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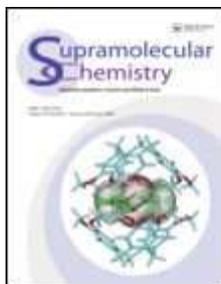
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**Synthesis and characterization of partially substituted at lower rim phosphorus containing calix(4)arenes**

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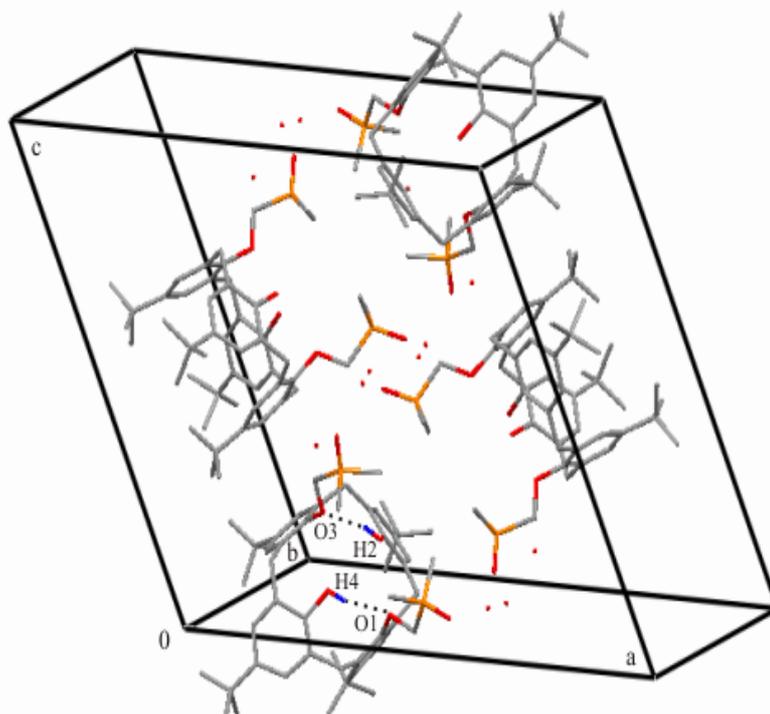
**Table 4. Crystal data and structure refinement for VI**

Empirical formula	C <sub>50</sub> H <sub>76</sub> O <sub>9</sub> P <sub>2</sub>	
Formula weight	883.05	
Temperature	140(2) K	
Wavelength	0.71073 Å	
Crystal system	monoclinic	
Space group	P2 <sub>1</sub> /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 <sup>3</sup>	
Z	4	
Density (calculated)	1.033 Mg/m <sup>3</sup>	
Absorption coefficient	0.122 mm <sup>-1</sup>	
F(000)	1912	
Crystal size	0.23 x 0.20 x 0.13 mm <sup>3</sup>	
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 <sup>2</sup>	
Data / restraints / parameters	7745 / 162 / 550	
Goodness-of-fit on F <sup>2</sup>	0.918	
Final R indices [I > 2σ(I)]	R <sub>1</sub> = 0.0976, wR <sub>2</sub> = 0.2144	
R indices (all data)	R <sub>1</sub> = 0.3783, wR <sub>2</sub> = 0.3505	
Largest diff. peak and hole	0.510 and -0.228 e. Å <sup>-3</sup>	

**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.



**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 $\nu$ (cm <sup>-1</sup> )
			Found, %				Calculated, %					
			C	H	N	P	C	H	N	P		
<b>1. IV</b> C <sub>68</sub> H <sub>74</sub> O <sub>6</sub> P <sub>2</sub> 1049.28 <b>Method A IVA</b>	19.5	260-262	77.61	7.22	-	5.87	77.84	7.11	-	5.90	1049.8 (M+H) <sup>+</sup> 1066.8 (M+H <sub>2</sub> O+H) <sup>+</sup>	(P=O) 1183 (s), 1202 (s), 1241(vs), (P-O-C) 918 (s)
<b>Method B IVB</b>	29	257-259	76.92	7.31	-	5.80					1049.6 M 1050.6 (M+H) <sup>+</sup> 391.3 (M+C <sub>8</sub> H <sub>10</sub> +H <sub>2</sub> O)/3 371.4 (M+C <sub>2</sub> H <sub>5</sub> OH+H <sub>2</sub> O)/3	(P=O) 1177 (s), 1192 (s), (P-O-C) 910 (s) (Ar-OH) 3530 (vs)
<b>2. Vb</b> C <sub>56</sub> H <sub>89</sub> N <sub>6</sub> O <sub>7</sub> P <sub>3</sub> 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) <sup>+</sup>	(P=O) 1179(vs), 1194 (s), (P-N-CH <sub>3</sub> ) 1308 (vs) (Ar) 1462 (vs), 1481(vs), 1599(vs) (Ar-OH) 3567 (vs)
<b>3. VI</b> C <sub>50</sub> H <sub>70</sub> O <sub>6</sub> P <sub>2</sub> .H <sub>2</sub> O 847.05 <b>Method A VIA</b>	90	365-370	71.19	8.68	-	7.29	70.90	8.57	-	7.31	829.80 (M+H) <sup>+</sup> 846.32 (M+H <sub>2</sub> O) 851.81 (M+Na) <sup>+</sup>	(P=O) 1172 (s), 1186 (vs), (Ar) 1486 (s), 1594 (s) (Ar-OH) 3449 (vs)
<b>Method B VIB</b>	78	368-370	71.03	8.65	-	7.26					829.5 (M+H) <sup>+</sup> 851.6 (M+Na) <sup>+</sup>	(P=O) 1169 (s), 1192 (s) (Ar) 1468 (s), 1586(s)
<b>4. VII</b> C <sub>66</sub> H <sub>102</sub> O <sub>6</sub> P <sub>2</sub> 1053.48	86	270-273	73.23	9.55	-	5.75	75.25	9.76	-	5.78	1053.6 (M+H) <sup>+</sup> 1075.6 (M+Na) <sup>+</sup>	(P=O) 1167 (s), 1191 (vs), (P-CH <sub>3</sub> ) 1364 (m) (Ar) 1477 (s), 1595 (s) (Ar-OH) 3421 (vs)

Table 2. <sup>1</sup>H- and <sup>31</sup>P-NMR data of Partially Substituted Phosphorylated Calix(4)arenes (δ in ppm).

Compd Index	Ar-H	OH*	Ar-CH <sub>2</sub> -Ar	CH <sub>2</sub> -P	(CH <sub>3</sub> ) <sub>2</sub> P	C(CH <sub>3</sub> ) <sub>3</sub>	C (CH <sub>3</sub> ) <sub>2</sub>	CCH <sub>2</sub> C	P-N(CH <sub>3</sub> ) <sub>2</sub>	P-Ar-H	<sup>31</sup> P{ <sup>1</sup> H}
<b>1.</b> <b>IVA</b>	6.96(s) , 6.57(s) 8H	5.29(s), 2H	4.20,2.96(dd)8H <sup>2</sup> J <sub>HH</sub> =17.5 Hz, <sup>2</sup> J <sub>HH</sub> =17.2 Hz	-	-	1.25(s) 0.81(s) 36H	-	-	-	7.96(dd)7.38(dt) 7.54(dt), 20H	34.60 (s)
<b>IVB</b>	7.06(s), 6.62(s) 8H	5.35(s) 2H	4.66, 2.83(dd) <sup>2</sup> J <sub>HH</sub> =14.5 Hz <sup>2</sup> J <sub>HH</sub> =14.7 Hz	-	-	1.29(s), 0.86(s) 36H	-	-	-	8.08(d), 7.42 (dt) 7.55(dt), 20H	34.50 (s)
<b>2.</b> <b>Vb</b>	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) <sup>2</sup> J <sub>HH</sub> = 13.5- 13.7 4.31 (d),3.40(d) <sup>2</sup> J <sub>HH</sub> = 14.2-14.5 8H	-	-	1.38(s), 1.35(s), 0.88(s) 36H	-	-	2.78(d), 12 H <sup>3</sup> J <sub>PH</sub> = 9.9 Hz 2.58(d), 12 H <sup>3</sup> J <sub>PH</sub> = 9.9 Hz 2.74(d), 12 H <sup>3</sup> J <sub>PH</sub> = 9.5 Hz	-	18,66(s), 18.00(s), ratio 2:1
<b>3.</b> <b>VIA</b>	7.12(s), 6.71(s) , 8H	6.18(s) 2H	4.11, 3.39 (dd) <sup>2</sup> J <sub>PH</sub> =13.3 Hz, <sup>2</sup> J <sub>PH</sub> =13.1 Hz, 8H	4.26, (d) <sup>2</sup> J <sub>PH</sub> = 8 Hz, 4H	1.87(d), <sup>2</sup> J <sub>PH</sub> = 13.1Hz 12H	1.32(s), 0.86(s) 36H	-	-	-	-	41.21 (s)
<b>VIB</b>	7.09(s), 6.75(s), 8H	6.26(s) 2H	4.29, 3.32 (dd) <sup>2</sup> J <sub>PH</sub> =13.3 Hz, <sup>2</sup> J <sub>PH</sub> =13.2 Hz, 8H	4.43 (d) <sup>2</sup> J <sub>PH</sub> =7.7 Hz, 4H	1.88 (d) <sup>2</sup> J <sub>PH</sub> =13.3 Hz, 12H	1.30(s), 0.85(s) 36H	-	-	-	-	40.89 (s)
<b>4.</b> <b>VII</b>	7.08 (s), 2H 6.81(s), 2H	6.57(s) 2H	4.13(d), <sup>2</sup> J <sub>PH</sub> =12.5 3.40(d), <sup>2</sup> J <sub>PH</sub> =12.6 8H	4.20 (d) <sup>2</sup> J <sub>PH</sub> = 7.7 Hz 4H	1.96(d) <sup>2</sup> J <sub>PH</sub> = 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.  $^{13}\text{C}$ - NMR data of Partially Substituted Phosphorylated Calix(4)arenes, ( $\delta$  in ppm)

Compd. Index	C ( Ar)	Ar- $\text{CH}_2$ -Ar	C( $\text{CH}_3$ ) <sub>3</sub>	C-( $\text{CH}_3$ ) <sub>2</sub>	C-( $\text{CH}_3$ ) <sub>3</sub>	C( $\text{CH}_3$ ) <sub>2</sub>	C- $\text{CH}_2$ -C	( $\text{CH}_3$ ) <sub>2</sub> P	$\text{CH}_2$ -P	P-N( $\text{CH}_3$ ) <sub>2</sub>	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), <sup>2</sup> J <sub>PC</sub> =133.8 Hz 129.1(d) <sup>3</sup> J <sub>PC</sub> =163.0 Hz 125.5(d) <sup>4</sup> J <sub>PC</sub> =150.9 Hz 126.4(d) <sup>5</sup> J <sub>PC</sub> =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) <sup>2</sup> J <sub>PC</sub> = 68.1Hz,	74.0, 73.2(d) <sup>2</sup> J <sub>PC</sub> = 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) <sup>2</sup> J <sub>PC</sub> = 68.3Hz,	74.3, 73.0(d) <sup>2</sup> J <sub>PC</sub> = 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-,  $^1\text{H}$ -,  $^{13}\text{C}$ -,  $^{31}\text{P}\{^1\text{H}\}$  – 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

1  
2  
3  
4 inclusion of calixarenes into polymer molecules or their immobilization onto  
5  
6 polymer supports have been reported in the literature [15-22]. This leaves open  
7  
8 a potential way to the improvement of the complexation and extraction ability of  
9  
10 calixarene copolyethers and copolyesters, containing phosphoryl fragment.  
11  
12

13  
14 It is therefore of particular interest to synthesize new phosphorus containing  
15  
16 calixarenes, partially substituted at lower rim, aiming at their potential reactivity  
17  
18 as co-monomers in polymerization [23,24]. In this article we report the synthesis  
19  
20 and characterization of calix(4)arenes partially substituted at the lower rim and  
21  
22 bearing mainly a phosphine oxide moiety. They can be used both as co-  
23  
24 monomers in polymerizations and as complexation agents for metal ions or  
25  
26 extractants of nuclear waste solutions on their own right [17,25-28].  
27  
28  
29  
30  
31  
32

## 33 2. RESULTS AND DISCUSSION

### 34 2.1. Synthesis and Structure Identification

35  
36 Partially phosphorylated calix(4)arenes are obtained in a two step  
37  
38 procedure. First, some of the OH groups of the initial calix(4)arenes I or II are  
39  
40 deprotonated by a base, e.g. BuLi, triethylamine (TEA) or most conveniently  
41  
42 sodium methoxide (NaOCH<sub>3</sub>) in methanol followed by addition of xylene. After  
43  
44 subsequent phosphorylation with various phosphorus compounds four new  
45  
46 calix(4)arenes are obtained (**Scheme 1**): **IV(A)** - with diphenyl phosphinic acid  
47  
48 chloride (DPPAC), **IV(B)** – with diphenyl phosphine oxide (DPPO), **V**- with  
49  
50 bis(dimethylamino) phosphinic acid chloride (DMPAC), **VI** and **VII**- with  
51  
52 chloromethyl dimethyl phosphine oxide (CDMPO). Two routes are used to  
53  
54 prepare **IV** and **VI**.  
55  
56  
57  
58  
59  
60

**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 Et<sub>3</sub>N 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-, <sup>1</sup>H-, <sup>13</sup>C-, <sup>31</sup>P{<sup>1</sup>H}- NMR spectroscopy and mass spectrometry. The obtained data of these products were almost identical. The ES–MS of compound

1  
2  
3  
4  
5 **IVA**, namely 5,11,17,23-tetra-*p-t*-butyl-25,27-dihydroxy-26,28-bis(diphenyl  
6  
7 phosphinoyl-oxy)calix(4)arene, **shows** one basic molecular peak at  $m/z = 1049,8$   
8  
9  $(M+H)^+$ , (*calc.* 1049,3) and an additional peak at 1066,80 (probably  $M + H_2O +$   
10  
11  $H)^+$  (method **A**) and  $m/z = 1049,6 ; 1050,6 ; 391,3 ; 371,4 ;$  and 279,3 probably due  
12  
13 to  $M$ ,  $(M+H)^+$ ,  $[M+ (CH_3)_2C_6H_4 + H_2O]/3$ ,  $(M+ C_2H_5OH +H_2O)/3$  and  $[M+$   
14  
15  $C_2H_5OH +H_2O + H^+]/4$  resp., *calcd.* 1049.3, 1050.3, 391.2, 371.1 and 278.6 for  
16  
17 **IVB** (method **B**).

20  
21 The  $^1H$  – NMR spectrum is in agreement with the assumed structure of the  
22  
23 di-substituted product. There are two pairs of doublets at  $\delta = 4,92$  and 2,91 ppm  
24  
25 characteristic for the protons of methylene bridges (method **A**). That means the  
26  
27 molecule is symmetrical – esterified at **positions 26 and 28** and in **the** cone  
28  
29 conformation [30]. **Should** the esterification **take place at positions** 27 and 28, the  
30  
31  $^1H$  – NMR spectrum would have three different pairs of doublets. Three kinds of  
32  
33 protons for the methylene bridges have to be present for such molecules. **We**  
34  
35 **however only observe** one singlet for OH at 5,29 ppm and two singlets for  
36  
37 aromatic protons. One singlet at  $\delta = 34,60$  ppm is observed in the  $^{31}P\{^1H\}$ -NMR  
38  
39 spectrum. These data also support **esterification at** the 26,28-position. The data  
40  
41 for **IVB** are shown in Table 2.

42  
43 In addition, the  $^{13}C$ -NMR spectrum of **IVA** shows two singlets at  $\delta = 31,9$   
44  
45 and 30,6 ppm for  $C(CH_3)_3$ , one singlet at  $\delta = 32,7$  ppm for  $Ar - CH_2 - Ar$  and four  
46  
47 doublets for the ring **C**s. (**Table 3**).

48  
49 A direct lower rim esterification with DPPAC is used instead of DPPO  
50  
51 because the first one was more convenient and available reagent, but the yield  
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4 was lower. To synthesize the calixarene with higher yield we pursue a different  
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6 procedure leading to the same product.  
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9  
10 In order to obtain a tetra-esterified product intermediate **III** is reacted with  
11 DMPAC at ratio of 1:5. In this case the outcome is a mixture of esterified  
12 calixarenes, containing mainly di- **Va** and tri-substituted **Vb**. There are traces of  
13 mono- and tetra-substituted calixarenes. The yield of the crude product (mixture)  
14 from our experiments is 72 – 80 %. After separating the di- and tri-ester  
15 phosphoramides from the mixture by fractional crystallization from  
16 dimethylsulfoxide (DMSO), we isolate 27-31% di-substituted product 5,11,17,23-  
17 tetra-*p-t*-butyl-25,27-dihydroxy-26,28-bis(tetramethyl-diamidophosphinoyl-oxy)  
18 calix(4) arene **Va**. This product, which is soluble in chloroform, alcohols, acetone,  
19 toluene and ethylacetate has been described previously [31]. The filtrate is  
20 further allowed to crystallize and after a few days 54-60% tri-esterified product,  
21 namely 5,11,17,23- tetra-*p-t* -butyl-25-hydroxy-26,27,28-tris(tetramethyl diamido  
22 phosphinoyl)-oxy)calix(4) arene **Vb** can be isolated too. It is a white crystalline  
23 substance, which melts at 260 - 265 °C and is soluble in chloroform, alcohols,  
24 acetone, toluene, ethylacetate, DMSO and diethylether. Thin layer  
25 chromatography of **Vb** on Silica gel 60 F<sub>254</sub> (Merck) shows only one spot, R<sub>f</sub> =  
26 0,43 (CH<sub>2</sub>Cl<sub>2</sub>/CH<sub>3</sub>OH, 10 : 1, v/v). Its structure is confirmed by IR-, NMR-  
27 spectroscopy and ES mass spectral data. The ES – MS displays only a peak for  
28 the triester phosphoramide at 1051,9 corresponding to the [M + H]<sup>+</sup> mass (*calc.*  
29 C<sub>56</sub>H<sub>89</sub>N<sub>6</sub>O<sub>7</sub>P<sub>3</sub> = 1051,3) and no peaks corresponding to the mono-, di- or tetra-  
30 substituted products (mono-, C<sub>48</sub>H<sub>67</sub>N<sub>2</sub>O<sub>5</sub>P, 783,04; di-, C<sub>52</sub>H<sub>78</sub>N<sub>4</sub>O<sub>6</sub>P<sub>2</sub>, 917,12;  
31 and tetra-, C<sub>60</sub>H<sub>106</sub>N<sub>8</sub>O<sub>8</sub>P<sub>4</sub>, 1185,41 respectively). Moreover, the <sup>31</sup>P{<sup>1</sup>H}-NMR  
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4 spectrum **shows** two singlet signals for the two kind of phosphorus atoms at  $\delta =$   
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6  
7 18,00 and  $\delta = 18,66$  ppm, at integral intensity ratio of 1 : 2, as expected. The  $^1\text{H}$  –  
8  
9  
10 NMR spectrum also **shows** peaks for three kinds of C(CH<sub>3</sub>) at  $\delta = 0,88$ ,  $\delta = 1,35$   
11  
12 and  $\delta = 1,38$  ppm, in ratio 1 : 2 : 1. For the protons of N-CH<sub>3</sub> we observed **a**  
13  
14  
15 doublet of doublets at  $\delta = 2,58$  and at  $\delta = 2,78$  ppm with  $^3J_{\text{PH}} = 9,9$  Hz and a  
16  
17  
18 doublet at  $\delta = 2,74$  ppm with  $^3J_{\text{PH}} = 9,5$  Hz, in ratio 2:1. Two doublets of doublets  
19  
20  
21 arising from the bridge methylene groups at  $\delta = 3,33$  ppm,  $^2J_{\text{PH}} = 13,7$  Hz,  $\delta =$   
22  
23  
24 5,11 ppm,  $^2J_{\text{PH}} = 13,5$  Hz,  $\delta = 3,40$  ppm,  $^2J_{\text{PH}} = 14,3$  Hz and  $\delta = 4,31$  ppm,  $^2J_{\text{PH}} =$   
25  
26  
27 14,5 Hz **are** observed, too. The  $^{13}\text{C}$  – NMR spectra and elemental analysis data  
28  
29  
30 **agree with the suggested structure**. The IR – spectrum of the compound (**Table**  
31  
32  
33 **1**) contains bands for phosphoryl (P=O) groups **at** 1179, 1194 and 1231  $\text{cm}^{-1}$ ,  
34  
35  
36 for P–N–CH<sub>3</sub> **at** 1308  $\text{cm}^{-1}$  and for phenolic hydroxyl groups at 3567  $\text{cm}^{-1}$ .

37  
38  
39 Finally, the di-substituted calixarenes **VI** and **VII** (according to the **Scheme**  
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41  
42 **1**) were obtained in good yields (90% and 86 % resp.). We use two equivalent of  
43  
44  
45 NaOCH<sub>3</sub> to ensure the deprotonation only of two hydroxyl groups, because the  
46  
47  
48 presence of extra base leads to the deprotonation of all OH groups thus leading  
49  
50  
51 to the tetra substituted products. There **are** data in the literature [27,28] about **the**  
52  
53  
54 complexation ability of the calixarenes and a way to improve their extractability **is**  
55  
56  
57 to change the substituents at the upper rim. The exchange of tert-Bu with tert-Oct  
58  
59  
60 can improve solubility **of** both the calixarenes and their complexes.

61  
62  
63 The implementation of two different deprotonating agents **results** into the  
64  
65  
66 identical product **VI**. It **is** soluble in chloroform, alcohols, acetone, ethylacetate  
67  
68  
69 **and insoluble** in water, toluene, xylene. The ES – MS of **VI(A)** shows only peaks  
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71  
72 at  $m/z = 829,8$  and  $846.8$  referred respectively to  $(M + H)^+$  and  $(M+H_2O+H)^+$  and

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4 at 851,8 – for  $(M + Na)^+$ . The calculated molecular mass  $M$  is 829,05. Regarding  
5  
6 the  $^1H$  – NMR spectrum of compound **VI(A)**, there are only a singlet for the  
7  
8 hydroxyl group at  $\delta = 6,18$  ppm, two singlets at  $\delta = 6,71$  ppm and at  $\delta = 7,12$  ppm  
9  
10 for H – Ar and two singlets for  $(CH_3)_3C-$  at  $\delta = 0,86$  and  $\delta = 1,32$  ppm. There are  
11  
12 also doublets at  $\delta = 1,87$  ppm with  $^2J_{PH} = 13,1$  Hz and at  $\delta = 4,26$  ppm with  $^2J_{PH} =$   
13  
14 8,0 Hz, characteristic for  $CH_2-P$  and  $(CH_3)_2 P$  resp. Two doublets are observed  
15  
16 at  $\delta = 4,10$  ppm and at  $\delta = 3,38$  ppm for the methylene bridges (Ar- $CH_2$ -Ar).  
17  
18 There is only a signal for the methylene bridges in the  $^{13}C$  – NMR spectrum , two  
19  
20 singlets for  $-C(CH_3)_3$  and  $-C(CH_3)_3$  and doublets for  $CH_2-P$  at  $\delta = 15,3$  with  
21  
22  $^2J_{PC} = 68,1$  Hz and at  $\delta = 73,6$  ppm with  $^2J_{PC} = 81,2$  Hz for  $(CH_3)_2 P$ . Similar data  
23  
24 are observed for **VI(B)**. In the  $^{31}P\{^1H\}$ -NMR spectrum there is a singlet at  $\delta =$   
25  
26 41,21 ppm for **VI(A)** and 40.89 ppm for **VI(B)**. These data are evidence that the  
27  
28 molecules of the calixarene are symmetrical.  
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36 Product **VII** is well soluble in methanol, toluene, dioxane, ethylacetate, methylene  
37  
38 chloride, chloroform and insoluble in water, acetone, hexane. The spectroscopic  
39  
40 data of this compound were close to those of product **VI**, except for the presence  
41  
42 of peaks for the t-octyl substituent instead of the t-Bu one. In the ES-MS  
43  
44 spectrum, there are two peaks  $m/z = 1053,6$  ( $M + H$ ) $^+$  and  $m/z = 1075,6$  ( $M +$   
45  
46  $Na$ ) $^+$  (calcd 1053.48) and no other peaks in the 500 to 2000 region. The  $^1H$  –  
47  
48 NMR spectrum shows a doublet at 4,20 ppm for  $CH_2-P$  with  $^2J_{PH} = 7,7$  Hz and a  
49  
50 doublet at  $\delta = 1,96$  ppm for  $(CH_3)_2 P-$  with  $^2J_{PH} = 13,1$  Hz. A doublet of doublets at  
51  
52  $\delta = 3,40$  and 4,13 ppm,  $^2J_{PH} = 12,6$  Hz shows the presence of Ar- $CH_2$ -Ar. The  
53  
54 singlet signals and their integrals correspond to the protons of the t-octyl group.  
55  
56 The  $^{31}P\{^1H\}$ -NMR spectrum shows a singlet at  $\delta = 40,27$  ppm.  
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4 The NMR data for all substituted calix(4)arenes indicated that the  
5  
6 molecules were symmetrical and in cone conformation, which is further confirmed  
7  
8 in the solid state by the structure of **VI(A)** determined by X-ray crystallography.  
9  
10

## 11 12 13 14 **2.2. X-ray Crystallographic Investigations**

15  
16 The molecular structure of calix(4)arene **VI(A)** is shown on **Figure 1**. The crystal  
17  
18 data and structure refinement are listed in **Table 4** and the relevant geometrical  
19  
20 parameters are shown in **Table 5**. The bond values and torsion angles are in  
21  
22 agreement with those reported in the literature for such **this type of** geometry. For  
23  
24 instance, the aromatic rings, which lie below the reference plane passing through  
25  
26 the four CH<sub>2</sub> bridging groups, are forming the hydrophobic part of the molecule  
27  
28 and the orientation of the rings determine the flattened cone conformation. The  
29  
30 hydrophilic part of the molecule is formed by both hydroxyl and phosphine oxide  
31  
32 groups, situated above the reference plane. The dihedral angles between phenyl  
33  
34 moieties are as follows: A / B - 83.6(3)°; A / C - 14.8(5)°; A / D 88.5(4)°; B / C -  
35  
36 86.7(3)°; B / D 77.3(5)°. The A and C opposite rings are quite parallel, while the  
37  
38 other two B and D are almost perpendicular one to another. The distances  
39  
40 between the opposite *t*-butyl groups are [C35... C43 = 6.52Å; C47 ...  
41  
42 C39=11.71Å]. The geometrical parameters characterizing the phosphine oxide  
43  
44 groups are in good agreement with the presence of double bonds between P1-  
45  
46 O5 and P2-O6. The values of the C1-O1-C29-P1 and C15-O3-C32-P1 torsion  
47  
48 angles are 176.6 and 172.4 Å respectively and the orientation of the phosphine  
49  
50 oxide groups towards the aromatic part of the molecule is almost the same.  
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52 Although the calixarene substitutes are symmetrically positioned, the whole  
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4 molecule does not possess symmetry elements. This is explained by the higher  
5  
6 conformational degree around C-C and C-O bonds. Two strong intramolecular  
7  
8 hydrogen bonds - O(2)-H(2) ... O(3) and O(4)-H(4) ...O(1) are observed within  
9  
10 the molecule. The three dimensional packing of the molecules is stabilized by  
11  
12 intensive hydrogen bonding between the phosphonic parts of the molecules and  
13  
14 two of the water molecules, while the third O(9) water molecule is not involved in  
15  
16 the hydrogen bonding network (**Figure 2**). The O(7) water molecule acts as a  
17  
18 bridging ligand to O6 atoms from the calixarene molecule and O(8) to O(5). Thus  
19  
20 O(6)...O(7)...O6[-x,-y,1-z]...O7[-x,-y,1-z] hydrogen bonding cyclic motif is  
21  
22 formed. They are connected by O(5) [-x,-1/2+y,1/2-z] ...O(8)[-x,-1/2+y,1/2-z] and  
23  
24 O8...O5 hydrogen bonds, which stabilize the formation of pseudo hydrophilic  
25  
26 cavities of the molecules. There are two additional  $\pi$  interaction between the B  
27  
28 phenyl ring and the methyl part of the phosphine oxide groups stabilizing the  
29  
30 pseudolayer arrangement [C10 ...C34 = 3.62Å; C12...C31=3.78 Å].  
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### 40 3. EXPERIMENTAL

#### 41 3.1. Reagents and physical measurements

42 Compounds I and II are synthesized according to the literature procedures [6,32].

43 Toluene and xylene are distilled over Na and stored over molecular sieves 4Å  
44  
45 (Merck).

46 Methanol is distilled after drying by a procedure with Mg . Other solvents and  
47  
48 chemicals are of reagent grade and are used as received from Merck and Fluka.

49 TLC is done using plates coated with Merck Kieselgel 60 F<sub>254</sub>.  
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4 Melting points are determined on microhot stage Boetius PHMK and are  
5 uncorrected. The IR spectra are measured on Mattson Alpha Centaury FT  
6 spectrometer as KBr pellets.  $^1\text{H}$  – NMR spectra are recorded on Bruker 400  
7 spectrometer in  $\text{CDCl}_3$ ,  $^{31}\text{P}\{^1\text{H}\}$ -NMR spectra are registiered on the same  
8 instrument at 161.9 MHz in  $\text{CDCl}_3$  as solvent. Chemical shifts are measured  
9 relative to TMS as internal standard for ( $^1\text{H}$ ) or external -  $\text{H}_3\text{PO}_4$  (85%), for  
10  $^{31}\text{P}\{^1\text{H}\}$ .  $^{13}\text{C}$ -NMR spectra are recorded on Bruker Avance DRX 250 MHz.  
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20 The ES-MS are performed on a Finnigan SSQ 710C spectrometer using a  
21 capillary temperature of  $200^\circ\text{C}$  and acceleration potential of 4.5 kV.  $10^{-4}$  –  $10^{-5}$  M  
22 solutions of substances in methanol are infused in a mixture of  
23  $\text{CH}_3\text{OH}/\text{H}_2\text{O}/\text{HCOOH}$  (50:50:1, v/v). The elemental analysis are carried out by  
24 Dr. H.J.Eder from the Microchemical Laboratory of the University of Geneva (for  
25 determination of C, H and N) and by Ilse Beetz Laboratory (96301 Kronach,  
26 Germany) for determination of phosphorus content.  
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### 40 **3.2. Crystal structure determination of 5,11,17,23-tetra-*p*-*t*-butyl-25,27-** 41 **dihydroxy-26,28,-bis(dimethylphosphinoyl-methoxy)-calix(4)arene.**

42 The crystals of **VI** were prepared by slow crystallization from a diluted  
43 ethylacetate solution at room temperature with the possibility of partial  
44 evaporation of the solvent.  
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51 Data collection were performed at 140(2) K using Mo K  $\alpha$  radiation on a four-  
52 circle kappa goniometer with an Oxford Diffraction KM4 Sapphire CCD. Cell  
53 refinement and data reduction were carried out with the aid of CrysAlis RED 1.7.1  
54  $\beta$  release [33]. No absorption correction was applied to the data set. All  
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4 structures were refined using the full-matrix least-squares on  $F^2$  with all non-H  
5  
6 atoms anisotropically defined. The hydrogen atoms were placed in calculated  
7  
8 positions using the "riding model". Structure refinement and geometrical  
9  
10 calculations were carried out with SHELXTL 5.1. [34]. Crystallographic data  
11  
12 (excluding structure factors) for the structure reported in this paper are deposited  
13  
14 with the Cambridge Crystallographic Data Centre as supplementary publication  
15  
16 No. **CCDC 296492**.  
17  
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### 23 **3.3. Synthesis**

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25  
26 5,11,17,23-tetra(*p*-*t*-butyl)-25,27-dihydroxy-26,28-  
27  
28 *bis*(diphenylphosphinoxy)calix(4)-arene. (IV)  
29

30 **Method A:** To a transparent colorless solution of 5,11,17,23-tetra(*p*-*t*-butyl)-  
31  
32 calix(4)-arene **I** (1.07 g, 1.66 mmol) in a mixture of toluene (100 ml) and TEA (18  
33  
34 g, 178 mmol) a transparent colorless solution of DPPAC (2.36 g, 9.97 mmol) in  
35  
36 toluene (50 ml) was added by a dropping funnel. The reaction mixture was stirred  
37  
38 at nitrogen atmosphere and at room temperature for 3 hours and at 90°C for 48  
39  
40 hrs. After cooling to room temperature the reaction mixture was filtered to  
41  
42 separate the white sediment, mainly TEA hydrochloride. The filtrate was  
43  
44 evaporated and the residue dissolve in 120 ml fresh toluene. The resulting  
45  
46 solution was washed with 12x50 ml distilled water, dried over MgSO<sub>4</sub> and  
47  
48 toluene was evaporated. The solid white residue was washed 6x50 ml with *n*-  
49  
50 hexane (stirring and refluxing for 15 min.) and 4x50 ml water-ethanol (stirring for  
51  
52 15 min at 50°C). The resulting white powder was dried at 60°C and high vacuum  
53  
54 for 24 hr. Yield 0.34 g (19.5%), m.p. 260 – 262 °C.  
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4 **Method B:** To a solution of 5,11,17,23-tetra(*p-t*-butyl)- calix(4)arene **I** (1.0 g, 1.54  
5 mmol) in dry toluene (90 ml) in a four necked flask provided with mechanical  
6 stirrer, thermometer, argon inlet and condenser were added DPPO (1.6 g, 7.92  
7 mmol) and TCM (2.7 g, 17.6 mmol). A solution of TEA (1.3 ml, 0.94 g, 9.3  
8 mmol) in toluene (15 ml) was added via dropping funnel to the reaction mixture at  
9 0°C. The mixture was stirred 3 hrs at room temperature and 10 hrs at 70-75 °C.  
10 The reaction mixture was cooled, filtered and the filtrate successively worked up  
11 with dilute HCl, dilute NaOH, water and water-ethanol (2:1), dried over Na<sub>2</sub>SO<sub>4</sub>  
12 and the solvents evaporated. Yield 0.46 g, (29%) white mass, m.p.257-259°C,  
13 TLC on Silica gel 60 F<sub>254</sub> (n-hexane/chloroform/acetic acid=10 : 6 : 1, R<sub>f</sub> = 0,62).  
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31 5,11,17,23-tetra-(*p-t*-butyl)-25-hydroxy-26,27,28-

32 tris(tetramethyldiamidophosphinoyl)oxy) calix(4)arene (**Vb**)

33  
34 To a solution of NaOCH<sub>3</sub> (Na, 0.117 g, 5.08 mmol, in 30 ml dry methanol) at  
35 room temperature, under argon atmosphere and stirring was added 5,11,17,23-  
36 tetra-(*p-t*-butyl)-25,26, 27,28- tetra hydroxy-calix(4)arene **I** (1g, 1.54 mmol) and  
37 50 ml dry xylene. The solution was stirred 30 min at room temperature and the  
38 methanol was removed. The resulted mixture was heated to reflux and a solution  
39 of DMPAC (0.867 g, 5.1 mmol) in 50 ml dry xylene was added via a dropping  
40 funnel. After 40 hrs reflux, the reaction mixture was cooled and NaCl filtered off,  
41 the filtrate was washed with water and then dried over Na<sub>2</sub>SO<sub>4</sub>. The solvent was  
42 evaporated on a rotary evaporator and a crude product 1,3 g, (80%) yielded. It  
43 was mixture of di- and tri- esterified calixarenes. That mixture was purified by  
44 fractional crystallization from DMSO and 0.35 g (27%) di-esterified calixarene **Va**  
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[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 Na<sub>2</sub>SO<sub>4</sub>, 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<sub>4</sub>) 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%),

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4 recrystallized from ethylacetate – methylene chloride, m.p. 368 – 370 °C,  
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7 isolated with 1 molecule water as crystalline hydrate.  
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14 5,11,17,23- tetra-(p-t-octyl)-25,27-dihydroxy-26,28- bis(dimethylphosphinoyl-  
15  
16 methoxy)calix(4)arene (VII)  
17

18 Prepared in a manner analogous to **Vb**. To a solution of NaOCH<sub>3</sub>, (Na, 0.063g,  
19 2.7 mmol in 15 ml of dry methanol) was added **II** (1.1g, 1.26 mmol) in 50 ml of  
20  
21 xylene and via dropping funnel CDMPO (0.38 g, 3.0 mmol) in 10 ml of xylene.  
22  
23 The reaction mixture was heated at reflux 22 hrs. The solvent was evaporated at  
24  
25 reduced pressure and the residue worked up with ethanol (2x25 ml) and  
26  
27 evaporated. The product was dissolved in chloroform and washed with 50 ml  
28  
29 dilute HCl and water (3x50 ml). The solution was dried (Na<sub>2</sub>SO<sub>4</sub>) filtered and  
30  
31 evaporated. Yield: 1.15 g, (86%), white product, recrystallized from toluene, m.p.  
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33 270-273°C.  
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#### 43 4. CONCLUSIONS

44  
45 In this paper we describe the synthesis of several new calix(4)arenes  
46  
47 partially substituted at the lower rim with **phosphorus** compounds – chloromethyl  
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49 dimethyl phosphine oxide, diphenyl phosphine oxide, bis(dimethylamino)  
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51 phosphinic acid chloride **and** diphenyl phosphinic acid chloride. In order to limit  
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53 the full esterification we use a smaller amount of deprotonating and  
54  
55 **phosphorylating** agents. The obtained new compounds **are** characterized by  
56  
57 elemental analysis, IR-, <sup>1</sup>H-, <sup>13</sup>C-, <sup>31</sup>P{<sup>1</sup>H} – NMR-spectroscopy, mass  
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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 NaOCH<sub>3</sub> 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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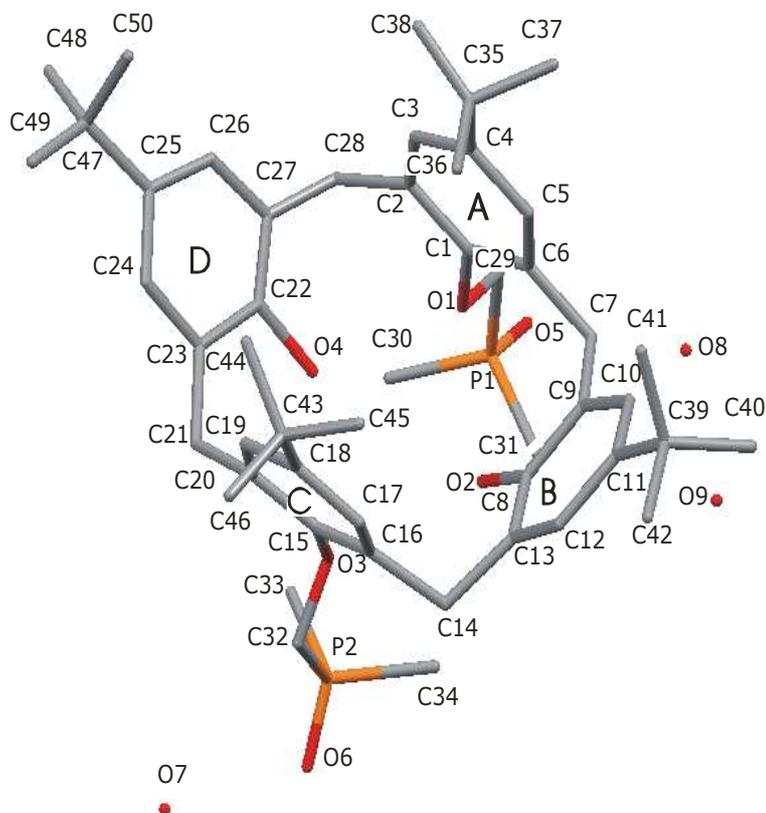


Figure 1. The molecular structure of VI determined by single-crystal x-ray diffraction.