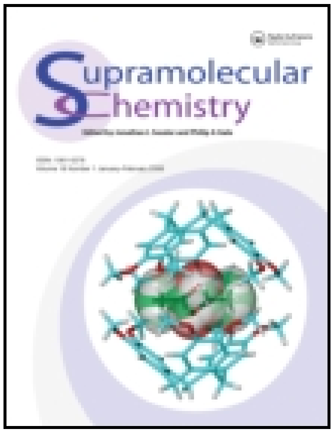

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Tetra-CMPO-derivatives of calix[4]arenes fixed in the *1,3-alternate* conformation

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Calix[4]arene derivatives fixed in the *1,3-alternate* conformation and substituted at one side by four carbamoylmethyl-phosphine oxide (CMPO) residues were synthesised. Two CMPO groups are directly attached to the wide rim, while the second pair is bound to the narrow rim via a tri- or tetramethylene spacer. Similar compounds, in which two CMPO groups at the wide rim are combined with two picolinamide groups or two ionisable carboxylic groups at the narrow rim, were also prepared. Some of these calixarene derivatives were studied as extractants for lanthanides (La^{3+}, Eu^{3+}, Yb^{3+}) and thorium (Th^{4+}) from acidic solution into methylene chloride. For selected samples, stability constants in methanol were determined by spectrophotometric titrations. Three compounds (**1b**′, **13**, **17**) in the *1,3-alternate* conformation and one intermediate in the *cone* conformation (**18**) were confirmed by a crystal structure.

Keywords: lanthanides; calix[4]arenes; complexation; extraction; crystal structures

1. Introduction

Carbamoylmethylphosphine oxides (CMPOs) are efficient extractants for actinides (and lanthanides), and, especially, the *N*,*N*-diisobutyl derivative is used on a technical scale (TRUEX process) (*1*). CMPO is a bidentate ligand and a trivalent cation surely binds more than one molecule of the ligand in its complex. Thus, it appeared reasonable to attach several CMPO functions to a common platform. In fact, tri-CMPO derivatives of triphenylmethanes (*2*) and tetra-CMPO derivatives of calix[4]arenes (*3*) are much more efficient extractants than CMPO itself. This is true for compounds where the CMPO functions are attached to the wide rim (*4*) or to the narrow rim (*5*). Better extraction results are even obtained with linear (*6*) oligo-CMPOs and with calix[4]arenes bearing only two or three CMPO functions (*7*).

Calix[4]arenes bearing ether residues equal to or larger than propyl are fixed in one of the four basic conformations (*cone*, *partial cone*, *1,2-* and *1,3-alternate*). Nearly all the calix[4]arene-derived ligands of the podand type are based on the *cone* conformation (*8*) where all oxygens (and all *p*-positions) point in the same direction, although rare examples with other conformations are known (*9–11*). It should be possible, however, to use also the *1,3-alternate* conformation as a scaffold (*12*), if the ligating groups are attached alternatingly to the wide and to the narrow rim, where an appropriate spacer could bring them to the same level. The *1,3-alternate* skeleton is more rigid compared to the *cone* isomers, which still can change between two 'pinched' *cone* conformations. Considering the fact that a tetra-CMPO derived from a rigid biscrown-3 calix[4]arene is by a factor of 10 more efficient as an extractant (*13*), this rigidity could be even advantageous.

It should also be worthwhile to attach different ligating functions to the wide and narrow rim of the calix[4]arene in its *1,3-alternate* conformation. Picolinamide groups, for instance, should lead to a better selectivity than CMPO functions alone (*14–16*). Carboxylic acids could potentially act as anion exchanger and reduce the number of nitrate anions to be extracted into the organic phase. Lipophilic carboxylic acids are often used as synergisers for neutral ligands in nuclear waste treatment (*17*), while polycarboxylic acids are proven to efficiently complex actinide (*18*) and lanthanide (*19*) cations (*20*).

2. Results and discussion

2.1 Syntheses

Amino groups attached to the wide rim of a calix[4]arene are usually obtained by the reduction of nitro groups which are often introduced via *ipso*-nitration (*21*). For the attachment at the narrow rim, the alkylation by *N*-(ω-bromoalkyl)phthalimides (or by ω-bromoalkylnitriles)

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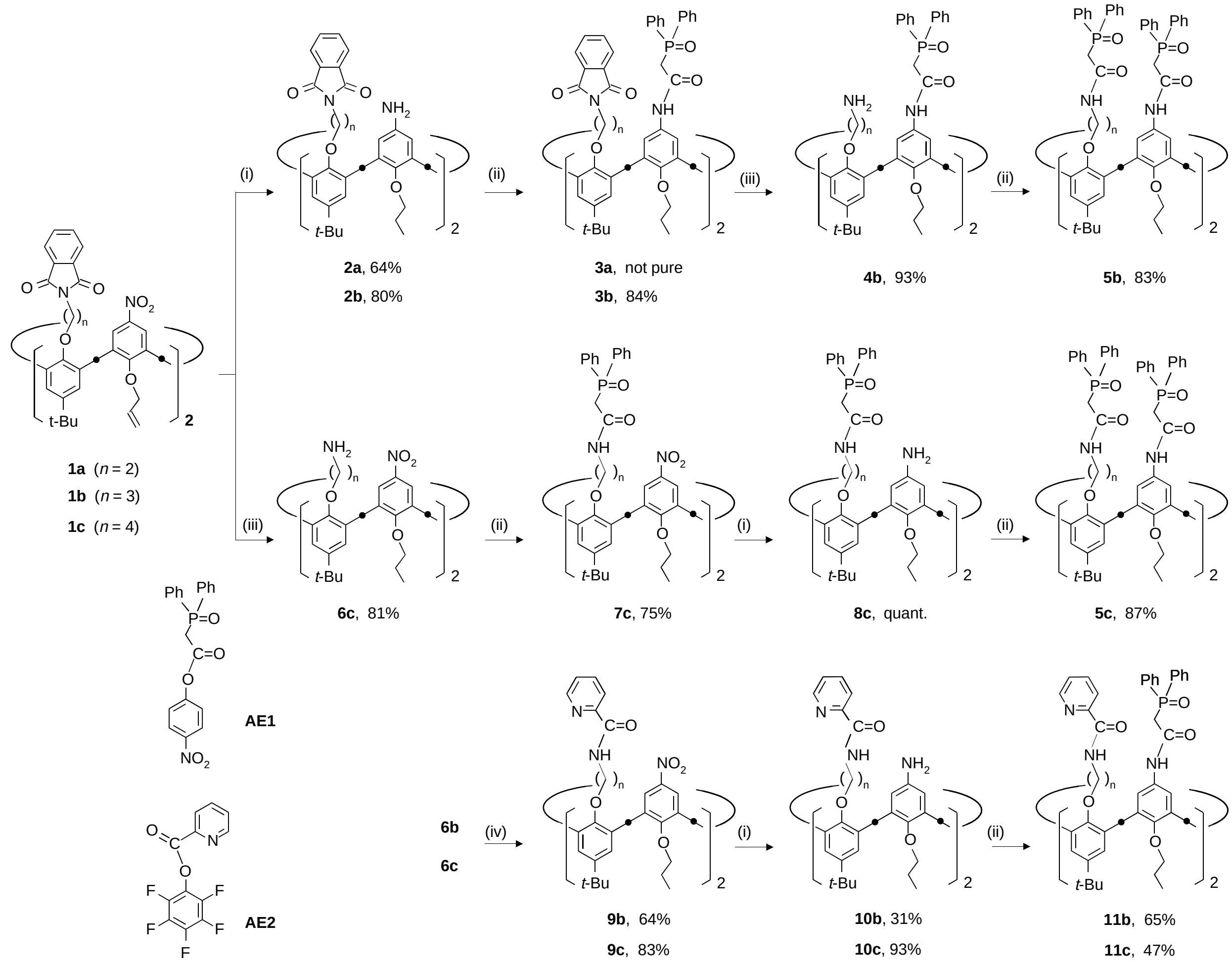


Scheme 1. Syntheses of tetra-CMPO derivatives of calix[4]arenes in the *1,3-alternate* conformation and of compounds bearing two CMPO and two picolinamide residues. (i) H_2, Raney-Ni, THF, r.t.; (ii) **AE1**, CH_2Cl_2, r.t.; (iii) hydrazine, EtOH, reflux and (iv) **AE2**, CH_2Cl_2, r.t.

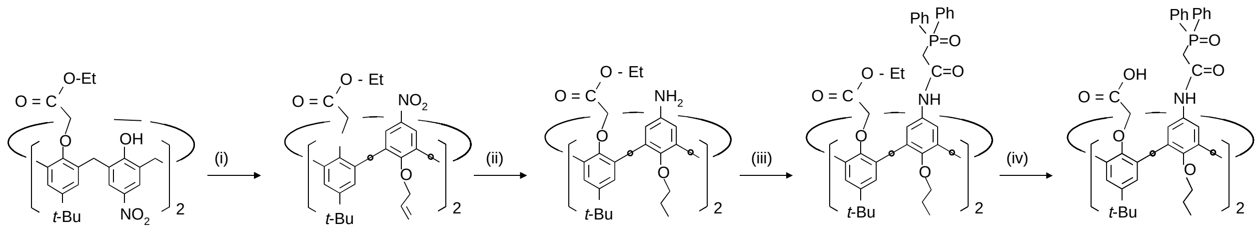
followed by hydrazinolysis of the phthalimide groups (or by reduction of the nitrile groups) are convenient methods.

Since selective substitutions are possible only at the wide rim distinguishing phenol and phenol ether units,[1] the following two pathways (Scheme 1) were checked, starting with the known *1,3-alternate* derivative **1** (*22*).

(a) Catalytic hydrogenation leads in excellent yields to the propoxy aniline derivative (amino propyl ether) **2a**,**b** ($n = 3, 4$) which was acylated by the active ester **AE1** (*3*, *13*) to give **3b** in 84% yield. (For $n = 2$, the product could not be sufficiently purified; for $n = 4$, this pathway was not further followed.) Cleavage of the phthalimide by hydrazine (93% of **4b**) and acylation of the aliphatic amino groups by **AE1** (83% of **5b** ($n = 3$)) occurred without problems.

(b) Alternatively (as studied for $n = 4$), cleavage of the phthalimide groups (of **1c**) with hydrazine occurred with the simultaneous hydrogenation of the allyl groups to give 81% of **6c**. Subsequent acylation by **AE1** (75% of **7c**) followed by quantitative hydrogenation of the nitro groups to **8c** and a second acylation step by **AE1** (87% of **5c** ($n = 4$)) was also possible without any problem. It should be mentioned that the allyl groups must not be quantitatively hydrogenated during the cleavage of the phthalimide groups, since this will be completed in the next step. It is important, however, that the cleavage of the phthalimide groups is quantitative while the nitro groups remain unchanged.

A direct conversion of **1** to the respective tetraamine (simultaneous or subsequent cleavage of the phthalimide groups and reduction of the nitro groups) was not attempted, although it should be more economic for those cases where only one acyl residue has to be attached.



Scheme 2. Synthesis of *1,3-alternate* derivatives combining two CMPO with two carboxylic groups. (i) Allylbromide, Cs_2CO_3, DMF, 50°C; (ii) H_2, Raney-Ni, THF, r.t.; (iii) **AE1**, CH_2Cl_2, r.t. and (iv) LiOH, THF–MeOH, r.t.

Two similar calixarene derivatives combining two picolinamide functions[2] at the narrow rim (attached via three or four methylene groups) with two CMPO functions at the wide rim were prepared in analogy to pathway (b). Acylation of **6b**,**c** with **AE2**, the hexafluorophenyl ester of α-picolinic acid (*24*) (64%/83% of **9b**,**c**), was followed by reduction of the nitro groups (31%/93% of **10b**,**c**) and acylation with **AE1** (65%/47% of **11b**,**c**). The partly striking difference in the yield for the last steps indicates that the reaction conditions are not optimised. These syntheses of extractants **5** and **11** are summarised in Scheme 1.

In order to (partly) compensate the positive charge of the extracted cation, we prepared compound **16**, where two CMPO functions are combined with two carboxylic groups. The synthesis starts with the known (*25*) diester **12** which is fixed in the *1,3-alternate* conformation as di-allyl ether **13** (isolated yield 21%, together with 39% of the isomer in the *partial cone* conformation). Reduction/hydrogenation and direct acylation of the crude diamine **14** furnished the diester **15** (92%), which was hydrolysed by aqueous LiOH to give the di-CMPO-di-acid **16** in 96% yield (see Scheme 2).

2.2 *Extraction and complexation*

The extraction of selected cations (lanthanides and thorium) from 1.0 M nitric acid into dichloromethane was studied for two tetra-CMPO compounds (**5b**, **5c**). The respective extraction percentages (*%E*) and distribution coefficients (*D*) are given in Table 1 and compared with the values previously obtained (*5–7*) for calixarenes fixed in the *cone* conformation and substituted at the wide or narrow rim by four CMPO functions. These data show that the extraction ability of lanthanides is similar for **5b** and **5c** (and practically identical for La^{3+}, Eu^{3+}, Yb^{3+}), but 5–20 times lower than for the analogues in the *cone* conformation. The stability constants of the complexes, however, are distinctly higher (by factors of 6–80) for **5b** than for **5c** (Table 2).

By all criteria, however, wide as well as narrow rim tetra-CMPOs in the *cone* conformation are better extractants/ligands than the derivatives in the *1,3-alternate* conformation, which, in addition, are more difficult to synthesise. Both data-sets show no real selectivity within the lanthanide series in contrast to the lower and, especially, the upper rim derivatives.

Table 1. Extraction of selected lanthanides and thorium by tetra-CMPOs **5**, $c_L = 10^{-3}$ M ($c_L = 10^{-4}$ M).

	La^{3+}	Eu^{3+}	Yb^{3+}	Th^{4+}
5b				
%E	11	11	9	(17)
D	0.12	0.12	0.09	(0.2)
5c				
%E	12	10	11	48 (12)[a]
D	0.13	0.11	0.12	0.92 (0.13)[a]
Narrow rim (*5*) ($n = 3$)				
%E	70	68	37	(96)
D	2.33	2.12	0.58	(24)
Wide rim (*6*, *7*)				
%E	98	64	6.6	(61.8)
D	49	1.78	0.07	(1.62)

Note: Values for a narrow and a wide rim tetra-CMPO fixed in the *cone* conformation are included for comparison.
[a] Values for $c_L = 10^{-4}$ M.

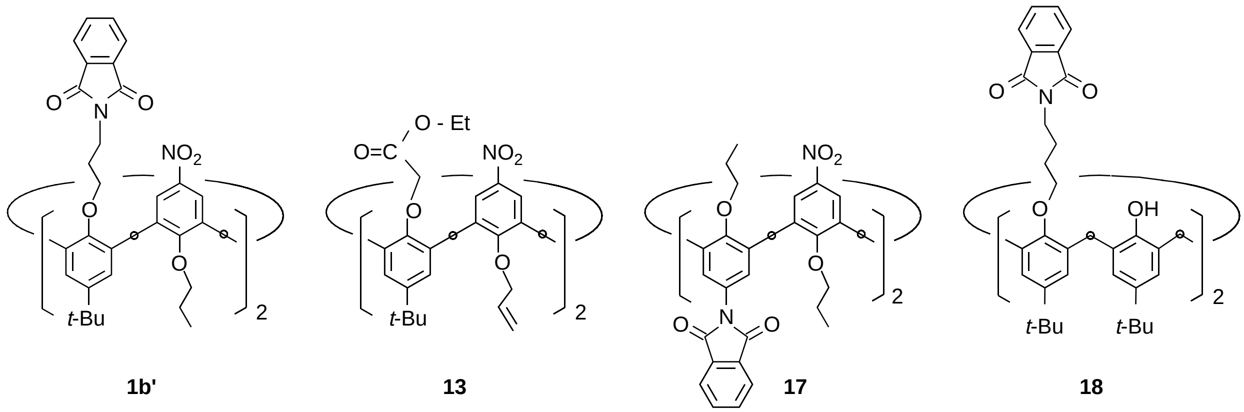
Table 2. Stability constants ($\log \beta \pm \sigma_{n-1}$) of the complexes of tetra-CMPOs **5** with some lanthanides in methanol at 25°C ($I = 10^{-2}$ M, Et_4NNO_3).

	La^{3+}	Eu^{3+}	Yb^{3+}
5b			
1:1	5.5 ± 0.2	4.7 ± 0.2	5.1 ± 0.2
5c			
1:1	4.2 ± 0.2	3.9 ± 0.2	3.2 ± 0.2
Wide rim (*23*)			
1:1	6.0	5.6	3.5
2:1	10.6	11.0	8.6

Note: Data for a wide rim tetra-CMPO in the *cone* conformation are included for comparison.

2.3 *Crystal structures*

Single crystals suitable for X-ray diffraction were obtained for three compounds fixed in the *1,3-alternate* confor-



1b' **13** **17** **18**

mation, **1b′** (obtained from **1b** by selective hydrogenation of the allyl groups, or by direct alkylation, using propyl- instead of allylbromide), **13** and **17** (a derivative with two different precursor functions for amino groups at the wide rim (*22*)). A crystal structure was also determined for the 1,3-diether **18** in the *cone* conformation (*26*), the very first step in the synthesis of **1c**.

Compound **18** assumes the usual pinched *cone* conformation where the aryl residues of the phenolic units are bent outwards, including angles of 148.7° and 132.2° with the reference plane defined by the four methylene bridge carbons. Consequently, the two ether aryl units are bent towards the cavity, with angles of 114.7° and 108.9°. This conformation (with interplanar angles between opposite calix[4]arene aryl planes of 100.9° and 43.6°) permits a slightly larger distance between the (bulky) ether residues (distances O12—O32 = 4.534 Å and O22—O42 = 3.222 Å). The orientation of the phthalimide planes is obviously mainly determined by packing requirements, since the $(CH_2)_4$-linker (tetramethylene linker) allows for conformational freedom.

The best plane through the C atoms of the bridging methylene groups is a suitable reference plane also for the derivatives in the *1,3-alternate* conformation, although the deviation from this common plane reaches 0.357 Å for **17**, with the four carbon atoms lying alternatingly on both sides (for **13** and **1b′**, this deviation is 0.243 and 0.076 Å, respectively). The shape of the molecule may then be characterised by the angle between the aromatic planes and this reference plane (see Table 3). The deviation of the reference plane from a geometrically exact plane can also be characterised by the angle between two triangles obtained by folding along the diagonal (C1—C3 or C2—C4). These angles are small (4.75°) for **1b′**, but larger for **13** (15.00°/15.64°) and **17** (21.70°/23.12°).

However, this folding does not entirely explain the strong differences found for the distances of opposite phenolic oxygens (largest for **1b′**, $\Delta = 0.561$ Å) and opposite *p*-aryl carbons (largest for **13**, $\Delta = 1.155$ Å). Most probably, packing effects are also responsible for such deviations in the exact shape of the *1,3-alternate* skeleton, since, especially, the *p*-substituents (*t*-butyl, nitro, phthalimido) are rather different in size, shape and polarity.

Further distances and angles of the three molecules with *1,3-alternate* conformation are compared in Table 3, which also contains data for **18**, a compound (precursor) in the *cone* conformation. The molecular conformation of compounds **1b′**, **13** and **17** is compared in Figure 1, while their packing is compared in Figure 2.

In the crystal lattice, **13**·$CHCl_3$ forms columns with alternating directionality parallel to the *b*-axis. Within the *a*–*b*-plane, these columns form double layers separated by channels which contain the chloroform molecules (Figure 2, middle). **17**·$CHCl_3$ forms similar columns along the *b*-axis, but, here, the molecules within each column are separated by solvent molecules, which are 'included' in the cavity surrounded by the phthalimide and the nitro groups. The larger size of this cavity, compared with **13**, may be the reason for this inclusion. Otherwise, both structures are rather similar. A description of the packing of **1b′** is more complicated. Figure 2 (top) shows a view along the *b*-axis in which the included acetone molecules are shown in 'ball and stick' representation.

3. Experimental part

3.1 Syntheses

Compounds **1b**, **1c**, **2b** and **6b** were prepared as described earlier (*23*).

3.1.1 5,17-Di-t-butyl-11,23-dinitro-26,28-diphthalimidoethyloxy-25,27-di-allyloxy-calix[4]arene (1a)

Compound **1a** was obtained (together with its partial *cone* isomer) as described for the analogous compounds **1b** and **1c** from the dinitro compound. A suspension of 5,17-di-*t*-butyl-11,23-dinitro-26,28-diphthalimidoethyloxy-calix

Table 3. Comparison of some typical data taken from the crystal structures of three different calix[4]arene derivatives in the *1,3-alternate* conformation (**1b′**, **13**, **17**) and one in the *cone* conformation (**18**).

Compounds		**1b′**	**13**·$CHCl_3$	**17**	**18**·$2H_2O$
Distances (Å)					
Within the reference plane	C1—C2	5.139	5.108	5.145	5.120
	C2—C3	5.110	5.137	5.134	5.105
	C3—C4	5.185	5.130	5.109	5.129
	C4—C1	5.144	5.125	5.123	5.105
	C1—C3	7.266	7.061	6.944	7.291
	C2—C4	7.278	7.365	7.412	7.173
Opposite phenolic oxygens	O12—O32	3.588	4.471	4.180	4.534
	O22—O42	4.149	4.585	4.546	3.222
Opposite *p*-C atoms	C15—C35	7.989	7.481	7.487	7.466
	C25—C45	7.377	6.326	6.580	9.548
Angles (°)					
Within the main plane	*p-t*Bu	112.3	113.1	120.6[a]	148.7
		131.9	109.5	104.5[a]	132.2
	p-NO_2	112.0	107.4	111.2	114.7
		115.4	99.9	100.7	108.9
Between opposite planes	*p-t*Bu	64.2	42.7	45.2	43.6
	p-NO_2	47.4	27.4	31.9	100.9
Within the main plane					
Folding C1—C3		4.8	15.0	21.7	2.5
Folding C2—C4		4.8	15.6	23.1	2.5

[a] Phthalimide instead of *t*-butyl.

[4]arene (2.9 g, 2.98 mmol) in dry DMF (40 ml) and Cs_2CO_3 (7.8 g, 23 mmol) was stirred under nitrogen at 50°C for 6 days. Water (50 ml) was added to stop the reaction and, after several washes (3× 50 ml water), the organic phase was dried over $MgSO_4$. The solvent was evaporated under reduced pressure. Colourless crystals (0.05 g, 2%) of the desired *1,3-alternate* isomer **1a** were isolated by column chromatography (chloroform–hexane, 1:2), together with the *partial cone* isomer (0.27 g, 9%). Clearly, these yields are not optimised.

3.1.2 Compound **1a**

Mp 251–253°C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.78 (s, 18H, *t*-Bu), 3.72, 3.86 (2d, 4/4H, $^2J = 15.6$ Hz, Ar—CH_2—Ar), 3.79 (m, 8H, O—CH_2—, —CH_2—N), 4.10 (d, 4H, $^2J = 5.16$ Hz, CH_2═CH—CH_2—O—), 5.08 (m, 4H, CH_2 ═CH—), 5.75 (m, 2H, CH_2═C*H*—), 6.95, 8.28 (2s, 4/4H, Ar*H*), 7.66–7.85 (m, 8H, Phth-*H*).

3.1.3 Partial cone isomer of **1a**

Mp 215–217°C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.00 (s, 18H, *t*-Bu), 3.24 (d, 2H, $^2J = 13.2$ Hz, Ar—CH_2—Ar), 3.70–4.25 (m, 18H, O—CH_2—, —CH_2—N, Ar—CH_2—Ar, —O—CH_2—CH═CH_2), 4.85, 5.22 (2m, 2/2H, CH_2 ═CH—), 5.56, 5.88 (2m, 1/1H, CH_2═C*H*—), 6.57, 6.88 (2d, 2/2H, $^4J = 2.2$ Hz, Ar*H*), 7.82 (m, 8H, Phth-*H*), 8.00, 8.42 (2s, 2/2H, Ar*H*).

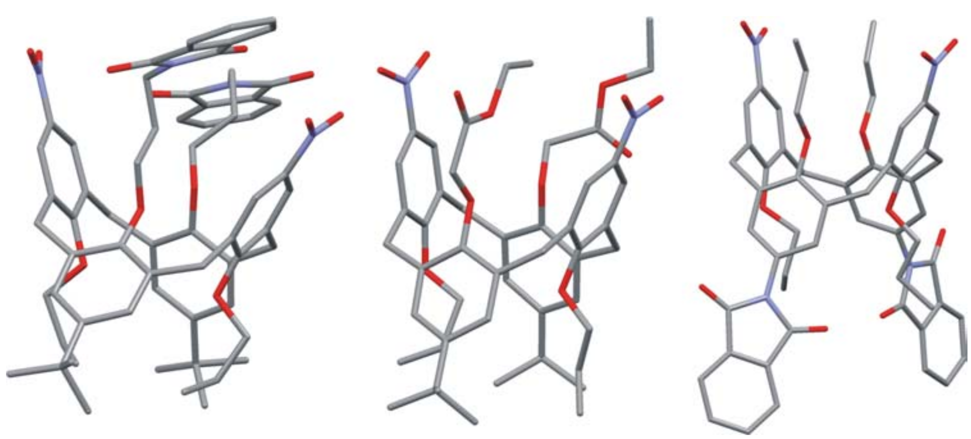


Figure 1. Molecular conformation of the three *1,3-alternate* derivatives **1b′**, **13** and **17** (from left to right).

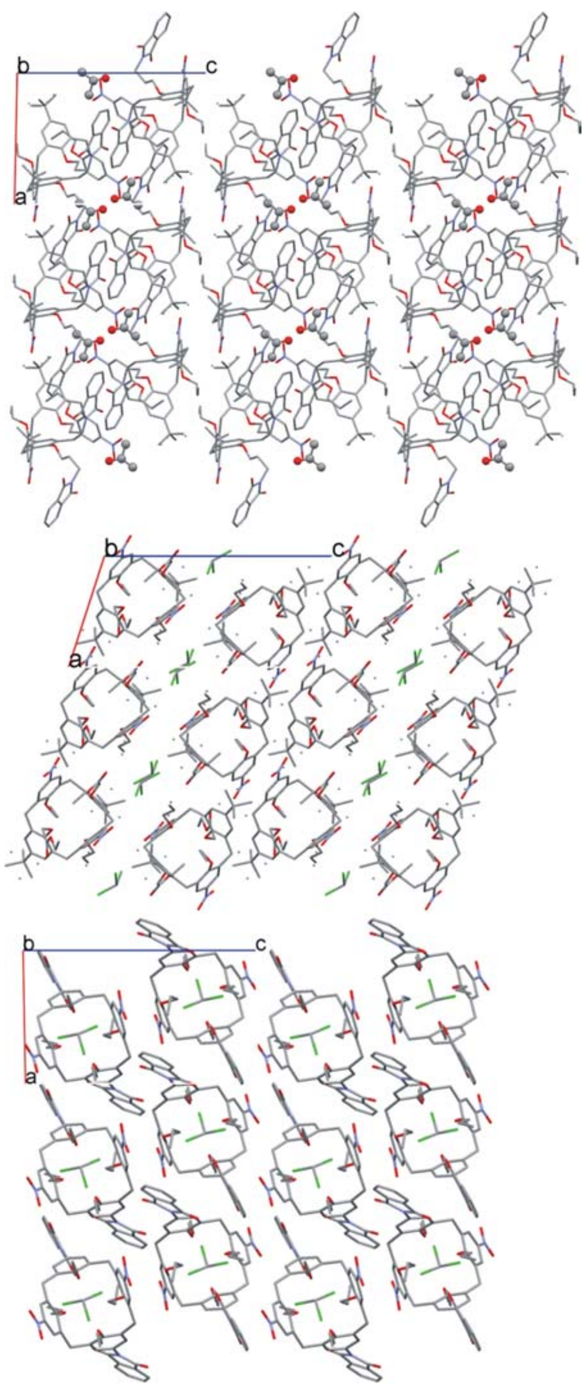


Figure 2. Packing of molecules seen along the *b*-axis in the lattice of **1b′**, **13** and **17** (from top to bottom); for **1b′**, the included acetone molecules are shown as 'ball and stick' models.

*3.1.4 5,17-Di-t-butyl-11,23-diamino-26,28-diphthalimidoethoxy-25,27-dipropoxy-calix[4]arene (**2a**)*

Diamine **2a** was prepared as described earlier for **2b**. A clear solution of **1a** (50 mg, 0.04 mmol) in THF (15 ml) was hydrogenated under normal pressure with Raney-Ni. The catalyst was filtered off, the solvent was evaporated and the dry residue was dissolved in $CHCl_3$ (3 ml) and reprecipitated with hexane to give **2a** as a yellow powder (30 mg, 64%); mp 315°C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.57 (t, 6H, $^3J = 7.16$ Hz, CH_3—CH_2—), 1.23 (s, 18H, *t*-Bu), 3.17 (br s, 4H, —NH_2), 3.45–3.60 (2br t, 4/4H, —CH_2—N, O—CH_2—), 3.74, 3.84 (2d, 4/4H, $^2J = 12.2$ Hz, Ar—CH_2—Ar), 6.88, 6.95 (2s, 4/4H, Ar*H*), 7.68–7.79 (2m, 8H, Phth-*H*).

*3.1.5 5,17-Di-t-butyl-11,23-di-CMPO-amido-26,28-diphthalimidopropoxy-25,27-dipropoxy-calix[4]arene (**3b**)*

p-Nitrophenyl carbamoylmethyl diphenyl phosphine oxide (**AE1**, 0.25 g, 0.65 mmol) was added to a clear solution of diamine **2b** (0.28 g, 0.27 mmol) and few drops of NEt_3 in dichloromethane (30 ml). The mixture was stirred at ambient temperature overnight. *p*-Nitrophenol formed during the acylation was extracted with an aqueous solution of NaOH (5%, 3× 100 ml). After drying over $MgSO_4$, the solvent was evaporated under reduced pressure and the residue was dissolved in dichloromethane (5 ml). Compound **3b** was obtained as a white powder by reprecipitation from hexane (0.4 g, 84%); mp 194–196°C; ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.65 (t, 6H, $^3J = 7.3$ Hz, —CH_2—CH_3), 1.20 (m, 22H, *t*-Bu, —CH_2—), 1.51 (m, 4H, —CH_2—), 3.26–3.69 (m, 24H, Ar—CH_2—Ar, O—CH_2—, —CH_2—P, —CH_2—N), 6.90, 6.95 (2s, 8H, Ar*H*), 7.40–7.75 (m, 28H, *m*, *p*-Ph_2*H*, *o*-Ph_2*H*, Pht-*H*), 8.84 (br s, 2H, N*H*); FD-MS, (M^++H) *m/z* = 1508.9.

*3.1.6 5,17-Di-t-butyl-11,23-di-CMPO-amido-26,28-diaminopropoxy-25,27-dipropoxy-calix[4]arene (**4b**)*

Hydrazine (1.6 ml) was added to a solution of **3b** (0.33 g, 0.2 mmol) in ethanol (15 ml). After 2 h under reflux, the reaction mixture was evaporated under reduced pressure; the residue was dissolved in chloroform (10 ml) and washed three times with water. The organic phase was dried over $MgSO_4$ and evaporated. The desired diamine was obtained as a white powder by reprecipitation from chloroform (5 ml) and hexane (25 ml) (0.25 g, 93%); mp 212–214°C; ^{1}H NMR (200 MHz, DMSO-d_6) δ 0.60 (t, 6H, $^3J = 6.8$ Hz, —CH_2—CH_3), 1.00 (m, 4H, —CH_2—), 1.19 (s, 18H, *t*-Bu), 1.46 (m, 4H, —CH_2—), 3.22–4.03 (m, 28H, NH_2, Ar—CH_2—Ar, O—CH_2—, —CH_2—P, —CH_2—N), 6.98, 7.23 (2s, 8H, Ar*H*), 7.55–7.92 (m, 20H, *m*, *p*-Ph_2*H*, *o*-Ph_2*H*), 10.24 (br s, 2H, N*H*); FD-MS, (M^++H) *m/z* = 1250.7.

*3.1.7 5,17-Di-t-butyl-11,23-di-CMPO-amido-26,28-di-CMPO-amidopropoxy-25,27-dipropoxy-calix[4]arene (**5b**)*

Tetra-CMPO **5b** was prepared by the same acylation procedure described above for **3b**. Starting from a solution of diamine **4b** (0.22 g, 0.14 mmol) in dichloromethane (30 ml) and **AE1** (0.16 g, 0.42 mmol), **5b** was obtained as a white powder (0.2 g, 83%); mp 152°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.61 (t, 6H, $^3J = 7.7$ Hz, —CH_2—CH_3), 1.20 (m, 22H, *t*-Bu, —CH_2—), 2.75 (m, 4H, —CH_2—), 2.72 (t, 4H, $^3J = 7.0$ Hz, —CH_2—N), 3.20 (t, 4H, $^3J = 7.3$ Hz, O—CH_2—), 3.50, 3.56 (2d, 8H, $^2J = 15.8$ Hz, Ar—CH_2—Ar), 3.61 (m, 8H, O—CH_2—, —CH_2—P), 3.76 (d, 4H, $^2J = 10.3$ Hz, —CH_2—P), 6.87, 7.09 (2s, 8H, Ar*H*), 7.38–7.81 (m, 40H, *m*, *p*-Ph_2H, *o*-Ph_2H), 8.96, 10.05 (2br s, 2/2H, N*H*); FD-MS, $(M^+ + H)$ $m/z = 1732.5$.

*3.1.8 5,17-Di-t-butyl-11,23-di-CMPO-amido-26,28-di-CMPO-amidobutyloxy-25,27-dipropoxy-calix[4]arene (**5c**)*

Tetra-CMPO **5c** was prepared as described for **5b**. Diamine **8c** (100 mg, 0.078 mmol) in dichloromethane (10 ml) was acylated with **AE1** (72 mg, 0.18 mmol). After purification by column chromatography, ($CHCl_3$–MeOH 98:2), **5b** (0.138 g, 87%) was obtained as a pink powder; mp 152°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.65 (t, 6H, $^3J = 7.7$ Hz, —CH_2—CH_3), 1.01–1.23 (m, 26H, *t*-Bu, 3 × —CH_2—), 2.93 (t, 4H, $^3J = 7.0$ Hz, —CH_2—N), 3.08, 3.27 (2t, 8H, $^3J = 7.3$ Hz, 2 × O—CH_2—), 3.37, 3.67 (2d, 4H, $^2J = 14.3$ Hz, CH_2—P), 3.65, 3.69 (2d, 8H, $^2J = 15.5$ Hz, Ar—CH_2—Ar), 6.92, 7.27 (2s, 8H, Ar*H*), 7.38–7.74 (m, 40H, *m*, *p*-Ph_2H, *o*-Ph_2H), 8.31, 10.20 (2br s, 2/2H, N*H*).

*3.1.9 5,17-Di-t-butyl-11,23-dinitro-26,28-diaminopropoxy-25,27-dibutyloxy-calix[4]arene (**6c**)*

Bis-phthalimide **1c** (0.45 g, 0.43 mmol) was dissolved in EtOH (30 ml), hydrazine (3 ml) was added and the reaction mixture was refluxed for 2 h. After the usual work-up, diamine **6c** was obtained as a yellow oil (0.3 g, 81%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.80 (t, 6H, $^3J = 7.4$ Hz, —CH_2—CH_3), 1.23 (m, 22H, *t*-Bu, —CH_2—), 1.47 (m, 4H, —CH_2—), 2.28 (br s, 4H, —NH_2), 2.69 (br t, 4H, —CH_2—), 3.51 (t, 4H, $^3J = 7.4$ Hz, N—CH_2—), 3.59 (br t, 4H, O—CH_2—), 3.63, 3.71 (2d, 4/4H, $^2J = 15.2$ Hz, Ar—CH_2—Ar), 6.98, 7.94 (2s, 4/4H, Ar*H*).

*3.1.10 5,17-Di-t-butyl-11,23-dinitro-26,28-di-CMPO-amidobutyloxy-25,27-dipropoxy-calix[4]arene (**7c**)*

The acylation of diamine **6c** by **AE1** was carried out at room temperature overnight as follows: **6c** (0.3 g, 0.35 mmol) dissolved in dichloromethane (15 ml) was reacted with **AE1** (0.32 g, 0.84 mmol); di-CMPO-amide **7c** (0.35 g, 75%) was obtained as a white powder; mp 142°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.80 (t, 6H, $^3J = 7.4$ Hz, —CH_2—CH_3), 1.22 (m, 26H, *t*-Bu, 2 × —CH_2—), 3.13 (m, 4H, —CH_2—), 3.07 (br t, 4H, —CH_2—N), 3.48 (2t, 4/4H, 2 × O—CH_2—), 3.66 (d, 4H, $^2J = 13.7$ Hz, —CH_2—P), 3.66, 3.75 (2d, 8H, $^2J = 15.2$ Hz, Ar—CH_2—Ar), 6.96, 7.88 (2s, 4/4H, Ar*H*), 7.38–7.81 (m, 2/2H, *m*, *p*-Ph_2H, *o*-Ph_2H, N*H*).

*3.1.11 5,17-Di-t-butyl-11,23-diamino-26,28-di-CMPO-amidobutyloxy-25,27-dipropoxy-calix[4]arene (**8c**)*

A solution of **7c** (110 mg, 0.082 mmol) and hydrazine (1 ml) in ethanol (15 ml) was refluxed for 2 h with Raney-Ni as the catalyst. The solvent was evaporated under reduced pressure; the formed residue was dissolved in chloroform (10 ml) and washed three times with water. The organic phase was dried over $MgSO_4$ and the solvent was evaporated under reduced pressure. Diamine **8c** was obtained as a yellow oil, which was used in the next step without further purification.

*3.1.12 5,17-Di-t-butyl-11,23-dinitro-26,28-dipicolinamidopropoxy-25,27-dipropoxy-calix[4]arene (**9b**)*

The active ester **AE2** (0.21 g, 0.73 mmol) was added to a suspension of diamine **6b** (0.25 g, 0.3 mmol) in chloroform (30 ml). The mixture was stirred at room temperature until the TLC shows that no starting material was left. The pentafluorophenol formed during the reaction was extracted with a solution of Na_2CO_3 (5%, 4× 100 ml) and the organic phase was dried over $MgSO_4$. The solvent was evaporated under reduced pressure, and the residue was dissolved in dichloromethane (5 ml) from which the desired compound was obtained by reprecipitation with hexane as a yellow powder (0.2 g, 64%); mp 127–129°C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.78 (t, 6H, $^3J = 7.35$ Hz, —CH_2—CH_3), 1.21 (s, 18H, *t*-Bu), 1.41 (m, 4H, —CH_2—CH_2—CH_2—), 1.71 (m, 4H, —CH_2—CH_3), 3.45–3.50 (m, 8H, —CH_2—N, O—CH_2—), 3.65–3.81 (m, 12H, Ar—CH_2—Ar, O—CH_2—), 6.95 (s, 4H, Ar*H*), 7.40 (m, 2H, H_b), 7.80 (m, 2H, H_c), 7.99 (s, 4H, Ar*H*), 8.17 (m, 2H, H_d), 8.29 (br t, 2H, —N*H*), 8.58 (m, 2H, H_a).

*3.1.13 5,17-Di-t-butyl-11,23-dinitro-26,28-dipicolylamidobutyloxy-25,27-dipropoxy-calix[4]arene (**9c**)*

Starting from diamine **6c** (0.25 g), containing traces of compounds with unhydrogenated allyl groups, the desired compound **9c** was obtained as the analogous mixture with the respective allyl compounds as described for **9b**, and was isolated as a white powder (0.25 g, 83%). The signals belonging to the protons of **9c** are listed below. ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.84 (t, 6H, $^3J = 7.35$ Hz, —CH_2-—CH_3), 1.21 (s, 18H, *t*-Bu), 1.20–1.66 (m, 12H,

—CH$_2$—C*H*$_2$—C*H*$_2$—CH$_2$—,—C*H*$_2$—CH$_3$), 3.46–3.86 (m, 20H, —C*H*$_2$—N, 2 × O—C*H*$_2$—, Ar—C*H*$_2$—Ar), 6.96 (s, 4H, Ar*H*), 7.39 (m, 2H, H_b), 7.81 (m, 2H, H_c), 7.92 (s, 4H, Ar*H*), 8.20 (m, 2H, H_d), 8.25 (br t, 2H, —N*H*), 8.56 (m, 2H, H_a).

*3.1.14 5,17-Di-t-butyl-11,23-diamino-26,28-di-picolinamidopropyloxy-25,27-dipropoxy-calix[4]arene (**10b**)*

Raney-Ni was added to a clear solution of **9b** (740 mg, 0.70 mmol) in THF (20 ml), and the reaction mixture was stirred under hydrogen for 4 days. When the hydrogen uptake was complete, the catalyst was filtered off and the solvent evaporated under reduced pressure. The residue was dissolved in chloroform (10 ml) and the desired amine was precipitated with hexane (15 ml) as a white powder (200 mg, 31%); mp 120°C; ^{1}H NMR (300 MHz, CDCl$_3$) δ 0.59 (t, 6H, $^3J = 7.7$ Hz, —CH$_2$—C*H*$_3$), 1.01–1.08 (m, 4H, —C*H*$_2$—), 1.22 (s, 18H, *t*-Bu), 1.55–1.59 (m, 4H, —C*H*$_2$—), 2.89 (br s, 4H, —N*H*$_2$), 3.17–3.22 (m, 8H, —C*H*$_2$—N, —C*H*$_2$—O), 3.51 (t, 4H, $^3J = 7.3$ Hz, O—C*H*$_2$—), 3.65, 3.74 (2d, 4/4H, $^2J = 15.8$ Hz, Ar—C*H*$_2$—Ar), 6.48, 6.92 (2s, 4/4H, Ar*H*), 7.38 (m, 2H, H_b), 7.80 (m, 2H, H_c), 8.13 (m, 2H, H_d), 8.26 (br t, 2H, —N*H*), 8.51 (m, 2H, H_a).

*3.1.15 5,17-Di-t-butyl-11,23-diamino-26,28-dipicolinamidobutyloxy-25,27-dipropoxy-calix[4]arene (**10c**)*

Diamine **10c** was prepared analogously. For a solution of mixture **9c** (0.25 g) in THF (20 ml), the hydrogenation was complete after 30 h. The diamine was reprecipitated from chloroform–hexane (~20 ml, 1:3) as a white powder (220 mg, 93%); mp 132°C; ^{1}H NMR (300 MHz, CDCl$_3$) δ 0.64 (t, 6H, $^3J = 7.7$ Hz, —CH$_2$—C*H*$_3$), 1.09–1.22 (m, 26H, 2 × —C*H*$_2$—, *t*-Bu), 1.82–1.86 (m, 4H, —C*H*$_2$—), 3.21–3.73 (m, 20H, —C*H*$_2$—N, —C*H*$_2$—O, Ar—C*H*$_2$—Ar), 6.42 (s, 4H, —N*H*$_2$), 6.92, 6.97 (2s, 4/4H, Ar*H*), 7.38 (m, 2H, H_b), 7.81 (m, 2H, H_c), 8.18 (m, 2H, H_d), 8.30 (br t, 2H, —N*H*), 8.54 (m, 2H, H_a).

*3.1.16 5,17-Di-t-butyl-11,23-di-CMPO-26,28-dipicolinamidopropyloxy-25,27-dipropoxy-calix[4]arene (**11b**)*

The final acylation was done as described above for **6b**. Diamine **10b** (200 mg, 0.20 mmol) dissolved in dichloromethane (30 ml) was reacted with active ester **AE1** (490 mg, 2.4 mmol). **11b** (170 mg, 65%) was isolated as a white powder; mp 108–109°C; ^{1}H NMR (300 MHz, DMSO-d_6) δ 0.93 (t, 6H, $^3J = 7.2$ Hz, —CH$_2$—C*H*$_3$), 1.18 (s, 18H, *t*-Bu), 1.44 (m, 4H, —C*H*$_2$—), 3.05–3.78 (m, 24H, —C*H*$_2$—N, —C*H*$_2$—O, Ar—C*H*$_2$—Ar, —C*H*$_2$—P), 6.32 (s, 2H, —N*H*), 6.95, 7.12 (2s, 4/4H, Ar*H*), 7.49–7.99 (m, 22H, *m*, *p*-Ph$_2$*H*, *o*-Ph$_2$*H*, H_b), 8.34 (m, 2H, H_c), 8.50 (m, 2H, H_d), 8.73 (br t, 2H, —N*H*,), 9.77 (m, 2H, H_a).

*3.1.17 5,17-Di-t-butyl-11,23-di-CMPO-26,28-dipicolinamidobutyloxy-25,27-dipropoxy-calix[4]arene (**11c**)*

Diamine **10c** (220 mg, 0.23 mmol) in dichloromethane (30 ml) was reacted analogously with **AE1** (325 mg, 0.55 mmol) to yield **11c** as a white powder (160 mg, 47%); mp 117–119°C; ^{1}H NMR (200 MHz, DMSO-d_6) δ 0.60 (t, 6H, $^3J = 7.2$ Hz, —CH$_2$—C*H*$_3$), 1.21 (m, 30H, *t*-Bu, —C*H*$_2$—), 3.06–3.72 (m, 24H, —C*H*$_2$—N, —C*H*$_2$—O, Ar—C*H*$_2$—Ar, —C*H*$_2$—P), 6.90, 7.06 (2s, 4/4H, Ar*H*), 7.40–7.80 (m, 22H, *m*, *p*-Ph$_2$*H*, *o*-Ph$_2$*H*, H_b), 8.11 (m, 2H, H_c), 8.34–8.50 (m, 6H, H_d, —N*H*, H_a), 9.45 (s, 2H, N*H*).

*3.1.18 5,17-Di-t-butyl-11,23-dinitro-25,27-diallyloxy-26,28-di-ethoxycarbonylmethoxy-calix[4]arene **13*** (1,3-alternate) *and **13a*** (partial cone)

A stirred suspension of dinitro-calixarene **12** (1.3 g, 1.6 mmol) and Cs$_2$CO$_3$ (4 g, 12.8 mmol) in dry DMF (40 ml) was heated to 40°C under nitrogen. After 1 h, allylbromide (1.1 ml, 12.8 mmol) was added and the reaction was continued for 7 days. DMF was removed under reduced pressure and the residue was treated with chloroform (25 ml) and water (75 ml). The organic phase was washed with water (2× 75 ml), dried (MgSO$_4$) and the solvent was evaporated to give a yellow oil. Analysis by TLC showed the presence of two compounds, which were separated and purified by column chromatography (CHCl$_3$) and identified by NMR as the *1,3-alternate* and the *partial cone* isomers.

*3.1.19 Compound **13*** (1,3-alternate)

White–yellow crystals, yield 0.3 g, 21%; mp 199–201°C; ^{1}H NMR (300 MHz, CDCl$_3$) δ 1.24 (t, 6H, $^3J = 6.1$ Hz, —CH$_2$—C*H*$_3$), 1.24 (s, 18H, *t*-Bu), 3.66, 4.07 (2d, 4/4H, $^2J = 14.7$, 15.1 Hz, Ar—C*H*$_2$—Ar), 3.99 (s, 4H, —C*H*$_2$—O—), 4.19 (m, 8H, O—C*H*$_2$), 5.14 (m, 4H, C*H*$_2$═CH—), 5.78 (m, 2H, CH$_2$═C*H*—), 6.98, 8.02 (2s, 4/4H, Ar*H*).

*3.1.20 Compound **13a*** (partial cone)

Yellow powder, yield 0.54 g, 39%; mp 222–223°C; ^{1}H NMR (300 MHz, CDCl$_3$) δ 1.00 (s, 18H, *t*-Bu), 1.31 (t, 6H, $^3J = 7.3$ Hz —CH$_2$—C*H*$_3$), 3.22, 3.65, 4.07 (3d, 2/2/2H, $^2J = 13.6$, 13.9, 13.6 Hz, Ar—C*H*$_2$—Ar), 4.15–4.37 (m, 14H, 3 × O—C*H*$_2$—, Ar—C*H*$_2$—Ar), 4.94, 5.40 (2m, 2/2H, —CH═C*H*$_2$), 6.06, 6.12 (2m, 2/2H, —C*H*═CH$_2$), 6.50, 6.88 (2d, 2/2H, $^4J = 2.5$, 2.5 Hz, Ar*H*), 8.03, 8.37 (2s, 2/2H, Ar*H*).

3.1.21 5,17-Di-t-butyl-11,23-di-CMPO-25,27-dipropoxy-26,28-diethoxycarbonylmethoxy-calix[4]arene (15)

Pd/C (0.1 g) was added to a solution of the dinitro compound **13** (0.3 g, 0.34 mmol) in THF (15 ml) and the suspension was stirred under hydrogen atmosphere at room temperature. After the hydrogen uptake was complete, the catalyst was filtered off and the solvent was evaporated. The residue was dissolved in dichloromethane (15 ml) to form a clear solution. **AE1** (80 mg, 0.09 mmol) and few drops of triethylamine were added, and the mixture was stirred at room temperature for 12 h. An aqueous solution of NaOH (30 ml, 5%) was added and the stirring was continued for an additional 30 min. Then, the organic phase was separated, washed three times with diluted aqueous NaOH (3× 30 ml), dried over $MgSO_4$ and evaporated under reduced pressure. The product was reprecipitated from $CHCl_3$–hexane (15 ml, 1:2) to give a white powder (0.11 g, 92%); mp 210–212°C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.73, 1.13 (2t, 6/6H, $^3J = 7.7, 7.3$ Hz, 2 × —CH_2—CH_3), 1.20 (m, 22H, *t*-Bu, —CH_2—), 3.35, 4.01 (2t, 4/4H, $^3J = 7.7$, 6.9 Hz, 2 × O—CH_2—), 3.44 (d, 4H, $^2J = 12.9$ Hz, —CH_2—P), 3.57 (s, 4H, O—CH_2—), 3.64, 3.93 (2d, 4/4H, $^2J = 15.8$ Hz, Ar—CH_2—Ar), 6.92, 7.15 (2s, 4/4H, Ar*H*), 7.43–7.78 (m, 20H, *m*, *p*-Ph$_2$*H*, *o*-Ph$_2$*H*), 9.06 (br s, 2H, N*H*).

3.1.22 5,17-Di-t-butyl-11,23-di-CMPO-25,27-dipropoxy-26,28-dicarboxymethoxy-calix[4]arene (16)

An aqueous solution of LiOH (98 mg, 2 ml water) was added to the solution of **15** (0.11 g, 0.09 mmol) in THF (7 ml) and MeOH (4 ml), and the mixture was stirred at room temperature overnight and neutralised with diluted HCl. The desired acid was isolated by precipitation with water. The white precipitate was filtered, washed with water and dried. Diacid **16** (0.1 g, 96%) was obtained as a white powder; mp 264°C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 0.65 (t, 6H, $^3J = 7.4$ Hz, —CH_2—CH_3), 1.15 (m, 4H, —CH_2 —CH_3), 1.23 (s, 18H, *t*-Bu), 1.96 (s, 2H, —COO*H*), 3.31 (t, 4H, $^3J = 7.4$ Hz, O—CH_2—), 3.67, 3.92 (2d, 4/4H, $^2J = 16.2$ Hz, Ar—CH_2—Ar), 3.76 (d, 4H, $^2J = 16.0$ Hz, —CH_2—P), 3.69 (s, 4H, O—CH_2—), 7.00, 7.16 (2s, 4/4H, Ar*H*), 7.51–7.84 (m, 20H, *m*, *p*-Ph$_2$*H*, *o*-Ph$_2$*H*), 9.46 (br s, 2H, N*H*).

3.2 Binding studies

Extraction experiments of lanthanide and thorium nitrates ($C_M = 10^{-4}$ M) from 1 M nitric acid into dichloromethane were performed at 20°C. A colorimetric method using Arsenazo-III was applied to determine the concentration of the metal ions before and after extraction in the aqueous phase. The full procedure, the starting materials and the calculations of the distribution coefficients (*D*) and the percentage extraction (%*E*) have already been described in detail (*3*). Complexation data, i.e. the stoichiometry and the stability constants (log β) of the species formed in methanol, were derived from spectrophotometric titrations at 25°C. The experimental procedure (*27*) and the data processing by the program Specfit (*28*) have been previously published. The ligand concentrations were ranging between 5×10^{-5} and 10^{-4} M and the ionic strength was settled as constant using 10^{-2} M Et_4NNO_3 as the background electrolyte.

Stock solutions of lanthanide and thorium nitrates used in extraction and complexation experiments were standardised by complexometric titrations with EDTA in the presence of xylenol orange as the coloured indicator.

3.3 Crystallographic data

Single crystals were obtained from a solution in acetone/methanol (**1b′**) or chloroform/methanol (**13**, **17**, **18**) which was overlaid in a test tube with an excess of methanol. The two molecules of water found per molecule **18** in its crystal structure were obviously absorbed from the atmosphere.

Intensity data were collected on a STOE IPDS II two-circle diffractometer with graphite-monochromated Mo-K_α radiation at 173 K (Table 4). For **13** and **17**, an empirical absorption correction was performed using the MULABS (*29*) option in PLATON (*30*). The structures were solved by direct methods using the program SHELXS (*31*) and refined against F^2 with full-matrix least-squares techniques using the program SHELXL (*31*). Hydrogen atoms were included at calculated positions with fixed displacement parameters. In **1b′**, one *tert*-butyl group is disordered over two positions (site occupation factors 0.491(6)/0.509(6)). In **13**, the two *tert*-butyl groups (site occupation factors 0.449(6)/0.551(5) and 0.320(2)/0.680(2)) and the terminal two C atoms of a propenoxy group (site occupation factors 0.40(2)/0.60(2)) are disordered over two positions. The C—C bond lengths in the disordered *tert*-butyl groups were restrained to 1.54(1) Å and the C═C double bonds in the propenoxy groups were restrained to 1.30(1) Å. In **18**, the water H atoms could not be located and were omitted from refinement. The geometric parameters of the side chain O32 to N324 were restrained to be equal to those of O12 to N124.

Crystallographic data in CIF format have been deposited with the Cambridge Crystallographic Data Centre: reference numbers: **1b′** CCDC 734171; **13** CCDC 734172; **17** CCDC 734173; **18** CCDC 734174.

4. Conclusions

Calix[4]arenes fixed in the *1,3-alternate* conformation have been used for the first time as the basic skeleton for the attachment of four CMPO residues or two CMPO functions in combination with two picolinamide or

Table 4. Crystal data and structure refinement details for **1b′**, **13**, **17** and **18**.

Compound	**1b′**	**13**	**17**	**18**
Empirical formula	$C_{64}H_{68}N_4O_{12}\cdot CH_3COCH_3$	$C_{50}H_{58}N_2O_{12}\cdot CHCl_3$	$C_{56}H_{52}Cl_3N_4O_{12}\cdot CHCl_3$	$C_{68}H_{78}N_2O_8\cdot 2H_2O$
Colour	Colourless	Colourless	Light yellow	Colourless
Shape	Block	Block	Block	Block
fw (g/mol)	1143.30	998.35	1092.38	1087.36
Temperature (K)	173	173	100	173
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073
Crystal system	Triclinic	Triclinic	Triclinic	Monoclinic
Space group	*P*-1	*P*-1	*P*-1	$P2_1/c$
Z	2	2	2	4
Cell parameters				
a (Å)	12.924(3)	10.4879(6)	9.8020(7)	13.0264(9)
b (Å)	14.094(3)	14.0724(8)	15.6199(11)	24.5795(15)
c (Å)	17.881(4)	19.2015(11)	17.9197(13)	19.9439(16)
α (°)	78.44(3)	96.336(4)	72.276(6)	90
β (°)	87.30(3)	104.191(4)	88.546(6)	105.126(6)
γ (°)	70.72(3)	111.084(4)	88.444(6)	90
Volume (Å^3)	3011.5(10)	2501.0(2)	2612.0(3)	6164.4(8)
Calcd density (mg/m^3)	1.261	1.326	1.389	1.172
Abs. coeff. (mm^{-1})	0.088	0.247	0.244	0.078
Crystal size (mm^3)	$0.42 \times 0.40 \times 0.22$	$0.32 \times 0.18 \times 0.14$	$0.43 \times 0.41 \times 0.36$	$0.25 \times 0.19 \times 0.17$
$2\theta_{max}$ (°)	55.24	55.52	59.62	51.64
Index ranges	$-16 \le h \le 16$, $-18 \le k \le 18$, $-23 \le l \le 22$	$-13 \le h \le 13$, $-18 \le k \le 17$, $-25 \le l \le 25$	$-13 \le h \le 13$, $-21 \le k \le 19$, $-24 \le l \le 24$	$-15 \le h \le 15$, $-29 \le k \le 29$, $-23 \le l \le 24$
No. of rflns collected	114,465	66,572	55,297	64,136
No. of indep. rflns	13,916	11,731	14,801	11,636
R_{int}	0.0786	0.0701	0.0777	0.1496
Absorption correction	None	Multi-scan	Multi-scan	None
T_{min}, T_{max}	–	0.917, 0.970	0.902, 0.917	–
Data/restraints/parameter	13,916/1/787	11,731/5/688	14,801/0/685	11,636/9/721
Goodness of fit	1.017	1.010	0.896	0.961
R_1,wR_2 [$I > 2\sigma(I)$]	0.0659, 0.1758	0.0479, 0.1229	0.0464, 0.1104	0.1027, 0.2671
R_1,wR_2 (all data)	0.0822, 0.1873	0.0729, 0.1317	0.0793, 0.1189	0.1723, 0.3205
Largest diff. peak and hole (eÅ^3)	0.883, −0.650	0.691, −0.542	0.474, −0.514	0.674, −0.751

Note: Data collection with a STOE-IPDS-II two-circle diffractometer, solution and refinement with SHELXS and SHELXL.

(potentially ionisable) carboxylic groups. Preliminary extraction and complexation studies with selected lanthanides, however, showed that this new arrangement does not lead to improved properties in comparison to narrow or wide rim tetra-CMPO derivatives of calix[4]-arenes in the *cone* conformation. Most probably, this is not caused by the more rigid scaffold, which might be even beneficial, but by an inappropriate mutual situation of the ligating functions. MD simulations should be helpful to find their best arrangement.

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Notes

1. Selective substitutions at the narrow rim cannot be controlled in a similar fashion by substituents at the wide rim.
2. For the extraction of lanthanides; actinides by calixarene-based picolinamides see Ref. (*16*).

References

(1) Horwitz, E.P.; Kalina, D.G.; Diamond, H.; Vandegrift, G.F.; Schulz, W.W. *Solvent Extr. Ion Exch.* **1985**, *3*, 75–109.
(2) Peters, M.W.; Werner, E.J.; Scott, M. *Inorg. Chem.* **2002**, *41*, 1707–1716; Rudzevich, V.; Schollmeyer, D.; Braekers, D.; Desreux, J.F.; Diss, R.; Wipff, G.; Böhmer, V. *J. Org. Chem.* **2005**, *70*, 6027–6033.
(3) Arnaud-Neu, F.; Böhmer, V.; Dozol, J.-F.; Grüttner, C.; Jakobi, R.A.; Kraft, D.; Mauprivez, O.; Rouquette, H.; Schwing-Weill, M.-J.; Simon, N.; Vogt, W. *J. Chem. Soc., Perkin Trans. 2* **1996**, 1175–1182.
(4) Delmau, L.H.; Simon, N.; Schwing-Weill, M.-J.; Arnaud-Neu, F.; Dozol, J.F.; Eymard, S.; Tournois, B.; Grüttner, C.; Musigmann, C.; Tunayar, A.; Bohmer, V. *Sep. Sci. Techn.* **1999**, *34*, 863–876.
(5) Barboso, S.; Carrera, A.G.; Matthews, S.E.; Arnaud-Neu, F.; Böhmer, V.; Dozol, J.-F.; Rouquette, H.; Schwing-Weill, M.-J. *J. Chem. Soc., Perkin Trans. 2* **1999**, 719–723.
(6) Matthews, S.E.; Saadioui, M.; Böhmer, V.; Barboso, S.; Arnaud-Neu, F.; Schwing-Weill, M.-J.; Carrera, A.G. *J. Prakt. Chem.* **1999**, *341*, 264–273.
(7) Arnaud-Neu, F.; Barboso, S.; Böhmer, V.; Brisach, F.; Delmau, L.; Dozol, J.-F.; Mogck, O.; Paulus, E.F.; Saadioui, M.; Shivanyuk, A. *Aust. J. Chem.* **2003**, *56*, 1113–1119.
(8) For early examples see: (a) Arduini, A.; Pochini, A.; Reverberi, S.; Ungaro, R. *J. Chem. Soc., Chem. Commun.* **1984**, 981–982. (b) Arduini, A.; Pochini, A.; Reverberi, S.; Ungaro, R.; Andreetti, G.D.; Ugozzoli, F. *Tetrahedron* **1986**, *42*, 2089–2100. (c) Arnaud-Neu, F.; Collins, E.M.; Deasy, M.; Ferguson, G.; Harris, S.J.; Kaitner, B.; Lough, A.J.; McKervey, M.A.; Marques, E.; Ruhl, B.L.; Schwing-Weill, M.-J.; Seward, E.M. *J. Am. Chem. Soc.* **1989**, *111*, 8681–8691.
(9) Mono- and bis-crown ethers derived from the *1,3-alternate* conformation are important examples, see: (a) Hill, C.; Dozol, J.-F.; Lamare, V.; Rouquette, H.; Eymard, S.; Tournois, B.; Vicens, J.; Asfari, Z.; Bressot, C.; Ungaro, R.; Casnati, A. *J. Incl. Phenom.* **1994**, *19*, 399–408. (b) Casnati, A.; Pochini, A.; Ungaro, R.; Ugozzoli, F.; Arnaud, F.; Fanni, S.; Schwing, M.J.; Egberink, R.J.M.; De Jong, F.; Reinhoudt, D.N. *J. Am. Chem. Soc.* **1995**, *117*, 2767–2777.
(10) For an example where the complexation occurs with the *partial cone* conformation see: van der Veen, N.J.; Egberink, R.J.M.; Engbersen, J.F.J.; van Veggel, F.J.C.M.; Reinhoudt, D.N. *Chem. Commun.* **1999**, 681–682.
(11) For bis-crown ethers fixed in the *1,2-alternate* conformation see: Arduini, A.; Domiano, L.; Pochini, A.; Secchi, A.; Ungaro, R.; Ugozzoli, F.; Struck, O.; Verboom, W.; Reinhoudt, D.N. *Tetrahedron* **1997**, *53*, 3767–3776.
(12) For a recent review see: Baklouti, L.; Harrowfield, J.; Pulpoka, B.; Vicens, J. *Mini-Rev. Org. Chem.* **2006**, *3*, 355–384.
(13) Arduini, A.; Böhmer, V.; Delmau, L.; Desreux, J.-F.; Dozol, J.-F.; Carrera, M.A.G.; Lambert, B.; Musigmann, C.; Pochini, A.; Shivanyuk, A.; Ugozzoli, F. *Chem. Eur. J.* **2000**, *6*, 2135–2144.
(14) (a) Nigond, L.; Condamines, N.; Cordier, P.Y.; Livet, J.; Madic, C.; Cuillerdier, C.; Musikas, C.; Hudson, M.J. *Sep. Sci. Technol.* **1995**, *30*, 2075–2099. (b) Casnati, A.; Della, C.; Fontanella, M.; Sansone, F.; Ugozzoli, F.; Ungaro, R.; Liger, K.; Dozol, J.-F. *Eur. J. Org. Chem.* **2005**, *11*, 2338–2348.
(15) Baaden, M.; Berny, F.; Madic, C.; Schurhammer, R.; Wipff, G. *Solvent Extr. Ion Exch.* **2003**, *21*, 199–220.
(16) Casnati, A.; Della, C.; Fontanella, M.; Sansone, F.; Ugozzoli, F.; Ungaro, R.; Liger, K.; Dozol, J.-F. *Eur. J. Org. Chem.* **2005**, *11*, 2338–2348.
(17) Kolarik, Z. *Chem. Rev.* **2008**, *108*, 4208–4252.
(18) Dean, N.E.; Hancock, R.D.; Cahill, C.L.; Frisch, M. *Inorg. Chem.* **2008**, *47*, 2000–2010.
(19) Bianchi, A.; Calabi, L.; Corana, F.; Fontana, S.; Losi, P.; Maiocchi, A.; Paleari, L.; Valtancoli, B. *Coord. Chem. Rev.* **2000**, *204*, 309–393.
(20) For a recent review of actinide/lanthanide separation with multidentate ligands see: Dam, H.H.; Reinhoudt, D.N.; Verboom, W. *Chem. Soc. Rev.* **2007**, *36*, 367–377.
(21) Jakobi, R.A.; Böhmer, V.; Grüttner, C.; Kraft, D.; Vogt, W. *New J. Chem.* **1996**, *20*, 493–501.
(22) Danila, C.; Bolte, M.; Böhmer, V. *Org. Biomol. Chem.* **2005**, *3*, 172–184.
(23) Herschbach, H.; Brisach, F.; Haddaoui, J.; Saadioui, M.; Leize, E.; Van Dorsselaer, A.; Arnaud-Neu, F.; Böhmer, V. *Talanta* **2007**, *74*, 39–46.
(24) See: (a) Zhao, H.; Burke, T.R., Jr. *Tetrahedron* **1997**, *53*, 4219–4230. (b) Christensen, J.B. *Molecules* **2001**, *6*, 47–51.
(25) Bolte, M.; Danila, C.; Böhmer, V. *Acta Crystallogr. Sect. E* **2003**, *59*, o533–o534.
(26) Lambert, T.N.; Dasaradhi, L.; Huber, V.J.; Gopalan, A.S. *J. Org. Chem.* **1999**, *64*, 6097–6101.
(27) Arnaud-Neu, F.; Schwing-Weill, M.J.; Ziat, K.; Cremin, S.; Harris, S.J.; McKervey, M.A. *New J. Chem.* **1991**, *15*, 33–37.
(28) Gampp, H.; Maeder, M.; Meyer, C.J.; Zuberbühler, A.D. *Talanta* **1985**, *32*, 257–264.
(29) Blessing, R.H. *Acta Crystallogr. Sect. A* **1995**, *51*, 33–38.
(30) Spek, A.L. *Acta Crystallogr. Sect. D* **2009**, *65*, 148–155.
(31) Sheldrick, G.M. *Acta Crystallogr. Sect. A* **2008**, *64*, 112–122.