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Calix[4]resorcinols Functionalized with Amino Acid Residues

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Abstract—By the Mannich reaction in ternary systems calix[4]resorcinol–amino acid (amino acid ester, amino acid ester hydrochloride)–formaldehyde calix[4]resorcinols were obtained functionalized on the upper molecule rim by amino acid residues.

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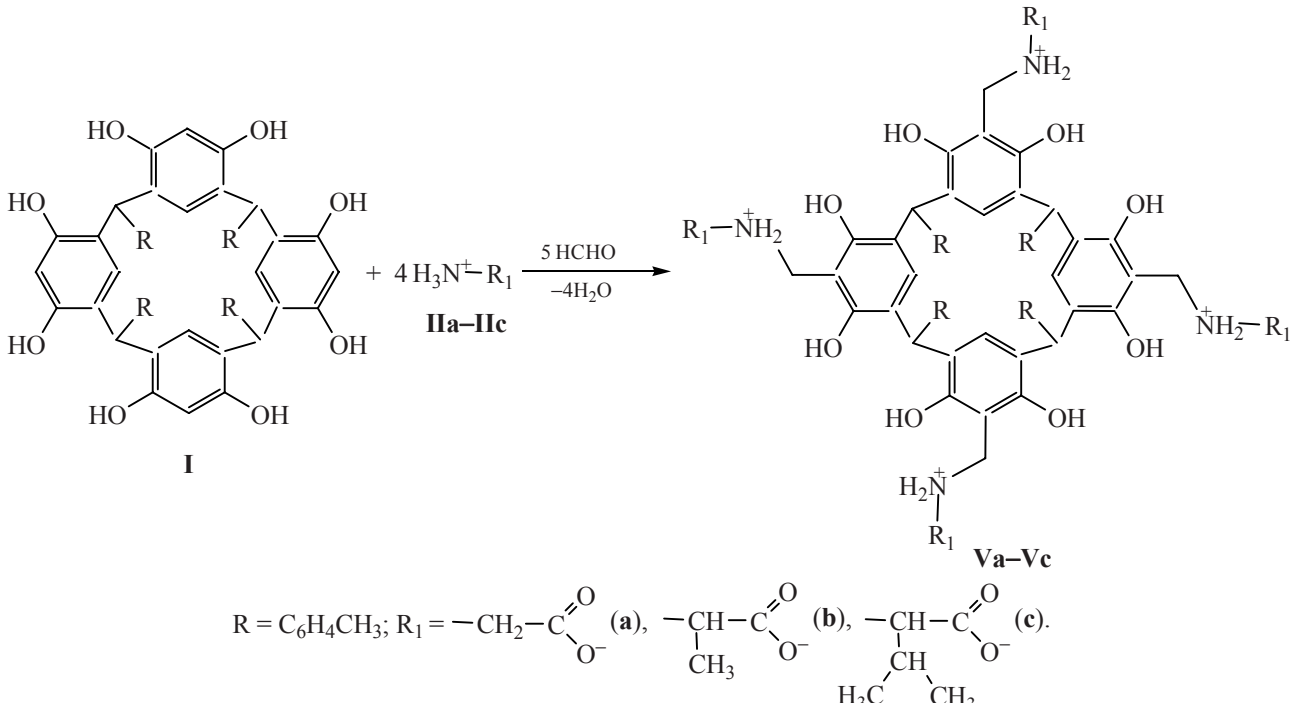
Production of supramolecular materials is one of the promising lines in solving of the nowadays scientific problems, namely, the information processing and storage, the producing of new generation drugs, complexing agents, and metal extractants [1–3]. Recently an active interest arose in the chemistry of calixresorcinols and their functionalized derivatives playing an important role in the supramolecular systems production. One of the most widespread methods for incorporating nitrogen-containing fragments into the *ortho*-position relative to hydroxy groups of the calixarene molecule is the aminomethylation by the Mannich reaction. There are some published reports devoted to aminomethylation of calix[4]resorcinols, involving alkyl groups on the upper molecule rim, using secondary amines [4–6]. Recently we described a preparation of aminoalkylated calix[4]resorcinols having aryl fragments on the lower molecule rim [7]. Calix[4]resorcinols containing amino acid residues are undoubtedly interesting for the study of their biological activity. There was an only report on calix-resorcinols aminomethylation with amino acids [4].

In this work calix[4]resorcinol **I** having tolyl groups on the lower molecule rim was used as an investigation object [8]. Amino acids glycine, *D,L*-alanine and *D,L*-valine, their ethyl esters and hydrochlorides of the latter were used as amines in the Mannich reaction. Reactions of calix-resorcinol **I,** water solutions of amino acids **IIa–IIc**, and formaldehyde in the ethanol-benzene mixture in the ratio 1:4:4 result in calix[4]-resorcinols **Va–Vc** in about 65% yield.

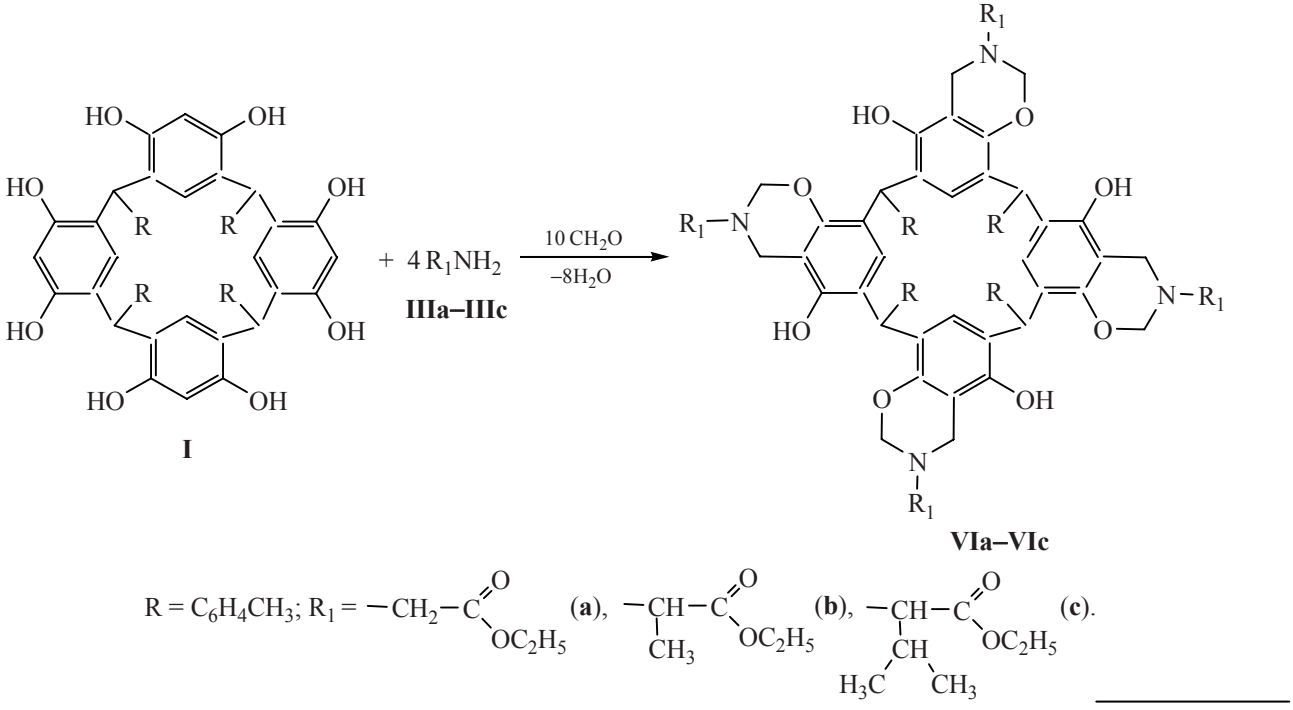
The calix[4]resorcinols aminoalkylation involving primary amines is known from the literature to give sometimes oxazine derivatives due to the participation of the second hydrogen atom of the primary amine [9]. The reaction might stop on the stage of Mannich base formation, when sterically hindered primary amines were used [10]. Spectral data showed that the reaction products obtained **Va–Vc** had a zwitterions structure characteristic of amino acids. Hence oxazine structure formation was not observed. In the IR spectra of aminomethylated calix[4]resorcinols **Va–Vc** a strong absorption band appears in the range 3000–2400 cm^{-1} belonging to the stretching vibrations of NH_2^+ group [11]. The signal of methylene protons of $C_{Ar}CH_2$–N fragment in the ^1H NMR spectrum of **Va–Vc** is observed as a singlet at 3.75, 3.88 and 3.62 ppm respectively in agreement with the literature data [4–6] (Scheme 1).

Reaction of compound **I** with formaldehyde using amino acid esters **IIIa–IIIc** (ratio 1:4:5) yields calixarenes having four oxazine fragments on the upper molecule rim formed through participation of both protons of the primary amino group in the condensation. In the ^1H NMR spectra of compounds **VIa–VIc** besides the signal of C_{Ar}–CH_2–N moiety methylene protons in the range 3.9–4.0 ppm (multiplet) there is a resonance signal at 4.8 ppm (multiplet) belonging to methylene protons of the oxazine fragment O–CH_2N (Scheme 2).

Scheme 1.



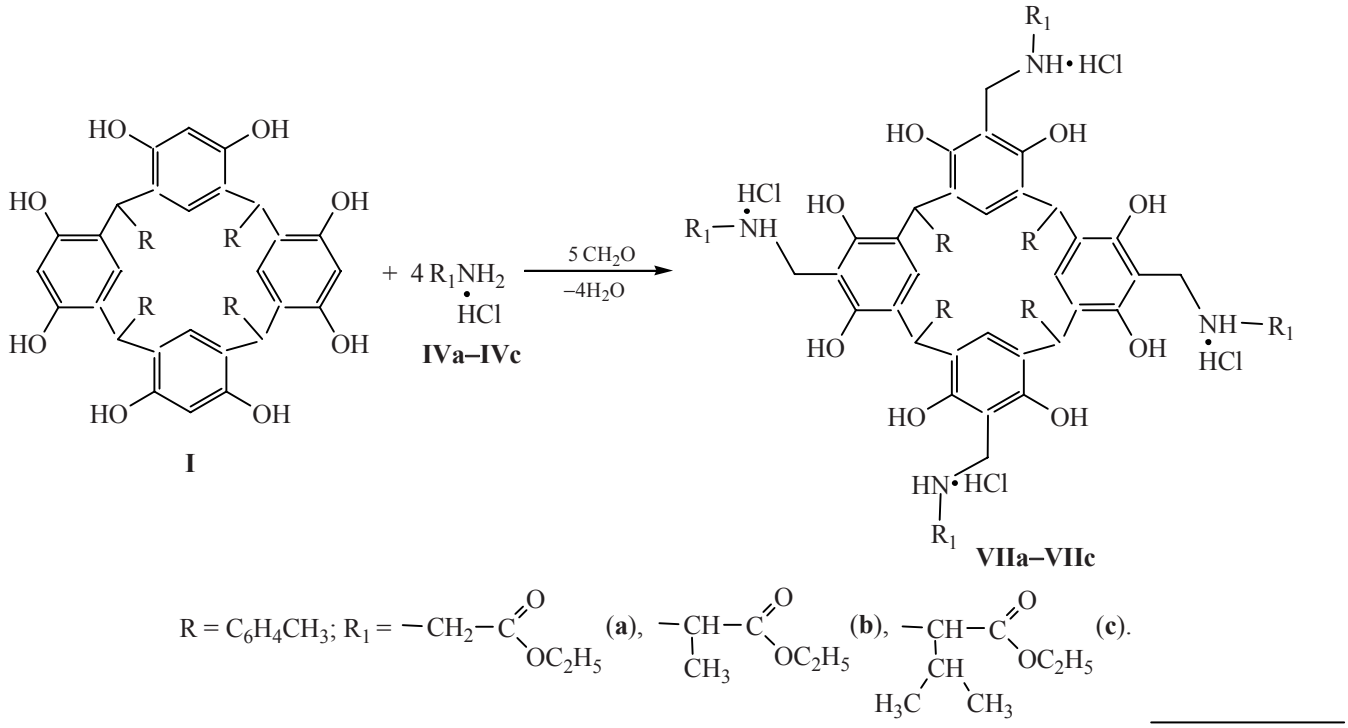
Scheme 2.



Reactions of resorcinol **I**, amino acid ethyl esters **IIIa–IIIc**, and formaldehyde in dioxane give rise to aminoalkylated calix[4]resorcinols **VIIa–VIIc** containing a quaternary nitrogen atom (Scheme 3).

The signal of methylene protons of C_{Ar}–CH_2–N moiety in the spectra of compounds **VIIa–VIIc** is observed as a singlet at 3.80, 3.86, 3.67 ppm respectively. In the IR spectra there are broad

Scheme 3.



absorption band in the range 3100–3500 cm^{-1} originating from hydroxy and ammonium groups.

We performed the biological activity prediction for compounds obtained **Va–Vc**, **VIa–VIc** and **VIIa–VIIc** using PASS program package. By these calculations, calix[4]resorcinols functionalized with amino acid residues may possess biological activity like sedative, antiherpes, antiseborrhea, transaminase and phosphatase inhibitors.

EXPERIMENTAL

The ^1H NMR spectra were registered on a Bruker MSL-400 device (400.13 MHz) relative to signals of residual protons of the deuterated solvent ($CDCl_3$, DMSO-d_6). The IR spectra were recorded on a UR-20 spectrophotometer in the range 400–3600 cm^{-1} from KBr pellets. The biological activity spectrum was predicted using PASS C&T program package (http://www.ibmh.msk.su/PASS/default.htm).

4,6,10,12,16,18,22,24-Octahydroxy-5,11,17,23-tetra(1-carboxylate)ammoniomethyl-2,8,14,20-tetra-(4-methyl)phenylpentacyclo[19.3.1.1^{3,7}.1^{9,13}.1^{15,19}]-octacoza-1(25),3,5,7(28),9,11,13(27),15,17,19(26),21,23-dodecaene (Va). To a solution of 0.3 g (0.00035 mol) of calix[4]resorcinol **I** in 30 ml of benzene–ethanol mixture (volume ratio 1:1) were added in succession under stirring 0.106 g (0.0014 mol) of glycine **IIa** dissolved in water and 0.053 g (0.00175 mol) of formaldehyde (40% water solution). The reaction mixture was refluxed for 20 h and cooled to room temperature. The precipitate was separated, washed with freshly distilled ethanol and dried under an oil pump vacuum (3 h, 80–90°C, 0.4 mm Hg). Yield 0.256 g (62%), mp >308°C. ^1H NMR spectrum [$(CD_3)_2SO$)], δ, ppm: 2.46 s (12H, C_{Ar}–CH_3), 3.75 s (16H, CH_2–N), 5.7 s (4H, C*H*), 6.32 s (4H, *m*–$CH_{Ar}C_6H_2$), 6.7 d (8H, C_6H_4, $^3J_{HH}$ 7.6 Hz), 7.1 d (8H, C_6H_4, $^3J_{HH}$ 7.6 Hz). IR spectrum, ν, cm^{-1}: 1603 (C=C_{Ar}), 3020 (NH_2^+), 3418 (OH). Found, %: C 69.11; H 5.88; N 4.97. $C_{68}H_{64}N_4O_{16}$. Calculated, %: C 68.46; H 5.36; N 4.70.

4,6,10,12,16,18,22,24-Octahydroxy-5,11,17,23-tetra(1-carboxylate-1-methyl)-ammoniomethyl-2,8,14,20-tetra(4-methyl)phenylpentacyclo-[19.3.1.1^{3,7}.1^{9,13}.1^{15,19}]octacoza-1(25),3,5,7(28),9,11,13-(27),15,17,19(26),21,23-dodecaene (Vb) was prepared similarly from 0.3 g (0.00035 mol) of calix[4] resorcinol **I** in 30 ml of benzene-ethanol mixture (volume ratio 1:1), 0.125 g (0.0014 mol) of *D,L*-alanine **IIb** and 0.531 g (0.0177 mol) of formaldehyde (40% water solution). Yield 0.28 g (63%), mp > 258°C.

^{1}H NMR spectrum [$(CD_3)_2SO$)], δ, ppm: 1.3 d (12H, CH_3–CH, $^3J_{HH}$ 7.0 Hz); 2.4 s (12H, C_{Ar}–CH_3), 3.5 br.m (4H, –CH–N), 3.88 s (8H, C_{Ar}–CH_2–N), 5.65 s (4H, CH), 6.3 s (4H, *m*–CH_{Ar} C_6H_2), 6.6 d (8H, C_6H_4, $^3J_{HH}$ 7.6 Hz), 6.9 d (8H, C_6H_4, $^3J_{HH}$ 7.6 Hz). IR spectrum, ν, cm^{-1}: 1621 (C=C_{Ar}), 3019 (NH_2^+), 3393 (OH). Found, %: C 70.01; H 6.10; N 5.17. $C_{72}H_{72}N_4O_{16}$. Calculated, %: C 69.23; H 5.77; N 4.49.

4,6,10,12,16,18,22,24-Octahydroxy-5,11,17,23-tetra(1-carboxylate-2-methyl)-propyl-ammoniomethyl-2,8,10,20-tetra(4-methyl)phenylpentacyclo-[19.3.1.1^{3,7}.1^{9,13}.1^{15,19}]octacoza-1(25),3,5,7(28),9,11,13-(27),15,17,19(26),21,23-dodecaene (Vc) was prepared similarly from 0.3 g (0.00035 mol) of calix[4] resorcinol **I** in 30 ml of benzene-ethanol mixture (volume ratio 1:1), 0.1645 g (0.0014 mol) of *D,L*-valine **IIc** 0.0525 g (0.00175 mol) of formaldehyde (40% water solution). Yield 0.333 g (69%), mp >284°C. ^{1}H NMR spectrum [$(CD_3)_2SO$)], δ, mp: 0.83 d.d [24H, CH(CH_3)$_2$, $^3J_{HH}$ 6.85 Hz], 2.38 s (12H, C_{Ar}–CH_3), 3.3 br.m (4H, –CH–N), 3.62 s (8H, C_{Ar}–CH_2–N), 5.7 s (4H, CH), 6.2 s (4H, *m*–CH_{Ar}, C_6H_2), 6.6 d (8H, C_6H_4, $^3J_{HH}$ 7.6 Hz), 6.9 d (8H, C_6H_4, $^3J_{HH}$ 7.6 Hz). IR spectrum, ν, cm^{-1}: 1621 (C=C_{Ar}), 2967 (NH_2^+), 3426 (OH). Found, %: C 71.42; H 7.27; N 4.51. $C_{80}H_{92}N_4O_{16}$. Calculated, %: C 70.59; H 6.47; N 4.12.

4,14,24,34-Tetrahydroxy-2,12,22,32-tetra(4-methylphenyl)-7,17,27,37-tetra(1-ethoxy-carbonyl)methyl-7,17,27,37-tetraazanocyclo[31.7.1.1^{3,11}.1^{13,21}.1^{23,31}.0^{5,15}.-0^{15,20}.0^{25,30}]-tetratetraconta-(41),3,5(10),11(44),13,15-(20),21(43),23,25(30),31(42),33,35(40)-dodecaene (VIa). To a solution of 0.3 g (0.00035 mol) of calix[4]-resorcinol **I** in 100 ml of ethanol-methylene chloride mixture (volume ratio 1:1) were added in succession 0.144 g (0.0014 mol) of glycine ethyl ester **IIIa**, and 0.106 g (0.00354 mol) of formaldehyde (40% water solution) under stirring. The reaction mixture was kept for 24 h at 20°C. The solvents were removed under a water-jet pump vacuum and the residue was reprecipitated from chloroform with *n*-pentane. The product isolated was dried under an oil pump vacuum (3 h, 80–90°C, 0.4 mm Hg). Yield 0.322 g (67%), mp >300°C. ^{1}H NMR ($CDCl_3$), δ, ppm: 1.12 t (12H, O–CH_2–CH_3, $^3J_{HH}$ 6.85 Hz), 2.3 s (12H, C_{Ar}CH_3), 3.1 s (8H, CH_2–N), 3.9 m (8H, C_{Ar}CH_2N), 4.2 q (8H, OCH_2CH$_3$, $^3J_{HH}$ 6.85 Hz), 4.8 m (8H, OCH_2–N), 5.6 br.s (4H, CH), 6.2 s (4H, CH_{Ar}, C_6H_2), 6.67 d (8H, CH_{Ar}, C_6H_4, $^3J_{HH}$ 7.6 Hz), 6.9 d (8H, CH_{Ar} C_6H_4, $^3J_{HH}$ 7.6 Hz). IR, ν, cm^{-1}: 1610 (C=C_{Ar}), 1740 (C=O), 3502 (OH). Found, %: C 71.17; H 6.45; N 4.21. $C_{80}H_{84}N_4O_{16}$. Calculated, %: C 70.80; H 6.19; N 4.13.

4,14,24,34-tetrahydroxy-2,12,22,32-tetra(4-methylphenyl)-7,17,27,37-tetra[1-ethoxy-carbonyl(1-methyl)]-ethyl-7,17,27,37-tetraazanocyclo[31.7.1.1^{3,11}.1^{13,21}.-1^{23,31}.0^{5,15}.0^{15,20}.0^{25,30}]-tetratatraconta-1(41),3,5(10),11-(44),13,15(20),21(43),23,25(30),31(42),33,35(40)-dodecaene (VIb) was prepared similarly from 0.3 g (0.00035 mol) of calix[4]resorcinol **I** in 100 ml of ethanol–methylene chloride mixture (volume ratio 1:1), 0.164 g (0.0014 mol) of *D,L*-alanine ethyl ester **IIb**, and 0.106 g (0.00354 mol) of formaldehyde (40% water solution). Yield 0.323 g (64%), mp >320°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.28 d (12H, CH_3CH, $^3J_{HH}$ 7.0 Hz), 1.37 t (12H, OCH_2CH_3, $^3J_{HH}$ 6.85 Hz), 2.36 s (12H, $C_{Ar}CH_3$), 3.3 br.m (4H, CH–N), 3.78 m (8H, $C_{Ar}CH_2N$), 4.12 q (8H, OCH_2CH_3, $^3J_{HH}$ 6.85 Hz), 5.0 m (8H, OCH_2–N), 5.56 br.s (4H, CH), 6.18 s (4H, CH_{Ar}, C_6H_2), 6.68 d (8H, CH_{Ar}, C_6H_4, $^3J_{HH}$ 7.6 Hz), 7.0 d (8H, CH_{Ar}, C_6H_4, $^3J_{HH}$ 7.6 Hz). IR spectrum, ν, cm^{-1}: 1610 (C=C_{Ar}), 1736 (C=O), 3485 (OH). Found, %: C 72.24; H 7.11; N 4.15. $C_{84}H_{92}N_4O_{16}$. Calculated, %: C71.39; H 6.51; N 3.97.

4,14,24,34-tetrahydroxy-2,12,22,32-tetra(4-methylphenyl)-7,17,27,37-tetra[1-ethoxy-carbonyl(2-methyl)]-propyl-7,17,27,37-tetraazanocyclo-[31.7.1.1^{3,11}.1^{13,21}.-1^{23,31}.0^{5,15}.0^{15,20}.0^{25,30}]tetratetraconta-1(41),3,5(10),11-(44),13,15(20),21(43),23,25(30),31(42),33,35(40)-dodecaene (VIc) was prepared similarly from 0.3 g (0.00035 mol) of calix[4]resorcinol **I** in 100 ml of ethanol–methylene chloride mixture (volume ratio 1:1), 0.2 g (0.0014 mol) of *D,L*-valine ethyl ester **IIc**, and 0.106 g (0.0035 mol) of formaldehyde (40% water solution). Yield 0.28 g (51.8%), mp >320°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 0.7 d.d [24H, CH(CH_3)$_2$, $^3J_{HH}$ 6.85 Hz], 1.27 d (12H, OCH_2CH_3, $^3J_{HH}$ 6.85 Hz), 1.9 m [4H, CH(CH$_3$)$_2$], 2.3 s (12H, $C_{Ar}CH_3$), 3.1 br.m (4H, CH–N), 3.9 m (8H, $C_{Ar}CH_2N$), 4.2 q (8H, OCH_2CH_3, $^3J_{HH}$ 6.85 Hz), 4.8 m (8H OCH_2–N), 5.6 br.s (4H, CH), 6.2 s (4H, *m*-CH_{Ar}, C_6H_2), 6.67 d (8H, *m*-CH_{Ar}, C_6H_4, $^3J_{HH}$ 7.6 Hz), 6.9 d (8H, CH_{Ar}, C_6H_4, $^3J_{HH}$ 7.6 Hz). IR spectrum, ν, cm^{-1}: 1610 (C=C_{Ar}), 1733 (C=O), 3493 (OH). Found, %: C 71.04; H 7.58; N 3.17. $C_{92}H_{108}$ N_4O_{16}. Calculated, %: C 72.44; H 7.08; N 3.7.

4,6,10,12,16,18,22,24-Octahydroxy-5,11,17,23-tetra(1-ethoxycarbonyl)ammoniomethyl-2,8,14,20-tetra(4-methyl)phenylpentacyclo[19.3.1.1^{3,7}.1^{9,13}.1^{15,19}]-octacoza-1(25),3,5,7(28),9,11,13(27),15,17,19(26),21,23-dodecaene (VIIa). To a solution of 0.3 g (0.00035 mol) of calix[4]resorcinol **I** in 50 ml of dioxane were added in succession under stirring 0.195 g (0.0014 mol) of

hydrochloride **IVa** and 0.0525 g (0.00175 mol) of paraformaldehyde. The mixture was acidified with HCl to pH 1.0–2.0. The reaction mixture was refluxed for 24 h. The solvent was removed under a water-jet pump vacuum and residue was reprecipitated from ethanol with diethyl ether. The product isolated was dried under an oil pump vacuum (3 h, 80–90°C, 0.4 mm Hg). Yield 0.343 g (73%), mp >117°C. ^{1}H NMR spectrum [$(CD_3)_2SO$], δ, ppm: 1.27 t (12H, OCH_2CH_3, $^3J_{HH}$ 6.85 Hz), 2.46 s (12H, C_{Ar}–CH_3), 3.80 s (16H, CH_2–N), 4.12 q (8H OCH_2CH_3, $^3J_{HH}$ 6.85 Hz), 5.7 s (4H, CH), 6.32 s (4H, *m*-CH_{Ar}, C_6H_2), 6.7 d (8H, C_6H_4, $^3J_{HH}$ 7.6 Hz), 7.1 d (8H, C_6H_4, $^3J_{HH}$ 7.6 Hz). IR spectrum, ν, cm^{-1}: 1599 (C=C_{Ar}), 1743 (C=O), 2984 (NH_2^+), 3406 (OH). Found, %: C 63.02; H 6.26; N 4.07; Cl 10.11. $C_{76}H_{84}N_4O_{16}$·4HCl. Calculated, %: C 62.72; H 6.05; N 3.85; Cl 9.77.

4,6,10,12,16,18,22,24-Octahydroxy-5,11,17,23-tetra[1-ethoxycarbonyl(1-methyl)]-ammoniomethyl-2,8,14,20-tetra(4-methyl)phenylpentacyclo[19.3.1.1^{3,7}.1^{9,13}.1^{15,19}]octacoza-1(25),3,5,7(28),9,11,13(27),15,17,19(26),21,23-dodecaene (VIIb) was prepared similarly from 0.3 g (0.00035 mol) of calix[4]resorcinol **I** in 50 ml of dioxane, 0.21 g (0.0014 mol) of hydrochloride **IVb**, and 0.106 g (0.00175 mol) of paraformaldehyde. Yield 0.379 g (71%), mp >104°C. ^{1}H NMR spectrum [$(CD_3)_2SO$)], δ, ppm: 1.3 d (12H, CH_3CH, $^3J_{HH}$ 7.0 Hz), 1.67 t (12H, OCH_2CH_3, $^3J_{HH}$ 6.85 Hz), 2.4 s (12H, C_{Ar}–CH_3), 3.5 br.m (4H, –CH–N), 3.86 s (8H, C_{Ar}–CH_2–N), 4.23 q (8H, OCH_2CH_3, $^3J_{HH}$ 6.85 Hz), 5.65 s (4H, CH), 6.3 s (4H, *m*-CH_{Ar}, C_6H_2), 6.6 d (8H, C_6H_4, $^3J_{HH}$ 7.6 Hz), 6.9 d (8H, C_6H_4, $^3J_{HH}$ 7.6 Hz). IR spectrum (KBr), ν, cm^{-1}: 1600 (C=C_{Ar}), 1740 (C=O), 3020 (NH_2^+), 3421 (OH). Found, %: C 64.19; H 6.52; N 4.03; Cl 10.09. $C_{80}H_{92}N_4O_{16}$ ·4HCl. Calculated, %: C 63.58; H 6.36; N 3.71; Cl 9.40.

4,6,10,12,16,18,22,24-Octahydroxy-5,11,17,23-tetra[1-ethoxycarbonyl(2-methyl)]-propylammoniomethyl-2,8,14,20-tetra(4-methyl)phenylpentacyclo-[19.3.1.1^{3,7}.1^{9,13}.1^{15,19}]-octacoza-1(25),3,5,7(28),9,11,13-(27),15,17,19(26),21,23-dodecaene (VIIc) was prepared similarly from 1 g (0.00118 mol) of calix[4]resorcinol **I** in 50 ml of dioxane, 0.86 g (0.0047 mol) of hydrochloride **IVc**, and 0.354 g (0.0118 mol) of paraformaldehyde. Yield 1.09 g (60%), mp >90°C. ^{1}H NMR spectrum [$(CD_3)_2SO$)], δ, ppm: 0.83 d.d [24H, $CH(CH_3)_2$, $^3J_{HH}$ 6.85 Hz], 1.27 t (12H, OCH_2CH_3, $^3J_{HH}$ 6.85 Hz), 2.38 s (12H, C_{Ar}–CH_3), 3.3 br.m (4H, –CH–N), 3.72 s (8H, C_{Ar}–CH_2–N), 4.1 q (8H, OCH_2CH_3, $^3J_{HH}$ 6.85 Hz), 5.7 s (4H, CH), 6.2 s (4H, *m*-CH_{Ar}, C_6H_2), 6.6 d (8H, C_6H_4, $^3J_{HH}$ 7.6 Hz), 6.9 d (8H, C_6H_4, $^3J_{HH}$ 7.6 Hz). IR spectrum, ν, cm^{-1}: 1607 (C=C_{Ar}), 1737 (C=O), 2968 (NH_2^+), 3404 (OH). Found, %: C 65.52; H 7.28; N 4.01; Cl 9.15. $C_{88}H_{108}N_4O_{16}$ ·4HCl. Calculated, %: C 65.10; H 6.91; N 3.45; Cl 8.76.

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