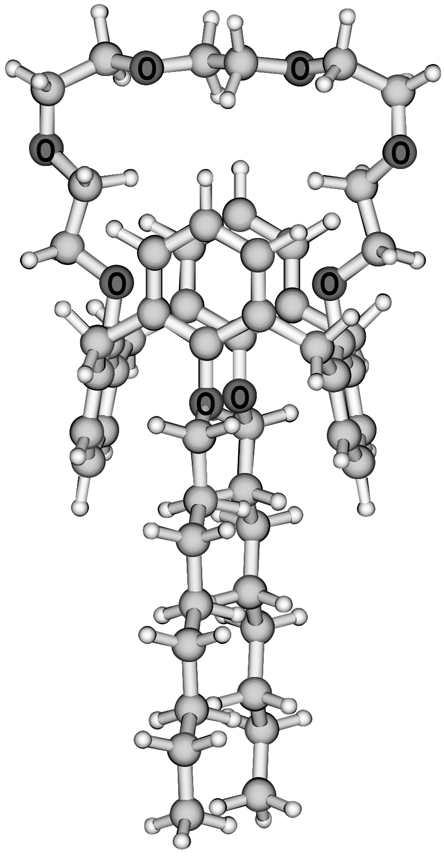

Fig. 1 DFT optimized structure of free **1** (*B3LYP*/6–31G(d))

$(\mathbf{1} \cdot H_3O^+) = 6.3 \pm 0.2$. This means that in the mentioned medium the stability constants of the considered cationic complex species $\mathbf{1} \cdot Na^+$ and $\mathbf{1} \cdot H_3O^+$ are comparable.

Quantum mechanical calculations

The quantum mechanical calculations were carried out at the density functional level of theory (DFT, *B*3*LYP* functional) using the Gaussian 03 suite of programs [18]. The 6–31G(d) basis set was used and the optimizations were unconstrained. Although a possible influence of a polar solvent on the detailed structures of **1** and $\mathbf{1} \cdot H_3O^+$ could be imagined, our quantum calculations in similar cases, performed in an analogous way, showed very good agreement of experiment with theory [19–21].

In the model calculations, we optimized the molecular geometry of the parent calix[4]arene-crown-6 ligand **1** and its complex with H_3O^+. The optimized structure of **1** is shown in Fig. 1. In Fig. 2, the optimized structures A and B of the $\mathbf{1} \cdot H_3O^+$ complex obtained by the full DFT optimization are illustrated with the lengths of the corresponding hydrogen bonds. In both of the mentioned structures of the $\mathbf{1} \cdot H_3O^+$ cationic complex species, the considered H_3O^+ ion is bound by three strong hydrogen bonds to two phenoxy oxygen atoms of the ligand **1** (structure A) or two ethereal oxygens of **1** (structure B) and further, to one carbon of the respective benzene ring of **1** (structures A, B).

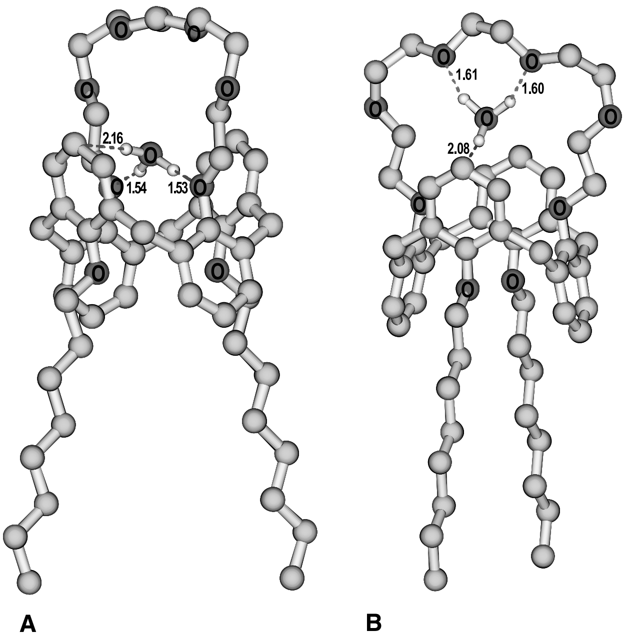

Fig. 2 DFT optimized structures (A, B) of the $\mathbf{1} \cdot H_3O^+$ complex (*B*3*LYP*/6–31G(d)) (hydrogen atoms omitted for clarity except those of H_3O^+). *Structure A* H-bond lengths of H_3O^+ to two phenoxy oxygens of **1**: 1.53, 1.54 Å; H-bond length of H_3O^+ to one carbon of the corresponding benzene ring of **1**: 2.16 Å. *Structure B* H-bond lengths of H_3O^+ to two ethereal oxygens of **1**: 1.61, 1.60 Å; H-bond length of H_3O^+ to one carbon of the corresponding benzene ring of **1**: 2.08 Å

In conclusion, it should be emphasized that the binding energy of structure A ($-361.2\,\mathrm{kJ\,mol^{-1}}$) is substantially higher than that of structure B ($-303.5\,\mathrm{kJ\,mol^{-1}}$) and therefore the mentioned structure A evidently corresponds to the experimentally proved complex species $\mathbf{1} \cdot H_3O^+$.

Experimental

Cesium dicarbollylcobaltate (Cs*DCC*) was purchased from Katchem, Řež, Czech Republic. A nitrobenzene solution of H*DCC* [22] was prepared from Cs*DCC* by the procedure described in Ref. [23]. The equilibration of the nitrobenzene solution of H*DCC* with stoichiometric NaOH, which was dissolved in an aqueous solution of NaCl (0.2 *M*), yielded the corresponding Na*DCC* solution in nitrobenzene. Compound **1** (*cf.* Scheme 1) was kindly supplied by Prof. *V.I. Kalchenko*, Institute of Organic Chemistry, NASU, Kiev, Ukraine. The other chemicals used (Lachema, Brno, Czech Republic) were of reagent grade purity. The radionuclide $^{22}Na^+$ (DuPont, Belgium) was of standard radiochemical purity.

The extraction experiments were carried out in 10 cm^3 glass test-tubes covered with polyethylene stoppers. 2 cm^3 of an aqueous solution of HCl of a concentration in the range from 1×10^{-3} to $1 \times 10^{-2}\,M$ and microamounts of $^{22}Na^+$ were added to 2 cm^3 of a nitrobenzene solution of **1** and Na*DCC*, whose initial concentrations varied also from 1×10^{-3} to $1 \times 10^{-2}\,M$ (in all experiments, the initial concentration of **1** in nitrobenzene, $C_1^{\mathrm{in,nb}}$, was equal to the initial concentration of Na*DCC* in this medium, $C_{\mathrm{Na}DCC}^{\mathrm{in,nb}}$). The test-tubes filled with the solutions were shaken for 24 h, using a laboratory shaker. Then the phases were separated by centrifugation. Afterwards, 1 cm^3 samples were taken from each phase and their γ-activities were measured using a well-type NaI(Tl) scintillation detector connected to a γ-analyzer NK 350 (Gamma, Budapest, Hungary). The equilibrium distribution ratio of sodium, D_{Na}, was determined as the ratio of the measured radioactivities of $^{22}Na^+$ in the nitrobenzene and aqueous samples.

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References

1. Böhmer V (1995) Angew Chem 34:713
2. Alfieri C, Dradi E, Pochini A, Ungaro R, Andreetti GD (1983) J Chem Soc Chem Commun:1075
3. Asfari Z, Wenger S, Vicens J (1994) J Incl Phenom Mol Recogn 19:137
4. Gutsche CD (1998) Calixarenes Revisited. The Royal Society of Chemistry, Cambridge
5. Ungaro R, Casnati A, Ugozzoli F, Pochini A, Dozol JF, Hill C, Rouquette H (1994) Angew Chem 33:1506
6. Casnati A, Pochini A, Ungaro R, Ugozzoli F, Arnaud F, Fanni S, Schwing MJ, Egberink RJM, de Jong F, Reinhoudt DN (1995) J Am Chem Soc 117:2767
7. Thuery P, Nierlich M, Bryan JC, Lamare V, Dozol JF, Asfari Z, Vicens J (1997) J Chem Soc Dalton Trans:4191
8. Makrlík E, Vaňura P (2006) Monatsh Chem 137:1185
9. Dybal J, Makrlík E, Vaňura P (2007) Monatsh Chem 138:541
10. Kříž J, Dybal J, Makrlík E, Budka J, Vaňura P (2007) Monatsh Chem 138:735
11. Dybal J, Makrlík E, Vaňura P, Selucký P (2007) Monatsh Chem 138:1239
12. Rais J (1971) Collect Czech Chem Commun 36:3253
13. Daňková M, Makrlík E, Vaňura P (1997) J Radioanal Nucl Chem 221:251
14. Makrlík E, Hálová J, Kyrš M (1984) Collect Czech Chem Commun 49:39
15. Makrlík E, Vaňura P (1996) J Radioanal Nucl Chem 214:339
16. Makrlík E, Vaňura P (2006) Monatsh Chem 137:157
17. Makrlík E, Vaňura P (2008) (unpublished results)
18. Frisch MJ, Trucks GW, Schlegel HB, Scuseria GE, Robb MA, Cheeseman JR, Montgomery JA Jr, Vreven T, Kudin KN, Burant JC, Millam JM, Iyengar SS, Tomasi J, Barone V, Mennucci B, Cossi M, Scalmani G, Rega N, Petersson GA, Nakatsuji H, Hada M, Ehara M, Toyota K, Fukuda R, Hasegawa J, Ishida M, Nakajima T, Honda Y, Kitao O, Nakai H, Klene M, Li X, Knox JE, Hratchian HP, Cross JB, Bakken V, Adamo C, Jaramillo J, Gomperts R, Stratmann RE, Yazyev O, Austin AJ, Cammi R, Pomelli C, Ochterski JW, Ayala PY, Morokuma K, Voth GA, Salvador P, Dannenberg JJ, Zakrzewski VG, Dapprich S, Daniels AD, Strain MC, Farkas O, Malick DK, Rabuck AD, Raghavachari K, Foresman JB, Ortiz JV, Cui Q, Baboul AG, Clifford S, Cioslowski J, Stefanov BB, Liu G, Liashenko A, Piskorz P, Komaromi I, Martin RL, Fox DJ, Keith T, Al-Laham MA, Peng CY, Nanayakkara A, Challacombe M, Gill PMW, Johnson B, Chen W, Wong MW, Gonzalez C, Pople JA (2004) Gaussian 03, Revision C. 02, Gaussian Inc., Wallingford, CT
19. Kříž J, Dybal J, Makrlík E (2006) Biopolymers 82:536
20. Kříž J, Dybal J, Makrlík E, Vaňura P, Lang J (2007) Supramol Chem 19:419
21. Kříž J, Dybal J, Makrlík E, Vaňura P (2008) Supramol Chem (in press)
22. Makrlík E, Vaňura P (1985) Talanta 32:423
23. Makrlík E (1992) Collect Czech Chem Commun 57:289