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Synthesis and Characterization of Partially Substituted at Lower Rim Phosphorus Containing Calix(4)arenes

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The synthesis and characterization of several new phosphorus-containing partially lower rim substituted derivatives of 5,11,17,23-tetra(*t*-butyl) calix(4)arene (I) and 5,11,17,23-tetra(*t*-octyl)calix(4)arene (II), namely 5,11,17,23-tetra(*t*-butyl)-25,27-dihydroxy-26,28-bis(diphenylphosphinoyl-oxy) calix(4)arene (IV); 5,11,17,23-tetra(*t*-butyl)-25-hydroxy-26,27,28-tris(tetramethyldiamidophosphinoyl-oxy) calix(4)arene (Vb); 5,11,17,23-tetra(*t*-butyl)-25,27-dihydroxy-26,28-bis(dimethyl-phosphinoylmethoxy) calix(4)arene (VI); 5,11,17,23-tetra (*t*-octyl)-25,27-dihydroxy-26,28-bis(dimethyl-phosphinoyl-methoxy) calix(4)arene (VII) are reported. The structure of the synthesized calix(4)arene derivatives are identified and confirmed by elemental analysis, IR, ^{1}H, ^{13}C, $^{31}P\{^{1}H\}$ NMR spectroscopy and mass spectrometry as and X-ray crystallographic analysis of 5,11,17,23-tetra(*t*-butyl)-25,27-dihydroxy-26,28-bis(dimethyl-phosphinoyl-methoxy) calix(4)arene VI. According to the NMR spectra, all calix(4)arenes are in cone conformation.

Keywords: Calix(4)arenes; Phosphorus containing calixarenes; Phosphine oxide; Tetra(*t*-octyl) calix(4)arene; X-ray analysis; NMR-spectroscopy

INTRODUCTION

Calixarenes are a class of macrocycles which can be prepared from p-substituted phenols and formaldehyde by a condensation reaction [1]. The growing interest in calixarene chemistry comes from the fact that they can be easily modified chemically at both their lower and upper rims, which can lead to the synthesis of derivatives with selected groups and various properties [2–7]. It is well known that calixarenes with different substituents at the lower rim possess versatile extracting and complexation properties toward metal cations [8–11]. On the other hand the introduction of a phosphorus moiety into calixarene molecules increases their complexation ability [12–15]. Nevertheless, immobilization of calixarenes on polymeric supports and the synthesis of polymers with calixarenes as co-monomers are still not widely popular. A few studies on the inclusion of calixarenes into polymer molecules or their immobilization onto polymer supports have been reported in the literature [16–26]. This leaves open a potential way to the improvement of the complexation and extraction ability of calixarene copolyethers and copolyesters, containing phosphoryl fragment.

It is therefore of particular interest to synthesize new phosphorus containing calixarenes, partially substituted at lower rim, aiming at their potential reactivity as co-monomers in polymerization [27,28]. In this article the synthesis and characterization of calix(4)arenes partially substituted at the lower rim and bearing mainly a phosphine oxide moiety is reported. They can be used both as co-monomers in polymerizations and as complexation agents for metal ions or extractants of nuclear waste solutions on their own right [18,19,29–32].

RESULTS AND DISCUSSION

Synthesis and Structure Identification

Partially phosphorylated calix(4)arenes were obtained in a two step procedure. First, some of the OH groups of the initial calix(4)arenes **I** or **II** were

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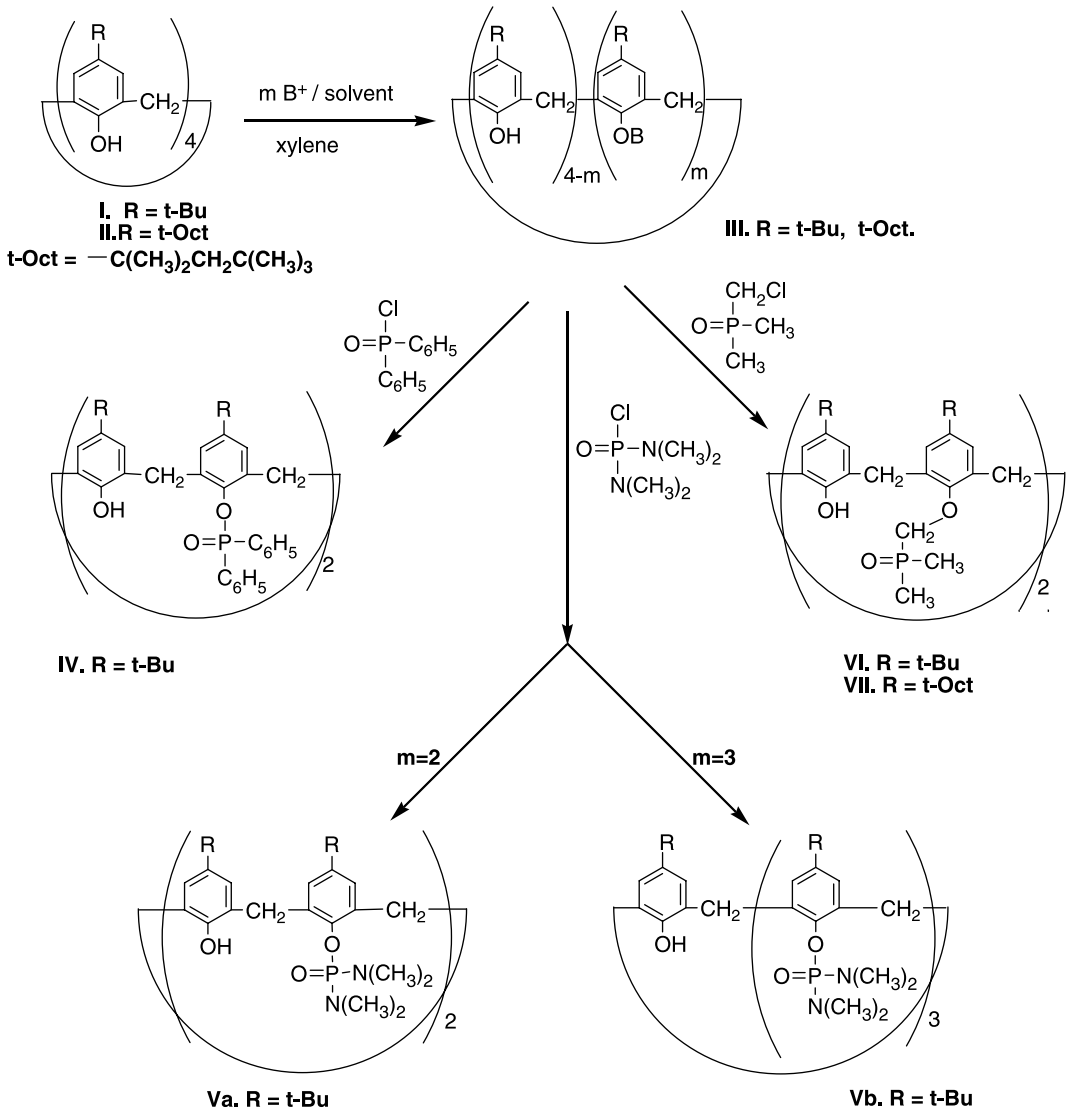
deprotonated by a base, e.g. BuLi, triethylamine (TEA) or most conveniently sodium methoxide ($NaOCH_3$) in methanol followed by addition of xylene. After subsequent phosphorylation with various phosphorus compounds four new calix(4)-arenes were obtained (Scheme 1): **IV(A)**—with diphenyl phosphinic acid chloride (DPPAC), **IV(B)**—with diphenyl phosphine oxide (DPPO), **V** with bis(dimethylamino) phosphinic acid chloride (DMPAC), **VI** and **VII** with chloromethyl dimethyl phosphine oxide (CDMPO). Two routes were used to prepare **IV** and **VI**.

Following method A for **IV**, the initial calix(4)-arene **I** reacted with DPPAC (in a ratio of 1:6) in toluene and TEA. Up to 100 times mole excess of Et_3N may need to be added in order to ensure complete dissolution of tetra (p-*t*-butyl) calix(4)arene. After the end of the reaction the resulted monoester and the excess of diphenyl phosphinic acid chloride were removed from the mixture by treating the crude product with warm n-hexane and water–ethanol (1:1). Disubstituted ester **IVA** is isolated as a white powder (m.p. 260–262°C) with a low yield (19%), probably due to its poor solubility in the above solvents.

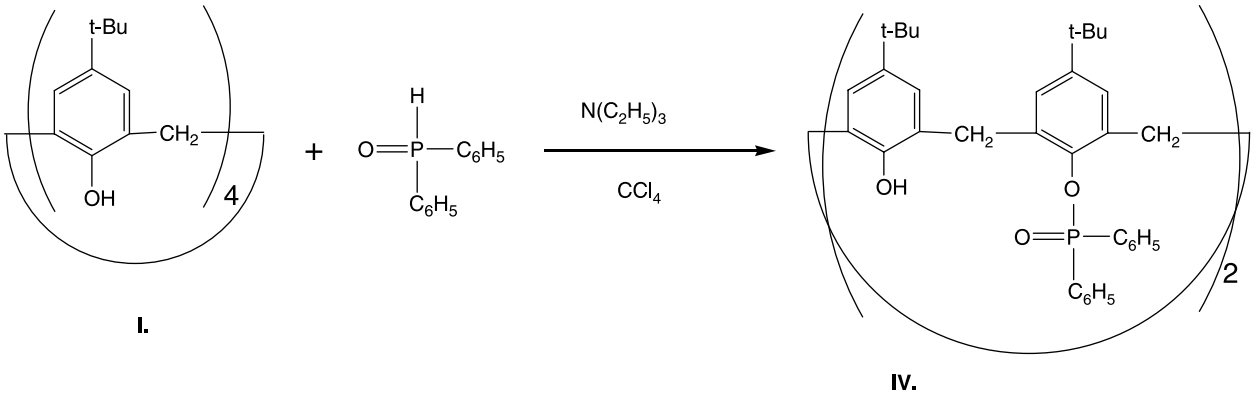
Method B: Alternatively the Todd–Atherton reaction was used to obtain **IVB** [33]; diphenyl phosphine oxide (DPPO) and tetrachloromethane (TCM) are added to a solution of **I** in toluene, followed by adding dropwise via a dropping funnel TEA at a molar ratio (**I**):DPPO:TCM:TEA = 1:5:5:6 (Scheme 2). The yield of the product as a white powder after purification was 29%, m.p. 257–259°C.

The melting point of the calixarene **IVB** was a little bit lower, but the reaction time was significantly shorter. The other reaction data are similar and some of these for the synthesized calixarene by the two methods are shown in Tables I and II.

The structure of the products prepared by both routes was established by elemental analysis, IR, ^1H,



SCHEME 1 Synthesis of calix(4)arenes IV–VII.



SCHEME 2 Method B. Synthesis of calix(4)arene IV via Todd–Atherton reaction.

^{13}C, $^{31}P\{^1H\}$ NMR spectroscopy and mass spectrometry. The obtained data of these products were almost identical. The ES-MS of compound **IVA**, namely 5,11,17,23-tetra-p-*t*-butyl-25,27-dihydroxy-26,28-bis(diphenyl phosphinoyl-oxy)calix(4)arene, shows one basic molecular peak at m/z = 1049,8 $(M + H)^+$, (calc. 1049.3) and an additional peak at 1066,80 (probably $M + H_2O + H)^+$ (method A) and m/z = 1049.6; 1050.6; 391.3; 371.4; and 279.3 probably due to M, $(M + H)^+$, $[M + (CH_3)_2C_6H_4 + H_2O]/3$, $(M + C_2H_5OH + H_2O)/3$ and $[M + C_2H_5OH + H_2O + H^+]/4$ resp., calcd. 1049.3, 1050.3, 391.2, 371.1 and 278.6 for **IVB** (method B).

The ^1H NMR spectrum is in agreement with the assumed structure of the di-substituted product. There were two pairs of doublets at $\delta = 4.92$ ppm and 2.91 ppm characteristic for the protons of methylene bridges (method A). That means the molecule was symmetrical—esterified at positions 26 and 28 and in the cone conformation [34]. Should the esterification take place at positions 27 and 28, the ^1H NMR spectrum would have three different pairs of doublets. Three kinds of protons for the methylene bridges have to be present for such molecules. Only one singlet was observed for OH at 5.29 ppm and two singlets for aromatic protons. One singlet at $\delta = 34{,}60$ ppm is observed in the $^{31}P\{^1H\}$-NMR spectrum. These data also support esterification at the 26,28-position. The data for **IVB** are shown in Table II.

In addition, the ^{13}C-NMR spectrum of **IVA** shows two singlets at $\delta = 31.9$ ppm and 30.6 ppm for $C(CH_3)_3$, one singlet at $\delta = 32.7$ ppm for $Ar—CH_2—Ar$ and four doublets for the ring *C*'s (Table III).

A direct lower rim esterification with DPPAC is used instead of DPPO because the first one was more convenient and available reagent, but the yield was lower. To synthesize the calixarene with higher yield a different procedure was pursued leading to the same product.

In order to obtain a tetra-esterified product intermediate **III** was reacted with DMPAC at a ratio of 1:5. In this case the outcome is a mixture of esterified calixarenes, containing mainly di- **Va** and tri-substituted **Vb**. There were traces of mono- and tetra-substituted calixarenes. The yield of the crude product (mixture) from our experiments was 72–80%. After separating the di- and tri-ester phosphoramides from the mixture by fractional crystallization from dimethylsulfoxide (DMSO), 27–31% di-substituted product 5,11,17,23-tetra-p-*t*-butyl-25,27-dihydroxy-26,28-bis(tetramethyl-diamidophosphinoyl-oxy) calix(4)arene **Va** was isolated. This product, which is soluble in chloroform, alcohols, acetone, toluene and ethylacetate has been described previously [35]. The filtrate is further allowed to crystallize and after a few days 54–60% tri-esterified product, namely 5,11,17,23-tetra-p-*t*-butyl-25-hydroxy-26,27,28-tris(tetramethyl diamido phosphinoyl)-oxycalix(4) arene **Vb** can be isolated too. It is a white crystalline substance, which melts at 260–265°C and is soluble in chloroform, alcohols, acetone, toluene, ethylacetate, DMSO and diethylether. Thin layer chromatography of **Vb** on Silica gel 60 F_{254} (**Merck**) shows only one spot, $R_f = 0.43$ (CH_2Cl_2/CH_3OH, 10:1, v/v). Its structure is confirmed by IR, NMR spectroscopy and ES mass spectral data. The ES-MS displays only a peak for the triester phosphoramide at 1051.9 corresponding to the $[M + H]^+$ mass (*calc.* $C_{56}H_{89}N_6O_7P_3 = 1051.3$) and no peaks corresponding to the mono-, di- or tetra-substituted products (mono-, $C_{48}H_{67}N_2O_5P$, 783.04; di-, $C_{52}H_{78}N_4O_6P_2$, 917.12; and tetra-, $C_{60}H_{106}N_8O_8P_4$, 1185.41 respectively). Moreover, the $^{31}P\{^1H\}$-NMR spectrum shows two singlet signals for the two kind of phosphorus atoms at $\delta = 18.00$ ppm and $\delta = 18.66$ ppm, at integral intensity ratio of 1:2, as expected. The ^1H NMR spectrum also shows peaks for three kinds of $C(CH_3)$ at $\delta = 0.88$ ppm, 1.35 ppm and 1.38 ppm, in the ratio 1:2:1. For the protons of $N—CH_3$ a doublet of doublets at $\delta = 2.58$ and at $\delta = 2.78$ ppm was observed with $^3J_{PH} = 9.9$ Hz and a doublet at $\delta = 2.74$ ppm with $^3J_{PH} = 9.5$ Hz, in the ratio 2:1. Two doublets of doublets arising from the bridge methylene groups at $\delta = 3.33$ ppm, $^2J_{PH} = 13.7$ Hz,

TABLE I Some preparative and analytical data of partially substituted phosphorylated calix(4)arenes

Product, Mol. wt.	Yield %	m.p. °C	Elemental analysis								ESMS m/z (Species)	IR spectra data ν (cm^{-1})
			Found, %				Calculated, %					
			C	H	N	P	C	H	N	P		
1. IV $C_{68}H_{74}O_6P_2$ 1049.28												
Method A IVA	19.5	260–262	77.61	7.22	–	5.87	77.84	7.11	–	5.90	1049.8 $(M + H)^+$ 1066.8 $(M + H_2O + H)^+$	P═O 1183 (s), 1202 (s), 1241 (vs), (P—O—C) 918 (s)
Method B IVB	29	257–259	76.92	7.31	–	5.80					1049.6 M 1050.6 $(M + H)^+$ 391.3 $(M + C_8H_{10} + H_2O)/3$ 371.4 $(M + C_2H_5OH + H_2O)/3$	(P═O) 1177 (s),1192 (s), (P—O—C) 910 (s) (Ar—OH) 3530 (vs)
2. Vb $C_{56}H_{89}N_6O_7P_3$ 1051.28	80	260–265	60.70	8.64	7.82	8.39	60.98	8.53	7.99	8.84	1051.87 $(M + H)^+$	(P═O) 1179(vs),1194 (s), (P—N—CH_3) 1308 (vs) (Ar) 1462 (vs),1481(vs), 1599(vs) (Ar—OH) 3567 (vs)
3. VI $C_{50}H_{70}O_6P_2{\cdot}H_2$ 847.05												
Method A VIA	90	365–370	71.19	8.68	–	7.29	70.90	8.57	–	7.31	829.80 $(M + H)^+$ 846.32 $(M + H_2O)$ 851.81 $(M + Na)^+$	(P═O) 1172 (s),1186 (vs), (Ar) 1486 (s), 1594 (s) (Ar—OH) 3449 (vs)
Method B VIB	78	368–370	71.03	8.65	–	7.26					829.5 $(M + H)^+$ 851.6 $(M + Na)^+$	(P═O) 1169 (s), 1192 (s) (Ar) 1468 (s), 1586(s)
4. VII $C_{66}H_{102}O_6P_2$ 1053.48	86	270–273	73.23	9.55	–	5.75	75.25	9.76	–	5.78	1053.6 $(M + H)^+$ 1075.6 $(M + Na)^+$	(P═O) 1167 (s), 1191 (vs), (P—CH_3) 1364 (m) (Ar) 1477 (s), 1595 (s) (Ar—OH) 3421 (vs)

TABLE II ^{1}H- and ^{31}P-NMR data of partially substituted phosphorylated calix(4)arenes (δ in ppm)

Compd Index	Ar–H	OH*	Ar–CH_2–Ar	CH_2–P	$(CH_3)_2P$	$C(CH_3)_3$	C $(CH_3)_2$	CCH_2C	P–$N(CH_3)_2$	P–Ar–H	$^{31}P\{^{1}H\}$
IVA	6.96(s), 6.57(s) 8H	5.29(s), 2H	4.20,2.96(dd)8H $^{2}J_{HH} = 17.5$ Hz, $^{2}J_{HH} = 17.2$ Hz	–	–	1.25(s) 0.81(s) 36H	–	–	–	7.96(dd), 7.38(dt) 7.54(dt), 20H	34.60 (s)
IVB	7.06(s), 6.62(s) 8H	5.35(s) 2H	4.66, 2.83(dd) $^{2}J_{HH} = 14.5$ Hz $^{2}J_{HH} = 14.7$ Hz			1.29(s), 0.86(s) 36H				8.08(d), 7.42 (dt) 7.55(dt), 20H	34.50 (s)
Vb	7.27(s),7.12(s) 7.02(s), 6.73(d),6.50(d) 8H	4.91(s) 1H	5.11(d),3.33(d) $^{2}J_{HH} = 13.5–13.7$ 4.31(d),3.40(d) $^{2}J_{HH} = 14.2–14.5$ 8H	–	–	1.38(s), 1.35(s), 0.88(s) 36H	–	–	2.78(d), 12 H $^{3}J_{PH} = 9.9$ Hz 2.58(d), 12 H $^{3}J_{PH} = 9.9$ Hz 2.74(d), 12 H $^{3}J_{PH} = 9.5$ Hz	–	18,66(s), 18.00(s), ratio 2:1
VIA	7.12(s), 6.71(s), 8H	6.18(s) 2H	4.11, 3.39 (dd) $^{2}J_{PH} = 13.3$ Hz, $^{2}J_{PH} = 13.1$ Hz, 8H	4.26, (d) $^{2}J_{PH} = 8$ Hz, 4H	1.87(d), $^{2}J_{PH} = 13.1$ Hz 12H	1.32(s), 0.86(s) 36H	–	–	–	–	41.21 (s)
VIB	7.09(s), 6.75(s), 8H	6.26(s) 2H	4.29, 3.32 (dd) $^{2}J_{PH} = 13.3$ Hz, $^{2}J_{PH} = 13.2$ Hz, 8H	4.43 (d) $^{2}J_{PH} = 7.7$ Hz, 4H	1.88 (d) $^{2}J_{PH} = 13.3$ Hz, 12H	1.30(s), 0.85(s) 36H	–	–	–	–	40.89 (s)
VII	7.08 (s), 2H 6.81(s), 2H	6.57(s) 2H	4.13(d), $^{2}J_{PH} = 12.5$ 3.40(d), $^{2}J_{PH} = 12.6$ 8H	4.20 (d) $^{2}J_{PH} = 7.7$ Hz 4H	1.96(d) $^{2}J_{PH} = 13.1$ Hz 12H	0.77(s), 0.28(s) 36H	1.35(s), 1.04(s). 24H	1.73(s), 1.36(s) 8H	–	–	40.27 (s)

*-s—singlet; d—doublet; dd—doublet of doublets; dt—doublet of triplets; **-Exchangeable.

TABLE III ^{13}C-NMR data of partially substituted phosphorylated calix(4)arenes (δ in ppm)

Compd. Index	C (Ar)	Ar–CH_2–Ar	C(CH_3)$_3$	C–(CH_3)	C–(CH_3)$_3$	C (CH_3)$_2$	C–CH_2–C	(CH_3)$_2$P	CH_2–P	P–N(CH_3)$_2$	P–C (Ar)
IVA	150.5, 148.1 142.9, 142.0 133.8, 133.4 132.2, 131.8 (s)	32.7(s)	31.9(s), 30.6(s)	–	34.3(s), 34.0(s)	–	–	–	–	–	129.7(d), $^2J_{PC}$ = 133.8 Hz 129.1(d) $^3J_{PC}$ = 163.0 Hz 125.5(d) $^4J_{PC}$ = 150.9 Hz 126.4(d) $^5J_{PC}$ = 155.9 Hz
Vb	150.7, 146.7, 146.1, 143.2, 143.1, 143.0, 136.3, 134.3, 132.1 126.6, 125.9, 125.6 (s)	32.1(s), 33.1(s)	33.1(s) 32.1(s), 31.4(s)	–	37.3(s) 34.5(s) 34.3(s)	–	–	–	–	41.4(s), 37.8 (s) 37.7 (s)	–
VIA	150.5, 149.8, 149.7 148.5, 143.1, 131.7, 128.0, 126.4, 125.7 (s)	31.5(s)	32.1(s), 31.2(s)	–	34.3(s) 34.3(s)	–	–	15.5, 14.9(d) $^2J_{PC}$ = 68.1 Hz,	74.0, 73.2(d) $^2J_{PC}$ = 81.2Hz	–	–
VII	150.1, 149.8, 149.6 146.9, 141.5 130.9, 126.9, 127.1, 126.3 (s)	31.6(s)	32.0(s) 31.1(s)	31.7(s) 30.7(s)	32.4(s) 31.6(s)	37.8(s) 36.1(s)	57.3(s) 56.9(s)	15.5, 14.4(d) $^2J_{PC}$ = 68.3 Hz,	74.3, 73.0(d) $^2J_{PC}$ = 80.4 Hz	–	–

$\delta = 5.11$ ppm, $^2J_{PH} = 13.5$ Hz, $\delta = 3.40$ ppm, $^2J_{PH} = 14.3$ Hz and $\delta = 4.31$ ppm, $^2J_{PH} = 14.5$ Hz are observed, too. The ^{13}C NMR spectra and elemental analysis data agree with the suggested structure. The IR spectrum of the compound (Table I) contains bands for phosphoryl (P═O) groups at 1179 cm^{-1}, 1194 cm^{-1} and 1231 cm^{-1}, for P—N—CH_3 at 1308 cm^{-1} and for phenolic hydroxyl groups at 3567 cm^{-1}.

Finally, the di-substituted calixarenes **VI** and **VII** (according to Scheme 1) were obtained in good yields (90% and 86% resp.). Two equivalents of $NaOCH_3$ were used to ensure the deprotonation only of two hydroxyl groups, because the presence of extra bases leads to the deprotonation of all OH groups thus leading to the tetra substituted products. There are data in the literature [31,32] about the complexation ability of the calixarenes and a way to improve their extractability is to change the substituents at the upper rim. The exchange of tert-Bu with tert-Oct can improve solubility of both the calixarenes and their complexes.

The implementation of two different deprotonating agents results into the identical product **VI**. It is soluble in chloroform, alcohols, acetone, ethylacetate and insoluble in water, toluene, xylene. The ES-MS of **VI(A)** shows only peaks at m/z = 829.8 and 846.8 referred respectively to $(M + H)^+$ and $(M + H_2O + H)^+$ and at 851.8—for $(M + Na)^+$. The calculated molecular mass *M* is 829.05. Regarding the ^{1}H NMR spectrum of compound **VI(A)**, there is only a singlet for the hydroxyl group at $\delta = 6.18$ ppm, two singlets at $\delta = 6.71$ ppm and at $\delta = 7.12$ ppm for H–Ar and two singlets for $(CH_3)_3C$— at $\delta = 0.86$ and $\delta = 1.32$ ppm. There are also doublets at $\delta = 1.87$ ppm with $^2J_{PH} = 13.1$ Hz and at $\delta = 4.26$ ppm with $^2J_{PH} = 8.0$ Hz, characteristic for CH_2–P and $(CH_3)_2$ P resp. Two doublets are observed at $\delta = 4.10$ ppm and at $\delta = 3.38$ ppm for the methylene bridges (Ar—CH_2—Ar). There is only a signal for the methylene bridges in the ^{13}C NMR spectrum, two singlets for —$C(CH_3)_3$ and —$C(CH_3)_3$ and doublets for CH_2—P at $\delta =$ 15.3 ppm with $^2J_{PC} = 68.1$ Hz and at $\delta = 73.6$ ppm with $^2J_{PC} = 81.2$ Hz for $(CH_3)_2$P. Similar data are observed for **VI(B)**. In the ^{31}P{^{1}H}-NMR spectrum there is a singlet at $\delta = 41.21$ ppm for **VI(A)** and 40.89 ppm for **VI(B)**. These data are evidence that the molecules of the calixarene are symmetrical.

Product **VII** is well soluble in methanol, toluene, dioxane, ethylacetate, methylene chloride, chloroform and insoluble in water, acetone, hexane. The spectroscopic data of this compound were close to those of product **VI**, except for the presence of peaks for the *t*-octyl substituent instead of the *t*-Bu one. In the ES-MS spectrum, there are two peaks m/z = 1053.6 $(M + H)^+$ and m/z = 1075.6 $(M + Na)^+$ (calcd 1053.48) and no other peaks in the 500 to 2000 region. The ^{1}H NMR spectrum shows

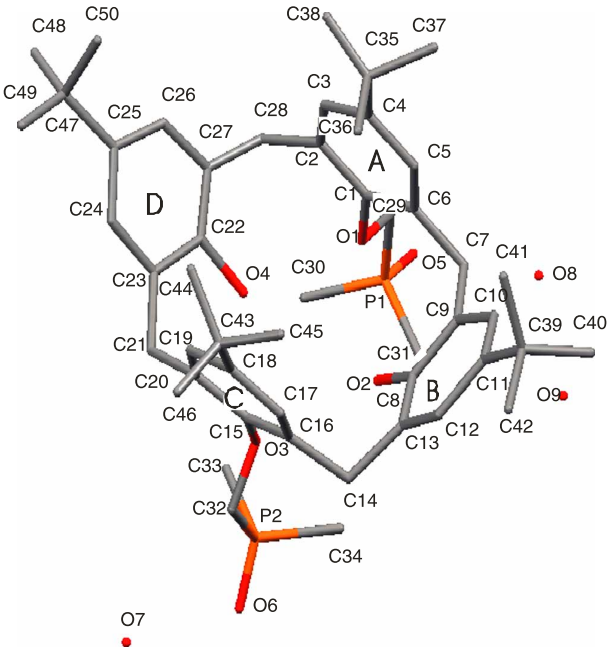


FIGURE 1 The molecular structure of VI determined by single-crystal X-ray diffraction.

a doublet at 4.20 ppm for CH_2—P with $^2J_{PH} = 7.7$ Hz and a doublet at $\delta = 1.96$ ppm for $(CH_3)_2$ P- with $^2J_{PH} = 13.1$ Hz. A doublet of doublets at $\delta = 3.40$ ppm and 4.13 ppm, $^2J_{PH} = 12.6$ Hz shows the presence of Ar—CH_2—Ar. The singlet signals and their integrals correspond to the protons of the t-octyl group. The $^{31}P\{^1H\}$-NMR spectrum shows a singlet at $\delta = 40.27$ ppm.

The NMR data for all substituted calix(4)arenes indicated that the molecules were symmetrical and in cone conformation, which is further confirmed in the solid state by the structure of **VI(A)** determined by X-ray crystallography.

X-ray Crystallographic Investigations

The molecular structure of ca\lix(4)arene **VI(A)** is shown in Fig. 1. The crystal data and structure refinement are listed in Table IV and the relevant geometrical parameters are shown in Table V. The band values and torsion angles are in agreement with those reported in the literature for this type of geometry. For instance, the aromatic rings, which lie below the reference plane passing through the four CH_2 bridging groups, are forming the hydrophobic part of the molecule and the orientation of the rings determine the flattened cone conformation. The hydrophilic part of the molecule is formed by both hydroxyl and phosphine oxide groups, situated above the reference plane. The dihedral angles between phenyl moieties are as follows: A/B—83.6(3)°; A/C—14.8(5)°; A/D—88.5(4)°; B/C—86.7(3)°; B/D—77.3(5)°. The A and C opposite rings are quite parallel, while the other two B and D are almost perpendicular to one another. The distances between the opposite *t*-butyl groups are [C35…C43 = 6.52 Å; C47…C39 = 11.71 Å]. The geometrical parameters characterizing the phosphine oxide groups are in good agreement with the presence of double bonds between P1–O5 and P2–O6. The values of the C1—O1—C29—P1 and C15—O3—C32—P1 torsion angles are 176.6 Å and 172.4 Å respectively and the orientation of the phosphine oxide groups towards the aromatic part of the molecule is almost the same. Although the

TABLE IV Crystal data and structure refinement for **VI**

Empirical formula	C50 H76 O9 P2	
Formula weight	883.05	
Temperature	140(2) K	
Wavelength	0.71073 Å	
Crystal system	monoclinic	
Space group	P21/c	
Unit cell dimensions	a = 23.188(11) Å	α = 90°
	b = 13.096(4) Å	β = 114.14(5)°
	c = 20.499(10) Å	γ = 90°
Volume	5680(4) Å^3	
Z	4	
Density (calculated)	1.033 Mg/m^3	
Absorption coefficient	0.122 mm^{-1}	
F(000)	1912	
Crystal size	0.23 × 0.20 × 0.13 mm^3	
Theta range for data collection	2.89 to 22.99°	
Index ranges	−25 < = h < = 25, −13 < = k < = 13, −22 < = l < = 22	
Reflections collected	26505	
Independent reflections	7745 [R(int) = 0.1862]	
Completeness to theta = 0.30°	98%	
Max. and min. Transmission	0.9843 and 0.9724	
Refinement method	Full-matrix least-squares on F^2	
Data/restraints/parameters	7745/162/550	
Goodness-of-fit on F^2	0.918	
Final R indices [I > 2sigma(*I*)]	R1 = 0.0976, wR2 = 0.2144	
R indices (all data)	R1 = 0.3783, wR2 = 0.3505	
Largest diff. peak and hole	0.510 and −0.228 e. Å^{-3}	

TABLE V Selected bond lengths [Å] and angles [°] for **VI**

P(1)—O(5)	1.522(8)	
P(1)—C(30)	1.795(12)	
P(1)—C(29)	1.797(12)	
P(1)—C(31)	1.829(12)	
P(2)—O(6)	1.398(11)	
P(2)—C(33)	1.821(16)	
P(2)—C(32)	1.840(12)	
P(2)—C(34)	1.873(16)	
O(5)—P(1)—C(30)	112.4(6)	
O(5)—P(1)—C(29)	111.8(6)	
C(30)—P(1)—C(29)	106.2(6)	
O(5)—P(1)—C(31)	113.5(5)	
C(30)—P(1)—C(31)	108.0(6)	
C(29)—P(1)—C(31)	104.4(6)	
O(6)—P(2)—C(33)	116.2(9)	
O(6)—P(2)—C(32)	113.8(7)	
C(33)—P(2)—C(32)	105.0(7)	
O(6)—P(2)—C(34)	108.5(9)	
C(33)—P(2)—C(34)	103.5(8)	
C(32)—P(2)—C(34)	109.2(7)	
C(1)—C(2)—C(3)—C(4)		−3(2)
C(2)—C(3)—C(4)—C(5)		3(2)
C(3)—C(4)—C(5)—C(6)		−1.9(19)
C(2)—C(1)—C(6)—C(5)		0.0(17)
C(13)—C(8)—C(9)—C(10)		3.6(18)
C(13)—C(8)—C(9)—C(7)		−175.4(11)
C(8)—C(9)—C(10)—C(11)		−6.7(18)
C(11)—C(12)—C(13)—C(8)		0.1(18)
C(20)—C(15)—C(16)—C(17)		2(2)
C(20)—C(15)—C(16)—C(14)		−174.9(13)
C(18)—C(19)—C(20)—C(15)		−3(2)
C(27)—C(22)—C(23)—C(24)		4(2)
C(27)—C(22)—C(23)—C(21)		−174.1(15)
C(20)—C(21)—C(23)—C(22)		75.8(16)
C(22)—C(23)—C(24)—C(25)		−1(2)

Symmetry transformations used to generate equivalent atoms.

calixarene substitutes are symmetrically positioned, the whole molecule does not possess symmetrical elements. This is explained by the higher conformational degree around C—C and C—O bonds. Two strong intramolecular hydrogen bonds —O(2)—H(2)...O(3) and O(4)—H(4)...O(1) are observed within the molecule. The three dimensional packing of the molecules is stabilized by intensive hydrogen bonding between the phosphonic parts of the molecules and two of the water molecules, while the third O(9) water molecule is not involved in the hydrogen bonding network (Fig. 2). The O(7) water molecule acts as a bridging ligand to O6 atoms from the calixarene molecule and O(8) to O(5). Thus O(6)...O(7)...O6[$-x, -y, 1-z$]...O7 [$-x, -y, 1-z$] hydrogen bonding cyclic motif is formed. They are connected by O(5) [$-x, -1/2+y, 1/2-z$]...O(8)[$-x, -1/2+y, 1/2-z$] and O8...O5 hydrogen bonds, which stabilize the formation of pseudo hydrophilic cavities of the molecules. There are two additional π interactions between the B phenyl ring and the methyl part of the phosphine oxide groups stabilizing the pseudo-layer arrangement [C10...C34 = 3.62 Å; C12...C31 = 3.78 Å].

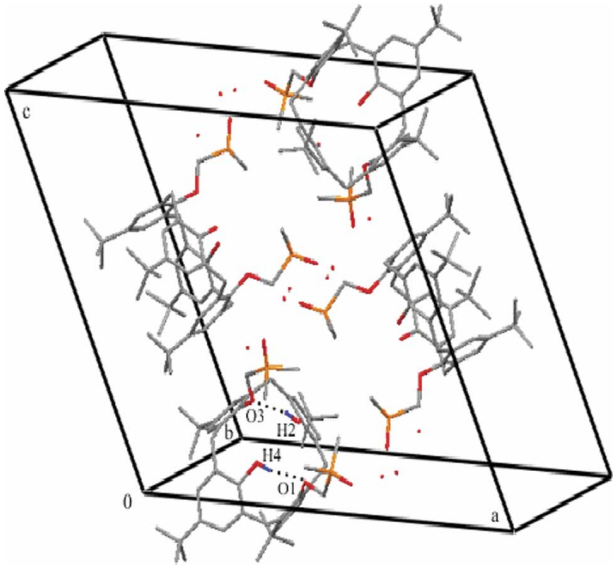


FIGURE 2 Packing of the molecules of VI determined by single-crystal X-ray diffraction.

EXPERIMENTAL

Reagents and Physical Measurements

Compounds **I** and **II** were synthesized according to the literature procedures [6,7,36].

Toluene and xylene were distilled over Na and stored over molecular sieves 4 Å (Merck).

Methanol was distilled after drying by a procedure with Mg. Other solvents and chemicals were of reagent grade and were used as received from Merck and Fluka.

TLC was conducted using plates coated with Merck Kieselgel 60 F_{254}.

Melting points were determined on microhot stage Boetius PHMK and were uncorrected. The IR spectra were measured on Mattson Alpha Centaury FT spectrometer as KBr pellets. ^{1}H-NMR spectra were recorded on Bruker 400 spectrometer in $CDCl_3$, $^{31}P\{^{1}H\}$-NMR spectra were registered on the same instrument at 161.9 MHz in $CDCl_3$ as solvent. Chemical shifts were measured relative to TMS as internal standard for (^{1}H) or external—H_3PO_4 (85%), for $^{31}P\{^{1}H\}$. ^{13}C-NMR spectra were recorded on Bruker Avance DRX 250 MHz.

The ES-MS were performed on a Finnigan SSQ 710C spectrometer using a capillary temperature of 200°C and acceleration potential of 4.5 kV. 10^{-4}–10^{-5} M solutions of substances in methanol were infused in a mixture of CH_3OH/H_2O/HCOOH (50:50:1, v/v). The elemental analyses were carried out by Dr. H.J.Eder from the Microchemical Laboratory of the University of Geneva (for determination of C, H and N) and by Ilse Beetz Laboratory (96301 Kronach, Germany) for determination of phosphorus content.

Crystal Structure Determination of 5,11,17,23-tetra-p-*t*-butyl-25,27-dihydroxy-26,28,-bis(dimethylphosphinoyl-methoxy)-calix(4)arene

The crystals of **VI** were prepared by slow crystallization from a diluted ethylacetate solution at room temperature with the possibility of partial evaporation of the solvent.

Data collection were performed at 140(2) K using Mo K α radiation on a four-circle kappa goniometer with an Oxford Diffraction KM4 Sapphire CCD. Cell refinement and data reduction were carried out with the aid of CrysAlis RED 1.7.1 β release [37]. No absorption correction was applied to the data set. All structures were refined using the full-matrix least-squares on F^2 with all non-H atoms anisotropically defined. The hydrogen atoms were placed in calculated positions using the "riding model". Structure refinement and geometrical calculations were carried out with SHELXTL 5.1 [38]. Crystallographic data (excluding structure factors) for the structure reported in this paper are deposited with the Cambridge Crystallographic Data Centre as supplementary publication No. CCDC 296492.

Synthesis

5,11,17,23-tetra(p-t-butyl)-25,27-dihydroxy-26,28-bis(diphenylphosphinoyloxy)calix(4)-arene (IV)

Method A

To a transparent colorless solution of 5,11,17,23-tetra(p-*t*-butyl)-calix(4)-arene **I** (1.07 g, 1.66 mmol) in a mixture of toluene (100 ml) and TEA (18 g, 178 mmol) a transparent colorless solution of DPPAC (2.36 g, 9.97 mmol) in toluene (50 ml) was added by a dropping funnel. The reaction mixture was stirred at nitrogen atmosphere and at room temperature for 3 hours and at 90°C for 48 hrs. After cooling to room temperature the reaction mixture was filtered to separate the white sediment, mainly TEA hydrochloride. The filtrate was evaporated and the residue dissolve in 120 ml fresh toluene. The resulting solution was washed with 12 × 50 ml distilled water, dried over $MgSO_4$ and toluene was evaporated. The solid white residue was washed 6 × 50 ml with n-hexane (stirring and refluxing for 15 min) and 4 × 50 ml water–ethanol (stirring for 15 min at 50°C). The resulting white powder was dried at 60°C and high vacuum for 24 hr. Yield 0.34 g (19.5%), m.p. 260–262°C.

Method B

To a solution of 5,11,17,23-tetra(p-*t*-butyl)-calix(4)-arene **I** (1.0 g, 1.54 mmol) in dry toluene (90 ml) in a four necked flask provided with mechanical stirrer, thermometer, argon inlet and condenser were added DPPO (1.6 g, 7.92 mmol) and TCM (2.7 g, 17.6 mmol). A solution of TEA (1.3 ml, 0.94 g, 9.3 mmol) in toluene (15 ml) was added via dropping funnel to the reaction mixture at 0°C. The mixture was stirred 3 hrs at room temperature and 10 hrs at 70–75°C. The reaction mixture was cooled, filtered and the filtrate successively worked up with dilute HCl, dilute NaOH, water and water–ethanol (2:1), dried over Na_2SO_4 and the solvents evaporated. Yield 0.46 g, (29%) white mass, m.p. 257–259°C, TLC on Silica gel 60 F_{254} (n-hexane/chloroform/acetic acid = 10:6:1, $R_f = 0{,}62$).

5,11,17,23-tetra-(p-t-butyl)-25-hydroxy-26,27,28-tris(tetramethyldiamidophosphinoyl)oxy) calix(4)arene (Vb)

To a solution of $NaOCH_3$ (Na, 0.117 g, 5.08 mmol, in 30 ml dry methanol) at room temperature, under argon atmosphere and stirring 5,11,17,23- tetra-(p-*t*-butyl)-25,26,27,28- tetra hydroxy-calix(4)arene **I** (1 g, 1.54 mmol) and 50 ml dry xylene were added. The solution was stirred for 30 min at room temperature and the methanol was removed. The resulting mixture was heated to reflux and a solution of DMPAC (0.867 g, 5.1 mmol) in 50 ml dry xylene was added via a dropping funnel. After 40 h reflux, the reaction mixture was cooled and NaCl filtered off, the filtrate was washed with water and then dried over Na_2SO_4. The solvent was evaporated on a rotary evaporator and a crude product 1.3 g, (80%) yielded. It was a mixture of di- and tri- esterified calixarenes. That mixture was purified by fractional crystallization from DMSO and 0.35 g (27%) di-esterified calixarene **Va** [35], m.p. 305–310°C and 0.73 g (56%) tri-esterified product **Vb**, a white crystal substance, m.p. 260–265°C were isolated.

5,11,17,23- Tetra-(p-t-butyl)-25,27-dihydroxy-26,28-bis(dimethylphosphinoyl-methoxy)calix(4)arene (VI)

Method A

Prepared in an analogous manner to **Vb**. Na (0.4 g, 17.4 mmol), 60 ml dry methanol, **I** (5.37 g, 8.3 mmol), 100 ml xylene, CDMPO (2.27 g, 17.9 mmol) in 80 ml xylene. The reaction mixture was heated under reflux for 16 hrs. The solvent was evaporated under reduced pressure and the residue worked up with 100 ml chloroform. The precipitate was centrifuged to remove NaCl, the solution was washed with water, dried over Na_2SO_4, filtered and evaporated. Yield: 6.2 g, (90%) white solid product, recrystallized from ethylacetate, m.p. 365–370°C. **VI(A)** was isolated with 1 molecule water as crystalline hydrate.

Method B

Product **VI** was also prepared by deprotonation of initial calixarene **I** with BuLi under an inert argon atmosphere. To a mixture of **I** (1.95 g, 3.0 mmol) in 60 ml dry tetrahydrofuran (THF)

(freshly distilled above $LiAlH_4$) under an argon atmosphere 4.3 ml (0.45 g, 7 mmol) of a 15% solution of BuLi in hexane were added. The mixture was boiled for 40 min. and a solution of CDMPO (0.76 g, 6 mmol) in 10 ml dry THF was added. The reaction mixture was refluxed for 15 hrs and after removing the solvent, 100 ml of methylene chloride and 20 ml of water were added to the residue. It was acidified with 10 ml of diluted HCl (1:5) and the organic layer was separated and washed twice with water, dried with sodium sulfate and the solvent evaporated. The yield of crude product was 1.95 g (78%), recrystallized from ethylacetate–methylene chloride, m.p. 368–370°C, isolated with 1 molecule water as crystalline hydrate.

5,11,17,23-tetra-(p-t-octyl)-25,27-dihydroxy-26,28-bis(dimethylphosphinoyl-methoxy)calix(4)arene (VII)

Prepared in a manner analogous to **Vb**. To a solution of $NaOCH_3$, (Na, 0.063 g, 2.7 mmol in 15 ml of dry methanol) was added **II** (1.1 g, 1.26 mmol) in 50 ml of xylene and via dropping funnel CDMPO (0.38 g, 3.0 mmol) in 10 ml of xylene. The reaction mixture was heated at reflux 22 hrs. The solvent was evaporated at reduced pressure and the residue worked up with ethanol (2 − 25 ml) and evaporated. The product was dissolved in chloroform and washed with 50 ml dilute HCl and water (3 × 50 ml). The solution was dried (Na_2SO_4) filtered and evaporated. Yield: 1.15 g, (86%), white product, recrystallized from toluene, m.p. 270–273°C.

CONCLUSIONS

In this paper the synthesis of several new calix(4)arenes, partially substituted at the lower rim with phosphorus compounds—chloromethyl dimethyl phosphine oxide, diphenyl phosphine oxide, bis(dimethylamino) phosphinic acid chloride and diphenyl phosphinic acid chloride, are described. In order to limit the full esterification a smaller amount of deprotonating and phosphorylating agents was used. The obtained new compounds are characterized by elemental analysis, IR, ^1H, ^{13}C, $^{31}P\{^1H\}$ NMR spectroscopy, mass spectrometry and X-ray crystallographic analysis of **VIA**. NMR spectra indicate that under the specified conditions (bases and phosphorylating agents) the formed symmetrical calixarenes are in cone conformation. A direct lower rim esterification with DPPAC is used instead of DPPO because the first one was more convinient and readily available reagent, even though the yield of **IVA** is lower. Using $NaOCH_3$ as deprotonating agent instead of BuLi for **VI** leads to a higher yield of the product. The authors want to synthesize the calixarenes in higher yields and to show that the same products can be prepared by other ways.

Phosphorylated calixarenes offer numerous possibilities for strong complexation with metal ions. The synthesis and characterization of polymers with the obtained calix(4)arenes is currently under investigation.

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