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Dedicated to Full Member of the Russian Academy of Sciences I.P. Beletskaya on Her Jubilee

Synthesis and Conformations of Adamantylated Calix[5]- and -[6]arenes

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Abstract—Procedures have been developed for the preparation of completely and partially adamantylated calix[*n*]arenes (*n* = 5, 6) by reaction of 3-R-substituted 1-hydroxyadamantanes (R = H, 4-MeC_6H_4, 4-$MeSO_2C_6H_4$, 4-HO-3-$HOCOC_6H_3$, $HOCOCH_2$) with *p*-H-calix[*n*]arenes (*n* = 5, 6) and 5,11,23,29-tetra-*tert*-butylcalix[6]arene in trifluoroacetic acid. Lower- and upper-rim modification of the prepared compounds has been studied. According to the ^1H NMR data, adamantylcalix[6]arenes possessing carboxymethyl groups in the adamantane moieties are characterized by reduced conformational mobility.

Calix[*n*]arenes are third-generation host molecules [1–3] following crown ethers and cyclodextrins. These compounds attract a keen attention of researchers engaged in the field of supramolecular chemistry, specifically concerning molecular recognition problems. Calixarenes are promising compounds for creation of molecular receptors due to the presence in their molecules of a hydrophobic aromatic cavity and the possibilities for ready functionalization of the upper and lower rims and immobilization of the macroring in a certain conformation.

Calixarenes usually acquire their useful properties via appropriate regio- and/or stereoselective functionalization of the lower-rim phenolic oxygen atoms and/or aromatic *para* positions at the upper rim [1, 2, 4]. Methods for modification of calix[4]arenes have been developed most extensively; as a result, very promising selective receptors have been synthesized. Calixarenes with a medium-size macroring (*n* = 5, 6) are expected to be more suitable than calix[4]arenes for creation of receptors for large neutral molecules and ions. However, unlike calix[4]arenes, methods for selective modification of calix[5]- and -[6]arenes and problems concerning their conformational properties have been studied to a considerably lesser extent.

The goal of the present work was to synthesize new medium-size calix[*n*]arenes (*n* = 5, 6) having adamantyl substituents on the upper rim and to study their chemical and conformatinal properties. Introduction of a bulky lipophilic group should increase the size of the hydrophobic cavity, and functional groups present in the adamantane fragment should provide the possibility for further modification and conformational organization of the molecule.

Adamantylation of *p*-H-calix[5]- and -[6]arenes. We recently showed [5–8] that calix[4]arenes undergo complete or partial adamantylation by reaction with 1-hydroxyadamantane or its 3-substituted derivatives in trifluoroacetic acid (TFA). These results prompted us to examine the reaction of 3-substituted 1-hydroxyadamantanes with *p*-H-calix[5]- and -[6]arenes in TFA. Like *p*-H-calix[4]arene, *p*-H-calix[5]- and -[6]arenes **Ia** and **Ib** reacted with 1-hydroxyadamantane (**IIa**) in TFA–$ClCH_2CH_2Cl$ (or $CHCl_3$; 1:1, by volume) to give completely adamantylated *p*-(1-adamantyl)calix[*n*]arenes **IVa** (*n* = 5) and **VIa** (*n* = 6) in high yields (see table). Exhaustive adamantylation also occurred in the reaction of *p*-H-calix[6]arene with 1-hydroxy-3-(*p*-tolyl)adamantane (**IIb**), and *p*-[3-(*p*-tolyl)-1-adamantyl]calix[6]arene (**VIb**) was obtained in 75% yield (Scheme 1).

As we noted in [6], electrophilic substitution at the *para* positions of the phenolic fragments in calix[4]arene in TFA is very sensitive to substituent in the adamantylating agent. By reaction with 1-hydroxy-3-(*p*-methylsulfonylphenyl)adamantane (**IIc**) having a strong electron-accpeptor substituent we succeeded

Adamantylation of *p*-H-calix[5]- and -[6]arenes in trifluoroacetic acid

Calixarene	1-Hydroxyadamantane, equiv.	Temperature, °C	Reaction time, h	Yield of *para*-substituted products, %				
				di	tri	tetra	penta	hexa
Ia	**IIa**, 9	55	9	–	–	–	**IVa**, 80	–
Ia	**IIc**, 7	60	6	6	32	**III**, 59	–	–
Ia	**IIc**, 7[a]	80	9	–	+	**III**, 7	**IVb**, 80	–
Ib	**IIa**, 9	55	9	–	–	–	–	**VIa**, 95
Ib	**IIb**, 12	70	8	–	–	–	–	**VIb**, 75
Ib	**IIc**, 5	50	12	21	14	10	–	–
Ib	**IIc**, 5	60	8	+	12	28	**V**, 16	–
Ib	**IIc**, 7.5	65	36	+	14	31	**V**, 35	**VIc**, 7
Ib	**IIc**, 9[a]	75	12	–	–	11	**V**, 45	**VIc**, 36
Ib	**IIc**, 9[a]	85	9	–	–	1	**V**, 7	**VIc**, 63
Ib	**IId**, 12	90	7	–	–	–	–	**VId**, 89

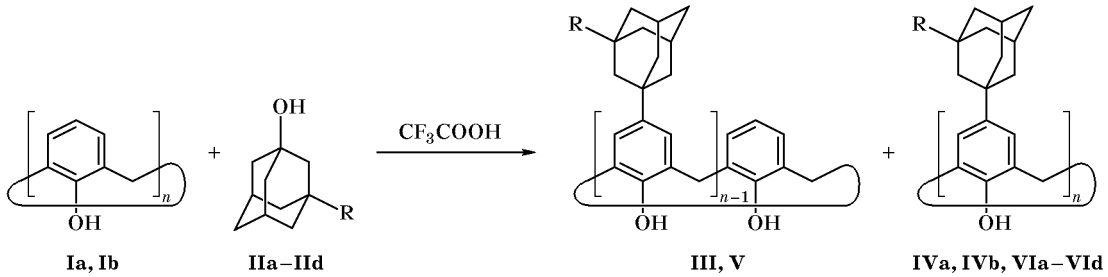
[a] In the presence of lithium perchlorate.

in obtaining partially adamantylated products. The corresponding di- and trisubstituted derivatives were isolated in preparative yields.

Selective upper-rim modification of *p*-H-calix[5]- and -[6]arenes with free lower-rim hydroxy groups has not been reported. Naturally, it was interesting to examine the possibility for selective reaction of the above macrocyclic compounds with 1-hydroxy-3-(*p*-methylsulfonylphenyl)adamantane. Depending on the reaction conditions, partially or exhaustively adamantylated derivatives can be obtained in satisfactory yield (see table). In the adamantylation of calix[6]arene **Ib**, products containing two, three, or four adamantyl groups on the upper rim were mainly formed at 50–65°C. Pentaadamantylation was observed at 70–75°C, and exhaustively adamantylated product was obtained by heating of the reaction mixture to 85°C. The two latter reactions were carried out in the presence of a catalytic amount of lithium perchlorate. The reaction mixtures were separated by column chromatography, and tetraadamantylcalix[5]-arene **III** and pentaadamantylcalix[6]arene **V** were isolated as individual compounds in fairly good yields. This is the first example of direct selective modification of the upper rim in calix[5]- and -[6]arenes having free lower-rim hydroxy groups.

Adamantylation of selectively modified calix[6]-arenes. A few known examples of selective upper-rim modification of calix[6]arenes involve either preliminary selective modification of the lower rim (which makes *para* positions of the phenolic fragments nonequivalent) or the use of partially de-*tert*-butylated calixarenes [9, 10]. Both these approaches were tried to synthesize partially adamantylated calix[6]arenes. As starting compounds we selected calixarenes **VII**–**IX**. Compounds **VII** and **VIII** are selectively acylated

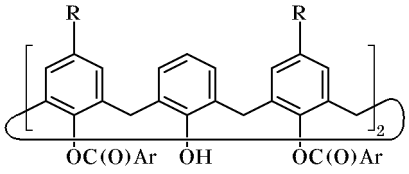
Scheme 1.



Ia, Ib **IIa–IId** **III, V** **IVa, IVb, VIa–VId**

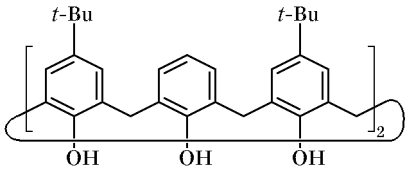
I, n = 5 (**a**), 6 (**b**); **II**, R = H (**a**), 4-MeC_6H_4 (**b**), 4-$MeSO_2C_6H_4$ (**c**), $HOCOCH_2$ (**d**); **III**, n = 5, R = 4-$MeSO_2C_6H_4$, 59%; **IV**, n = 5, R = H, 80% (**a**); n = 5, R = 4-$MeSO_2C_6H_4$, 80% (**b**); **V**, n = 6, R = 4-$MeSO_2C_6H_4$, 45%; **VI**, n = 6, R = H, 95% (**a**); n = 6, R = 4-MeC_6H_4, 75% (**b**); n = 6, R = 4-$MeSO_2C_6H_4$, 63% (**c**); n = 6, R = $HOCOCH_2$, 89% (**d**).

at the phenolic hydroxy groups. Calixarene **VII** has no upper-rim substituents, and **VIII** is partially alkylated at the upper rim. Calixarene **IX** has four *tert*-butyl groups on the upper rim and free hydroxy groups.



VII, VIII

VII, R = H, Ar = Ph; **VIII**, R = *t*-Bu, Ar = 4-$NO_2C_6H_4$.



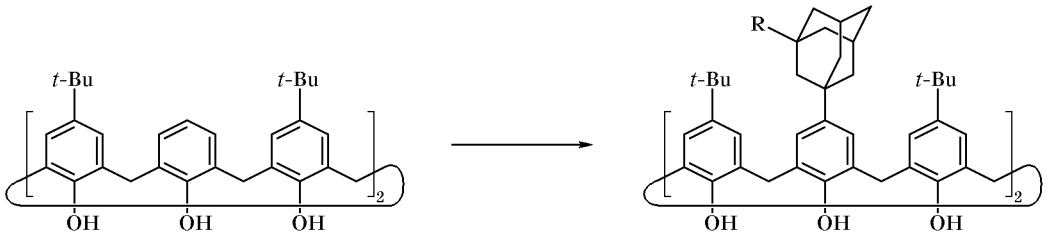
IX

It was quite surprising that calix[6]arenes **VII** and **VIII** failed to react with hydroxyadamantane in TFA, and they were quantitatively recovered from the reaction mixtures. By contrast, tetra-*p*-*tert*-butylcalix[6]-arene **IX** reacted with 1-hydroxyadamantane (**IIa**), 3-hydroxy-1-adamantylacetic acid (**IId**), and 2-hydroxy-5-(3-hydroxy-1-adamantyl)benzoic acid (**IIe**) in TFA–1,2-dichloroethane (1 : 1, by volume) to give the corresponding 5,11,23,29-tetra-*tert*-butyl-17,35-bis-(3-R-1-adamantyl)calix[6]arenes **Xa**–**Xc** in high yields (Scheme 2). It should be noted that the carboxy group in molecules **IId** and **IIe** is separated from the adamantane core by methylene or phenylene group. Our attempts to effect the reaction of **IX** with 1-hydroxyadamantane-3-carboxylic acid (**IIf**) were unsuccessful. Regardless of the reaction conditions, complex mixtures of products were obtained, which we failed to separate and identify.

Chemical transformations of adamantylated calix[6]arenes. We examined some reactions of newly synthesized adamantylcalix[6]arenes **VIa**, **VId**, and **Xb**. Using *p*-(1-adamantyl)calix[6]arene (**VIa**) as an example, we have demonstrated the possibility for both complete and selective modification of the lower rim. Like the corresponding *p*-*tert*-butylcalix[6]arene [11], compound **VIa** reacted with benzyl chloride in acetone in the presence of potassium carbonate to afford 36% of monobenzyl ether **XI**. The alkylation of **VIa** with ethyl bromoacetate according to the procedure reported in [12] gave 59% of hexa-*O*-ethoxycarbonylmethyl derivative **XII** (Scheme 3).

As a result of our study, completely and partially adamantylated calix[6]arenes having carboxy groups in the adamantane fragments (**VId** and **Xb**) became available. Taking into account that the nature of substituents, conformational parameters, and the size of

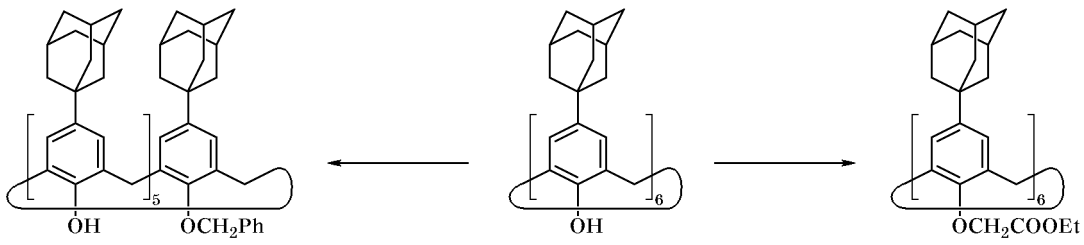
Scheme 2.



IX **Xa–Xc**

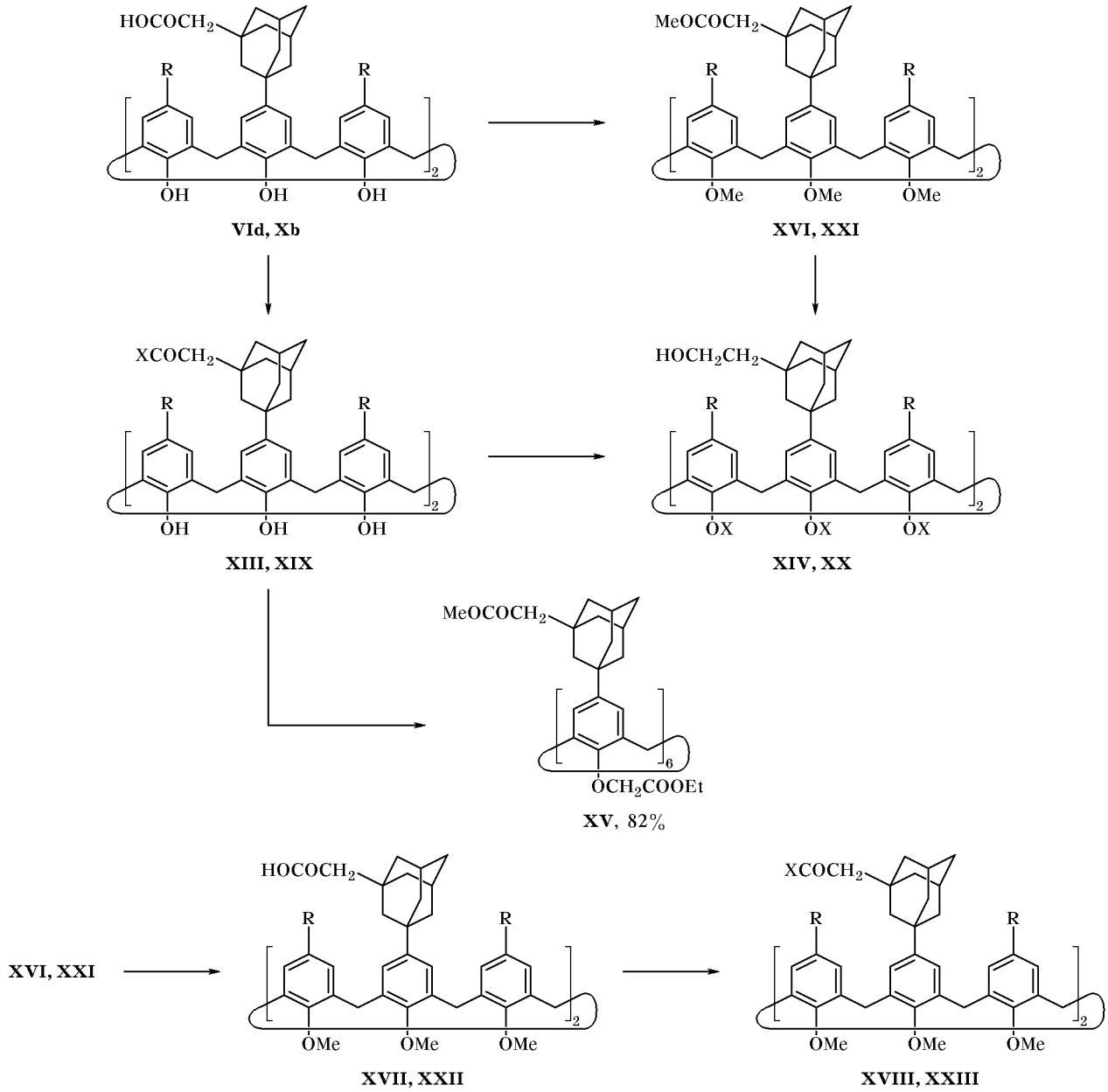
X, R = H, 56% (**a**), $HOCOCH_2$, 69% (**b**), 4-HO-3-$HOCOC_6H_3$, 65% (**c**).

Scheme 3.



XI, 36% **VIa** **XII**, 59%

Scheme 4.



VId, R = 3-HOCOCH$_2$-1-Ad; **Xb**, R = *t*-Bu; **XIII**, R = 3-HOCOCH$_2$-1-Ad, X = MeO, 94% (**a**), Et$_2$N, 98% (**b**), morpholino, 100% (**c**); **XIV**, R = 3-HOCH$_2$CH$_2$-1-Ad, X = H, 94% (**a**), Me, 84% (**b**); **XVI**, R = 3-MeOCOCH$_2$-1-Ad, 92%; **XVII**, R = 3-HOCOCH$_2$-1-Ad, 100%; **XVIII**, R = 3-HOCOCH$_2$-1-Ad, X = NH$_2$, 95% (**a**), MeOCOCH$_2$NH, 81% (**b**); **XIX**, R = *t*-Bu, X = MeO, 93% (**a**), Et$_2$N, 85% (**b**); **XX**, R = *t*-Bu, X = H, 89%; **XXI**, R = *t*-Bu, 84%; **XXII**, R = *t*-Bu, 100%; **XXIII**, R = *t*-Bu, X = piperidino, 98%.

the cavity in calixarene derivatives are crucial factors responsible for their behavior as host molecules, development of procedures for selective functionalization of the adamantane and/or phenolic fragments of the compounds under study is an important problem. Scheme 4 shows structures of some modified derivatives of carboxylic acids **VId** and **Xb**.

The carboxy groups in hexa- and dicarboxylic acids **VId** and **Xb** were modified without involving phenolic hydroxy groups via transformation into esters **XIIIa** and **XIXa** and amides **XIIIb**, **XIIIc**, and **XIXb**. Esters **XIIIa** and **XIXa** were synthesized in 94 and 59% yield, respectively, by treatment of **VId** and **Xb** with MeOH in THF under reflux in the presence of

concentrated sulfuric acid. The yield of ester **XIXa** can be increased to 93% by conversion of acid **Xb** into the corresponding dichloride and treatment of the latter with sodium methoxide in a mixture of MeOH with THF. Piperidine- and morpholine-containing derivatives **XIIIb**, **XIIIc**, and **XIXb** were obtained from the corresponding acid chlorides in anhydrous THF. Their yields were 98, 100, and 85%, respectively. Methyl esters **XIIIa** and **XIXa** were reduced to alcohols **XIVa** and **XX** by the action of $LiAlH_4$ in THF. The structure of compound **XIVa** deserves attention. Its molecule is a calixarene macrocycle with enlarged intramolecular cavity due to the presence of adamatane belt, which possesses six phenolic hydroxy groups on the lower rim and six hydroxyethyl fragments on the uppermost (adamantane) rim.

The alkylation of methyl ester **XIIIa** with ethyl bromoacetate in acetone in the presence of potassium carbonate gave hexa-*p*-(3-methoxycabonylmethyl-1-adamantyl)hexa(ethoxycarbonylmethoxy)calix[6]arene (**XV**) having 12 ester groups. The yield of **XV** was 82%. This compound is the first calixarene derivative in which ester groups are located at both upper and lower rims. Exhaustive methylation of acids **VId** and **Xb**, involving both carboxy and hydroxy groups, was effected with the aid of dimethyl sulfate in THF in the presence of sodium hydride. Products **XVI** and **XXI** were thus obtained in 92 and 84% yield, respectively. The ester groups in **XVI** and **XXI** are readily hydrolized with alcoholic alkali, affording the corresponding acids **XVII** and **XXII** in quantitative yield. The reduction of **XVI** with $LiAlH_4$ gave 84% of hydroxyethyl derivative **XIVb**.

Acids **XVII** and **XXII** were converted into acyl chlorides and then into amides **XVIIIa** (aqueous ammonia in dioxane, 95%), **XXIII** (piperidine in THF, 98%), and **XVIIIb** (glycine methyl ester hydrochloride in THF/Et_3N, 81%).

Conformations of adamantylated calix[6]arenes. Study of the conformational behavior of calixarenes is related primarily to one of the most important problems of supramolecular chemistry, molecular recognition. Conformation of the host molecule is often the principal factor in the creation of new synthetic receptors. An essential obstacle to application of medium-size calix[*n*]arenes (n = 5–8) in supramolecular chemistry is their conformational lability; therefore, conformational preorganization of such calixarenes becomes most significant. Using ^1H NMR spectroscopy we have studied the influence of adamantyl substituents on conformational properties of cyclic hexamers. *p*-Alkylcalix[6]arenes are much more conformationally labile compounds [13] than *p*-alkylcalix[4]arenes. Their coalescence temperatures (T_c) are considerably lower than ambient. For example, the coalescence temperatures of *p-tert*-butylcalix[4]arene and *p*-tert-butylcalix[6]arena in chloroform are 52°C and 11°C, respectively. Analysis of the ^1H NMR spectra at various temperatures showed that replacement of the upper-rim *tert*-butyl groups in calix[6]arene by adamantyl only slightly affects conformational mobility of the macrocycle (T_c 13°C; this value is almost the same as that found for the *tert*-butyl derivative).

It was shown previously [14, 15] that benzylation of one hydroxy group in *p-tert*-butylcalix[6]arene fixes its molecule in the *cone* conformation (T_c > 396 K in $C_2D_2Cl_4$). Mutual *syn* orientation of the phenolic fragments in this compound is held by a system of hydrogen bonds between the lower-rim hydroxy groups, including the benzylated oxygen atom. This conclusion was drawn on the basis of the

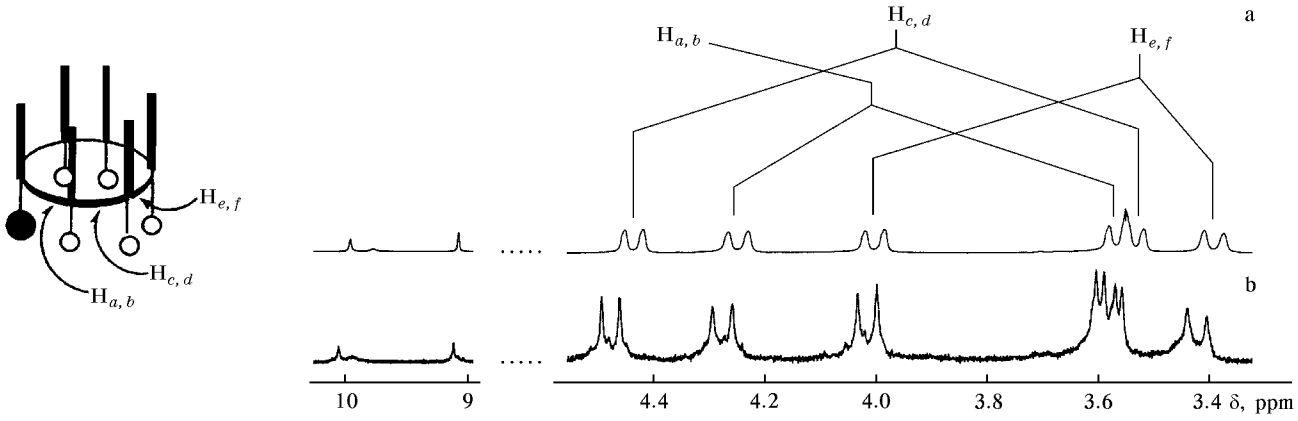
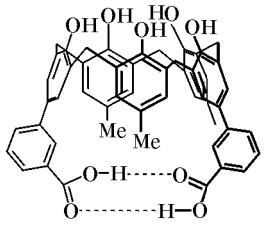


Fig. 1. Resonance signals from protons of the hydroxy and methylene groups in (a) monobenzylated *p-tert*-butylcalix[6]arene and (b) compound **XI**.

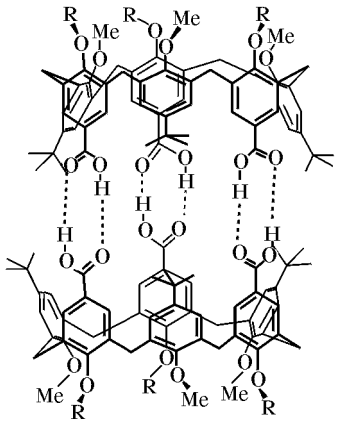
^{1}H NMR spectra. The *cone* conformer (Fig. 1a) was found to display in the spectrum three pairs of doublets corresponding to methylene groups. The distances between the pairs were sufficiently large: 0.90 (H_a, H_b), 0.69 (H_c, H_d), and 0.61 ppm (H_e, H_f) (at 25°C). The ^{1}H NMR spectrum of calix[6]arene **XI** at 25°C (Fig. 1b) also contains three pairs of doublets located at δ 4.47/3.56, 4.28/3.59, and 4.01/3.42 ppm, and the distances between them are very similar to those found for the *tert*-butyl derivative: 0.91 ppm for H_a/H_b, 0.69 ppm for H_c/H_d, and 0.59 ppm for H_e/H_f. The observed analogy between resonance signals of the methylene protons and protons of the hydroxy groups involved in hydrogen bonding for calix[6]-arene **XI** and *tert*-butylcalixarene led us to conclude that monobenzylated *p*-(1-adamantyl)calix[6]arene **XI** is also fixed in the *cone* conformation.

A possible way of reducing the conformational mobility of calixarenes consists of modification of the upper rim with functional groups capable of participating in nonvalence interactions, e.g., in intramolecular hydrogen bonding. Systematic studies on that topic were not performed, although the ability of, e.g., carboxy groups to form intra- and intermolecular hydrogen bonds should necessarily affect conformational behavior of the macroring.

As concerns calix[5]- and -[6]arenes, Haino *et al.* reported on reduction of conformational mobility in calix[5]arene **XXIV** as a result of formation of intramolecular hydrogen bonds between two benzoic acid fragments on the upper rim. The formation of self-assembled molecular cages by calix[6]arenetricarboxylic acid derivatives **XXV** via intermolecular hydrogen bonds was described in [17, 18].



XXIV



XXV

XXV, R = Me, C_8H_{17}.

Some calix[6]arenes synthesized in the present work contain carboxymethyl substituents in the adamantane fragments, which are capable of forming intra- and intermolecular hydrogen bonds. Due to the presence of polar groups, these compounds are readily soluble in water and aqueous alcohol at pH 8–10; nevertheless, lipophilic adamantane fragments in *p*-(3-carboxymethyl-1-adamantyl)calix[6]arene (**VId**) and 5,11,23,29-tetra-*tert*-butyl-17,35-bis(3-carboxymethyl-1-adamantyl)calix[6]arene (**Xb**) make them soluble to a sufficient extent in chloroform (up to a concentration of 15–20 mg/ml). Therefore, we were able to examine their conformational behavior in weakly polar organic media.

According to published data [19], at 293 K *p*-*tert*-butylcalix[6]arene exists mainly in completely asymmetric *winged cone* conformation (Fig. 2) in which four aromatic rings are oriented downward, forming a cavity, while the remaining two distal aromatic rings are arranged almost orthogonally to the above four.

Figure 3 shows the ^{1}H NMR spectrum of *p*-(3-carboxymethyl-1-adamantyl)calix[6]arene (**VId**). The observed pattern in the region of methylene and phenolic proton signals suggests that even at room temperature conformational mobility of this compound is strongly limited and that it also has a *winged cone* conformation. Presumably, this conformer is stabilized through formation of intramolecular hydrogen bonds. In order to exclude probable stabilization via intermolecular interactions, we recorded the ^{1}H NMR spectra of **VId** in the concentration range from 1.20 to 14.4 mM. The signals did not change their position throughout the examined range of concentration, indicating that intermolecular hydrogen bonds are not formed. The coalescence temperature of hexacarboxylic acid **VId** was estimated at ~60°C, i.e., it is typical of calix[4]-arenes (Fig. 4).

The ^{1}H NMR spectra of 5,11,23,29-tetra-*tert*-butyl-17,35-bis(3-carboxymethyl-1-adamantyl)calix[6]arene (**Xb**) and its methyl derivatives **XIXa**, **XXI**, and **XXII**, recorded at 25°C, revealed considerable reduction of conformational mobility only for dicarboxylic acid **Xb**. As follows from the ArC**H**$_2$Ar signal pattern, the coalescence temperature of **Xb** is higher than

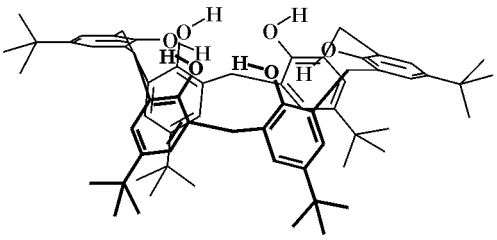


Fig. 2. *Winged cone* conformation of *p*-*tert*-butylcalix[6]-arene at 223 K.

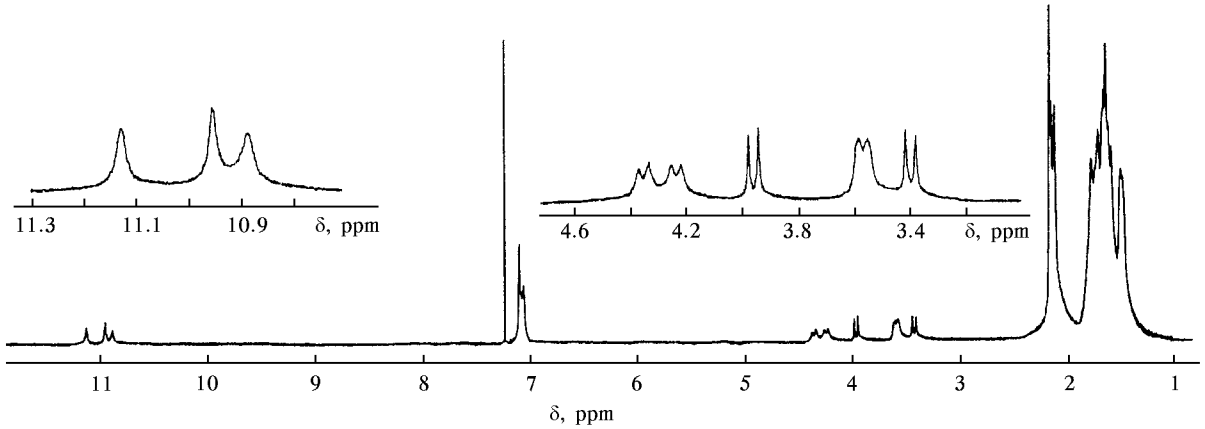


Fig. 3. ^{1}H NMR spectrum of *p*-(3-carboxymethyl-1-adamantyl)calix[6]arene (**VId**) at 298 K.

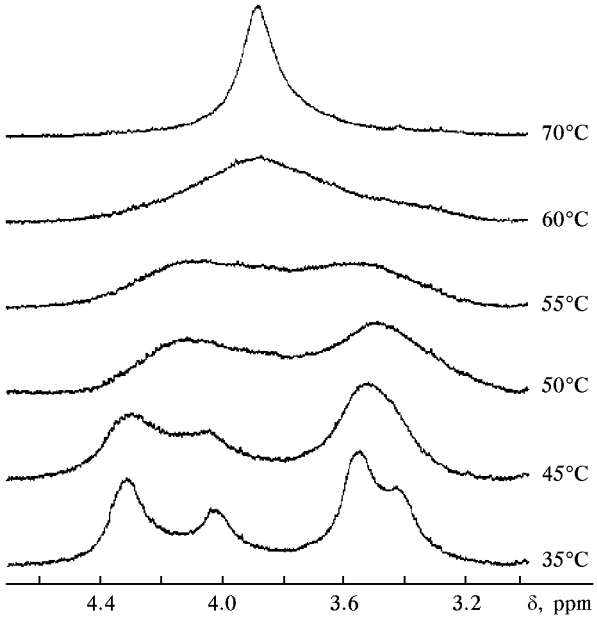


Fig. 4. Temperature dependence of the ^{1}H NMR spectrum of *p*-(3-carboxymethyl-1-adamantyl)calix[6]arene (**VId**) in the region of methylene proton signals.

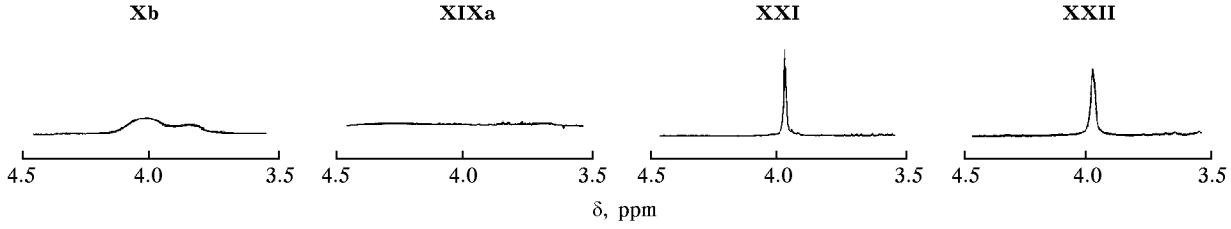


Fig. 5. Methylene proton signals in the ^{1}H NMR spectra of compounds **Xb**, **XIXa**, **XXI**, and **XXII** at 298 K.

25°C. Selective methylation of the upper-rim carboxy groups (compound **XIXa**) increases the mobility of the macroring ($T_c \approx 25$°C). Methylation of the lower-rim hydroxy groups (compounds **XXI** and **XXII**) considerably increases the conformational mobility: compounds **XXI** and **XXII** show in the ^{1}H NMR spectra sharp singlets in the region corresponding to methylene protons (Fig. 5).

Thus our results indicate a unigue reduction of conformational mobility of calix[6]arenes on intro-

duction of 3-carboxymethyl-1-adamantyl substituents at the upper rim. This reduction becomes appreciable even if only two carboxymethyl groups are present. *p*-(3-Carboxymethyl-1-adamantyl)calix[6]arene (**VId**) is characterized by the maximal coalescence temperature among known calix[6]arenes with free lower-rim hydroxy groups. Such compounds are the first examples demonstrating restriction of conformational mobility of calix[6]arenes through intramolecular H-bonding between functional groups located on the upper rim.

EXPERIMENTAL

The ^{1}H and ^{13}C NMR spectra were recorded on a Varian VRX-300 spectrometer (300 and 75.4 MHz, respectively) using $CDCl_3$ and DMSO-d_6 as solvents and tetramethylsilane as internal reference. Preparative column chromatography was performed on Silicagel 40/60. Silufol-254 and DC Alufolien Kieselgel 60 F254 (Merck) plates were used for TLC analysis; spots were visualized under UV light. *p*-H-Calix[5]-arene (**Ia**) [20], *p*-H-calix[6]arene (**Ib**) [21], 1-hydroxyadamantane (**IIa**) [22], 1-hydroxy-3-(4-methylphenyl)adamantane (**IIb**) [23], 1-hydroxy-3-(4-methylsulfonylphenyl)adamantane (**IIc**) [5], 3-hydroxy-1-adamantylacetic acid (**IId**) [24], 2-hydroxy-5-(3-hydroxy-1-adamantyl)benzoic acid (**IIe**) [5], 3-hydroxyadamantane-1-carboxylic acid (**IIf**) [25], 37,38,40,41-tetrabenzoyloxy-39,42-dihydroxycalix[6]arene (**VII**) [26], 11,17,29,35-tetra-*tert*-butyl-39,42-dihydroxy-37,38,40,41-tetrakis(4-nitrobenzoyloxy)calix[6]arene (**VIII**) [27], and 5,11,23,29-tetra-*tert*-butylcalix[6]-arene (**IX**) [28] were synthesized by known methods. All solvents used were dehydrated and purified by standard procedures.

General procedure for adamantylation of calixarenes Ia, Ib, and IX. The reactions were carried out in a round-bottom flask equipped with a reflux condenser (capped by a drying tube) and a system for supplying argon. The flask was charged with appropriate calixarene, adamantylating agent, and co-solvent and was filled with argon. Trifluoroacetic acid and, if necessary, lithium perchlorate were then added. The molar ratio calixarene–adamantylating agent–TFA was usually 1:(5–12):(50–120). The volume of the added solvent (1,2-dichloroethane or chloroform) was equal to the volume of trifluoroacetic acid. Lithium perchlorate was taken in an amount of 1×10^{-2} mol per mole of calixarene. The mixture was heated at a required temperature (see table) on an oil bath under continuous stream of argon. The progress of reactions was monitored by TLC. When the reaction was complete, the mixture was evaporated to dryness under reduced pressure, the residue was treated with water, and the precipitate was filtered off and washed with methanol.

General procedure for preparation of carboxylic acid chlorides (from acids VId, Xb, and XVII). A mixture of carboxylic acid, dry benzene, and thionyl chloride was refluxed for 2 h and cooled. Excess thionyl chloride and solvent were distilled off under reduced pressure at 30–35°C. Dry benzene was added to the residue and was distilled off under reduced pressure. The procedure was repeated three times. The solid residue was used in further syntheses without additional purification.

Tetra-*p*-[3-(*p*-methylsulfonylphenyl)-1-adamantyl]calix[5]arene (III) was synthesized from 0.27 g (0.5 mmol) of calix[5]arene **Ia**, 1.07 g (3.5 mmol) of 1-hydroxy-3-(*p*-methylsulfonylphenyl)-adamantane (**IIc**), and 2.7 ml (35 mmol) of trifluoroacetic acid. The solid residue was subjected to column chromatography using benzene–chloroform as eluent (gradient elution). Yield 0.51 g (59%), mp 185–186°C, R_f 0.65 (chloroform–benzene, 2:1). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: adamantane fragments: 156.80, 156.75 (1:1, C_{arom}); 137.63, 137.78 (1:1, C_{arom}); 127.17 (CH_{arom}); 125.93, 125.84 (1:1, CH_{arom}); 44.44 ($MeSO_2$); 36.33 (C^1); 48.77, 48.65 (1:1, C^2); 37.82, 37.78 (1:1, C^3); 42.10 br.s (C^4, C^8)*; 29.19 (C^5, C^7); 35.45 (C^6); 41.92 (C^9, C^{10})*; cavity: 149.91, 147.87, 147.78, 143.10, 143.06 (C_{arom}); 129.01 (CH_{arom}); 126.66, 126.39, 126.35, 126.33, 126.01 (C_{arom}); 125.27, 125.19, 125.14, 121.40 (CH_{arom}); 31.54 (CH_2). Found, %: C 74.02; H 7.70. $C_{103}H_{110}O_{13}S_4$. Calculated, %: C 73.45; H 7.61.

Penta-*p*-(1-adamantyl)calix[5]arene (IVa) was synthesized from 0.27 g (0.5 mmol) of calix[5]arene **Ia**, 0.68 g (4.5 mmol) of 1-hydroxyadamantane (**IIa**), and 2.1 ml (27 mmol) of trifluoroacetic acid. The residue (obtained after evaporation of the reaction mixture) was washed with boiling methanol. Yield 0.49 g (80%), mp 340–342°C, R_f 0.55 (chloroform–hexane, 2:1). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 9.72 s (5H, OH), 7.18 s (12H, H_{arom}), 4.00–3.70 br.s (10H, $ArCH_2Ar$), 2.07 s (15H, CH, Ad), 1.82 s (30H, CH_2, Ad), 1.67 s (30H, CH_2, Ad). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: adamantane fragments: 35.52 (2:1, C^1), 43.29 (2:1, C^2, C^8, C^9), 28.96 (C^3, C^5, C^7), 36.77 (C^6); cavity: 147.29, 144.51, 127.85 (C_{arom}),

* Hereinafter, alternative assignment is possible for the signals marked with an asterisk.

125.74 (CH_{arom}); 33.09 ($ArCH_2Ar$). Found, %: C 85.13; H 8.45. $C_{85}H_{100}O_5$. Calculated, %: C 84.96; H 8.39.

Penta-*p*-[3-(*p*-methylsulfonylphenyl)-1-adamantyl]calix[5]arene (IVb) was synthesized from 0.27 g (0.5 mmol) of calix[5]arene **Ia**, 1.07 g (3.5 mmol) of 1-hydroxy-3-(*p*-methyl-sulfonylphenyl)-adamantane (**IIc**), and 2.7 ml (35 mmol) of trifluoroacetic acid. The solid residue was subjected to column chromatography using benzene–chloroform as eluent (gradient elution). Yield 0.8 g (80%), mp 238–240°C (decomp.), R_f 0.60 (chloroform–benzene, 2:1). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 8.64 s (5H, OH), 7.79 d (10H, H_{arom}), 7.50 d (10H, H_{arom}), 7.18 s (10H, H_{arom}), 4.10 br.s (5H, $ArCH_2Ar$), 3.55 br.s (5H, $ArCH_2Ar$), 2.95 s (15H, SO_2Me), 2.23 br.s (10H, CH, Ad), 1.95–1.70 m (60H, CH_2, Ad). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: adamantane fragments: 156.71 (C_{arom}); 137.59 (C_{arom}); 127.10, 125.80 (CH_{arom}); 44.37 ($MeSO_2$); 36.28 (C^1); 48.63 (C^2); 37.73 (C^3); 42.05 (C^4, C^8)*; 29.14 (C^5, C^7); 35.40 (C^6); 41.87 (C^9, C^{10})*; cavity: 147.73, 142.98, 126.26 (C_{arom}); 125.07 (CH_{arom}); 31.49 ($ArCH_2Ar$). Found, %: C 73.98; H 6.70. $C_{120}H_{130}O_{15}S_5$. Calculated, %: C 73.06; H 6.64.

Penta-*p*-[3-(*p*-methylsulfonylphenyl)-1-adamantyl]calix[6]arene (V) was synthesized from 0.32 g (0.5 mmol) of calix[6]arene **Ib**, 1.07 g (3.5 mmol) of 1-hydroxy-3-*p*-methylsulfonylphenyl-adamantane (**IIc**), and 2.7 ml (35 mmol) of trifluoroacetic acid. The solid residue was subjected to column chromatography using benzene–chloroform as eluent (gradient elution). Yield 0.47 g (45%), mp 245–247°C, R_f 0.70 (chloroform–benzene, 2:1). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: adamantane fragments: 156.82 (C_{arom}); 137.76 (C_{arom}); 127.22 (CH_{arom}); 125.92 (CH_{arom}); 44.48 ($MeSO_2$); 36.52 (C^1); 48.88 (C^2); 37.88 (C^3); 42.09 br.s (C^4, C^8)*; 29.29 (C^5, C^7); 35.53 (C^6); 42.02 (C^9, C^{10})*; cavity: 147.59, 143.46 (C_{arom}); 125.67 (CH_{arom}); 32.60 br.s ($ArCH_2Ar$). Found, %: C 74.12; H 6.63. $C_{127}H_{136}O_{16}S_5$. Calculated, %: C 73.38; H 6.59.

Hexa-*p*-(1-adamantyl)calix[6]arene (VIa) was synthesized from 0.32 g (0.5 mmol) of calix[6]arene **Ib**, 2.1 g (4.5 mmol) of 1-hydroxyadamantane, and 2.1 ml (27 mmol) of trifluoroacetic acid. The residue was washed with boiling methanol. Yield 0.69 g (95%), mp >400°C, R_f 0.6 (chloroform–hexane, 2:1). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 10.53 s (6H, OH), 7.12 s (12H, H_{arom}), 4.30–3.50 br.s (12H, $ArCH_2Ar$), 2.10 s (18H, CH, Ad), 1.85 s (36H, CH_2, Ad), 1.68 s (36H, CH_2, Ad). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: adamantane fragments: 35.48 (2:1, C^1); 43.25 (2:1, C^2, C^8, C^9); 28.93 (C^3, C^5, C^7); 36.74 (C^6); cavity: 147.26, 144.49, 126.82 (C_{arom}); 125.71 (CH_{arom}); 33.04 ($ArCH_2Ar$). Found, %: C 85.21; H 8.43. $C_{102}H_{120}O_6$. Calculated, %: C 84.96; H 8.39.

Hexa-*p*-[3-(*p*-tolyl)-1-adamantyl]calix[6]arene (VIb) was obtained from 0.32 g (0.5 mmol) of calix-[6]arene **Ib**, 1.45 g (6.0 mmol) of 1-hydroxy-3-(*p*-tolyl)adamantane (**IIb**), and 4.6 ml (60 mmol) of trifluoroacetic acid. The residue was washed with boiling methanol. Yield 0.74 g (75%), mp 233–235°C, R_f 0.55 (chloroform–hexane, 2:1). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: adamantane fragments: 147.67 (C_{arom}); 134.93 (C_{arom}); 128.72, 124.60 (CH_{arom}); 20.80 (Me); 36.54 (C^1)*; 49.05 (C^2); 36.79; (C^3)*; 42.28 br.s (C^4, C^8, C^9, C^{10}); 29.49 (C^5, C^7); 35.78 (C^6); cavity: 146.50, 143.93 br.s, 126.95 (C_{arom}); 125.70 br.s (CH_{arom}); 32.90 br.s ($ArCH_2Ar$). Found, %: C 87.98; H 7.97. $C_{144}H_{156}O_6$. Calculated, %: C 87.23; H 7.93.

Hexa-*p*-[3-(*p*-methylsulfonylphenyl)-1-adamantyl]calix[6]arene (VIc) was synthesized from 0.32 g (0.5 mmol) of calix[6]arene **Ib**, 1.38 g (4.5 mmol) of 1-hydroxy-3-(*p*-methylsulfonylphenyl)-adamantane (**IIc**), and 3.5 ml (45 mmol) of trifluoroacetic acid. The solid residue was subjected to column chromatography using benzene–chloroform as eluent (gradient elution). Yield 0.75 g (63%), mp 288–290°C (decomp.), R_f 0.50 (chloroform–benzene, 2:1). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 8.64 s (5H, OH), 7.79 d (10H, H_{arom}), 7.50 d (10H, H_{arom}), 7.18 s (10H, H_{arom}), 4.10 br.s (5H, $ArCH_2Ar$), 3.55 br.s (5H, $ArCH_2Ar$), 2.95 s (15H, SO_2Me), 2.23 br.s (10H, CH, Ad), 1.95–1.70 m (60H, CH_2, Ad). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: adamantane fragments: 156.68 (C_{arom}); 137.62 (C_{arom}); 127.06, 125.80 (CH_{arom}); 44.32 ($MeSO_2$); 36.38 (C^1); 48.75 (C^2); 37.74 (C^3); 41.93 (C^4, C^8)*; 29.14 (C^5, C^7); 35.38 (C^6); 41.86 (C^9, C^{10})*; cavity: 147.50, 143.35, 127.0 (C_{arom}); 125.55 (CH_{arom}); 32.77 ($ArCH_2Ar$). Found, %: C 73.87; H 6.68. $C_{144}H_{156}O_{18}S_6$. Calculated, %: C 73.06; H 6.64.

Hexa-*p*-(3-carboxymethyl-1-adamantyl)calix[6]-arene (VId) was synthesized from 0.53 g (0.83 mmol) of calix[6]arene **Ib**, 1.58 g (7.5 mmol) of 3-hydroxy-1-adamantylacetic acid (**IId**), 5 ml (65 mmol) of trifluoroacetic acid, and 5 ml of 1,2-dichloroethane. The residue was washed with boiling methanol. Yield 1.33 g (89%), mp 343–345°C, R_f 0.4 (chloroform–ethanol, 20:1). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 10.82 m (6H, OH); 7.06 br.s (12H, H_{arom}); 4.30 d,

4.00 d, 3.55 d, 3.40 d (12H, $ArCH_2Ar$); 2.15 br.s (12H, CH, Ad; 12H, CH_2COOH); 1.90–1.40 m (72H, CH_2, Ad). ^{13}C NMR spectrum (DMSO-d_6), δ_C, ppm: adamantane fragments: 172.50 (COOH); 48.28 (CH_2COOH); 32.95 (C^1); 48.44 (C^2); 35.93 (C^3); 42.20 (C^4, C^8)*; 28.85 (C^5, C^7); 35.59 (C^6); 40.96 (C^9, C^{10})*; cavity: 149.04, 141.85, 127.42 (C_{arom}); 124.74 (CH_{arom}); 31.18 ($ArCH_2Ar$). Found, %: C 75.80; H 7.52. $C_{114}H_{132}O_{18}$. Calculated, %: C 76.48; H 7.43.

17,35-Bis(1-adamantyl)-5,11,23,29-tetra-*tert*-butylcalix[6]arene (Xa) was synthesized from 0.43 g (0.5 mmol) of calix[6]arene **IX** and 0.3 g (2 mmol) of 1-hydroxyadamantane (**IIa**) in a mixture of 3 ml (39 mmol) of trifluoroacetic acid and 3 ml of 1,2-dichloroethane in the presence of lithium perchlorate. The mixture was heated for 14 h at 65°C. The residue was washed with methanol and subjected to column chromatography using chloroform–hexane (1:1) as eluent. Yield 0.32 g (56%), mp 340–342°C, R_f 0.45 (chloroform–hexane, 3:4). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 10.53 s (6H, OH), 7.14 s (8H, H_{arom}), 7.11 s (4H, H_{arom}), 4.30–3.20 br.s (12H, $ArCH_2Ar$), 2.09 br.s (4H, CH, Ad), 1.86 br.s (12H, CH_2, Ad), 1.75 s (12H, CH_2, Ad), 1.30 s (36H, *t*-Bu). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: adamantane fragments: 35.46 (C^1); 43.26 (C^2, C^8, C^9); 28.92 (C^3, C^5, C^7); 36.72 (C^4, C^6, C^{10}); *t*-Bu: 33.93, 31.44; cavity: 147.18 br.s, 144.52, 144.14, 126.84 (C_{arom}); 126.14, 126.05, 125.68 (CH_{arom}); 33.05, 33.87 (2:1, $ArCH_2Ar$). Found, %: C 83.54; H 8.63. $C_{78}H_{96}O_6$. Calculated, %: C 82.94; H 8.57.

5,11,23,29-Tetra-*tert*-butyl-17,35-bis(3-carboxymethyl-1-adamantyl)calix[6]arene (Xb) was synthesized from 0.5 g (0.58 mmol) of calix[6]arene **IX** and 0.49 g (2.32 mmol) of 3-hydroxy-1-adamantylacetic acid (**IId**) in a mixture of 5 ml (65 mmol) of trifluoroacetic acid and 5 ml of 1,2-dichloroethane. The residue was washed with methanol and dissolved in a minimal amount of chloroform. The product was precipitated with hexane or isolated by column chromatography using chloroform–ethanol (20:1) as eluent. Yield of **Xb** 0.5 g (69%), mp 276–278°C, R_f 0.45 (chloroform–ethanol, 20:1). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 10.50 s (6H, OH), 7.13 s (8H, H_{arom}), 7.09 s (4H, H_{arom}), 4.30–3.40 m (12H, $ArCH_2Ar$), 2.16 br.s (4H, CH, Ad; 4H, CH_2COOH), 1.80–1.60 m (24H, CH_2, Ad), 1.22 s (36H, *t*-Bu). ^{13}C NMR spectrum (DMSO-d_6), δ_C, ppm: adamantane fragments: 172.41 (COOH); 48.19 (CH_2COOH); 32.88 (C^1); 48.30 (C^2); 35.79 (C^3); 42.10 (C^4, ^{10}); 28.70 (C^3, C^7); 35.52 (C^6); 40.86 (C^8, C^9); *t*-Bu: 34.43, 31.35; cavity: 149.19, 148.93, 141.60, 141.50, 127.26, 127.21, 127.15 (C_{arom}); 125.07, 124.71 (CH_{arom}); 31.01 ($ArCH_2Ar$). Found, %: C 77.90; H 8.04. $C_{82}H_{100}O_{10}$. Calculated, %: C 79.06; H 8.09.

5,11,23,29-Tetra-*tert*-butyl-17,35-bis[3-(3-carboxy-4-hydroxyphenyl)-1-adamantyl]calix[6]arene (Xc) was synthesized from 0.5 g (0.58 mmol) of calix[6]arene **IX** and 0.37 g (1.28 mmol) of 2-hydroxy-5-(3-hydroxy-1-adamantyl)benzoic acid (**IIe**) in a mixture of 5 ml (65 mmol) of trifluoroacetic acid and 5 ml of 1,2-dichloroethane. Yield 0.53 g (65%), mp 288–290°C, R_f 0.4 (chloroform–ethanol, 20:1). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 10.52 s (6H, OH), 7.89 br.s (2H, H_{arom}), 7.58 d (2H, H_{arom}), 7.16 br.s (12H, H_{arom}), 6.97 d (2H, H_{arom}), 4.40–3.30 br.s (12H, $ArCH_2Ar$), 2.32 br.s (4H, CH, Ad), 1.95–1.75 m (24H, CH_2, Ad), 1.25 s (36H, *t*-Bu). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: adamantane fragments: 174.88 (COOH); 160.26, 142.11 (C_{arom}); 134.16, 125.81, 117.52 (CH_{arom}); 110.69 (C_{arom}); 36.75 (C^1)*; 49.19 (C^2); 36.63 (C3)*; 42.40 (C^4, C^8)*; 29.53 (C^5, C^7); 35.76 (C^6); 41.93 (C^9, C^{10})*; *t*-Bu: 34.05, 31.54; cavity: 147.33, 144.35, 143.71, 129.36 (C_{arom}); 127.02, 126.81, 126.24 (CH_{arom}); 33.01 ($ArCH_2Ar$). Found, %: C 80.64; H 7.38. $C_{92}H_{104}O_{12}$. Calculated, %: C 78.83; H 7.48.

5,11,17,23,29,35-Hexa(1-adamantyl)-37-benzyl-38,39,40,41,42-pentahydroxycalix[6]arene (XI). A mixture of 0.29 g (0.2 mmol) of calix[6]arene **VIa**, 0.031 g (0.224 mmol) of potassium carbonate, and 30 ml of anhydrous acetone was heated for 2 h under reflux with stirring under dry nitrogen. The mixture was cooled, 0.026 ml (0.224 mmol) of benzyl chloride was added, the mixture was heated for 20 h under reflux with stirring and cooled, and 2 ml of aqueous ammonia (25%) was added. The mixture was acidified with 5% hydrochloric acid and extracted with methylene chloride. The combined extracts were washed with water until neutral reaction, dried over magnesium sulfate, and evaporated, and the residue was subjected to column chromatography using chloroform–hexane (2:1) as eluent. Yield 0.11 g (36%), mp 261–263°C (decomp.), R_f 0.35 (chloroform–hexane, 1:1). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 10.04 s (2H, OH), 9.95 br.s (1H, OH), 9.12 s (2H, OH), 7.78 d (2H, H_{arom}), 7.64 t (2H, H_{arom}), 7.45 t (1H, H_{arom}), 7.16 s (12H, H_{arom}), 7.13 s (6H, H_{arom}), 7.11 s and 7.08 s (2H, H_{arom}), 5.21 s (2H, CH_2Ph), 4.47 d (2H, $ArCH_2Ar$), 4.28 d (2H, $ArCH_2Ar$), 4.01 d (2H, $ArCH_2Ar$), 3.59 d (2H, $ArCH_2Ar$), 3.56 d (2H, $ArCH_2Ar$), 3.42 d (2H, $ArCH_2Ar$), 2.18–2.03 m (18H, CH, Ad), 1.90–1.60 m

(72H, CH_2, Ad). Found, %: C 87.24; H 8.37. $C_{109}H_{126}O_6$. Calculated, %: C 85.45; H 8.28.

5,11,17,23,29,35-Hexakis(1-adamantyl)-37,38,-39,40,41,42-hexakis(ethoxycarbonylmethoxy)calix-[6]arene (XII). A mixture of 0.66 g (0.46 mmol) of calix[6]arene **VIa** and 2.28 g (16.5 mmol) of K_2CO_3 in 30 ml of anhydrous acetone was refluxed for 10 min under stirring in a stream of dry nitrogen. It was then cooled, 1.82 ml (16.5 mmol) of ethyl bromoacetate was added, and the mixture was refluxed for 9 h under stirring in a stream of dry nitrogen and cooled to –12°C. The precipitate was filtered off and washed with 20 ml of acetone cooled to –12°C. The residue was washed on a filter with water, 3 N hydrochloric acid, and water again (until neutral reaction) and dried to obtain 0.32 g of compound **XII**. The acetone extract was evaporated until a glassy material was obtained. Acetone, 3 ml, was added, the mixture was cooled to –12°C, and the precipitate was washed with 8 ml of cold acetone and water, and dried to isolate an additional 0.21 g of compound **XII**. Yield 59%, mp 322–324°C, R_f 0.5 (chloroform–ethanol, 20:1). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 7.19 s (6H, OH), 4.40–3.65 m (12H, CH_2COOEt; 12H, $ArCH_2Ar$; 12H, CH_2Me), 2.08 s (18H, CH, Ad), 1.92–1.60 m (72H, CH_2, Ad), 1.10 br.s (18H, Me). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: adamantane fragments: 35.57 (2:1, C^1), 43.15 (2:1, C^2, C^8, C^9), 28.90 (C^3, C^5, C^7), 36.72 (C^6); ester: 168.95 (COOEt), 69.90 (CH_2COOEt), 60.28 ($COOCH_2Me$), 13.85 (Me); cavity: 152.62, 145.75, 132.09 (C_{arom}); 126.01 (CH_{arom}). Found, %: C 78.01; H 8.10. $C_{126}H_{156}O_{18}$. Calculated, %: C 77.27; H 8.03.

Hexa-*p*-(3-methoxycarbonylmethyl-1-adamantyl)calix[6]arene (XIIIa). A mixture of 1.79 g (1 mmol) of calix[6]arene **VId**, 16 ml (395 mmol) of methanol, 0.5 ml (9.39 mmol) of 98% sulfuric acid, and 30 ml of THF was heated for 15 h under reflux. The progress of the reaction was monitored by TLC. When the reaction was complete, the mixture was evaporated to dryness, the residue was treated with water, and the precipitate was filtered off and washed on a filter with water, hot isopropyl alcohol, and methanol. Yield 1.77 g (94%), mp 333–337°C, R_f 0.85 (chloroform–ethanol, 20:1). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 10.53 s (6H, OH), 7.17 s (12H, H_{arom}), 4.30–3.50 br.s (12H, $ArCH_2Ar$), 3.68 s (18H, COOMe), 2.21 s (12H, CH, Ad; 12H, CH_2COOMe), 1.90–1.60 m (72H, CH_2, Ad). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: adamantane fragments: 171.96 (COOMe), 51.05 ($COOMe$), 48.93 (CH_2COOMe), 33.67 (C^1), 48.41 (C^2), 36.38 (C^3), 42.33 (C^4, C^8),* 29.21 (C^5, C^7), 35.80 (C^6), 41.39 (C^9, C^{10})*; cavity: 147.50, 143.72, 126.97 (C_{arom}); 125.81 (CH_{arom}); 33.00 ($ArCH_2Ar$). Found, %: C 77.38; H 7.81. $C_{120}H_{144}O_{18}$. Calculated, %: C 76.89; H 7.74.

Hexa-*p*-(3-piperidinocarbonylmethyl-1-adamantyl)calix[6]arene (XIIIb). Calix[6]arene **VId**, 0.2 g (0.16 mmol) was converted into the corresponding acid chloride by treatment with 4 ml (55 mmol) of thionyl chloride in 8 ml of benzene (see general procedure given above). The product was dissolved in 10 ml of anhydrous THF, 0.94 ml (9.6 mmol) of piperidine was added, and the mixture was stirred for 2 h and was left to stand overnight. The precipitate was filtered off and washed on a filter with THF. The filtrate was evaporated, the residue was treated with water, and the precipitate was filtered off, washed on a filter with water, dried, and washed with ether. Yield 0.24 g (98%), mp 224–226°C (decomp.), R_f 0.45 (chloroform–ethanol, 20:1). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 6.99 br.s (12H, H_{arom}), 3.90–3.50 br.s (12H, $ArCH_2Ar$), 3.53 br.s (24H, NCH_2), 3.42 br.s (24H, $NCH_2C\mathbf{H}_2$), 2.19 s (12H, CH, Ad),* 2.13 s (12H, CH_2CON),* 1.85–1.45 m (72H, CH_2, Ad; 12H, $NCH_2CH_2C\mathbf{H}_2$). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: adamantane fragments: 169.22 (CON); 47.81 (CH_2CON); 45.59 (NCH_2); 26.37, 25.55 ($NCH_2\mathbf{C}H_2$); 24.35 ($NCH_2CH_2\mathbf{C}H_2$); 34.40 (C^1); 49.22 (C^2); 36.17 (C^3); 42.36 (C^4, C^8)*; 29.18 (C^5, C^7); 35.74 (C^6); 41.64 (C^9, C^{10})*; cavity: 141.50 br.s, 127.80 br.s (C_{arom}); 124.82 (CH_{arom}). Found, %: C 79.14; H 8.58; N 3.78. $C_{144}H_{186}N_6O_{12}$. Calculated, %: C 78.87; H 8.55; N 3.83.

Hexa-*p*-(3-morpholinocarbonylmethyl-1-adamantyl)calix[6]arene (XIIIc). Calix[6]arene **VId**, 0.2 g (0.16 mmol) was converted into the corresponding acid chloride by treatment with 4 ml (55 mmol) of thionyl chloride in 8 ml of benzene (see general procedure given above). The product was dissolved in 10 ml of anhydrous THF, 0.84 ml (9.6 mmol) of morpholine was added with stirring, and the mixture was stirred for 2 h and was left to stand overnight. The precipitate was filtered off and washed with THF on a filter. The filtrate was evaporated, the residue was treated with water, and the precipitate was filtered off, washed on a filter with water, and dried. Yield 0.25 g (100%), mp 228–230°C (decomp.), R_f 0.38 (chloroform–ethanol, 20:1). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 7.11 br.s (12H, H_{arom}), 3.90–3.70 br.s (12H, $ArCH_2Ar$), 3.67 br.s (24H, NCH_2), 3.55 br.s (24H, OCH_2), 2.25 s (12H, CH, Ad),* 2.21 s (12H, CH_2CON),* 1.85–1.55 m (72H, CH_2, Ad). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: adamantane

fragments: 169.48 (CON), 66.45 (OCH_2), 47.10 (CH_2CON), 45.19 (NCH_2), 34.41 (C^1), 48.93 (C^2), 36.21 (C^3), 42.14 (C^4, C^8),* 29.05 (C^5, C^7), 35.58 (C^6), 41.55 (C^9, C^{10})*; cavity: 148.24, 142.86, 126.90 (C_{arom}); 125.41 (CH_{arom}). Found, %: C 76.25; H 7.99; N 3.76. $C_{138}H_{174}N_6O_{18}$. Calculated, %: C 75.17; H 7.95; N 3.81.

Hexa-*p*-[3-(2-hydroxyethyl)-1-adamantyl]calix-[6]arene (XIVa). A solution of 0.19 g (0.1 mmol) of calix[6]arene **XIIIa** in anhydrous THF was added dropwise with stirring to a suspension of 0.1 g (2.63 mmol) of lithium aluminum hydride in 15 ml of anhydrous THF. The mixture was heated for 2 h under reflux with stirring and cooled, and 0.1 ml of water, 0.1 ml of a 3 N aqueous solution of sodium hydroxide, and 0.3 ml of water were added in succession under stirring. The precipitate was filtered off and washed on a filter with THF and then with a mixture of choroform or methylene chloride with ethanol (20 : 1). The filtrate was evaporated, the solid residue was dissolved in chloroform, and the solution was washed with 2 N hydrochloric acid and then with water until neutral reaction. The organic phase was evaporated, the residue was stirred in boiling methanol, the mixture was cooled, and the precipitate was filtered off, washed on a filter with methanol, and dried. Yield 0.16 g (94%), mp 262–264°C (decomp.), R_f 0.25 (chloroform–ethanol, 20 : 1). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 6.98 br.s (12H, H_{arom}), 3.80 s (12H, $ArCH_2Ar$), 3.48 t (12H, $CH_2C\mathbf{H}_2OH$), 2.04 br.s (12H, CH, Ad), 1.70–1.40 m (72H, CH_2, Ad), 1.29 t (12H, $C\mathbf{H}_2CH_2OH$). ^{13}C NMR spectrum (DMSO-d_6), δ_C, ppm: adamantane fragments: 56.26 (CH_2OH), 46.60 ($\mathbf{C}H_2CH_2OH$), 32.27 (C^1), 48.52 (C^2),* 35.74 (C^3), 42.37 (C^4, C^8),* 28.72 (C^5, C^7), 35.64 (C^6), 40.13 (C^9, C^{10})*; cavity: 148.69, 141.88, 127.14 (C_{arom}); 124.51 (CH_{arom}). Found, %: C 81.01; H 8.59. $C_{114}H_{144}O_{12}$. Calculated, %: C 80.24; H 8.51.

5,11,17,23,29,35-Hexakis[3-(2-hydroxyethyl)-1-adamantyl]-37,38,39,40,41,42-hexamethoxycalix[6]-arene (XIVb) was synthesized as described above for compound **XIVa** from 0.2 g (0.1 mmol) of calix-[6]arene **XVI** and 0.1 g (2.63 mmol) of lithium aluminum hydride in 15 ml of anhydrous THF. After removal of the solvent, the solid residue was dissolved in methylene chloride, and the solution was washed with 2 N hydrochloric acid and then with water until neutral reaction. The solvent was distilled off, and the residue was washed with methanol and dried. Yield 0.15 g (84%), mp 193–195°C, R_f 0.2 (chloroform–ethanol, 20 : 1). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 6.98 br.s (12H, H_{arom}), 4.27 br.s (6H, $CH_2CH_2O\mathbf{H}$), 3.84 br.s (12H, $ArCH_2Ar$), 3.48 t (12H, $CH_2C\mathbf{H}_2OH$), 2.83 br.s (18, OMe), 2.02 br.s (12H, CH, Ad), 1.70–1.40 m (72H, CH_2, Ad), 1.29 t (12H, $C\mathbf{H}_2CH_2OH$). ^{13}C NMR spectrum (DMSO-d_6), δ_C, ppm: adamantane fragments: 56.33 (CH_2OH); 46.73 ($\mathbf{C}H_2CH_2OH$); 32.37 (C^1); 48.54 (C^2)*; 35.80 (C^3); 42.52 (C^4, C^8)*; 28.83 (C^5, C^7); 35.75 (C^6); 40.13 (C^9, C^{10})*; COR: 59.36 (OMe); cavity: 153.63, 144.95, 132.90 (C_{arom}); 125.30 (CH_{arom}). Found, %: C 81.42; H 8.84. $C_{120}H_{156}O_{12}$. Calculated, %: C 80.50; H 8.78.

5,11,17,23,29,35-Hexakis(3-methoxycarbonyl-methyl-1-adamantyl)-37,38,39,40,41,42-hexakis-(ethoxycarbonylmethoxy)calix[6]arene (XV). A mixture of 0.19 g (0.1 mmol) of calix[6]arene **XIIIa** and 0.124 g (0.9 mmol) of potassium carbonate in 10 ml of anhydrous acetone was heated for 10 h under reflux with stirring. The mixture was cooled, 0.133 ml (1.2 mmol) of ethyl bromoacetate was added, and the mixture was heated for 13 h under reflux with stirring, cooled, treated with 20 ml of 2 N hydrochloric acid (with stirring), and extracted with methylene chloride. The organic extracts were combined, washed with water until neutral reaction, dried over magnesium sulfate, and evaporated to dryness. The residue was dissolved in a minimal amount of methylene chloride, and hexane was added. The precipitate was filtered off, washed with hexane on a filter, and dried. Yield 0.2 g (82%), mp 132–134°C, R_f 0.3 (chloroform–ethanol, 20 : 1). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 7.13 br.s (12H, H_{arom}), 4.20–3.80 br.s (12H, $ArCH_2Ar$; 12H, $C\mathbf{H}_2Me$; 12H, $C\mathbf{H}_2COOEt$), 3.63 s (18H, COOMe), 2.11 br.s (12H, CH, Ad; 12H, $C\mathbf{H}_2COOMe$), 1.90–1.60 m (72H, CH_2, Ad), 1.04 br.s (18H, Me). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: adamantane fragments: 171.80 (**C**OOMe), 50.91 (COO**Me**), 48.12 ($\mathbf{C}H_2COOMe$), 33.46 (C^1), 48.28 (C^2), 36.36 (C^3), 42.15 (C^4, C^8),* 29.03 (C^5, C^7), 35.62 (C^6), 41.17 (C^9, C^{10})*; COR: 168.99 (**C**OOEt), 69.90 ($\mathbf{C}H_2COOEt$), 60.21 ($\mathbf{C}H_2Me$), 13.84 (Me); cavity: 152.87, 144.94, 133.97 (C_{arom}); 125.94 (CH_{arom}). Found, %: C 73.41; H 7.65. $C_{144}H_{180}O_{30}$. Calculated, %: C 72.34; H 7.59.

37,38,39,40,41,42-Hexamethoxy-5,11,17,23,29,35-hexakis(3-methoxycarbonylmethyl-1-adamantyl)-calix[6]arene (XVI). A solution of 1.07 g (0.6 mmol) of *p*-(3-carboxymethyl-1-adamantyl)calix[6]arene (**VId**) in 20 ml of anhydrous THF was added with stirring to a suspension of 0.33 g (8.4 mmol) of sodium hydride (a 60% suspension in mineral oil was washed with THF) in 10 ml of anhydrous THF. The mixture was stirred for 15 min at room temperature,

and 0.69 ml (7.2 mmol) of dimethyl sulfate was added. The mixture was heated for 7 h under reflux and was left overnight. The precipitate was filtered off and washed with THF, the filtrate was evaporated on a rotary evaporator, the residue was dissolved in methylene chloride, and the solution was washed with 2 N hydrochloric acid and then with water until neutral reaction, dried over magnesium sulfate, and evaporated. Yield 1.08 g (92%), mp 110–112°C, R_f 0.7 (chloroform–ethanol, 20 : 1). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 7.02 s (12H, H_{arom}), 3.95 s (12H, $ArCH_2Ar$), 3.66 s (18H, COOMe), 3.02 s (18, OMe), 2.17 s (12H, CH, Ad; 12H, C**H**$_2$COOMe), 1.80–1.50 m (72H, CH_2, Ad). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: adamantane fragments: 171.79 (**C**OOMe), 50.92 (COO**Me**), 48.27 (**C**H_2COOMe), 33.47 (C^1), 48.27 (C^2), 36.37 (C^3), 42.35 (C^4, C^8),* 29.05 (C^5, C^7), 35.64 (C^6), 41.11 (C^9, C^{10})*; COR: 59.77 (OMe); cavity: 154.15, 144.78, 133.44 (C_{arom}); 125.40 (CH_{arom}). Found, %: C 79.09; H 8.04. $C_{126}H_{156}O_{18}$. Calculated, %: C 77.27; H 8.03.

5,11,17,23,29,35-Hexakis(3-carboxymethyl-1-adamantyl)-37,38,39,40,41,42-hexamethoxycalix[6]-arene (XVII). A mixture of 0.98 g (0.5 mmol) of calix[6]arene **XVI**, 9 ml of a 3 N aqueous solution of NaOH (27 mmol), and 72 ml of ethanol was heated for 7 h under reflux with stirring. The ethanol was distilled off, 2 N hydrochloric acid was added to the residue, and the precipitate was filtered off, washed with water, and dried. Yield 0.96 g (100%), mp 226–228°C, R_f 0.35 (chloroform–ethanol, 20 : 1). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 6.98 br.s (12H, H_{arom}), 3.85 br.s (12H, $ArCH_2Ar$), 2.83 br.s (18H, OMe), 2.05 s (12H, CHAd),* 2.00 s (12H, C**H**$_2$COOH),* 1.80–1.40 m (72H, CH_2, Ad). ^{13}C NMR spectrum (DMSO-d_6), δ_C, ppm: adamantane fragments: 172.44 (COOH), 48.22 (**C**H_2COOH), 32.84 (C^1), 48.06 (C^2),* 36.09 (C^3), 42.21 (C^4, C^8),* 28.74 (C^5, C^7), 35.50 (C^6), 40.76 (C^9, C^{10})*; COR: 59.40 (OMe); cavity: 153.73, 144.73, 132.96 (C_{arom}); 125.36 (CH_{arom}). Found, %: C 78.31; H 7.83. $C_{120}H_{144}O_{18}$. Calculated, %: C 76.89; H 7.74.

5,11,17,23,29,35-Hexakis(3-carbamoylmethyl-1-adamantyl)-37,38,39,40,41,42-hexamethoxycalix[6]-arene (XVIIIa). Calix[6]arene **XVII**, 0.19 g (0.1 mmol), was converted into the corresponding acid chloride by treatment with 4 ml (55 mmol) of thionyl chloride in 4 ml of benzene (see general procedure). The product was dissolved in 10 ml of anhydrous dioxane, 2 ml (29 mmol) of 25% aqueous ammonia was added, and the mixture was stirred for 2 h and was left overnight. The mixture was evaporated, and the residue was treated with water. The precipitate was filtered off, washed on a filter with water, and dried. Yield 0.18 g (95%), mp 252–254°C (decomp.), R_f 0.1 (chloroform–ethanol, 20 : 1). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 7.22 br.s (6H, $CONH_2$), 6.98 br.s (12H, H_{arom}), 6.71 br.s (6H, $CONH_2$), 3.85 br.s (12H, $ArCH_2Ar$), 2.82 br.s (18H, OMe), 2.05 s (12H, CH, Ad),* 1.85 s (12H, CH_2CON),* 1.80–1.40 m (72H, CH_2, Ad). ^{13}C NMR spectrum (DMSO-d_6), δ_C, ppm: adamantane fragments: 172.25 (CON), 49.61 (**C**H_2COMe),* 32.97 (C^1), 48.37 (C2),* 36.13 (C^3), 42.30 (C^4, C^8),* 28.82 (C^5, C^7), 35.63 (C^6), 41.16 (C^9, C^{10})*; COR: 59.41 (OMe); cavity: 153.69, 144.89, 132.92 (C_{arom}); 125.36 (CH_{arom}). Found, %: C 78.82; H 8.14; N 4.38. $C_{120}H_{150}N_6O_{12}$. Calculated, %: C 77.14; H 8.09; N 4.50.

37,38,39,40,41,42-Hexamethoxy-5,11,17,23,29,35-hexakis(3-methoxycarbonylmethylcarbamoyl-methyl-1-adamantyl)calix[6]arene (XVIIIb). Calix-[6]arene **XVII**, 0.14 g (0.075 mmol), was converted into the corresponding acid chloride by treatment with 3 ml (43 mmol) of thionyl chloride in 3 ml of benzene (see general procedure). The product was dissolved in 8 ml of anhydrous THF, and the solution was added with stirring to a suspension of 0.113 g (0.9 mmol) of glycine methyl ester hydrochloride in 6 ml of THF containing 0.2 ml (1.44 mmol) of triethylamine. The mixture was stirred for 2 h and was left overnight. It was evaporated, the residue was treated with water, and the precipitate was filtered off, washed on a filter with water, dried, and dissolved in a minimal amount of chloroform. The solution was passed through a thin layer of silica gel using chloroform–ethanol (20 : 1) as eluent. Yield 0.14 g (81%), mp 240–242°C, R_f 0.35 (chloroform–ethanol, 20 : 1). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 7.00 br.s (12H, H_{arom}), 6.54 br.s (6H, CONH), 4.10–3.80 m (12H, $ArCH_2Ar$; 12H, NCH_2), 3.70 s (18H, COOMe), 3.02 br.s (18H, OMe), 2.15 s (12H, CHAd),* 2.10 s (12H, CH_2CON),* 1.90–1.45 m (72H, CH_2, Ad). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: adamantane fragments: 171.05 (CON),* 170.29 (**C**OOMe),* 51.94 (COO**Me**), 50.71 (**C**H_2CON, N**C**H_2COOMe),* 33.62 (C^1), 48.64 (C^2), 36.38 (C^3), 42.30 (C^4, C^8),* 29.47 (C^5, C^7), 35.59 (C^6), 41.20 (C^9, C^{10})*; COR: 59.83 (OMe); cavity: 153.87, 144.92, 133.41 (C_{arom}); 125.35 (CH_{arom}); 30.72 ($ArCH_2Ar$). Found, %: C 73.59; H 7.65; N 3.47. $C_{138}H_{174}N_6O_{24}$. Calculated, %: C 72.04; H 7.62; N 3.65.

5,11,23,29-Tetra-*tert*-butyl-17,35-bis(3-methoxy-carbonylmethyl-1-adamantyl)calix[6]arene (XIXa). *a.* Compound **XIXa** was synthesized as described above for hexamethyl ester **XIIIa** from 0.15 g

(0.12 mmol) of calixarene **Xb**, 4.5 ml (111 mmol) of methanol, and 0.024 ml (0.45 mmol) of 98% sulfuric acid in 10 ml of THF. After evaporation of the reaction mixture, the residue was dissolved in methylene chloride and subjected to column chromatography using methylene chloride as eluent. Yield 0.09 g (59%), mp 332–335°C, R_f 0.9 (chloroform–ethanol, 20 : 1). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 10.60 s (6H, OH), 7.24 s (8H, H_{arom}), 7.17 s (4H, H_{arom}), 4.20–3.40 m (12H, $ArCH_2Ar$), 3.70 s (6H, COOMe), 2.20 s (4H, CH, Ad; 4H, C**H**$_2$COOMe), 1.86 br.s (8H, CH_2, Ad), 1.72 br.s (16H, CH_2, Ad), 1.33 s (36H, *t*-Bu). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: adamantane fragments: 171.87 (**C**OOMe), 50.95 (COO**Me**), 48.28 (**C**H_2COOMe), 33.56 (C^1), 48.35 (C^2), 36.27 (C^3), 42.27 (C^4, C^8),* 29.13 (C^5, C^7), 35.72 (C^6), 41.36 (C^9, C^{10})*; *t*-Bu: 33.92, 31.43; cavity: 147.48, 147.13, 144.17, 143.60, 126.94 (C_{arom}); 126.11, 125.66 (CH_{arom}); 32.98, 32.84 ($ArCH_2Ar$). Found, %: C 78.08; H 8.21. $C_{84}H_{104}O_{10}$. Calculated, %: C 79.21; H 8.23.

b. Calix[6]arene **Xb**, 0.2 g (0.16 mmol) was converted into the corresponding acid chloride by treatment with 4 ml (55 mmol) of thionyl chloride in 8 ml of benzene (see general procedure). The product was dissolved in a mixture of anhydrous methanol (4 ml) and anhydrous THF (2 ml), 4 ml of a 5% solution of sodium methoxide (2.93 mmol) in anhydrous methanol was added, and the mixture was stirred for 2 h and was left to stand overnight. The mixture was evaporated, the residue was treated with water, and the precipitate was filtered off, washed with water on a filter, dried, and dissolved in a minimal amount of chloroform or methylene chloride. The solution was passed through a thin layer of silica gel (preliminarily wetted with hexane) using chloroform or methylene chloride as eluent, and the eluate was evaporated. Yield 0.19 g (93%).

5,11,23,29-Tetra-*tert*-butyl-17,35-bis(3-piperidinocarbonylmethyl-1-adamantyl)calix[6]arene (XIXb). Calix[6]arene **Xb**, 0.15 g (0.12 mmol) was converted into the corresponding acid chloride by treatment with 2 ml (27 mmol) of thionyl chloride in 4 ml of benzene (see general procedure). The product was dissolved in 4 ml of anhydrous 1,4-dioxane, and the solution was added with stirring to a solution of 0.2 ml (2 mmol) of piperidine and 0.2 ml (1.44 mmol) of triethylamine in 4 ml of anhydrous dioxane. The mixture was stirred for 2 h and was left to stand overnight. It was then evaporated, the residue was treated with water, and the precipitate was filtered off, washed on a filter with water, and dissolved in a minimal amount of methylene chloride. The solution was passed through a thin layer of silica gel using methylene chloride–acetone (10 : 1) as eluent. Yield 0.14 g (85%), mp 227–228°C, R_f 0.65 (chloroform–ethanol, 20 : 1). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 7.14 s (8H, H_{arom}), 7.11 s (4H, H_{arom}), 4.20–3.60 m (12H, $ArCH_2Ar$), 3.57 br.s (8H, NCH_2), 3.45 br.s (8H, $NCH_2C\mathbf{H}_2$), 2.24 s (4H, CH, Ad), 2.17 s (4H, CH_2CON), 1.80–1.50 m (24H, CH_2, Ad; 4H, $NCH_2CH_2C\mathbf{H}_2$), 1.28 s (36H, *t*-Bu). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: adamantane fragments: 169.21 (CON), 47.84 ($NCH_2\mathbf{C}H_2$), 45.62 (NCH_2), 24.38 ($NCH_2CH_2C\mathbf{H}_2$), 34.40 (C^1), 48.92 (C^2), 36.32 (C^3), 42.25 (C^4, C^8),* 29.18 (C^5, C^7), 35.72 (C^6), 41.71 (C^9, C^{10})*; *t*-Bu: 33.88, 31.39; cavity: 144.07, 143.69, 126.90 (C_{arom}); 126.09 125.98, 125.65 (CH_{arom}); 32.94, 32.75 ($ArCH_2Ar$). Found, %: C 81.28; H 8.47; N 1.98. $C_{92}H_{118}N_2O_8$. Calculated, %: C 80.08; H 8.62; N 2.03.

5,11,23,29-Tetra-*tert*-butyl-17,35-bis[3-(2-hydroxyethyl)-1-adamantyl]calix[6]arene (XX) was synthesized as described above for compound **XIVa** from 0.2 g (0.16 mmol) of calix[6]arene **XIXa** and 0.1 g (2.63 mmol) of lithium aluminum hydride in 15 ml of THF. After removal of the solvent, the solid residue was washed with ether. Yield 0.17 g (89%), mp 340–342°C, R_f 0.25 (chloroform–ethanol, 20 : 1). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 7.04 s (8H, H_{arom}), 6.98 s (4H, H_{arom}), 4.60–3.80 br.s (12H, $ArCH_2Ar$), 3.66 t (4H, CH_2OH), 2.13 br.s (4H, CH, Ad), 1.70–1.50 m (24H, CH_2, Ad), 1.44 t (4H, C**H**$_2$$CH_2OH$), 1.26 s (36H, *t*-Bu). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: adamantane fragments: 57.48 (CH_2OH), 46.02 (**C**H_2CH_2OH), 32.27 (C^1), 48.03 (C^2), 35.79 (C^3), 42.26 (C^4, C^8),* 28.94 (C^5, C^7), 35.56 (C^6), 41.39 (C^9, C^{10})*; *t*-Bu: 33.27, 31.05; cavity: 131.85, 127.78 (C_{arom}); 124.53 124.05 (CH_{arom}). Found, %: C 82.07; H 8.73. $C_{82}H_{104}O_8$. Calculated, %: C 80.88; H 8.61.

5,11,23,29-Tetra-*tert*-butyl-37,38,39,40,41,42-hexamethoxy-17,35-bis(3-methoxycarbonylmethyl-1-adamantyl)calix[6]arene (XXI) was synthesized as described above for compound **XVI** from 0.5 g (0.4 mmol) of calix[6]arene **Xb**, 0.154 g (3.84 mmol) of 60% sodium hydride, and 0.36 ml (3.84 mmol) of dimethyl sulfate in 20 ml of THF. After evaporation of the extract, the residue was washed with cold methanol and dried. Yield 0.46 g (84%), mp 148–150°C, R_f 0.8 (chloroform–ethanol, 20 : 1). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 6.98 s (8H, H_{arom}), 6.95 s (4H, H_{arom}), 3.93 s (12H, $ArCH_2Ar$), 3.62 s (6H, $CH_2COO\mathbf{Me}$), 2.98 s (12H, OMe), 2.92 s (6H, OMe),

2.09 br.s (4H, CH, Ad; 4H, C**H**$_2$COOMe), 1.70–1.50 m (24H, CH_2, Ad), 1.12 s (36H, *t*-Bu). ^{13}C NMR cpectrum ($CDCl_3$), δ_C, ppm: adamantane fragments: 171.96 (**C**OOMe), 51.09 (COO**Me**), 48.43 (**C**H$_2$-COOMe), 33.60 (C^1), 48.47 (C^2), 36.51 (C^3), 42.49 (C^4, C^8),* 29.10 (C^5, C^7), 35.69 (C^6), 41.20 (C^9, C^{10})*; *t*-Bu: 34.10, 31.40; COR: 59.89 (OMe); cavity: 154.05, 153.87, 145.55, 145.12, 133.52, 133.45, 133.35 (C_{arom}); 125.98, 125.90, 125.52 (CH_{arom}); 30.93 ($ArCH_2Ar$). Found, %: C 78.14; H 8.51. $C_{90}H_{116}O_{10}$. Calculated, %: C 79.61; H 8.61.

5,11,23,29-Tetra-*tert*-butyl-17,35-bis(3-carboxymethyl-1-adamantyl)-37,38,39,40,41,42-hexamethoxycalix[6]arene (XXII) was synthesized as described above for compound **XVII** from 0.46 g (0.34 mmol) of calix[6]arene **XXI**, 3.75 ml (11.25 mmol) of a 3 N aqueous solution of sodium hydroxide and 30 ml of ethanol. Yield 0.46 g (100%), mp 200–202°C, R_f 0.45 (chloroform–ethanol, 20:1). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 7.00 br.s (4H, H_{arom}), 6.98 br.s (4H, H_{arom}), 6.95 s (4H, H_{arom}), 3.93 s (12H, $ArCH_2Ar$), 3.11 s (6H, OMe), 2.89 s (12H, OMe), 2.10 s (4H, CH, Ad),* 2.09 s (4H, C**H**$_2$COOH),* 1.70–1.50 m (24H, CH_2, Ad), 1.12 s (36H, *t*-Bu). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: adamantane fragments: 176.53 (**C**OOH), 48.25 (**C**H$_2$COOH), 33.48 (C^1), 48.28 (C^2), 36.49 (C^3), 42.31 (C^4, C^8),* 29.09 (C^5, C^7), 35.73 (C^6), 41.26 (C^9, C^{10})*; *t*-Bu: 34.11, 31.43; COR: 60.04, 59.82 (OMe); cavity: 153.94, 153.78, 145.57, 145.13, 133.71, 133.43, 133.20 (C_{arom}); 126.18, 126.01, 125.22 (CH_{arom}); 30.28 ($ArCH_2Ar$). Found, %: C 80.16; H 8.37. $C_{88}H_{112}O_{10}$. Calculated, %: C 79.48; H 8.49.

5,11,23,29-Tetra-*tert*-butyl-37,38,39,40,41,42-hexamethoxy-17,35-bis(3-piperidinocarbonylmethyl-1-adamantyl)calix[6]arene (XXIII). Calix[6]arene **XXII**, 0.12 g (0.09 mmol), was converted into the corresponding acid chloride by treatment with 2 ml (27 mmol) of thionyl chloride in 4 ml of benzene (see general procedure). The product was dissolved in 10 ml of anhydrous THF, and 0.176 ml (1.8 mmol) of piperidine was added with stirring. The mixture was stirred for 2 h and was left to stand overnight. It was then evaporated, the residue was treated with water, the precipitate was filtered off, washed with water on a filter, dried, and dissolved in a minimal amount of chloroform, and the solution was passed through a thin layer of silica gel using chloroform–ethanol (10:1) as eluent. Yield 0.13 g (98%), mp 148–148°C, R_f 0.4 (chloroform–ethanol, 20:1). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 6.93 s (8H, H_{arom}), 6.90 s (4H, H_{arom}), 3.87 s (12H, $ArCH_2Ar$), 3.50 br.s (8H, NCH_2), 3.37 br.s (8H, $NCH_2C\mathbf{H}_2$), 2.88 s (12H, OMe), 2.83 s (6H, OMe), 2.11 s (4H, CH, Ad), 2.03 s (4H, CH_2CON), 1.75–1.40 m (24H, CH_2, Ad; 4H, $NCH_2CH_2C\mathbf{H}_2$), 1.07 s (36H, *t*-Bu). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: adamantane fragments: 169.09 (CON), 47.70 ($NCH_2\mathbf{C}H_2$), 45.50 (NCH_2), 24.36 ($NCH_2CH_2\mathbf{C}H_2$), 34.27 (C^1), 49.09 (C^2), 36.44 (C^3), 42.26 (C^4, C^8),* 29.05 (C^5, C^7), 35.54 (C^6), 41.28 (C^9, C^{10})*; *t*-Bu: 33.93, 31.25; COR: 59.69 (OMe); cavity: 153.77, 153.71, 145.33, 145.16, 133.36, 133.18, 133.14 (C_{arom}); 125.86, 125.74, 125.39 (CH_{arom}); 30.14, 29.49 ($ArCH_2Ar$). Found, %: C 81.54; H 8.97; N 1.84. $C_{98}H_{130}N_2O_8$. Calculated, %: C 80.39; H 8.95; N 1.91.

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