Synthesis, Conformations and Extraction Properties of New Chromogenic Calix[4]arene Amide Derivatives

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The synthesis of a new series of chromogenic calix[4]arene derivatives is described. *p*-Tetrakis(phenylazo)calix[4]arenes substituted with tertiary amide groups at the lower rim were obtained. The *O*-substitution of 25,26,27,28-tetrahydroxy-11,23-bis(phenylazo)calix[4]arene (**2**) and 25,26,27,28-tetrahydroxy-5,17,11,23-tetrakis(phenylazo)calix[4]arene (**3**) to provide 26,28-bis{[(diethylamino)carbonyl]methoxy}-25,27-dihydroxy-11,23-bis(phenylazo)calix[4]arene (**4**), 26-{[(diethylamino)carbonyl]methoxy}-25,27,28-trihydroxy-5,11,17,23-tetrakis(phenylazo)calix[4]arene (**5**), 25,26,27,28-tetrakis{[(dialkylamino)carbonyl]methoxy}-5,11,17,23-tetrakis(phenylazo)calix[4]arene [alkyl = ethyl (**6a**), methyl (**7**)] and 26,28-bis{[(diethylamino)carbonyl]methoxy}-25,27-dihydroxy-5,11,17,23-tetrakis(phenylazo)calix[4]arene (**8a**) have been carried out by treatment of the precursors **2** and **3** with either α-chloro-*N*,*N*-diethylacetamide or α-chloro-*N*,*N*-dimethylacetamide. A potassium complex of **8** (**8b**) was isolated. The structures of these compounds have been studied by NMR spectroscopy. In addition, the conformations have been confirmed by single-crystal X-ray analysis in the cases of tetra-*O*-substituted azocalix[4]arenes (**6a** and **7**) and bis(*O*-substituted) azocalix[4]arenes (**8a** and **8b**). The resolved structures of **6a** and **7** show 1,3-alternate conformations while the bis(*O*-substituted) analogues **8** display cone conformations, their packing showing a zigzag chain of molecules for **8a** and a dimer for **8b**. Moreover, the extraction properties of **6a**, **6b** and **8a** towards different metal ions have been studied by liquid-liquid extraction and atomic absorption spectrometry and found to exhibit K^+ selectivity.

Introduction

Calixarenes are currently the subjects of study as chemical sensors[1] and selective receptors[2] due to their important functionalisation and complexation possibilities. Among these sensors, different calixarene derivatives may be found, thanks to their importance in the fields of medicine and the environment, in ion-selective electrodes[3−7] and in chromogenic sensors[8,9] that change colour in response to some variation in their environment. This can be achieved by the use of ionophores with chromogenic groups in the neighbourhood of the coordination sites. In the case of chromogenic compounds the most studied are azocalixarenes, first developed by Shinkai and al.,[10−12] and including amphiphilic azocalixarenes,[13] chemiluminescent azocalixarenes,[14] azocalix[9]arenes[15] and more recently chromoionophore azocalix[4]arene diazacrown ethers[16] and chromogenic 2,2′-bithiazolylcalix[4]arenes.[17] For endowment of the calixarene with selective recognition properties, however, it has been shown that the nature of the substituents plays an important role in their complexation efficiency.[18] Among these substituents, for instance, additional donor groups such as amide moieties show greater efficiency for metal ion complexation than oxo, ester and ether groups,[2,19] and have been grafted onto the lower rims of calix[4]arenes for the complexation of alkali[20,21] and alkaline earth metal ions,[22−25] lanthanide ions[26−29] and transition metal ions,[30−32] and also for the simultaneous complexation of cations and anions.[33] Some calix[4]arenes with pendant amide units have been used as selective extracting agents for metal ions.[34−37]

In order to introduce binding properties to azocalixarenes, we have introduced tertiary amide groups, due to their metal ion complexation efficiency. Here we report the syntheses of a number of amide-substituted azocalixarenes: **5**, bearing one tertiary amide group at the lower rim of the phenylazocalixarene, **4** and **8** with two, and **6** and **7** with four. Their conformations were studied by ^1H and ^{13}C NMR spectroscopy and X-ray diffraction analysis. Additionally we report an atomic absorption spectrometry study of the extraction properties of **6a**, **6b** and **8a** towards Na^+, K^+, Mg^{2+}, Ca^{2+}, Mn^{2+}, Ni^{2+}, Cu^{2+}, Pb^{2+} and Cd^{2+}.

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Results and Discussion

The starting phenylazocalix[4]arenes **2** and **3** were obtained from calix[4]arene by literature methods[9] (Figure 1).

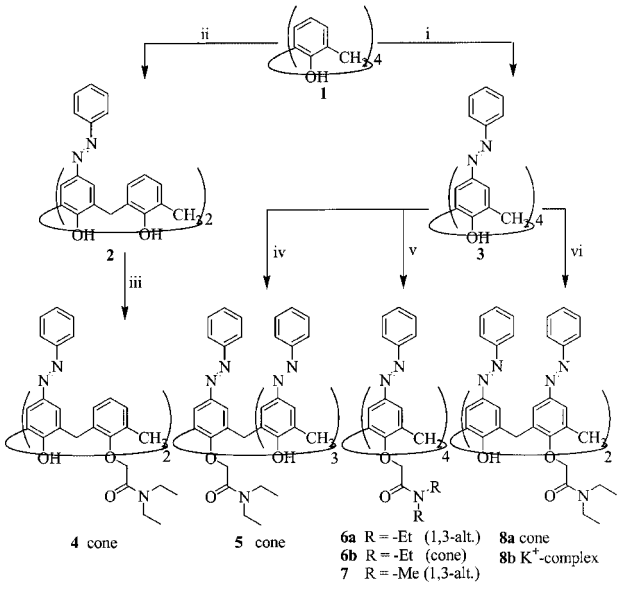

Figure 1. Reagents and reaction conditions: (i) **3**, BF_4 salt of benzodiazonium, pyridine, THF, 0 °C, 12 h, 40%; (ii) **2**, BF_4 salt of benzodiazonium, pyridine, THF, 0 °C, 12 h, 32%; (iii) 4, α-chloro-*N*,*N*-diethylacetamide, Cs_2CO_3, dry DMF, 80 °C, 48 h, 22%; (iv) **5**, α-chloro-*N*,*N*-diethylacetamide, K_2CO_3, KI, dry MeCN, reflux, 12 h, 64%; (v) **6a** and **7**, α-chloroacetamide, Cs_2CO_3, dry DMF, reflux, 74 h, 16% and 26%, respectively; **6b**, α-chloro-*N*,*N*-diethylacetamide, CaH_2, dry DMF, 80 °C, 50 h, 17%; (vi) **8a**, α-chloro-*N*,*N*-diethylacetamide, CaH_2, dry DMF, 80 °C, 24 h, 31%; **8b**, α-chloro-*N*,*N*-diethylacetamide, K_2CO_3 (excess), dry THF/DMF (9:1, v/v), 75 °C, 72 h, 3%

Syntheses and Conformational Properties of Calix[4]arene Derivatives

The syntheses of tetra-*O*-substituted calixarene derivatives **6a** and **7** were performed by the reaction sequence depicted in Figure 1. Compounds **6a** and **7** were obtained by similar procedures: treatment of *p*-tetrakis(phenylazo)calix[4]arene **3** with tertiary acetamide (α-chloro-*N*,*N*-diethylacetamide and α-chloro-*N*,*N*-dimethylacetamide, respectively) and Cs_2CO_3 in dry DMF gave compounds **6a** and **7**, each in a 1,3-alternate conformation as expected with this base.[38] This is confirmed by the presence of only one singlet for the $ArCH_2Ar$ groups − δ = 4.16 ppm for **6a** and δ = 3.99 ppm for **7** − in the ^1H NMR spectrum and one signal for the corresponding carbon atoms, at δ = 38.0 and 37.3 ppm, respectively, in the ^{13}C NMR spectrum.[39,40] The analogous reaction in the presence of CaH_2 as base gave **6b** in the cone conformation. The corresponding ^1H NMR and ^{13}C NMR spectra show two doublets (δ = 3.56 and 5.56 ppm, J = 13.5 Hz) for $ArCH_2Ar$ groups and one signal (at δ = 32.6 ppm) for the corresponding carbon atoms, respectively, both spectra indicating a cone conformation. In this case, we can see that the Ca^{2+} cation is capable of maintaining the cone conformation whereas for the synthesis of **6a**,[20] Cs^+ permits an 1,3-alternate conformation to be obtained, in accordance with the literature.[41,42]

Treatment of **3** with α-chloro-*N*,*N*-diethylacetamide and CaH_2 in DMF gave mainly the distal 1,3-disubstituted compound **8a**. The ^1H and ^{13}C NMR spectra show two characteristic doublets (δ = 3.85 and 5.14 ppm, J = 13.2 Hz) for the $ArCH_2Ar$ groups and one signal (δ = 32.0 ppm) for the corresponding carbon atoms, respectively, both indicating a cone conformation in compound **8a**. Similar treatment with an excess of K_2CO_3 gave the potassium complex of **8a** (complex **8b**). This complex was isolated by column chromatography as crystals suitable for X-ray structure analysis, which showed a cone conformation as depicted below. On the other hand, similar treatment of **3** in dry acetonitrile with K_2CO_3 as base gave the monosubstituted analogue **5** in good yield (64%). The ^1H and ^{13}C NMR spectra show the two characteristic AX systems (δ = 3.73, 4.50 ppm, J = 13.7 Hz and δ = 3.78, 4.77 ppm, J = 13.0 Hz) for the $ArCH_2Ar$ groups and two signals (δ = 32.5 and 32.8 ppm) for the corresponding carbon atoms, respectively, both again indicating a cone conformation in compound **5**. However, the calix[4]arene **4**, disubstituted both on the upper and lower rim with diazo and acetamide groups, respectively, was prepared by treatment of **2** with α-chloro-*N*,*N*-diethylacetamide, with Cs_2CO_3 as base in dry DMF. The HMBC spectrum of **4** showed that the alkylation had taken place only at those phenol groups that were not *p*-substituted (Figure 2): in fact the HMBC cross peaks indicate that OCH_2, 3′-H, 4′-H are correlated to C-1′ whereas 3-H is correlated to C-1 (Figure 3). The ^1H NMR spectrum shows an AX system for the $ArCH_2Ar$ groups, indicating a cone conformation in compound **4**.

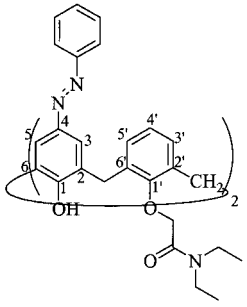

Figure 2. Numbering scheme for compound **4**

Single-Crystal X-ray Structures

Single crystals suitable for X-ray analysis were obtained for **6a** (from toluene), **7** (from toluene/pyridine), **8a** (from toluene/cyclohexane) and **8b** (from ethyl acetate). A summary of the crystallographic data for the molecules is listed in Table 1. The different Figures were calculated by use of PLATON.[43] In the four compounds, the skeleton of calix[4]arene is numbered conventionally (C1...C28, O25...O28) and the different substituents as depicted for the compound **8a** in Figure 4.

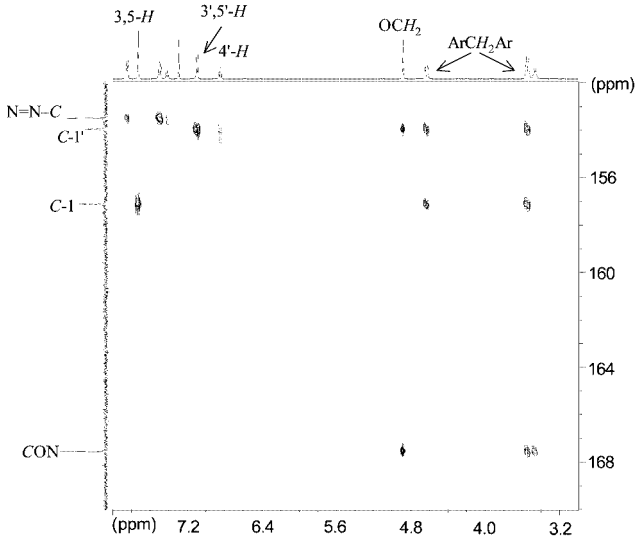

Figure 3. Expanded HMBC of compound **4**

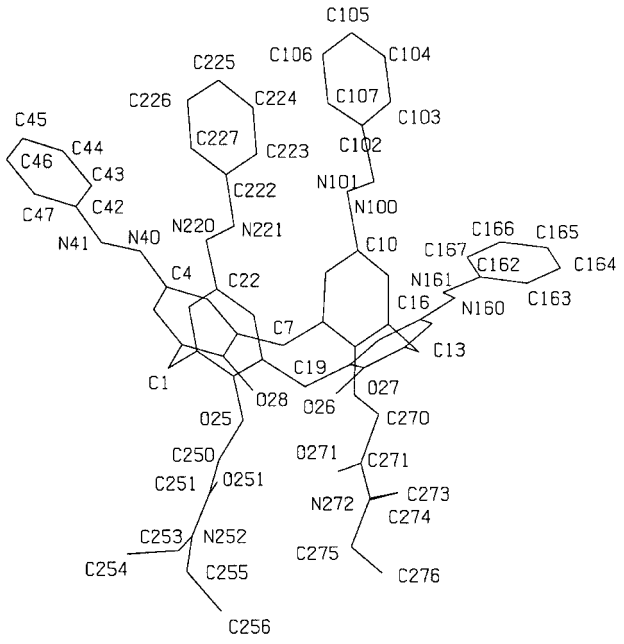

Figure 4. Numbering scheme for compound **8a**

The X-ray structure of **6a**, which is tetrasubstituted with four amide groups, confirms a 1,3-alternate conformation as observed by NMR spectroscopy, presumably due to the steric hindrance between the four substituents. The inclination angles of the aromatic units to the mean plane of the CH_2 bridges have similar values (Table 2). The dihedral angles between mean planes of the phenyl rings in each moiety (on both sides of each diazo group) are near 30° for two of them and near 7° for the two others (Table 3). Compound **6a** crystallises with two toluene molecules, one outside the cavity. The second toluene molecule is situated between two macrocycles translated along the *b* axis (Figure 5). Weak interactions are found between C(toluene)···C(diazophenyl ring) atoms, corresponding to distances of 3.722−3.880 Å. These results can be compared to, for instance, those observed in a similar molecule: 5,11,17,23-tetra-*tert*-butyl-25,26,27,28-tetrakis[(*N*,*N*-

Table 1. Crystallographic data for compounds **6a**, **7**, **8a** and **8b**

	6a	**7**	**8a**	Compound **8b**
Empirical formula	$C_{76}H_{84}N_{12}O_8{\cdot}2C_7H_8$	$C_{68}H_{68}N_{12}O_8{\cdot}2C_7H_8$	$C_{64}H_{62}N_{10}O_6{\cdot}C_7H_8$	$C_{64}H_{60}N_{10}O_6K{\cdot}2C_4H_8O_2$
Formula mass	1477.82	1365.61	1155.34	1280.53
Temperature [K]	173(2)	293(2)	173(2)	123(2)
Crystal system	triclinic	tetragonal	monoclinic	triclinic
Space group	$P\bar{1}$	$P4/n$	$P2_1/c$	$P\bar{1}$
Unit cell dimensions [Å, °]	a = 10.315(2)	a = 14.516(2)	a = 11.392(2)	a = 13.369 (3)
	b = 18.172(4)	b = 14.516(2)	b = 26.041(5)	b = 14.959(5)
	c = 22.038(4)	c = 17.484(4)	c = 21.006(4)	c = 17.971(4)
	α = 82.55(3)			α = 100.32(3)
	β = 79.50(3)		β = 95.40(3)	β = 90.91(3)
	γ = 85.38(3)			γ = 114.67(3)
Volume [Å^3]	4020.6(1)	3684.3(1)	36204(2)	3196.4(11)
Z, calcd. density [Mg·m^{-3}]	2, 1.221	2, 1.231	4, 1.237	2, 1.330
Absorption coeff. [mm^{-1}]	0.079	0.081	0.081	0.153
F(000)	1576	1448	2440	1354
Limiting indices	$-13 \le h \le 13$	$-26 \le h \le 16$	$-12 \le h \le 12$	$0 \le h \le 15$
	$-21 \le h \le 23$	$-11 \le k \le 11$	$-29 \le k \le 29$	$-17 \le k \le 15$
	$-25 \le l \le 28$	$-17 \le l \le 19$	$-23 \le l \le 23$	$-20 \le l \le 20$
Reflections coll./unique	28599/18310	5105/2743	17161/9496	10534/10534
Data/restraints/parameters	18309/24/1054	2743/21/260	9496/0/838	10534/0/846
Goodness-of-fit on F^2	0.994	1.032	0.978	0.629
Final R indices [$I > 2\sigma(I)$]	$R1$ = 0.0647	$R1$ = 0.1049	$R1$ = 0.0724	$R1$ = 0.0560
R indices (all data)	$wR2$ = 0.1553	$wR2$ = 0.2922	$wR2$ = 0.1940	$wR2$ = 0.1530
	$R1$ = 0.1369	$R1$ = 0.1607	$R1$ = 0.1585	$R1$ = 0.0941
	$wR2$ = 0.2004	$wR2$ = 0.3509	$wR2$ = 0.2542	$wR2$ = 0.2072
Largest diff. peak/hole [e·Å^3]	0.453/−0.296	0.476/−0.469	0.386/−0.323	0.458

Table 2. Inclination angles of aromatic units to the mean plane of methylene groups [°]

6a	**7**	**8a**	**8b**
104.58(6)	99.2(2)	138.0(2)	147.0(1)
106.09(7)	–	99.6(1)	97.40(7)
104.87(6)	–	145.0(1)	145.4(1)
102.29(6)	–	103.9(1)	106.42(8)
1,3-alternate	1,3-alternate	cone	cone

Table 3. Angles between the aromatic rings on either side of the −N=N− groups [°]

6a	**7**	**8a**	**8b**
32.6(1)	29.4(3)	1.8(4)	5.3(2)
6.9(2)	–	10.5(3)	44.9(1)
28.2(1)	–	33.5(1)	37.5(2)
6.9(1)	–	10.7(3)	15.6(2)

diethyl-2-carbamoyl)methoxy]calix[4]arene ($\mathbf{L_1}$). The only differences between $\mathbf{L_1}$ and **6a** are in the substituents on the upper rim of the calixarene: *tert*-butyl groups for $\mathbf{L_1}$ and diazo groups for **6a**. $\mathbf{L_1}$ can be obtained either in a cone conformation[44] or in a 1,3-alternate conformation,[45] depending on the kind of bases employed in the synthesis, crystallising as sodium and dipotassium complexes, respectively, whereas in our case we have obtained an organic complex. It is interesting to note that this kind of compounds can crystallise without ions.

Like **6a**, compound **7** (Figure 6) crystallises in a tetragonal group and the asymmetric unit consists of only one moiety. Two disordered toluene molecules lie in the network between the macrocycles. The macrocycle is in the 1,3-alternate conformation, as is to be expected when four substituents are grafted on the lower rim of this kind of azocalixarenes. The macrocycle shows a "4bar" symmetry with the inclination angles of aromatic units to the mean plane of CH_2 bridges as quoted in Table 2. The packing of **7** is drawn along the "4bar" axis and permits the symmetry and the disordered solvent molecules that lie in the network between the macrocycles to be observed (Figure 7).

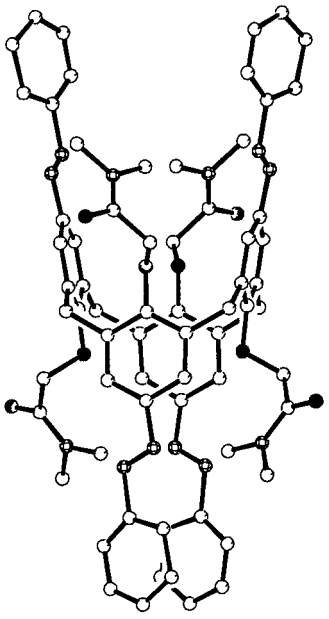

Figure 6. 1,3-Alternate conformation of compound **7**

The X-ray structure of the di-*O*-substituted amide azocalix[4]arene **8a** shows that the ethyl group of one amide substituent is disordered with occupation factors of 0.51 and 0.49. One toluene molecule is present as a guest in the structure, but is disordered: one toluene molecule is found at 0.39 occupation and a second one with 0.61. For the latter, the methyl group is also disordered, with 0.30−0.70 occupations. The macrocycle has a distorted cone conformation, as indicated by the inclination angles (Tables 2 and 3). The two moieties with free OH groups each have a large inclination (138 and 145°). The corresponding dihedral angles between the aromatic rings of each moiety are very different: one moiety is almost coplanar (1.8°) while the value of this angle for the other moiety is 33.5°. The four phenolic oxy-

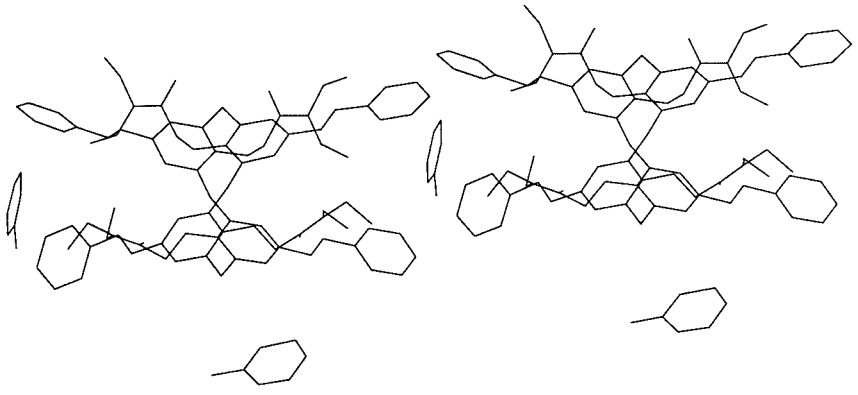

Figure 5. Packing of compound **6a**

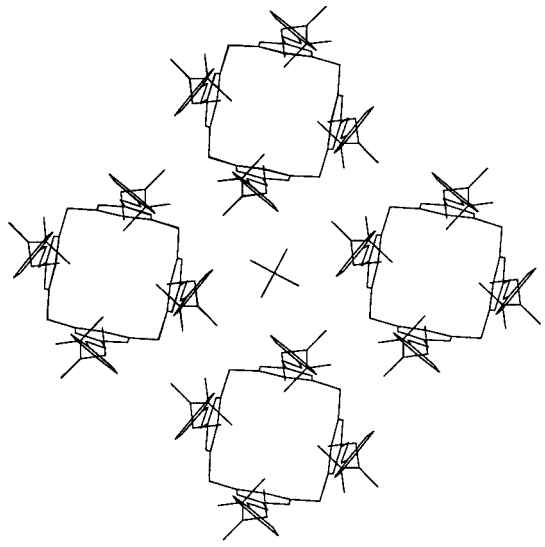

Figure 7. Packing of compound **7**

gen atoms and the one carbonyl oxygen atom are involved in intramolecular hydrogen bonds (Table 4) corresponding to O26 and O27 and the other is bifurcated between O28, O25 and O251. This situation is similar to those previously described by M. Bochenska et al.[46] concerning a *p-tert*-butylcalix[4]arene substituted with two amide groups on proximal OH groups.

Table 4. Hydrogen bonds for compound **8a**

	O−H [Å]	H···O [Å]	O···O [Å]	O−H···O [°]
O26−H26···O27	0.84	2.118	2.925	160.85
O28−H28···O25	0.84	2.062	2.845	154.83
O28−H28···O251	0.84	2.375	2.950	126.10

However, the structure of **8a** shows a very interesting packing, with one disordered toluene molecule lying between the calixarenes and one of the amide substituents situated in the cavity of a neighbouring macrocycle. The distance between C253 (carbonyl function) of one molecule and C42...C47 (the centroid of the diazo aromatic group) of the neighbouring molecule is 3.718 Å. This situation is repeated along the *b* axis, giving a zigzag chain of molecules. This packing is similar to that of *p-tert*-butylcalix[4]arene di-*O*-substituted by CH_2CO_2Et, a regular cone-shaped conformation that enclathrates the ethoxy residue of one of the ester groups of a neighbouring molecule.[47] In both cases there is a self-inclusion producing a one-dimensional polymeric chain with the molecules aligned in a zigzag fashion and alternating in opposite directions between successive chains (Figure 8).

The same calixarene can also be crystallised as potassium complex **8b** (Figure 9) with two ethyl acetate molecules: one of these participates in the coordination of K^+ while the second is a guest in the network between the calixarene units. The conformation of the macrocycle is very close to that of compound **8a**, with two large inclination angles. The dihedral angles between rings show large deviations from coplanarity, with one exception (Table 3). Characteristic bonds and angles around the potassium ion are given in Table 5. The coordination number is seven: with the four oxygen atoms of the hydroxy groups, two oxygen atoms of the amide substituents and one oxygen atom of the solvent. The shortest distances are those with the oxygen atoms of the hydroxy groups (2.155 and 2.218 Å), while the smallest angles are those with the two oxygen atoms of the amide

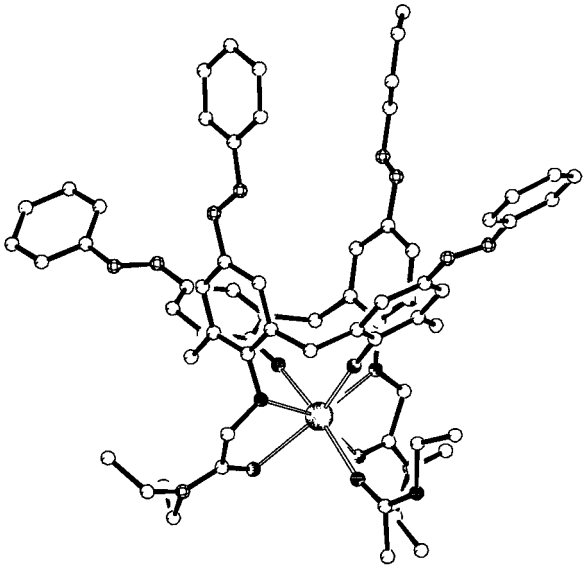

Figure 9. Cone conformation of potassium complex **8b**

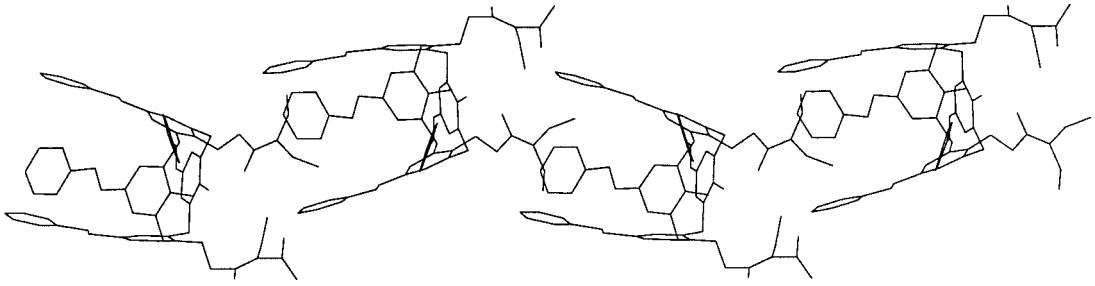

Figure 8. Zigzag chain of molecules in **8a**

Table 5. Selected bond lengths and angles around the potassium ion

	Bond lengths [Å]		Bond lengths [Å]
K1−O25	2.544(2)	K1−O253	2.445(2)
K1−O26	2.155(2)	K1−O273	2.444(2)
K1−O27	2.580(2)	K1−O500	2.394(3)
K1−O28	2.218(2)		
	Bond angles [°]		Bond angles [°]
O25−K1−O26	81.49(8)	O500−K1−025	96.90(9)
O26−K1−O27	73.40(8)	O500−K1−O26	173.8(1)
O27−K1−O28	74.87(8)	O500−K1−O27	111.22(9)
O28−K1−O26	95.5(1)	O500−K1−O28	89.8(1)
O28−K1−O25	74.56(8)	O27−K1−O25	137.92(7)
O25−K1−O253	62.65(8)	O25−K1−O273	159.70(8)
O26−K1−O253	92.29(9)	O26−K1−O273	102.72(9)
O27−K1−O253	149.17(8)	O27−K1−O273	61.19(8)
O28−K1−O253	134.74(9)	O28−K1−O273	124.06(9)
O500−K1−O253	81.68(9)	O500−K1−0273	76.76(9)
O273−K1−O253	97.17(9)		

groups (62.65 and 61.19°). For precedents to the potassium coordination, a notable example can be found in the structure of calix[4]dibenzocrowns-6, in which the potassium ion is bonded to the six oxygen atoms of the molecule and the seventh coordination is occupied by a strongly bound water molecule.[48]

Another comparable structure of **8b** is the 5,11,17,23-tetra-*tert*butyl-26,28-[(*N*,*N*-diethyl-2-carbamoyl)ethoxy]-25,27-dimeth-oxycalix[4]arene sodium triiodide structure, in which the compound is also in a cone conformation and the sodium ion is hexacoordinate with the oxygen atoms of the amide and ether substituents.[36] Moreover, the packing of **8b** shows that one equivalent of ethyl acetate solvent is incorporated in the network. Two calixarene molecules, connected by a centre of symmetry, lie in such a way that the diazo substituents of one lies in the cavity of the second (Figure 10): the distances between C222...C227 (the centroid of diazo aromatic ring) and C8...C27, C20...C25 (the centroids of two aromatic rings of the calixarene), respectively, are 3.787 and 4.102 Å.

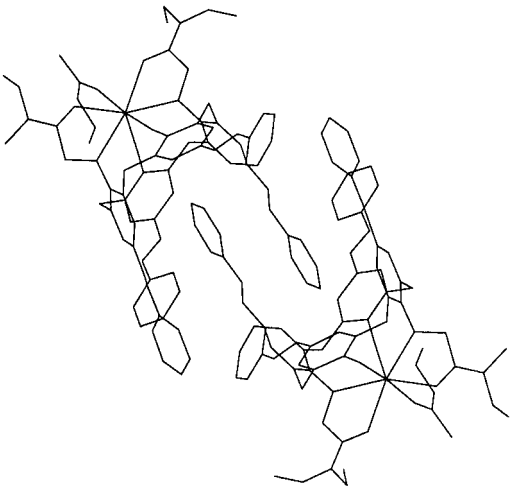

Figure 10. Dimer in the packing of **8b**

These crystallographic results give sufficient information regarding the conformations of the calixarenes in the solid state, which correspond to those obtained in solution.

Extraction Properties

The results given in Figure 11 correspond to the percentage of cation extracted (% Extraction) from solutions of **6a**, **6b** and **8a**. Each of these ligands show a significant extraction level only for sodium, potassium and calcium, K^+ always being the best extracted.[49] This result correlates with the potassium complex **8b** that we isolated, in which the potassium ion is coordinated with the oxygen atoms of the amide group. The tetraamide derivative **6b** (cone conformation) is the most efficient one for the extraction of Na^+ (51%), K^+ (75%) and Ca^{2+} (48%). In the case of compound **6a** (1,3-alternate conformation), the extraction percentages are close to those of **6b**, 52% for K^+ and 42% for Ca^{2+} but very low for Na^+ (4%) and Mn^{2+} (4%). The diamide derivative **8a** extracts the same metal ions as **6a** and **6b**, but exhibits significant differences. These differences in the extraction behaviour are attributable to the number of amide units attached to the calixarene.

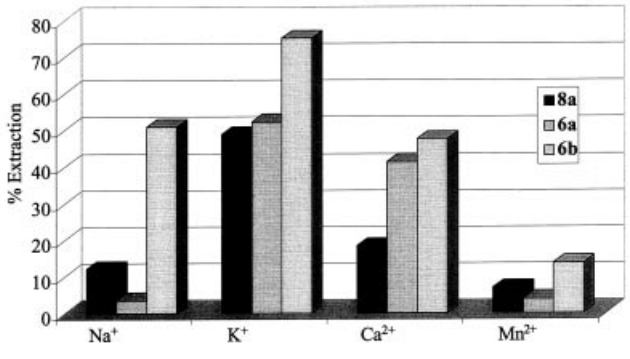

Figure 11. Extraction percentage of cations as a function of the nature of the ligands

These results have confirmed previous studies, which showed that calixarene amide derivatives are efficient ligands for alkali and alkaline earth metal ions.[50]

Conclusion

This paper describes the first syntheses of calixarenes bearing both diazo and acetamide groups, found on the basis of their ^1H and ^{13}C NMR spectra to exist either in cone or 1,3-alternate conformations. Most of them have been analysed in the solid state by X-ray crystallography, confirming the conformations observed in solution. In the solid-state structure of **8a**, the calixarene diamide is in a cone conformation, enclathrating one of the amide groups of a neighbouring molecule. This self-inclusion produces an interesting one-dimensional polymeric chain. These new azocalixarene amide derivatives **6a**, **6b** and **8a** clearly favour the efficient extraction of K^+.

Experimental Section

General Remarks: Melting points were determined with an Electrothermal 9100 capillary apparatus. ^1H and ^{13}C NMR spectra were recorded with a Bruker DRX 300 spectrometer (^1H: 300 MHz; ^{13}C: 75 MHz; solvent, chemical shifts in ppm, J in Hertz). $^{13}C/^1H$ HMBC was recorded with a Bruker AM 500 machine. Mass spectra were obtained by the electrospray technique, positive mode (ES-MS). IR spectroscopy was performed with a Mattson 5000 FT apparatus ($\tilde{\nu}$ in cm^{-1}). Macherey−Nagel plates were used for TLC analyses (SiO_2, Roth, polygram Sil G/UV 254) and silica gel 60 (Merck, particle size 0.040−0.063 mm) was used for chromatography columns. All solvents were purified by standard procedures before use. Dry solvents were obtained by literature methods and stored over molecular sieves. All other reagents (reagent-grade quality) as obtained from commercial suppliers were used without further purification. All reactions were carried out under nitrogen. Compound **1** was synthesised by a literature procedure.[51]

Extraction: The extraction of metal ions (Na^+, K^+, Mg^{2+}, Ca^{2+}, Mn^{2+}, Ni^{2+}, Cu^{2+}, Pb^{2+} and Cd^{2+}) by **6a**, **6b** and **8a** ligands was investigated with acetate and chloride salts. The organic solutions were made by dissolving a weighed amount of the ligand in dichloromethane. The aqueous solution was buffered to pH = 4.8 with tris(hydroxymethyl)aminomethane − HCl (0.05 M) (99%, Acros) and the ionic strength was maintained at $\mu = 0.1$ with tetramethylammonium chloride (0.1 M) (98%, Acros). Liquid-liquid extraction experiments were carried out in a flask by shaking 25 mL of an aqueous phase containing metal salt (10^{-4} M) and 5 mL of organic phase containing **6a**, **6b** and **8a** ($5\ 10^{-4}$ M) for 12 h in a thermostatted bath (30 °C). The aqueous phase was separated and centrifuged, 1% of HNO_3 was then added to these solutions and analysis was carried out by atomic absorption spectrometry (Perkin−Elmer 3110) with an air/acetylene flame, the measurements being made with standard conditions calibration. The percentages of extraction (Ex%) were determined from Equation (1)[52], where $[M]_{blank}$ and $[M]_{final}$ represent the metal concentrations in the aqueous phase extracted with pure dichloromethane and in the dichloromethane solutions containing ligands, respectively. $Ex\% = ([M]_{blank} - [M]_{final}) \times 100/[M]_{blank}$ (1)

Synthesis of 26,28-Bis{[(diethylamino)carbonyl]methoxy}-25,27-dihydroxy-11,23-bis(phenylazo)calix[4]arene (4). Cone Conformation: 25,26,27,28-Tetrahydroxy-11,23-bis(phenylazo)calix[4]arene (**2**, 0.1 g, 0.158 mmol), α-chloro-*N*,*N*-diethylacetamide (0.054 mL, 0.395 mmol) and Cs_2CO_3 (0.26 g, 0.79 mmol) were stirred in dry DMF (15 mL) and heated at 80 °C for 48 h. To this solution was added water (20 mL). The resulting precipitate was filtered off and treated with HCl (10%, 12 mL) and $CHCl_3$ (15 mL). The organic phase was separated and dried with $MgSO_4$, and the solvents were evaporated to dryness. Purification of the resulting residue by column chromatography [SiO_2, ethyl acetate/hexane = 6:4 (v/v)] gave **4** as a yellow-orange powder (0.03 g, 22%). M.p. 182−184 °C. IR: $\tilde{\nu}$ = 3330.8 (OH), 2971.2, 2927.9 (CH), 1638.9 (CO), 1582.6, 1474.3, 1444.2, 1424.5 (C=C, N=N) cm^{-1}. ^1H NMR ($CDCl_3$): δ = 1.06 (t, J = 7.1 Hz, 6 H, CH_3CH_2N), 1.13 (t, J = 7.1 Hz, 6 H, CH_3CH_2N), 3.29 (q, J = 6.0 Hz, 4 H, CH_2N), 3.37 (q, J = 6.1 Hz, 4 H, CH_2N), 3.38, 4.47 ('q', AX, J_{AX} = 13.0 Hz, 4 H, $ArCH_2Ar$), 4.70 (s, 4 H, CH_2O), 6.66 (t, J = 7.6 Hz, 2 H, H_{Ar}), 6.93 (d, J = 7.5 Hz, 4 H, H_{Ar}), 7.33, 7.23 (m, 6 H, $H_{m,p}$-diazo), 7.54 (s, 4 H, H_{Ar}), 7.67 (d, J = 7.3 Hz, 4 H, H_o-diazo), 8.92 (s, 2 H, OH) ppm. ^{13}C NMR ($CDCl_3$): δ = 13.4 (NCH_2CH_3), 14.7 (NCH_2CH_3), 32.1 ($ArCH_2Ar$), 40.7 (NCH_2CH_3), 41.4 (NCH_2CH_3), 73.8 (CH_2O), 122.7, 124.3, 126.0, 129.3, 129.9, 130.2 (CH_{Ar}), 129.0, 133.7, 145.9, 153.5, 154.0, 157.1 (C_{Ar}), 167.5 (CO) ppm. $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$, HMBC): δ = 13.4 (NCH_2CH_3/NCH_2CH_3), 14.7 (NCH_2CH_3/NCH_2CH_3), 32.1 ($ArCH_2Ar/H_{Ar}$), 40.7, 41.4 (NCH_2CH_3/NCH_2CH_3), 73.8 (CH_2O/CH_2O), 122.7 (C_o-diazo/$H_{o,m,p}$-diazo), 124.3, 126.0 (CH_{Ar}/H_{Ar}, $ArCH_2Ar$), 129.0 (C_{Ar}/H_{Ar}, $ArCH_2Ar$), 129.3 (C_m-diazo/$H_{o,m,p}$-diazo), 129.9 (CH_{Ar}/H_{Ar}, $ArCH_2Ar$), 130.2 (C_p-diazo/$H_{o,m,p}$-diazo), 133.7, 145.9 (C_{Ar}/H_{Ar}, $ArCH_2Ar$), 153.5 (N=NC-/$H_{o,m,p}$-diazo), 154.0 ($COCH_2CON/H_{Ar}$, $ArCH_2Ar$, OCH_2), 157.1 (COH/H_{Ar}, $ArCH_2Ar$), 167.5 (CON/OCH_2, NCH_2CH_3, NCH_2CH_3) ppm. ES-MS: m/z = 858.52 $[M + H]^+$ (calcd. 858.41), 881.48 $[M + Na]^+$ (calcd. 881.40). $C_{52}H_{54}N_6O_6$ (859.04): calcd. C 72.79, H 6.46, N 9.73; found C 72.71, H 6.34, N 9.78.

Synthesis of 26-{[(diethylamino)carbonyl]methoxy}-25,27,28-trihydroxy-5,11,17,23-tetrakis(phenylazo)calix[4]arene (5). Cone Conformation: A mixture of **3** (0.3 g, 0.36 mmol), K_2CO_3 (0.11 g, 0.8 mmol), KI (0.133 g, 0.8 mmol) and α-chloro-*N*,*N*-diethylacetamide (0.1 mL, 0.72 mmol) was stirred in dry MeCN (25 mL). This mixture was heated at reflux temperature for 12 h. The resulting precipitate was removed by filtration. The filtrate was concentrated to dryness and the residue was treated with HCl (1 M, 35 mL) and CH_2Cl_2 (40 mL). The organic phase was separated, washed with water (20 mL) and dried with Na_2SO_4. The solvent was removed by evaporation. Purification of the resulting residue by column chromatography [SiO_2, chloroform/petroleum ether/acetonitrile = 5:4:1 (v/v)] gave **5** as a red solid (0.22 g, 64%). M.p. 283−285 °C. IR: $\tilde{\nu}$ = 3320.0 (OH), 2912.0 (CH), 1619.3 (C=O), 1593.7, 1543.1, 1487.4, 1439.0 (C=C, N=N) cm^{-1}. ^1H NMR ($CDCl_3$): δ = 1.32 (t, J = 7.0 Hz, 6 H, NCH_2CH_3), 1.33 (t, J = 7.0 Hz, 6 H, NCH_2CH_3), 3.36 (q, J = 7.2 Hz, 2 H, NCH_2CH_3), 3.64 (q, J = 7.0 Hz, 2 H, NCH_2CH_3), 3.73, 4.50 ('q', AX, J_{AX} = 13.7, 4 H, $ArCH_2Ar$), 3.78, 4.77 ('q', AX, J_{AX} = 13.0 Hz, 4 H, $ArCH_2Ar$), 5.10 (s, 2 H, CH_2O), 7.37−7.49 (m, 14 H, H_{Ar}), 7.73−7.78 (m, 14 H, H_{Ar}), 10.22 (br. s, 3 H, OH) ppm. ^{13}C NMR ($CDCl_3$): δ = 13.4 (NCH_2CH_3), 14.5 (NCH_2CH_3), 32.8, 32.5 ($ArCH_2Ar$), 41.3 (NCH_2CH_3), 72.5 (CH_2O), 122.8, 122.9, 123.2, 124.57, 124.63, 124.7, 129.03, 129.05, 129.1, 129.35, 129.4, 129.45 (CH_{Ar}), 130.5, 130.7, 135.7, 147.4, 150.5, 153.3, 153.3, 153.6, 153.7, 153.9, 157.2, 168.9 (C_{Ar}), 171.5 (CO) ppm. ES-MS: m/z = 954.3 $[M + H]^+$ (calcd. 954.40), 976.3 $[M + Na]^+$ (calcd. 976.39). $C_{58}H_{51}N_9O_5$

(954.40): calcd. C 73.01, H 5.39, N 13.21; found C 73.11, H 5.32, N 13.15.

General Procedure for the Synthesis of Tetraamide-Substituted Tetrakis(phenylazo)calix[4]arenes 6a and 7. 1,3-Alternate Conformation: *p*-Tetrakis(phenylazo)calix[4]arene (0.3 g, 0.36 mmol) and Cs_2CO_3 (1.408 g, 4.32 mmol) were stirred at reflux temperature under nitrogen in dry DMF (30 mL) for 2 h. α-Chloroacetamide (8.64 mmol) was added to this solution. After 3 d, the reaction mixture was allowed to cool to room temperature, and water (50 mL) was added. The orange precipitate was recovered by filtration and washed three times with water (3 × 20 mL). The residue was dissolved in $CHCl_3$ (30 mL) and HCl (10%, 35 mL). The organic phase was separated and dried with Na_2SO_4. After evaporation to dryness, a red product was obtained and purified either by recrystallisation or column chromatography.

25,26,27,28-Tetrakis{[(diethylamino)carbonyl]methoxy}-5,11,17,23-tetrakis(phenylazo)calix[4]arene (6a). 1,3-Alternate Conformation: Purification of the residue by column chromatography [SiO_2, ethyl acetate/hexane/acetonitrile/methanol = 5:4.4:0.4:0.2 (v/v)] gave **6a** as a red solid (0.042 g, 16%). M.p. 214−216 °C. IR: ṽ= 2971, 2932, 2878 (CH), 1640.6(C=O), 1598.0, 1450.0 (N=N, C=C) cm^{-1}. ^1H NMR ($CDCl_3$): δ = 0.62 (t, *J* = 7.0 Hz, 12 H, NCH_2CH_3), 1.13 (t, *J* = 7.1 Hz, 12 H, NCH_2CH_3), 3.06 (q, *J* = 7.0 Hz, 8 H, NCH_2CH_3) 3.37 (q, *J* = 7.0 Hz, 8 H, NCH_2CH_3), 4.16 (s, 8 H, $ArCH_2Ar$), 4.44 (s, 8 H, CH_2O), 7.44−7.51 (m, 12 H, $H_{m,p}$-diazo), 7.75 (s, 8 H, H_{Ar}), 7.83 (d, *J* = 7.8 Hz, 8 H, H_o-diazo) ppm.^{13}C NMR ($CDCl_3$): δ = 13.3 (NCH_2CH_3), 14.4 (NCH_2CH_3), 38.0 ($ArCH_2Ar$), 41.2, 42.7 (NCH_2CH_3), 72.3 (CH_2O), 122.8, 125.4, 129.5, 131.0 (CH_{Ar}), 134.8, 147.9, 152.9, 161.7 (C_{Ar}), 167.7 (CO) ppm. ES-MS: *m*/*z* =1293.5 $[M + H]^+$ (calcd. 1293.65). $C_{76}H_{84}N_{12}O_8$ (1293.58): calcd. C 70.57, H 6.55, N 12.99; found C 70.77, H 6.61, N 13.00.

25,26,27,28-Tetrakis{[(dimethylamino)carbonyl]methoxy}-5,11,17,23-tetrakis(phenylazo)calix[4]arene (7). 1,3-Alternate Conformation: Purification of the residue by recrystallisation from acetone and column chromatography [SiO_2, chloroform/petroleum ether/acetonitrile/methanol = 5:4.4:0.4:0.2 (v/v)] gave **5** as a red powder (0.11 g, 26%). M.p. 328−330 °C. IR ṽ = 2928.4 (CH), 1645.8 (C=O), 1584.4, 1469.5, 1448.6 (N=N, C=C) cm^{-1}. ^1H NMR (C_5D_5N): δ = 2.44 [s, 12 H, $N(CH_3)_2$], 2.99 [s, 12 H, $N(CH_3)_2$], 3.99 (s, 8 H, $ArCH_2Ar$), 4.51 (s, 8 H, CH_2O), 7.47−7.53 (m, 12 H, $H_{m,p}$-diazo), 7.67 (s, 8 H, H_{Ar}), 7.83 (d, *J* = 7.8 Hz, 8 H, H_o-diazo) ppm. ^{13}C NMR (C_5D_5N): δ = 35.6 (NCH_3), 36.9 (NCH_3), 37.3 ($ArCH_2Ar$), 73.8 (CH_2O), 122.5, 125.4, 129.9, 132.3 (CH_{Ar}), 135.9, 148.1, 153.2, 162.0 (C_{Ar}), 168.2 (CO) ppm. ES-MS: *m*/*z* = 1181.4 $[M + H]^+$ (calcd. 1181.53), 1203.3 $[M + Na]^+$ (calcd. 1203.52). $C_{68}H_{68}N_{12}O_8$ (1181.36): calcd. C 69.14, H 5.80, N 14.23; found C 69.22, H 5.80, N 14.21.

Synthesis of 25,26,27,28-Tetrakis{[(diethylamino)carbonyl]-methoxy}-5,11,17,23-tetrakis(phenylazo)calix[4]arene (6b). Cone Conformation: *p*-Tetrakis(phenylazo)calix[4]arene (0.3 g, 0.36 mmol) and CaH_2 (0.23 g, 6.6 mmol) were stirred at 70 °C under nitrogen in dry DMF (20 mL) for 2 h. After the mixture had cooled to room temperature, α-chloroacetamide (0.3 mL, 8.64 mmol) was added. The mixture was stirred for 48 h at 80 °C, and water (40 mL) was then added. The resulting precipitate was recovered by filtration. The residue was dissolved in $CHCl_3$ (40 mL) and HCl (1 M, 35 mL). The organic phase was separated, washed with water (2 × 20 mL) and dried with $MgSO_4$. After concentration to dryness, purification of the compound by recrystallisation from acetone gave **6b** as a yellow-orange powder (0.08 g, 17%). M.p. 186−188 °C. IR: ṽ = 2970.8, 2931.3 (CH), 1653.5 (CO), 1581.4, 1459.5, 1431.1 (C=C, N=N) cm^{-1}. ^1H NMR ($CDCl_3$): δ = 1.16 (t, *J* = 7.1 Hz, 12 H, CH_3CH_2N), 1.23 (t, *J* = 7.0 Hz, 12 H, CH_3CH_2N), 3.43−3.34 (m, 16 H, CH_2N), 5.13 (s, 8 H, CH_2O), 3.56, 5.56 ('q', AX, J_{AX} = 13.5 Hz, 8 H, $ArCH_2Ar$), 7.32−7.30 (m, 12 H, $H_{m,p}$-diazo), 7.43 (s, 8 H, H_{Ar}), 7.68 (d, *J* = 7.8 Hz, 8 H, H_o-diazo) ppm. ^{13}C NMR ($CDCl_3$): δ = 13.5 (NCH_2CH_3), 14.7 (NCH_2CH_3), 32.6 ($ArCH_2Ar$), 40.5 (NCH_2CH_3), 41.3 (NCH_2CH_3), 72.3 (CH_2O), 122.9, 124.1, 129.2, 130.3 (CH_{Ar}), 135.9, 148.8, 153.2, 159.9 (C_{Ar}), 168.6 (CO) ppm. ES-MS: *m*/*z* =1293.5 $[M + H]^+$ (calcd. 1293.65). $C_{76}H_{84}N_{12}O_8$ (1293.58): calcd. C 70.57, H 6.55, N 12.99; found C 70.31, H 6.55, N 12.99.

26,28-Bis{[(diethylamino)carbonyl]methoxy}-25,27-dihydroxy-5,11,17,23-tetrakis(phenylazo)calix[4]arene (8a): *p*-Tetrakis(phenylazo)calix[4]arene (**3**, 0.3 g, 0.36 mmol) and CaH_2 (0.14 g, 3.3 mmol) in dry DMF (20 mL) were stirred at 70 °C for 2 h. After the mixture had cooled to room temperature, α-chloro-*N*,*N*-diethylacetamide (0.1 mL, 0.72 mmol) was added. The mixture was then stirred at 80 °C for 22 h. Water (80 mL) was added to this solution. The resulting precipitate was filtered off and treated with HCl (1 M, 35 mL) and $CHCl_3$ (40 mL). The organic phase was separated, washed with water (20 mL) and dried with $MgSO_4$. After concentration to dryness, purification of the residue by recrystallisation from acetone gave **8** as a red powder (0.12 g, 31%). M.p. 187−189 °C. IR: ṽ = 3345.8 (OH), 2971.8, 2930.2 (CH), 1655.2 (C=O), 1584.3, 1471.8, 1444.8 (C=C, N=N) cm^{-1}. ^1H NMR (C_5D_5N): δ = 1.15 (t, *J* = 7.1 Hz, 12 H, NCH_2CH_3), 3.39 (q, *J* = 7.0 Hz, 4 H, NCH_2CH_3), 3.51 (q, *J* = 7.2 Hz, 4 H, NCH_2CH_3), 5.14, 3.85 ('q', AX, J_{AX} = 13.2 Hz, 8 H, $ArCH_2Ar$), 5.29 (s, 4 H, CH_2O), 7.67−7.19 (m, 28 H, H_{Ar}), 10.15 (br. s, 2 H, OH) ppm. ^{13}C NMR (C_5D_5N): δ = 12.8 (NCH_2CH_3), 13.9 (NCH_2CH_3), 32.0 ($ArCH_2Ar$), 40.4 (NCH_2CH_3), 40.9 (NCH_2CH_3), 73.6 (CH_2O), 122.7, 123.3, 124.6, 124.63, 128.9, 134.9, 135.3, 135.6 (CH_{Ar}), 146.0, 149.3, 149.6, 150.0, 151.2, 152.6, 153.1, 157.5 (C_{Ar}), 167.8 (CO) ppm. ES-MS: *m*/*z* =1067.3 $[M + H]^+$ (calcd. 1067.49), 1089.2 $[M + Na]^+$ (calcd. 1089.48), 1105.3 $[M + K]^+$ (calcd. 1105.59). $C_{64}H_{62}N_{10}O_6$ (1067.26): calcd. C 72.03, H 5.86, N 13.12; found C 71.96, H 5.83, N 13.05.

Potassium 26,28-Bis{[(diethylamino)carbonyl]methoxy}-25,27-dihydroxy-5,11,17,23-tetrakis(phenylazo)calix[4]arene Complex (8b): *p*-Tetrakis(phenylazo)calix[4]arene (**3**, 0.5 g, 0.6 mmol) and an excess of K_2CO_3 were stirred at reflux temperature under nitrogen in dry THF/DMF (9:1, v/v, 50 mL) for 1 h. α-Chloro-*N*,*N*-diethylacetamide (0.42 mL, 12 mmol) was then added to this solution. The mixture was stirred for 3 d at 75 °C. After concentration, the residue was dissolved in dichloromethane (50 mL) and washed with HCl (1 M, 20 mL) and water (2 × 20 mL). The organic layer was dried with $MgSO_4$ and filtered, and the solvents were evaporated to dryness. The resulting powder was chromatographed [SiO_2, ethyl acetate/hexane/methanol; 6:3:1 (v/v)] to give a pure fraction of **8b** (20 mg, 3%) as red crystals suitable for X-ray analyse.

X-ray Crystallographic Study: Data collection was performed with a Nonius Kappa CCD with Mo-K_α radiation. The structures were solved by direct methods by use of SHELXS[53] and refined by successive cycles of full-matrix, least-squares refinement with SHELXL.[53] As usual, non-H atoms were refined isotropically except for some disordered solvent molecules. Hydrogen atoms were calculated at theoretical positions and refined riding. For compound **7**, the H atoms of the methyl group were omitted; the carbon atom of this group lies on the 4bar axis, so the hydrogen atoms are very disordered. The crystallographic data for **6a**, **7**, **8a** and **8b**

are reported in Table 1. CCDC-174990 (**6a**), -174756 (**7**), -174663 (**8a**) and -174629 (**8b**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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