ISSN 1070-3632, Russian Journal of General Chemistry, 2013, Vol. 83, No. 9, pp. 1738–1743. © Pleiades Publishing, Ltd., 2013.
Original Russian Text © E.A. Alekseeva, S.S. Basok, A.V. Mazepa, A.P. Luk'yanenko, O.V. Snurnikova, A.I. Gren', 2013, published in Zhurnal Obshchei Khimii, 2013, Vol. 83, No. 9, pp. 1519–1525.

p-tert-Butylcalix[4]arenes Containing Azacrown Ether Substituents at the Lower Rim as Potential Polytopic Receptors

E. A. Alekseeva, S. S. Basok, A. V. Mazepa, A. P. Luk'yanenko, O. V. Snurnikova, and A. I. Gren'

Bogatskii Institute of Physical Chemistry, National Academy of Sciences of Ukraine, Lustdorfskaya doroga 86, Odessa 65080, Ukraine
e-mail: Alyeksyeyeva@rambler.ru

Received August 2, 2012

Abstract—A series of disubstituted *p-tert*-butylcalix[4]arenes with *N*-methoxycarbonylmonoazacrown ether and *N*-ethoxymonoazacrown ether residues at the lower rim has been prepared via the reaction of di(carboxymethoxy)-*p-tert*-butylcalix[4]arene with azacrown ethers and subsequent reduction of the resulting amide derivatives. Using UV titration and ^{1}H NMR spectroscopy we have demonstrated the ability of the calixarene with two *N*-carbonylmonoaza-18-crown-6-ether substituents to form the 1:3 complexes with K^+ and Na^+ and the 1:2 complexes with Cs^+, Sr^{2+}, Cu^{2+}, and Zn^{2+}. The calixarene with two fragments of *N*-ethoxymonoazo-18-crown ether has formed binuclear complexes with alkali metals cations and mononuclear complexes with transition metals cations.

DOI: 10.1134/S1070363213090181

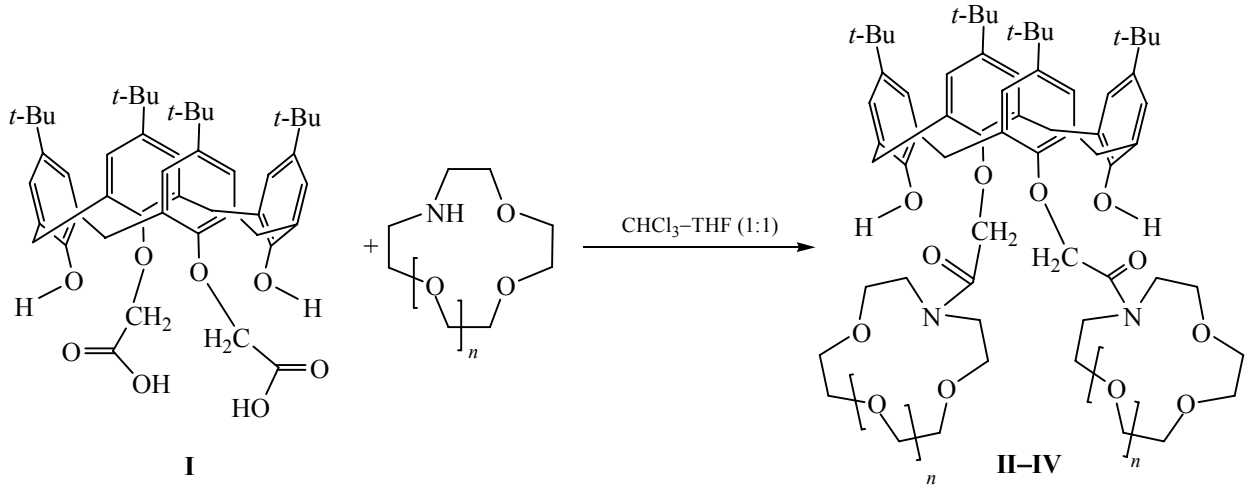
The search for the methods to prepare new macrocyclic compounds with intramolecular cavity is an important field of the developing supramolecular chemistry area. Such compounds are capable of binding metal cations, anions and neutral molecules by the *host-guest* mechanism. The calix[*n*]arenes are especially promising in this context: their numerous derivatives are known for the exciting complexing and extraction properties [1–4], and they are easily functionalized at both the small and the large rims of the macrocycle. New polytopic receptors can result from combining calixarenes with the well known complexones, crown ethers [5, 6], through a linker that simultaneously acts as an additional donor center. As the calixarene core is relatively rigid and there is a short linker between the fragments of calixarene and the substituent, a certain structural pre-organization of the molecule can be expected promoting the formation of sandwich or pseudo-sandwich type complexes with metal cations of large ionic radius.

So far only a few examples of such calixarene derivatives have been described in the literature. For example, [7–9] have reported the ability of calix[4]-arenes and calix[6]arenes with *N*-alkylcarbonyldiaza-18-crown-6 ether substituents at the upper rim to carry the ions across the phospholipid membrane. In the same papers, it has been demonstrated that the calix[4]-arene containing *N*-dodecyl-*N'*-benzyl-18-diazacrown-6 ether residues forms ion-selective channels in the membrane. It has been shown that *p-tert*-butylcalix[4]-arenes, di- and tetrasubstituted at the small rim with *N*-methoxycarbonylbenzo-15-crown ether fragments, form complexes with metal cations and anions [10].

In this work, we synthesized a series of disubstituted derivatives of *p-tert*-butylcalix[4]arene containing azacrown ethers attached via amide or *N*-ethoxy groups at the small rim as in order to obtain new polytopic receptors.

The starting material to prepare compounds containing *N*-methoxycarbonylazacrown ether substituents was 1,3-dicarboxymethoxy derivative of *p-tert*-butylcalix[4]arene (**I**) (Scheme 1). Previously, we showed that the modified carbodiimide method involving hydroxybenzotriazole was effective to reach high yields of the *p-tert*-butylcalix[4]arene derivatives with varied degree of substitution containing amide

Scheme 1.



n = 1 (**II**), 2 (**III**), 3 (**IV**).

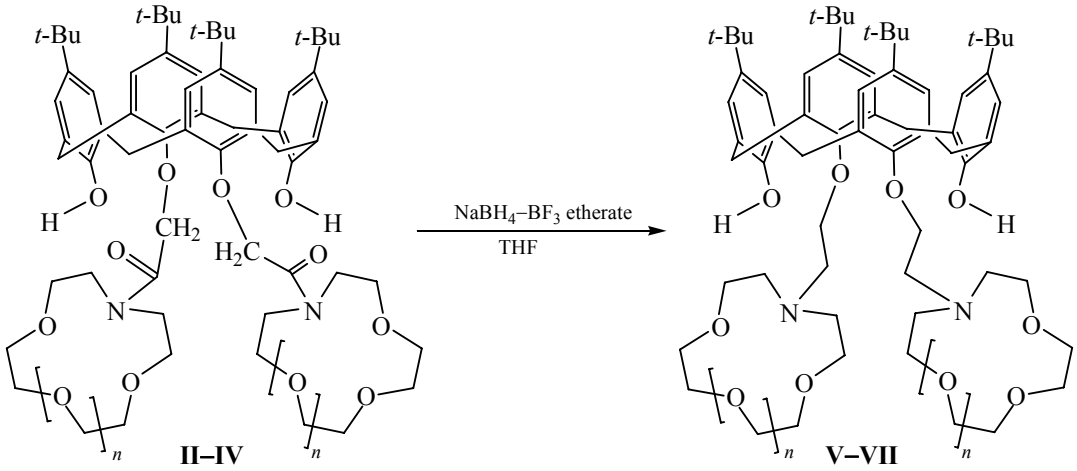
groups at the lower rim [11]. The same method was used in this work for the preparation of **II–IV**. The ^{1}H NMR data of the synthesized derivatives revealed the cone conformation of the molecules.

Upon reduction of **II–IV** with $LiAlH_4$ in boiling THF, several processes occurred simultaneously: the C–N bond hydrogenolysis and partial destruction of the ether bond of phenol oxygen and of azacrown ether fragment; that led to the complex mixture of products containing the unsubstituted calixarene. Replacing the $LiAlH_4$ with the $NaBH_4$–BF_3 etherate system (Scheme 2) and changing the reaction temperature to 15–20°C allowed obtaining of the target calixarenes substituted with azacrown ether-*N*-ethoxy fragments (**V–VII**) with yields of 35–55%.

Preliminary study of the extraction ability of the prepared substituted calixarenes showed that compounds **II–IV** almost completely recovered sodium and potassium cations from aqueous solutions of their salts. Replacement of the amide group with amino-ethoxy fragment (compounds **V–VII**) led to a sharp decrease of the calixarenes binding ability towards the alkali metal cations.

Complexing properties of the prepared compounds were studied by spectrophotometric and ^{1}H NMR titrations in methanol and CD_3OD, respectively. The

Scheme 2.



n = 1 (**V**), 2 (**VI**), 3 (**VII**).

Stability constants (log β) and composition of the calixarenes **II–V** and **VII** complexes with metal cations[a]

Comp. no.	Na^+	K^+	Cs^+	Sr^{2+}	Zn^{2+}	Cu^{2+}
II	8.22±0.03 (1:1)	5.39±0.07 (1:1)	7.9±0.03 (1:1)	4.25±0.02 (1:1)	[b]	6.38±0.08 6.37±0.06 (1:2)
III	5.66±0.01 7.8±0.04 7.88±0.04 (1:3)	6.21±0.05 9.55±0.03 (1:2)	7.76±0.03 (1:1)	5.34±0.01 7.98±0.01 (1:2)	3.21±0.04 6.58±0.04 (1:2)	2.07±0.01 (1:1)
IV	7.71±0.03 11.24±0.05 11.38±0.05 (1:3)	8.32±0.07 13.45±0.01 13.56±0.01 (1:3)	7.9±0.03 (1:1)	4.53±0.01 7.26±0.01 (1:2)	3.88±0.04 7.54±0.04 (1:2)	<2 3.82±0.04 (1:2)
VII	2.53±0.06 7.57±0.08 (1:2)	3.12±0.05 8.11±0.05 (1:2)	3.99±0.02 (1:1)	2.79±0.04 (1:1)	3.75±0.03 (1:1)	<2 (1:1)

[a] Metal chlorides of Na^+, K^+, Cs^+, Sr^{2+}, and Cu^{2+}; acetate of Zn^{2+}. [b] No visible changes in absorption spectra.

experiments were performed at 20°C by adding the corresponding salt solution to the ligand solution of constant concentration. The results were processed using SIRKO software [12]. The obtained stability constants (log β) and the complexes composition are presented in the table.

Titration of **II** (containing 12-azacrown-4 ether fragment attached via amide linker) by NaCl, KCl, and $SrCl_2$ indicated the formation of mononuclear complexes of calixarene with the cations. In the presence of copper cations, **II** formed the 1:2 (ligand:metal) complexes with close values of log β_1 (6.38±5%) and log β_2 (6.37±5%), thus, the molecule parts of the same nature (the crown ether rings) were likely involved in the complex formation [13, 14]. In the interaction of calixarene **II** with CsCl, a mononuclear complex was formed, probably, of the pseudo-sandwich type (log β = 7.9).

Calixarene **III** formed trinuclear sodium and binuclear potassium complexes, whereas in the case of calixarene **IV**, both sodium and potassium complexes were trinuclear. In the both cases, there was a significant difference between log β_1 and log β_2 but the values of log β_2 and log β_3 were close (see the Table). The data from NMR-titration of calixarene **IV** (changes of the chemical shifts of *tert*-butyl, $OCH_2C{=}O$, and crown ether protons) suggested that inclusion of the second and the third cations (sodium or potassium) in the crown-ether fragments occurred after binding of the first cation inside the cavity formed by the amide and the hydroxyl groups of the calixarene.

Calixarene **IV** formed the 1:1 complexes with Cs^+, whereas with Sr^{2+}, Cu^{2+}, and Zn^{2+}, binuclear complexes were formed. The amine analog of **IV**, the calixarene **VII** bearing *N*-ethoxy-18-monoazacrown-6 ether substituents, gave only the 1:1 complexes with Cs^+, Sr^{2+}, Cu^{2+}, and Zn^{2+} and binuclear complexes with Na^+ and K^+; in the latter case, both the first and second complex stability constants were much lower as compared with those of **IV**. The result was consistent with [16, 17] where the essential contribution of the amide group to the complexation with metal cations was stated, both due to carbonyl oxygen additional complexing ability, and via strong binding of the counterion in the outer sphere.

In the ^1H NMR spectra of **II**–**IV**, the following signals were observed: two singlets from *tert*-butyl groups protons (1:1), a pair from doublets of methylene macrocycle bridge protons (*J* of 12.45–13.2 Hz), two singlets from aromatic protons of the calixarene core (1:1), and well resolved triplets from CH_2NCH_2 protons of the crown ether substituents. The ^1H NMR spectra of **II**–**IV** complexes with sodium, potassium, and cesium picrates showed significant changes in the shape and chemical shift of the signals of the protons of macrocyclic core groups, thus possibly indicating changes in the symmetry of calixarene molecules upon coordination with the metal cations. Signals from the protons of methylene bridges of calixarene core, appearing at 4.43–4.47 ppm in the spectra of free ligands, shifted upfield and overlapped with the signals of azacrown ether protons, the latter appeared as

poorly resolved multiplets. The ^{1}H NMR spectra of calixarenes **III** and **IV** complexes with sodium cations contained picrate anion proton signals at 8.67–8.8 ppm with the integral intensity of 6H, thus indicating the formation of 1:3 complexes.

In the ^{1}H NMR spectra of **II**–**IV** complexes with cesium picrate, the signals of picrate anion protons showed the integral intensity of 2H, indicating the formation of the 1:1 complex. As in that case, the chemical shifts of amide methylene protons did not change upon the interaction, the complexation should have occurred via the crown ether substituents exclusively, and the intramolecular sandwich-type complexes with Cs^+ were formed.

To conclude, the study of complexing properties of a series of calixarene derivatives, showed that the azacrown ether derivatives of *p-tert*-butylcalix[4]-arenes containing amide fragments were polytopic receptors, forming polynuclear complexes with some *s*- and *d*-elements cations. Replacement of the amide groups by the amino groups resulted in a sharp decrease in the complexes stability; such calixarene derivative did not act as polytopic receptors.

EXPERIMENTAL

The structure and conformation of the compounds obtained were determined from ^{1}H NMR spectra recorded with Bruker AVANCE DRX 500 spectrometer (500 MHz, ~10% solutions in $CDCl_3$, internal reference – TMS). The Fast Atom Bombardment mass spectra were recorded with VG 70-70EQ mass spectrometer (Xe atom beam of 8 kV energy and *m*-nitrobenzyl alcohol as a matrix). UV spectra were recorded with Specord M 40 and Hitachi U3210 spectrophotometers. The complex stability constants in methanol were determined by the molar ratios method at a constant concentration of the ligand (2×10^{-5} mol/l) and varied concentration of metal salts, the corresponding calixarene:metal molar ratio ranged from 1:0.01 to 1:20. The solutions absorbance was measured at 225–330 nm. Determination of the complexes stability constants in the CD_3OD solution by ^{1}H NMR titration was performed similarly, by tracking the changes in the chemical shifts of calixarene core and substituents protons.

Di(carboxymethoxy)-*p-tert*-butylcalix[4] arene **I** was prepared as described in [18].

General method for the preparation of *p-tert*-butylcalix[4]arene derivatives with methoxycarbonylmonoazacrown ether fragments. 0.62 g (3 mmol) of dicyclohexylcarbodiimide was added at 0°C to a solution of 0.764 g (1 mmol) of **I** and 0.432 g (3.2 mmol) of hydroxybenzotriazole in 15 ml of anhydrous CH_2Cl_2–THF (1:1) mixture. The reaction mixture was stirred for 1 h at 0°C. Then, a solution of 2.2 mmol of the appropriate azacrown ether in 5 ml of THF was added to the suspension. The reaction mixture was stirred for 5–6 h and left overnight. The precipitated dicyclohexylurea was filtered off, washed with THF, and the combined filtrates were dried by rotary evaporation. The dry residue was dissolved in a minimal amount of dioxane and left for 24 h at room temperature. The precipitated dicyclohexylurea was filtered off, washed with dioxane, and the organic solvent was evaporated under reduced pressure. The dry residue was dissolved in $CHCl_3$–C_6H_6 (1:2) mixture and washed successively with water (2×50 ml), 5% HCl (3×50 ml), and water (10×50 ml). After removal of the solvent, the desired product was extracted from the dry residue with heptane (2×300 ml). After removal of heptane, the target compound was isolated in the form of fine white powder.

5,11,17,23-Tetra-*tert*-butyl-25,27-bis[(1,4,7-trioxa-10-azacyclodec-10-yl)carbonylmethoxy]-26,28-dihydroxycalix[4]arene (II). Yield 95%. ^{1}H NMR spectrum, δ, ppm: 1.00 s [18H, $(CH_3)_3C$], 1.24 s [18H, $(CH_3)_3C$], 3.25 d (4H, $ArCH_2Ar$, *J* 12.76 Hz), 3.58 m (20H, OCH_2CH_2O, $C\underline{H}_2CH_2N$), 3.65 t (4H, $C\underline{H}_2CH_2N$), 3.8 t (4H, $CH_2C\underline{H}_2N$), 4.0 t (4H, $C\underline{H}_2CH_2N$), 4.42 d (4H, $ArCH_2Ar$, *J* 12.76 Hz), 4.89 s (4H, CH_2CO), 6.79 s (4H, H_{arom}), 6.95 s (4H, H_{arom}), 7.55 s (2H, OH). Mass spectrum, *m*/*z*: 1079 $[M + 1]^+$.

5,11,17,23-Tetra-*tert*-butyl-25,27-bis[(1,4,7,10-tetraoxa-13-azacyclodec-13-yl)carbonylmethoxy]-26,28-dihydroxycalix[4]arene (III). Yield 96.7%. ^{1}H NMR spectrum, δ, ppm: 1.00 s [18H, $(CH_3)_3C$], 1.23 s [18H, $(CH_3)_3C$], 3.26 d (4H, $ArCH_2Ar$, *J* 12.45 Hz), 3.64 m (36H, OCH_2CH_2O, $C\underline{H}_2CH_2N$), 3.73 t (4H, $CH_2C\underline{H}_2N$), 3.84 t (4H, $CH_2C\underline{H}_2N$), 4.42 d (4H, $ArCH_2Ar$, *J* 12.45 Hz), 4.84 s (4H, CH_2CO), 6.82 s (4H, H_{arom}), 6.96 s (4H, H_{arom}), 7.53 s (2H, OH). Mass spectrum, *m*/*z*: 1167 $[M + 1]^+$.

5,11,17,23-Tetra-*tert*-butyl-25,27-bis[(1,4,7,10,13-pentaoxa-16-azacyclodec-16-yl)carbonylmethoxy]-26,28-dihydroxycalix[4]arene (IV). Yield 98%. ^{1}H NMR spectrum, δ, ppm: 1.01 with [18H, $(CH_3)_3C$], 1.21 s [18H, $(CH_3)_3C$], 3.24 d (4H, $ArCH_2Ar$, *J* 12.45 Hz), 3.6–3.81 m (48H, OCH_2CH_2O, CH_2CH_2N), 4.42 d

(4H, $ArCH_2Ar$, *J* 12.45 Hz), 4.88 s (4H, CH_2CO), 6.82 s (4H, H_{arom}), 6.94 s (4H, H_{arom}), 7.64 s (2H, OH). Mass spectrum, *m*/*z*: 1254 $[M + 1]^+$.

Reduction of methoxycarbonyl derivatives of calixarene containing azacrown ether moiety. *Method* 1. 0.135 g (3.6 mmol) of $NaBH_4$ was added upon cooling to a solution of 0.7 mmol of the corresponding diamide derivative in 30 ml of anhydrous THF. At the end of the $NaBH_4$ addition, the temperature of the reaction mixture was raised to room temperature and a solution of 0.455 ml (3.6 mmol) of boron trifluoride etherate in 5 ml of THF was added. The reaction mixture was heated to boiling during 2 h with stirring, then refluxed with stirring during further 4 h, and finally left overnight. Diborane excess was decomposed with ice water upon ice bath cooling, and the mixture was refluxed for 2 h. After cooling, the precipitate formed was filtered off, and the filtrate was evaporated to dryness. To the residue, 15 ml of 20% HCl was added, and the mixture was heated for 2 h. Cooled reaction mixture was treated with aqueous LiOH to pH 8–9 and extracted with chloroform (5×20 ml). The organic phase was evaporated in a rotary evaporator. The dry residue was extracted with hot hexane (2×100 ml). The solvent was removed to dryness, and the crude product was purified by crystallization from water–ethanol mixture (1:2).

Method 2. A solution of 0.5 mmol of the corresponding diamide in 30 ml of THF was added to a suspension of 0.19 g (0.5 mmol) of $LiAlH_4$ in 15 ml of anhydrous THF under ice water cooling and vigorous stirring. Then the reaction mixture was refluxed for 6 h and left overnight. The $LiAlH_4$ excess was decomposed with ethyl acetate, and then with cold water under ice cooling. The resulting precipitate was filtered off, washed with THF, and the combined filtrates were evaporated to dryness with a rotary evaporator. The dry residue was dissolved in water, treated with aqueous LiOH to pH 8–9, and extracted with chloroform (5×20 ml). After removing the solvent, the product was isolated as described in *method* 1.

5,11,17,23-Tetra-*tert*-butyl-25,27-bis[(1,4,7-trioxa-10-azacyclodec-10-yl)ethoxy]-26,28-dihydroxycalix-[4]arene (V). Yield 55%. ^{1}H NMR spectrum, δ, ppm: 0.85 with [18H, $(CH_3)_3C$], 1.20 [18H, $(CH_3)_3C$], 3.01 t (4H, $OCH_2C\underline{H}_2N$), 3.26–3.32 m (12H, $ArCH_2Ar$, CH_2CH_2N), 3.5–3.57 m (16H, OCH_2CH_2O), 3.84 t (8H, $CH_2C\underline{H}_2N$), 4.1 t (4H, OCH_2CH_2N), 4.45 d (4H, $ArCH_2Ar$, *J* 13.45 Hz), 6.8 s (4H, H_{arom}), 6.93 s (4H, H_{arom}), 8.3 br.s (2H, OH). Mass spectrum, *m*/*z*: 1051 $[M + 1]^+$.

5,11,17,23-Tetra-*tert*-butyl-25,27-bis[(1,4,7-trioxa-10-azacyclodec-10-yl)ethoxy]-26,28-dihydroxycalix-[4]arene (VI). Yield 35%. ^{1}H NMR spectrum, δ, ppm: 0.96 s [18H, $(CH_3)_3C$], 1.21 s [18H, $(CH_3)_3C$], 2.97 t (4H, $OCH_2C\underline{H}_2N$), 3.24–3.33 m (12H, $ArCH_2Ar$, CH_2CH_2N), 3.5–3.56 m (24H, OCH_2CH_2O), 3.84 m (8H, CH_2CH_2N), 3.97 t (4H, $OC\underline{H}_2CH_2N$), 4.48 d (4H, $ArCH_2Ar$, *J* 13.3 Hz), 6.76 s (4H, H_{arom}), 6.89 s (4H, H_{arom}), 8.5 br.s (2H, OH). Mass spectrum, *m*/*z*: 1083 $[M + 1]^+$.

5,11,17,23-Tetra-*tert*-butyl-25,27-bis[(1,4,7,10,13-pentaoxa-16-azacyclodec-16-yl)ethoxy]-26,28-dihydroxycalix[4]arene (VII). Yield 35%. ^{1}H NMR spectrum, δ, ppm: 0.97 s [18H, $(CH_3)_3C$], 1.2 s [18H, $(CH_3)_3C$], 2.94 t (4H, $OCH_2C\underline{H}_2N$), 3.28–3.35 m (12H, $ArCH_2Ar$, $C\underline{H}_2CH_2N$), 3.56–3.68 m (32H, OCH_2CH_2O), 3.87–3.96 m (12H, CH_2CH_2N, OCH_2CH_2N), 4.45 d (4H, $ArCH_2Ar$, *J* 13.35 Hz), 6.84 s (4H, H_{arom}), 6.90 s (4H, H_{arom}), 8.56 br.s (2H, OH). Mass spectrum, *m*/*z*: 1227 $[M + 1]^+$.

Synthesis of the calixarenes II–IV complexes with alkali metal picrates. A weighed sample of 5 mmol of metal picrate was added to a solution of 1.25 mmol of calixarene in 10 ml of anhydrous CH_2Cl_2. The reaction mixture was stirred at room temperature for 4–5 h; then, the insoluble salt was filtered off, and the solvent was removed under reduced pressure.

[II-Na](Pic). ^{1}H NMR spectrum, δ, ppm: 1.24 s [18H, $(CH_3)_3C$], 1.27 s [18H, $(CH_3)_3C$], 3.29 d (4H, $ArCH_2Ar$, *J* 13.45 Hz), 3.62–3.71 m (24H, OCH_2·CH_2O, $C\underline{H}_2CH_2N$), 3.84 m (8H, $ArCH_2Ar$, $CH_2C\underline{H}_2N$), 4.02 m (4H, $CH_2C\underline{H}_2N$), 4.94 s (4H , CH_2CO), 6.76 s (2H, H_{arom}), 7.01 s (6H, H_{arom}), 8.7 s (2H, H_{Pic}).

[II-K](Pic). ^{1}H NMR spectrum, δ, ppm: 1.27 s [18H, $(CH_3)_3C$], 1.31 s [18H, $(CH_3)_3C$], 3.28 d (4H, $ArCH_2Ar$, *J* 13.6 Hz), 3.65–4.11 m (36H, OCH_2CH_2O, $C\underline{H}_2CH_2N$, $CH_2C\underline{H}_2N$, $ArCH_2Ar$), 4.85 s (4H, CH_2CO), 6.61 s (4H, H_{arom}), 7.03 s (4H, H_{arom}), 8.66 s (2H, H_{Pic}).

[III-3Na](Pic)$_3$. ^{1}H NMR spectrum, δ, ppm: 1.27 s, 1.28 s [36H, $(CH_3)_3C$], 3.31 d (4H, $ArCH_2Ar$, *J* 13.40 Hz), 3.48–3.89 m (42H, OCH_2CH_2O, $C\underline{H}_2CH_2N$, $CH_2C\underline{H}_2N$), 4.13 d (2H, $ArCH_2Ar$), 4.9 s (4H, CH_2CO), 6.73 s (4H, H_{arom}), 7.02 s (4H, H_{arom}), 8.73 s (6H, H_{Pic}).

[III-2K](Pic)$_2$. ^{1}H NMR spectrum, δ, ppm: 0.85 s [18H, $(CH_3)_3C$], 1.30 s [18H, $(CH_3)_3C$], 3.29 d (4H,

$ArCH_2Ar$, *J* 13.70 Hz), 3.64–4.13 m (44H, OCH_2CH_2O, $C\underline{H_2}CH_2N$, $CH_2C\underline{H_2}N$, $ArCH_2Ar$), 4.79 s (4H, CH_2CO), 6.62 s (2H, H_{arom}), 7.03 s (6H, H_{arom}), 8.68 s (4H, H_{Pic}).

[III-Cs](Pic). ^1H NMR spectrum, δ, ppm: 0.94 s [18H, $(CH_3)_3C$], 1.27 s [18H, $(CH_3)_3C$], 3.29 d (4H, $ArCH_2Ar$, *J* 13.45 Hz), 3.65–3.85 m (40H , OCH_2CH_2O, $C\underline{H_2}CH_2N$, $CH_2C\underline{H_2}N$), 4.37 d (4H, $ArCH_2Ar$), 4.83 s (4H, CH_2CO), 6.74 s (2H, H_{arom}), 6.99 s (6H, H_{arom}), 8.72 s (2H, H_{Pic}).

[IV-3Na](Pic)$_3$. ^1H NMR spectrum, δ, ppm: 0.88 s [18H, $(CH_3)_3C$], 1.28 s [18H, $(CH_3)_3C$], 3.3 d (4H, $ArCH_2Ar$, *J* 13.6 Hz), 3.65–3.91 m (48H, OCH_2CH_2O, $C\underline{H_2}CH_2N$), 4.11 d (4H, $ArCH_2Ar$, *J* 12.1 Hz), 4.91 s (4H, CH_2CO), 6.77 s (4H, H_{arom}), 7.02 s (4H, H_{arom}), 8.77 s (6H, H_{Pic}).

[IV-3K](Pic)$_3$. ^1H NMR spectrum, δ, ppm: 0.84 s [18H, $(CH_3)_3C$], 1.30 s [18H, $(CH_3)_3C$], 3.28 d (4H, $ArCH_2Ar$, *J* 13.70 Hz), 3.57–3.79 m (40H, OCH_2CH_2O, CH_2CH_2N), 4.09 m (12H, $ArCH_2Ar$, CH_2CH_2N), 4.83 s (4H, CH_2CO), 6.62 s (4H, H_{arom}), 7.02 s (4H, H_{arom}), 8.68 s (6H, H_{Pic}).

[IV-Cs](Pic). ^1H NMR spectrum, δ, ppm: 0.95 s [18H, $(CH_3)_3C$], 1.25 s [18H, $(CH_3)_3C$], 3.28 d (4H, $ArCH_2Ar$, *J* 13.45 Hz), 3.61–3.79 m (40H, OCH_2CH_2O, $C\underline{H_2}CH_2N$), 4.37 m (12H, $ArCH_2Ar$, $CH_2C\underline{H_2}N$), 4.88 s (4H, CH_2CO), 6.75 s (4H, H_{arom}), 6.97 s (4H, H_{arom}), 8.72 s (2H, H_{Pic}).

REFERENCES

1. Gutsche, C.D., *Calixarenes, An Introduction*, 2nd ed., Cambridge: RSC Publishing, 2008.
2. Creaven, B.S., Donlon, D.F., and McGinley, J., *Coord. Chem. Rev*., 2009, vol. 253, p. 893.
3. Vicens, J. and Harrowfield, J., *Calixarenes in the Tanoworld*, Dordrecht: Springer, 2007, p. 394.
4. Oueslati, I., *Tetrahedron*, 2007, vol. 63, no. 44, p. 10840.
5. Tsukanov, A.V., Dubonosov, A.D., Bren', V.A., and Minkin, V.I., *Chem. Heterocycl. Comp*., 2008, no. 8, pp. 899–923.
6. Ushakov, E.N., Alfimov, M.V., and Gromov, S.P., *Russ. Chem. Rev*., 2008, vol. 77, no. 1, p. 39.
7. Iglesias-Sanchez, J.C., Wang, W., Ferdani, R., Prados, P., de Mendoza, J., and Gokel, G.W., *New J. Chem*., 2008, vol. 32, no. 5, p. 878.
8. Yanaka, Y., Kobuke, Y., and Sokabe, M., *Angew. Chem. Int. Ed*., 1995, vol. 34, no. 6, p. 693.
9. Cacciapaglia, R., Casnati, A., DiStefano, S., Mandolini, L., Pulemili, D., Reinhoudt, D.N., Sartori, A., and Ungaro, R., *Chem. Eur. J*., 2004, vol. 10, no. 18, p. 4436.
10. Beer, P.D., Drew, M.G.B., Knubley, R.J., and Ogden, M.I., *J. Chem. Soc. Dalton Trans*., 1995, p. 3117.
11. Alekseeva, E.A., Luk'yanenko, A.P., Basok, S.S., Mazepa, A.V., and Gren', A.I., *Russ. J. Org. Chem*., 2010, vol. 46, no. 9, p. 1403–1408.
12. Vetrogon, V.I., Lukyanenko, N.G., Schwing-Weill, M.-J., and Arnaud-Neu, F., *Talanta*, 1994, vol. 41, p. 2105.
13. Bentouhami, E., Bouet, G.M., Schwing, M.-J., and Khan, M.A., *J. Solution Chem*., 2006, vol. 35, p. 889.
14. Kinard, W.F., Grant, P.M., and Baisden, P.A., *Polyhedron*, 1989, no. 8, p. 2385.
15. Roymon, J., Balaji, R., Amitabha, A., Anupam, K., and Chebrolu, P.R., *J. Org. Chem*., 2008, vol. 73, no. 15, p. 5745.
16. Casnati, A., Barboso, S., Rouquette, H., Schwing-Weill, M.-J., Arnaud-Neu, F., Dozol, J.-F., and Ungaro, R., *J. Am. Chem. Soc*., 2001, vol. 123, no. 49, p. 12182.
17. Kim, H.J., Kim, S.K., Lee, J.Y., and Kim, J.S., *J. Org. Chem*., 2006, vol. 71, no. 17, p. 6611.
18. Arnaud-Neu, F., Barrett, G., Fanni, S., Marrs, D., and McGregor, W., J. *Chem. Soc., Perkin Trans. 2*, 1995, no. 3, p. 453.