Synthesis and characterization of partially substituted at lower rim phosphorus containing calix(4)arenes

Emil Stefanov Tashev, Tania Dimitrova Tosheva, Stoycho Dimitrov Shenkov, Anne-Sophie Chauvin, Victoria Lachkova, Rosica Petrova Petrova, Rosario Scopelliti, Sabi Genchev Varbanov

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Synthesis and characterization of partially substituted at lower rim phosphorus containing calix(4)arenes

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Keywords:	calix(4)arenes, phosphorus containing calixarenes, phosphine oxide, tetra(t-octyl)calix(4)arene, X-ray analysis

Table 4. 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 x 0.20 x 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 > 2σ(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 5. 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.

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Figure 2 Packing of the molecules of VI determined by single-crystal x-ray diffraction

Table 1. 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 v (cm ⁻¹)
			Found, %				Calculated, %					
			C	H	N	P	C	H	N	P		
1. IV C ₆₈ H ₇₄ O ₆ P 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 ₂ O+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 ₈ H ₁₀ + H ₂ O)/3 371.4 (M+C ₂ H ₅ OH+H ₂ O)/3	(P=O) 1177 (s),1192 (s), (P-O-C) 910 (s) (Ar-OH) 3530 (vs)
2. Vb C ₅₆ H ₈₉ N ₆ O ₇ P 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 ₆ P ₂ .H ₂ O 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 ₂ O) 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 ₆ P 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)

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Table 2. ¹H- and ³¹P-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) ₂ P	C(CH ₃) ₃	C (CH ₃) ₂	CCH ₂ C	P-N(CH ₃) ₂	P-Ar-H	³¹ P{ ¹ H}
1. 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)
2. 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
3. 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} = 13.1Hz 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)
4. 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 3. ^{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) ₂	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)
1. 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), ² J _{PC} =133.8 Hz 129.1(d) ³ J _{PC} =163.0 Hz 125.5(d) ⁴ J _{PC} =150.9 Hz 126.4(d) ⁵ J _{PC} =155.9 Hz
2. V b	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)	-
3. 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) ² J _{PC} = 68.1Hz,	74.0, 73.2(d) ² J _{PC} = 81.2Hz	-	-
4. 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) ² J _{PC} = 68.3Hz,	74.3, 73.0(d) ² J _{PC} = 80.4Hz	-	-

Synthesis and characterization of partially substituted at lower rim phosphorus containing calix(4)arenes

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Abstract:

We report 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(diphenyl phosphinoyl-oxy) calix(4)arene (**IV**); 5,11,17,23-tetra(*t*-butyl)-25-hydroxy-26,27,28-tris(tetramethyldiamido-phosphinoyl-oxy) calix(4)arene (**Vb**); 5,11,17,23-tetra(*t*-butyl)-25,27-dihydroxy-26,28-bis(dimethyl- phosphinoyl-methoxy) calix(4)arene

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(VI); 5,11,17,23-tetra (*t*-octyl)-25,27-dihydroxy-26,28-bis(dimethyl-phosphinoyl-methoxy) calix(4)arene (VII). The structure of the synthesized calix(4)arene derivatives are identified and confirmed by elemental analysis, IR-, ^1H -, ^{13}C -, $^{31}\text{P}\{^1\text{H}\}$ – 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.

Phosphorus containing calix(4)arenes

Key words: calix(4)arenes; phosphorus containing calixarenes; phosphine oxide; tetra(*t*-octyl) calix(4)arene; X-ray analysis; NMR-spectroscopy.

1. 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 [2-6]. It is well known that calixarenes with different substituents at the lower rim possess versatile extracting and complexation properties toward metal cations [7-10]. On the other hand introducing of a phosphorus moiety into calixarene molecules increases their complexation ability [11-14]. 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 [15-22]. 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 [23,24]. In this article we report the synthesis and characterization of calix(4)arenes partially substituted at the lower rim and bearing mainly a phosphine oxide moiety. 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 [17,25-28].

2. RESULTS AND DISCUSSION

2.1. Synthesis and Structure Identification

Partially phosphorylated calix(4)arenes are obtained in a two step procedure. First, some of the OH groups of the initial calix(4)arenes I or II are deprotonated by a base, e.g. BuLi, triethylamine (TEA) or most conveniently sodium methoxide (NaOCH₃) in methanol followed by addition of xylene. After subsequent phosphorylation with various phosphorus compounds four new calix(4)arenes are 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 are used to prepare **IV** and **VI**.

Scheme 1.

Following **Method A** for **IV**, the initial calix(4)arene **I** reacts with DPPAC (in a ratio of 1:6) in toluene and TEA. Up to 100 times mole excess of Et₃N 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 are 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: We alternatively use the Todd – Atherton reaction to obtain **IVB** [29]; 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 is 29%, m.p. 257 – 259 °C.

Scheme 2.

The melting point of the calixarene **IVB** is 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 1 and 2**.

The structure of the products prepared by both routes is established by elemental analysis, IR-, ¹H-, ¹³C-, ³¹P{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 are two pairs of doublets at $\delta = 4,92$ and 2,91 ppm characteristic for the protons of methylene bridges (method **A**). That means the molecule is symmetrical – esterified at **positions 26 and 28** and in **the** cone conformation [30]. **Should** the esterification **take place at positions** 27and 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. **We however only observe** one singlet for OH at 5,29 ppm and two singlets for aromatic protons. One singlet at $\delta = 34,60$ ppm is observed in the ³¹P{¹H}-NMR spectrum. These data also support **esterification at** the 26,28-position. The data for **IVB** are shown in Table 2.

In addition, the ¹³C–NMR spectrum of **IVA** shows two singlets at $\delta = 31,9$ 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 3**).

A direct lower rim esterification with DPPAC is used instead of DPPO because the first one was more convinient and available reagent, but the yield

was lower. To synthesize the calixarene with higher yield we pursue a different procedure leading to the same product.

In order to obtain a tetra-esterified product intermediate **III** is reacted with DMPAC at ratio of 1:5. In this case the outcome is a mixture of esterified calixarenes, containing mainly di- **Va** and tri-substituted **Vb**. There are traces of mono- and tetra-substituted calixarenes. The yield of the crude product (mixture) from our experiments is 72 – 80 %. After separating the di- and tri-ester phosphoramides from the mixture by fractional crystallization from dimethylsulfoxide (DMSO), we isolate 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**. This product, which is soluble in chloroform, alcohols, acetone, toluene and ethylacetate has been described previously [31]. 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-oxy)calix(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 F₂₅₄ (Merck) shows only one spot, $R_f = 0,43$ (CH₂Cl₂/CH₃OH, 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.* C₅₆H₈₉N₆O₇P₃ = 1051,3) and no peaks corresponding to the mono-, di- or tetra-substituted products (mono-, C₄₈H₆₇N₂O₅P, 783,04; di-, C₅₂H₇₈N₄O₆P₂, 917,12; and tetra-, C₆₀H₁₀₆N₈O₈P₄, 1185,41 respectively). Moreover, the ³¹P{¹H}-NMR

spectrum shows two singlet signals for the two kind of phosphorus atoms at $\delta = 18,00$ 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 $\text{C}(\text{CH}_3)$ at $\delta = 0,88$, $\delta = 1,35$ and $\delta = 1,38$ ppm, in ratio 1 : 2 : 1. For the protons of N-CH_3 we observed a doublet of doublets at $\delta = 2,58$ and at $\delta = 2,78$ ppm with $^3J_{\text{PH}} = 9,9$ Hz and a doublet at $\delta = 2,74$ ppm with $^3J_{\text{PH}} = 9,5$ Hz, in ratio 2:1. Two doublets of doublets arising from the bridge methylene groups at $\delta = 3,33$ ppm, $^2J_{\text{PH}} = 13,7$ Hz, $\delta = 5,11$ ppm, $^2J_{\text{PH}} = 13,5$ Hz, $\delta = 3,40$ ppm, $^2J_{\text{PH}} = 14,3$ Hz and $\delta = 4,31$ ppm, $^2J_{\text{PH}} = 14,5$ 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 1) contains bands for phosphoryl (P=O) groups at 1179, 1194 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 the Scheme 1) were obtained in good yields (90% and 86 % resp.). We use two equivalent of NaOCH_3 to ensure the deprotonation only of two hydroxyl groups, because the presence of extra base leads to the deprotonation of all OH groups thus leading to the tetra substituted products. There are data in the literature [27,28] 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 $(\text{M} + \text{H})^+$ and $(\text{M} + \text{H}_2\text{O} + \text{H})^+$ and

at 851,8 – for $(M + Na)^+$. The calculated molecular mass M is 829,05. Regarding the 1H – NMR spectrum of compound **VI(A)**, there are 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 $\delta = 15,3$ 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 $^{31}P\{^1H\}$ -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 1H – NMR spectrum shows 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 $\delta = 3,40$ 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.

2.2. X-ray Crystallographic Investigations

The molecular structure of calix(4)arene **VI(A)** is shown on **Figure 1**. The crystal data and structure refinement are listed in **Table 4** and the relevant geometrical parameters are shown in **Table 5**. The bond values and torsion angles are in agreement with those reported in the literature for such **this type of** geometry. For instance, the aromatic rings, which lie below the reference plane passing through the four CH₂ 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 one to another. The distances between the opposite *t*-butyl groups are [C35... C43 = 6.52Å; C47 ... C39=11.71Å]. 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 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 calixarene substitutes are symmetrically positioned, the whole

molecule does not possess symmetry 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 (**Figure 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 interaction between the B phenyl ring and the methyl part of the phosphine oxide groups stabilizing the pseudolayer arrangement [C10 ...C34 = 3.62Å; C12...C31=3.78 Å].

3. EXPERIMENTAL

3.1. Reagents and physical measurements

Compounds **I** and **II** are synthesized according to the literature procedures [6,32]. Toluene and xylene are distilled over Na and stored over molecular sieves 4Å (Merck).

Methanol is distilled after drying by a procedure with Mg . Other solvents and chemicals are of reagent grade and are used as received from Merck and Fluka. TLC is done using plates coated with Merck Kieselgel 60 F₂₅₄.

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

The ES-MS are 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 are infused in a mixture of $\text{CH}_3\text{OH}/\text{H}_2\text{O}/\text{HCOOH}$ (50:50:1, v/v). The elemental analysis are 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.

3.2. 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 [33]. 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. [34]. 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**.

3.3. 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 12x50 ml distilled water, dried over MgSO_4 and toluene was evaporated. The solid white residue was washed 6x50 ml with *n*-hexane (stirring and refluxing for 15 min.) and 4x50 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 Na₂SO₄ and the solvents evaporated. Yield 0.46 g, (29%) white mass, m.p.257-259°C, TLC on Silica gel 60 F₂₅₄ (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 NaOCH₃ (Na, 0.117 g, 5.08 mmol, in 30 ml dry methanol) at room temperature, under argon atmosphere and stirring was added 5,11,17,23-tetra-(*p*-*t*-butyl)-25,26, 27,28- tetra hydroxy-calix(4)arene **I** (1g, 1.54 mmol) and 50 ml dry xylene. The solution was stirred 30 min at room temperature and the methanol was removed. The resulted 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 hrs reflux, the reaction mixture was cooled and NaCl filtered off, the filtrate was washed with water and then dried over Na₂SO₄. The solvent was evaporated on a rotary evaporator and a crude product 1,3 g, (80%) yielded. It was 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**

[31], 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 Na₂SO₄, 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 LiAlH₄) 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 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 NaOCH₃, (Na, 0.063g, 2.7 mmol in 15 ml of dry methanol) was added **II** (1.1g, 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 (2x25 ml) and evaporated. The product was dissolved in chloroform and washed with 50 ml dilute HCl and water (3x50 ml). The solution was dried (Na₂SO₄) filtered and evaporated. Yield: 1.15 g, (86%), white product, recrystallized from toluene, m.p. 270-273°C.

4. CONCLUSIONS

In this paper we describe 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. In order to limit the full esterification we use a smaller amount of deprotonating and **phosphorylating** agents. The obtained new compounds **are** characterized by elemental analysis, IR-, ¹H-, ¹³C-, ³¹P{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 convenient and **readily** available reagent, **even though** the yield of **IVA** **is** lower. Using NaOCH₃ as deprotonating agent instead of BuLi for **VI** **leads** to a higher yield of the product. We **want** to synthesize the calixarenes **in** higher yield 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 presently under investigation.

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Figure 1. The molecular structure of VI determined by single-crystal x-ray diffraction.