# NEW CALIX[4]ARENE-BASED AMIDES – THEIR SYNTHESIS, CONFORMATION, COMPLEXATION

Ivan STIBOR[a1,*], Martina RŮŽIČKOVÁ[a], Rostislav KRÁTKÝ[b], Michal VINDYŠ[a], Jaroslav HAVLÍČEK[b1], Evguenni PINKHASSIK[a2], Pavel LHOTÁK[a3], Asiya R. MUSTAFINA[c1], Yuliya E. MOROZOVA[c2], Ella Kh. KAZAKOVA[c3] and Valentina P. GUBSKAYA[c4]

[a] *Department of Organic Chemistry, Institute of Chemical Technology, Prague, Technická 5, 166 28 Prague 6, Czech Republic; e-mail: [1] stibori@vscht.cz, [2] epnkhssk@memphis.edu, [3] lhotakp@vscht.cz*

[b] *Department of Analytical Chemistry, Institute of Chemical Technology, Prague, Technická 5, 166 28 Prague 6, Czech Republic; e-mail: [1] havlicej@vscht.cz*

[c] *Department of Organic Chemistry, Kazan State University, 420008 Kazan, Russia; e-mail: [1] asiya@iopc.kcn.ru, [2] moroz@iopc.kcn.ru, [3] ella@iopc.kcn.ru, [4] in@iopc.kcn.ru*

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New chiral calix[4]arene-based diol-diamides **1a**, **1b**, tetraamides **2a**, **2b** and **7** as well as achiral diamide **3** and tetraamides **4**–**6** were prepared. The conformation of **1** has been studied in solution by NMR and in solid state by X-ray crystallography. The pinched-cone conformation of the calix[4]arene skeleton in **1** was found to be stabilized by a circular array of hydrogen bonds formed by two phenolic O–H and two amidic N–H bonds at lower rim. Whereas no significant complexation of $Na^+$ was observed in solution for diamides **1** and **3**, tetraamides **2**, **4**, **5**, and **6** give strong complexes with $Na^+$ as confirmed by NMR titrations of **2** and **4**. The influence of anions and the solvents used on complexation ability of **2** towards $Na^+$ is negligible.

**Keywords**: Complexation; Calix[4]arenes; Calixarenes; Conformation analysis; NMR spectroscopy; X-Ray diffraction; Receptors; Recognition.

Since the pioneering works of Gutsche[1], calix[*n*]arenes in general and calix[4]arene derivatives in particular[2,3], are still receiving much interest because of a unique combination of their features – relative ease of synthesis, rather wide variety of structures, interesting physical and chemical properties, and a wide range of applications including ion carriers[4], analytical sensors[5,6], model structures for biomimetics research[7], catalysts[8], and a tool for studying the role of H-bonding in molecular association[9–11].

Unsubstituted calix[4]arenes are not effective cation receptors, whereas their derivatives having the lower rim of the calix[4]arene skeleton substi-

tuted with amides, and esters have been shown to possess cation affinities[12–19]. Tetraesters[20–38] and tetraamides[39–50] are the most thoroughly studied compounds of this type. The recently developed selective hydrolysis of one ester group, leaving the other three untouched[51–53], has opened a versatile synthetic route to a number of ligands for trivalent cations with interesting photophysical properties[54,55]. Also distal (1,3) derivatives of calix[4]arenes are accessible by regioselective alkylation of the parent calix[4]arene[56,57]. These compounds have been used for the preparation of highly preorganized macrocyclic ligands[58–60]. Very recently, distal *N*-substituted carboxamides or sulfonamides of calix[4]arene have been shown to bind $Hg^{2+}$ with remarkable selectivity[61]. Chiral calix[4]arenes can be prepared (among other methods) by treatment of appropriate calix[4]arene derivative with chiral compounds. This is well documented[62–64], even for lower-rim substituted di- and tetraamides[64–66]. It was found[67] that in solid state (X-ray crystallography) distal(1,3)disubstituted calix[4]arenes adopt well organized conformation controlled by self inclusion and hydrogen bonding.

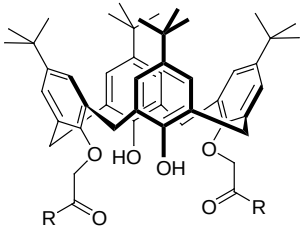
Here we report on the synthesis of new chiral amides with the calix[4]arene skeleton, namely: distal(1,3)disubstituted **1a**, **1b**, tetrasubstituted **2a**, **2b**, and **7**. Achiral amides **3**–**6** have also been synthesized. The complexation behaviour of both **1** and **2** was thoroughly studied in connection with the main aim of this study – the (chiral) recognition of anion which might be present in the form of tight ion-pair with complexed sodium cation. It is well documented in literature that such ion-pairs really exist even in polar solvents[68,69]. Analogously, closely related disubstituted amides have been found to facilitate the selective transport of ions through a polymer inclusion membrane[70].

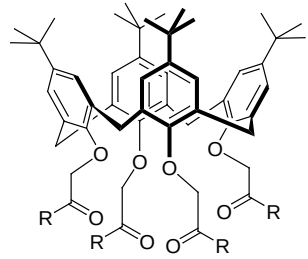
## RESULTS AND DISCUSSION

### *Synthesis*

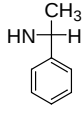
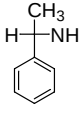
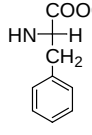
The synthesis of disubstituted compounds makes use of selective distal alkylation of parent calix[4]arene with ethyl bromoacetate to diester **8** transformed subsequently to diacid **10** and its dichloride[56] **12**. Analogously, the well-known tetraester[48] **9** is easily transformed to tetraacid[29] **11** and its tetrachloride[29] **13**. The syntheses of all amides have been accomplished using standard reaction of acyl chlorides **12** and **13** with corresponding (a)chiral amine in the presence of a tertiary amine in an inert solvent. Thus, **1a** and **1b** were obtained in 56 and 65% yields after crystallization from

methanol. Accordingly, **2a** and **2b** were obtained in 72 and 68% yields after crystallization from toluene or methanol. Amides **4**, **5**, and **6** were obtained in 74, 56, and 55% yields, respectively.





R =

| | | |
|---|---|---|
| **1a** |  | **2a** |
| **1b** |  | **2b** |
| **3** | $NHCH_2COOCH_3$ | **4** |
| | $NHCH_2COOH$ | **5** |
| | $NHCH_2CONHCH_2CH_2CH_3$ | **6** |
| |  | **7** |
| **8** | $OCH_2CH_3$ | **9** |
| **10** | OH | **11** |
| **12** | Cl | **13** |

*Conformation of Diamide* **1**

Conformation of compound **1a** was first studied using $^1H$ and $^{13}C$ NMR spectra. All the hydrogens and carbons were unequivocally assigned as shown below (Fig. 1 and Table I). The interpretation was based on 2D experiments COSY, HETCOR, and long-range HETCOR. Full details of the assignment have already been published[71].

As compound **1** possesses $C_{2v}$ symmetry, the *tert*-butyl, $CH_2$, $OCH_2$, and aromatic groups are duplicated. Two pairs of doublets belonging to $CH_2$ (positions 7 and 21, see Fig. 1) are characteristic for the cone conformation

of the calix[4]arene skeleton. In order to know more about conformation in solution, we have performed a thorough study of this compound using NOE interactions. The results are schematically shown below (Fig. 2).

Out of many trivial spatial NOEs, one deserves special attention and it is the NOE of amide proton to phenolic hydroxy group of neighbouring aro-

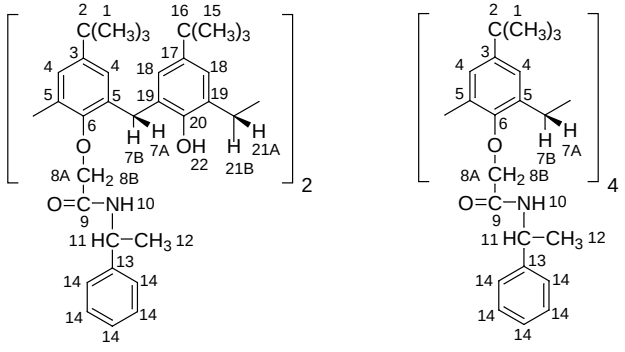


FIG. 1
Numbering of **1** and **2** for NMR spectra assignment

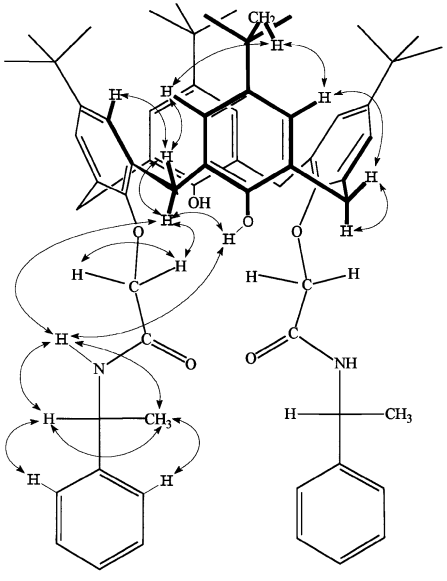


FIG. 2
NOE's in $^1$H NMR spectra of **1**

TABLE I
$^1$H and $^{13}$C NMR chemical shifts and coupling constants for compound **1a** (**1b**)

| Position | $^1$H ($CDCl_3$) | | | $^1$H ($CDCl_3$–$CD_3OD$–$D_2O$ 4 : 4 : 1) | | | $^{13}$C ($CDCl_3$) |
|---|---|---|---|---|---|---|---|
| | δ, ppm | *J*, Hz | H | δ, ppm | *J*, Hz | H | δ, ppm |
| 1 | 0.99 s | | 9 | 1.06 s | | 9 | 31.60 |
| 2 | | | | | | | 34.66 |
| 3 | | | | | | | 149.06 |
| 4 | 6.85 d | 4.0 | 2 | 6.97 d | 2.1 | 2 | 126.65<br>127.17 |
| 5 | | | | | | | 132.81<br>132.93 |
| 6 | | | | | | | 150.26 |
| 7A | 3.27 d | 13.2 | 1 | 3.36 d | 13.4 | 1 | 32.81 |
| 7B | 4.03 d | 13.6 | 1 | 4.04 d | 13.1 | 1 | |
| 8A | 4.26 d | 15.3 | 1 | 4.31 d | 15.5 | 1 | 75.70 |
| 8B | 4.59 d | 15.3 | | 4.59 d | 15.5 | 1 | |
| 9 | | | | | | | 168.14 |
| 10 | 9.16 d | 7.3 | 1 | 9.36 d | 7.4 | 1 | |
| 11 | 5.17 m | | 1 | 5.17 m | | 1 | 50.24 |
| 12 | 1.62 d | 6.9 | 3 | 1.65 d | 7.0 | 3 | 22.01 |
| 13 | | | | | | | 143.63 |
| 14 | 7.19–7.28 m | | 5 | 7.24–7.32 m | | 5 | 127.40<br>128.05<br>129.19 |
| 15 | 1.29 s | | 9 | 1.31 s | | 9 | 32.35 |
| 16 | | | | | | | 34.74 |
| 17 | | | | | | | 143.95 |
| 18 | 7.06 d | 3.6 | 2 | 7.13 d | 2.0 | 2 | 126.10<br>126.38 |
| 19 | | | | | | | 127.80<br>128.25 |
| 20 | | | | | | | 150.00 |
| 21A | 3.40 d | 13.6 | 1 | 3.48 d | 13.4 | 1 | 32.95 |
| 21B | 4.05 d | 13.4 | 1 | 4.07 d | 13.4 | 1 | |
| 22 | 7.39 s | | 1 | | | | |

matic unit. This interaction is a part of cyclic array of hydrogen bonds, probably very similar to that found in the solid state. This assumption is further supported by the NOE between amide proton and H-7A (see Fig. 1) of Ar–$CH_2$–Ar unit. The inspection of CPK models of compound **1** shows that these interactions can be rationalized by assuming the pinched cone conformation of **1**. The crystal structure of **1a** has been solved and a very similar arrangement of the lower rim was found. The spatial interactions in pinched cone conformation are clearly visible in Fig. 3.

Nitrogen N1–H forms bifurcated hydrogen bonds to both O1 (223 pm) and O3 (214 pm) and similarly nitrogen N2–H forms bifurcated hydrogen bonds to O2 (223 pm) and O5 (195 pm). These hydrogen bonds along with the O2–H···O3 (196 pm) and O1–H···O5 (195 pm) makes the pinched-cone conformation of the lower rim rigid. Very recently, a paper dealing with similar calix[4]arene amides has been published[72] where exactly the same conformation was found both in the solid state and solution. The pinched cone conformation was proved in both solid state as well as in solution

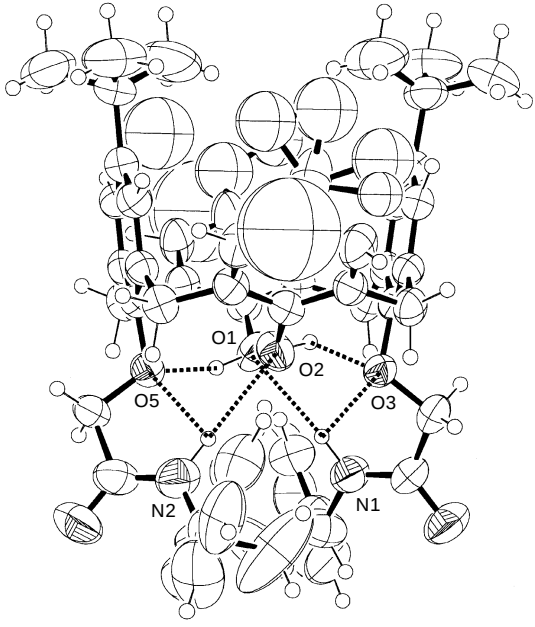



FIG. 3
Cyclic array of hydrogen bonds in **1** – crystal structure of **1a**

($CDCl_3$) using FTIR, $^1H$ NMR, and variable temperature (20–50 °C in $CDCl_3$ and 40–120 °C in $CDCl_2CDCl_2$) $^1H$ NMR.

The crystal packing is of interest in compound **1** as it forms layers. The orientation of the calixarene skeletons in each layer is shown in Fig. 4 with nicely visible pinched-cone conformations. We were not able to find any intermolecular contact between the molecules within one layer. Also interlayer interaction seems to be missing as the shortest distance we have found was around 500 pm.

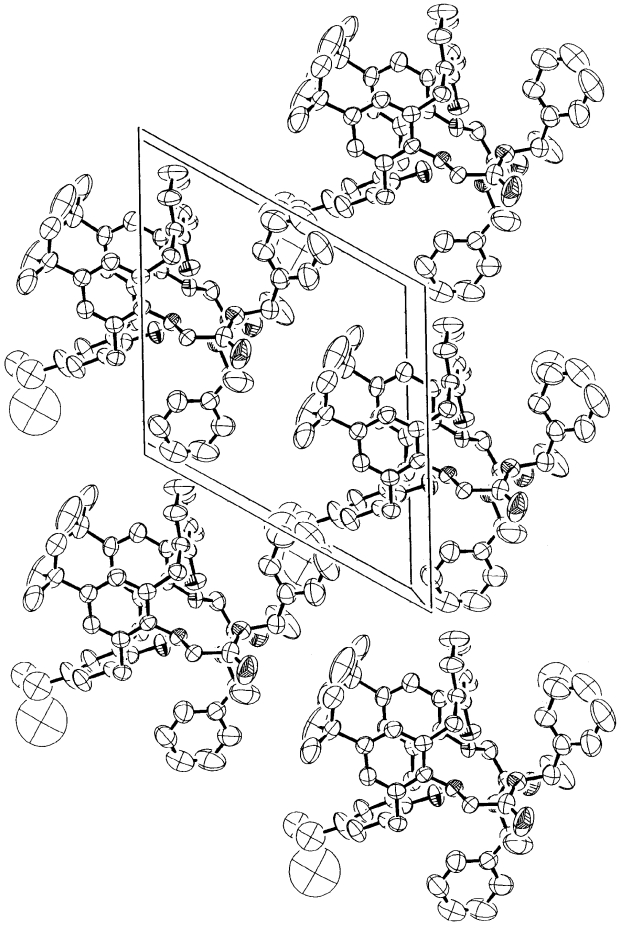


FIG. 4
Crystal packing of **1a**

*Conformation of Tetraamide **2***

The conformation of both free tetraamides of this type and their complexes with $Na^+$ are known. There are two recent reports dealing with this[72,73]. $^1H$ NMR spectra show that the complexation of $Na^+$ ion induces a change of the orientation of the amide groups from a network-like pattern with circular N–H···O=C intramolecular hydrogen bonding to a pattern in which the carbonyl group converge on the $Na^+$ ion. This was proved in solid state by crystal structure of both free ligands as well as its $Na^+$ complex[72]. This behavior is well documented for *N*,*N*-diethyltetraamide of type **2** and its complexes with $Na^+$, $K^+$, $Sr^{2+}$, and $Pb^{2+}$ ions[74].

In general we have found chemical shifts of the corresponding nuclei in $^1H$ and $^{13}C$ NMR spectra of **2a** to be very close to those of **1a**. The only ambiguities were associated with assignment of quaternary carbons, the problem was solved using HETCOR spectrum. All hydrogens and carbons have been assigned as shown below (Table II) using numbering of **2** given in Fig. 1.

The $^1H$ NMR spectra were measured in solvents with different polarities. This was necessary in order to be able to quantify the stability of sodium complexes (*vide infra*).

*Complexation*

Complexation ability of **1** was tested using standard NMR titration with $Na^+$ of NaSCN in $CDCl_3$–$CD_3OD$–$D_2O$ (4 : 4 : 1). This solvent mixture was the only possibility to attain the concentration of calixarene **1** needed for good NMR data (0.02 mol $l^{-1}$). Unfortunately, no interaction between the sodium cation and calixarene **1** was found. To overcome the solubility problems in alkali metal complexation with **1**, we turned our attention to UV and CD measurements.

UV and CD spectra were measured in acetonitrile using concentrations of **1a** range $5 \cdot 10^4$–$1 \cdot 10^3$ mol $l^{-1}$. The UV spectrum (Fig. 5) of free ligand **1a** in acetonitrile shows a broad band at 225–240 nm belonging to aromatics and a much weaker band at 284 nm characteristic of free phenolic hydroxy groups. As usual, the non-conjugated carbonyl group has low intensity ($\varepsilon$ = 15–20) but it can contribute to the absorption at 284 nm in UV spectrum of **1a**. In CD spectrum of free ligand **1a**, the following bands are present: two bands at 260 and 267 nm belonging to the $\pi$–$\pi^*$ transition, followed by the n–$\pi^*$ transition at 285 nm of the carbonyl attached to the lower rim.

An addition of neutral alkali salt (LiSCN, NaSCN, KSCN) to **1a** caused no changes in both UV and CD spectra in pure acetonitrile indicating no complexation of the respective cation. As it is well known that the formation of phenolate anion is usually accompanied by changes in UV spectra we have attempted an addition of alkali hydroxides. The UV as well as CD spectra were measured after addition of ten-fold excess of LiOH, NaOH, KOH or $N(C_2H_5)_4OH$. In UV spectra (Fig. 5), the formation of new band at

TABLE II
$^1H$ and $^{13}C$ NMR chemical shifts and coupling constants for **2**

| Position | $^1H$ $CDCl_3$ | | $^1H$ $CDCl_3$–$CD_3OD$ 3 : 1 | | $^1H$ $CDCl_3$–DMSO 4 : 3 | | $^1H$ $CDCl_3$–DMF 4 : 3 | | $^{13}C$ $CDCl_3$ |
|---|---|---|---|---|---|---|---|---|---|
| | δ, ppm | *J*, Hz | δ, ppm | *J*, Hz | δ, ppm | *J*, Hz | δ, ppm | *J*, Hz | |
| 1 | 1.06 s | | 1.07 s | | 1.07 s | | 1.09 s | | 31.35 |
| 2 | | | | | | | | | 33.87 |
| 3 | | | | | | | | | 145.61 |
| 4 | 6.67 d | 3.6 | 6.71 s | | 6.72 s | | 6.74 s | | 125.59 |
| 5 | | | | | | | | | 132.86 |
| 6 | | | | | | | | | 153.02 |
| 7A | 3.00 d | 13.2 | 2.98 d | 13.1 | 3.01 d | 12.8 | 2.97 d | 13.1 | 31.73 |
| 7B | 4.29 d | 13.2 | 4.35 d | 13.1 | 4.56 d | 12.8 | 4.53 d | 13.1 | |
| 8A | 4.34 d | | 4.27 d | 13.6 | 4.34 d | 13.2 | 4.35 d | 13.2 | 74.98 |
| 8B | 4.34 s | | 4.46 d | 13.6 | 4.57 d | 13.2 | 4.58 d | 13.2 | |
| 9 | | | | | | | | | 168.80 |
| 10 | 7.50 brs | | | | 8.82 d | 7.9 | 8.84 d | 8.1 | |
| 11 | 5.16 m | | 5.09 m | | 5.03 m | | 5.11 m | | 48.84 |
| 12 | 1.49 d | 7.0 | 1.47 d | 7.0 | 1.40 d | 7.0 | 1.46 d | 7.0 | 21.57 |
| 13 | | | | | | | | | 143.19 |
| 14 | 7.22 m | | 7.23 m | | 7.19 m | | 7.21 m | | 126.59<br>127.27<br>128.48 |

320–335 nm was clearly observed. The band was the highest for LiOH and successively lower for KOH and $N(C_2H_5)_4OH$, and almost negligible for NaOH. In contrast, no changes of CD spectra (Fig. 6) were observed for

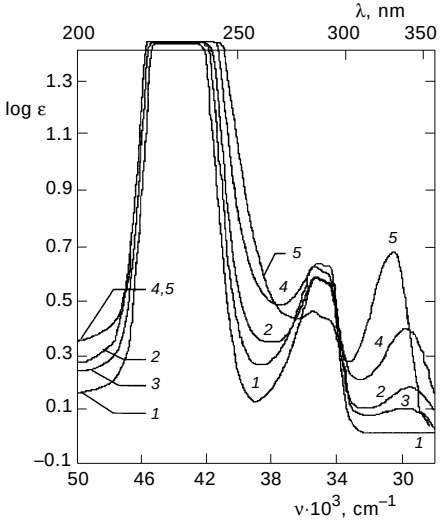



FIG. 5

UV spectra of compound **1a** in acetonitrile (*1*) and **1a** in acetonitrile with: $NEt_4OH$ (*2*), NaOH (*3*), KOH (*4*), LiOH (*5*) ($c_{\mathbf{1a}}$ = 0.001 mol $l^{-1}$, $c_{MOH}$ = 0.01 mol $l^{-1}$)

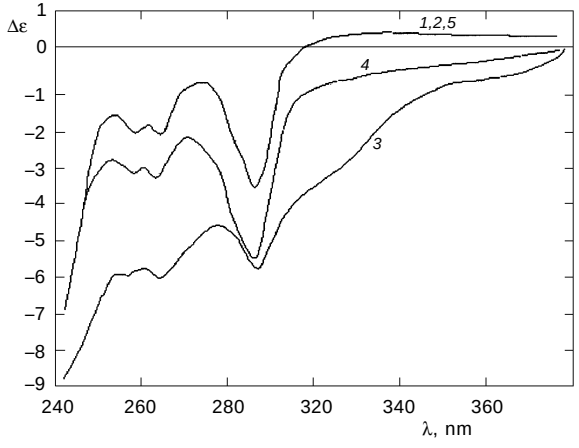



FIG. 6

CD spectra of compound **1a** in acetonitrile (*1*) and **1a** in acetonitrile with: $NEt_4OH$ (*2*), NaOH (*3*), KOH (*4*), LiOH (*5*) (*l* = 1 cm, $c_{\mathbf{1a}}$ = 0.001 mol $l^{-1}$, $c_{MOH}$ = 0.01 mol $l^{-1}$)

LiOH and $N(C_2H_5)_4OH$ whereas an addition of KOH or NaOH is even more accompanied by appearance of new diffuse bands at 310 and 350 nm.

We can give only speculative interpretation of these observations. The changes in UV spectra reflect the deprotonation of phenolic hydroxyl groups whereas the changes in CD spectra are closely associated with chiral chromophore, more specifically with interaction of the alkali cation with amide NH. On the other hand, it is very likely, that complexation of the alkali cation takes place after the deprotonation, thus changing the conformation of the whole lower rim of **1**.

Tetraamide **2** in accordance with literature data[72,73] was found to form strong complexes easily detectable by NMR titration. The following measurements were performed in the search for tight ion-pairs (*vide infra*).

Solubilization of Sodium Salts with **2a**

Ligand **2a** was found to be able to solubilize solid NaSCN in chloroform at ambient temperature. No solubilization was observed for sodium acetate, benzoate, and phenylacetate. The measurement was done by addition of two equivalents of a Na salt to 0.02 M solution of **2a** in $CDCl_3$ and solubilization was monitored (by spectral measurement) after sonication for (total) 5, 10, 20, 30, 40, 60, 90, 120 min and finally 5 h. As both complexed and uncomplexed **2a** are visible in spectra (due to slow exchange), the percentage of complexation can be easily assessed by simple integration. The induced chemical shifts observed in solubilization experiments in chloroform are summarized in Table III.

The highest CIS (complexation induced shift)[72] in $^1H$ NMR spectra were observed for protons in the following positions (CIS in Hz): 4 (96), 7A (73), and 7B (48). The aromatic hydrogen in position 4 is the only one reflecting the change in the electron donation ability of the lower-rim substituent caused by complexation while both hydrogens in position 7 react differently due to unequal distances from the sodium cation complexed. In $^{13}C$ NMR of **2a**, the following most remarkable CIS were observed: 6 (–241 Hz), 3 (162 Hz), 5 (96 and 98 Hz), and 7 (–94 Hz). It is interesting to note that all aromatic carbons of the calix[4]arene skeleton reflect a change in the donating character of the lower-rim substituent as transmitted to different positions. Also CIS in positions 8 and 9 are low, which is especially surprising in position 9 as the carbonyl oxygen is proved to be directly engaged into the complex formation[45,46,72–75].

Complexation of Sodium Salts with **2a** in Solution

Complexation of $Na^+$ was studied first in $CDCl_3$–$CD_3OD$ 3 : 1 (v/v) using sodium thiocyanate, benzoate, and phenylacetate. Again, different anions were tested in order to see whether spectral characteristics of anions are affected by cation complexation. In all cases, stability of the complex formed with sodium cation were too high to allow NMR assessment. The stoichiometry of the complexes formed was 1 : 1 in all cases. The highest CIS (fast exchange conditions) due to NaSCN were found for protons 4 (118 Hz), 7A (75 Hz), and 8A (–76 Hz). Interestingly, the differences in CIS of 8A–8B protons are bigger than 7A–7B implicating that the rigidity of lower rim substituents is comparable or higher than that of the cone-conformation of the calix[4]arene skeleton. Moreover, the difference in CIS of 8A, 8B protons is in excellent agreement with the calculated conformation of the so-

TABLE III
Complexation induced chemical shifts in $^1H$ and $^{13}C$ NMR spectra (in Hz) of **2a** due to addition of 2 equivalents of solid NaSCN in $CDCl_3$

| Position | $^1H$ NMR | $^{13}C$ NMR |
|---|---|---|
| 1 | 12 | –9 |
| 2 | | 16 |
| 3 | | 162 |
| 4 | 96 | 15, 16 |
| 5 | | 96, 98 |
| 6 | | –241 |
| 7 | 73, 48 | –94 |
| 8 | –24, –12 | 0 |
| 9 | | –21 |
| 10 | –35 | |
| 11 | –25 | 43 |
| 12 | –8 | 33 |
| 13 | | 3 |
| 14 | 12 | –18, 7, 12 |

dium–tetraester complex reported[45,46]. The changes due to complexation in the above solvent mixture are summarized in Table IV.

Trying to find conditions for association constants measurements, we have performed NMR titration experiments in $CDCl_3$–$(CD_3)_2SO$ 4 : 3 (v/v). CIS (fast exchange conditions) measured after addition of 5 equivalents of each salt are summarized below. It was found that chemical shifts of almost all protons in the ligands do not change by further addition of the salt within experimental error. Again, we have also examined whether the spectra of anions are affected by complexation of the sodium cation. We have found small changes in spectra of picrate and tosylate but, unfortunately, no significant changes in $^1H$ NMR spectra of anions were found in general, indicating that they form no tight ion-pairs with the sodium cation despite the fact that their influence on stability of the complex formed is apparent. All CIS as well as the calculated association constants are summarized in Table V.

Analogously, a similar study has also been performed in a mixture $CDCl_3$ and fully deterated DMF and the following results have been obtained. Chemical shifts of most protons change until 1.5 equivalents of Na salt is added except for protons 7B, 8A, and 8B, where further additions of salts are accompanied by CIS. Again, the influence of the anion used on the CIS observed is negligible if any. The data obtained are summarized in Table VI.

The decrease in stability of the sodium complex formed in the last two solvents can be explained in terms of competitive binding of the sodium cation and solvation of the amide carbonyl group by the dipolar aprotic solvents used. In this way the co-operative binding by eight oxygens organized at the lower rim[72,73] is destroyed. Protic solvents like methanol are

TABLE IV
Complexation induced chemical shifts in $^1H$ NMR spectra (in Hz) due to addition of 1 equivalent of Na salt to **2a** in $CDCl_3$–$CD_3OD$ (3 : 1)

| Salt | Position | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | 1 | 12 | 7A | 8A | 7B | 8B | 11 | 4 | 14 |
| NaSCN | 24 | 10 | 75 | –76 | –28 | –9 | 1 | 116 | 20 |
| Na benzoate | 20 | 8 | 60 | –71 | –25 | –7 | 2 | 99 | 16 |
| Na phenylacetate | 20 | 5 | 58 | –71 | –23 | –10 | 0 | 100 | 14 |

TABLE V
Complexation induced chemical shifts in $^1$H NMR spectra (in Hz) due to addition of 5 equivalents of Na salt to **2a** in $CDCl_3$–DMSO (4 : 3) and calculated association constants

| Salt | Position | | | | | | | | | | $K_{ass}$ l mol$^{-1}$ |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | 1 | 12 | 7A | 8A | 7B | 8B | 11 | 4 | 14 | 10 | |
| NaSCN | 20 | 20 | 62 | –106 | –82 | –24 | 27 | 107 | 29 | –147 | 297 ± 26 |
| Na trifluoroacetate | 19 | 17 | 56 | –95 | –74 | –21 | 25 | 98 | 26 | –123 | 265 ± 31 |
| Na phenylacetate | 15 | 10 | 42 | –65 | –54 | –16 | 17 | 75 | 19 | –44 | 240 ± 26 |
| Na phenolate | 18 | 16 | 51 | –87 | –78 | –22 | 24 | 95 | 25 | | 215 ± 27 |
| Na picrate | 19 | 20 | 59 | –102 | –78 | –21 | 28 | 104 | 28 | –152 | 192 ± 24 |
| Na tosylate | 20 | 15 | 57 | –98 | –80 | –26 | 24 | 103 | 26 | –137 | 325 ± 28 |

TABLE VI
Complexation induced chemical shifts in $^1$H NMR spectra (in Hz) due to addition of 5 equivalents of Na salt to **2a** in $CDCl_3$–DMF (4 : 3) and calculated association constants

| Salt | Position | | | | | | | | | | $K_{ass}$ l mol$^{-1}$ |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | 1 | 12 | 7A | 8A | 7B | 8B | 11 | 4 | 14 | 10 | |
| NaSCN | 13 | 12 | 78 | –78 | –61 | –20 | 21 | 109 | 29 | –126 | 1 468 ± 181 |
| Na trifluoroacetate | 13 | 11 | 81 | –76 | –56 | –12 | 23 | 115 | 30 | –116 | 313 ± 35 |
| Na phenylacetate | 9 | 2 | 56 | –41 | –31 | –5 | 10 | 80 | 21 | –12 | 357 ± 29 |
| Na phenolate | 13 | 5 | 68 | –67 | –65 | –17 | 14 | 109 | 30 | | 135 ± 15 |
| Na picrate | 11 | 11 | 70 | –75 | –55 | –16 | 22 | 100 | 24 | –136 | 1 296 ± 150 |
| Na tosylate | 13 | 9 | 74 | –67 | –50 | –10 | 19 | 106 | 26 | –135 | 1 312 ± 135 |

not capable of this effect as the solvation of the externally positioned NH function is more probable.

We have also examined the complexation behaviour of compounds **4**, **6**, and **7** using a standard $^1$H NMR titration protocol with respect to the lithium cation ($LiClO_4$) and sodium cation ($NaBPh_4$) in $CDCl_3$, $CDCl_3$–$CD_3CN$ 4 : 1 as well as in neat $CD_3CN$. For compound **4**, analogous tetra-*tert*-butyl ester was prepared and used for preparation of free tetraacid, but no complexation data was reported[76]. For all combinations with compounds **6** and **7**, only the expected 1 : 1 ligand : cation stoichiometry was found. For compound **4**, however, a more complicated complexation pattern was detected. An addition of one equivalent of sodium tetraphenylborate in $CDCl_3$–$CD_3CN$ 4 : 1 was accompanied by the expected change in chemical shifts corresponding to the formation of the 1 : 1 complex with the sodium cation sitting inside the pre-formed cavity of eight oxygens as described repeatedly in literature and in agreement with all that has been reported above for compound **2**. An addition of another equivalent of the sodium salt has a striking effect. The doublet ($J$ = 5.6 Hz, interaction with adjacent N–H) of methylene protons in position C-11 at 3.85 ppm has changed to pair of dublets centred at 3.64 and 3.72 ppm both having similar coupling constants to N–H. This means that rotation of N(10)–C(11) bond and(or) C(11)–CO bond is hindered by complexation. Inspection of analogous titration with "phenylalanine analogue" **7** has proved that this is a unique property of compounds **4**. It can be interpreted in terms of Fig. 7 where the complexation behavior of **4** is schematically shown. The complexation induced shifts due to complexation of sodium tetraphenylborate are summarized in Table VII.

TABLE VII
$^1$H NMR chemical shifts (in ppm) and coupling constants (in Hz) for selected protons in **4** titrated with 1 and 2 equivalents of $NaBPh_4$ in $CDCl_3$–$CD_3CN$ (4 : 1)

| Compound | Position | | | | | | |
|---|---|---|---|---|---|---|---|
| | 1 | 4 | 7A | 7B | 8AB | 10 | 11 |
| **4** | 0.98 | 6.78 | 3.20, $J$ = 12.8 | 4.42, $J$ = 12.8 | 4.44 | 7.83, $J$ = 5.8 | 3.98, $J$ = 5.8 |
| **4** + 1 $Na^+$ | 1.10 | 7.11 | 3.27, $J$ = 12.2 | 4.09, $J$ = 12.8 | 4.17 | 6.43, $J$ = 5.6 | 3.85, $J$ = 5.6 |
| **4** + 2 $Na^+$ | 1.12 | 7.13 | 3.28, $J$ = 11.0 | 3.99, $J$ = 11.0 | 4.01 | 6.05, $J$ = 5.9 | 3.72, $J$ = 5.9<br>3.64, $J$ = 5.9 |

Obviously, we are not sure, whether the second cation is bound by all four binding sites indicated in Fig. 7 co-operatively. The measurement is done in fast exchange conditions, so only averaged picture of the complexation can be obtained. This completely new binding motif is now under study in our laboratory.

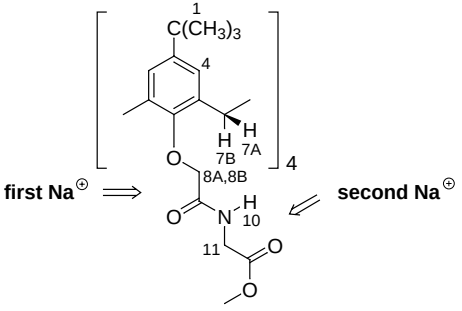



FIG. 7
Two sodium cations consecutively complexed with compound **4**

## CONCLUSIONS

In conclusion, chiral calix[4]arene-based diol-diamides and tetraamides were prepared. The conformation of diol-diamide **1** has been shown to be similar in solution and in the solid state. No significant complexation of the sodium cation has been observed in solution for **1** and **3**. Strong complexation of the sodium cation was observed for **2**, **4**–**6**, and **7**. The $^1$H NMR titrations experiments have revealed that complex with 1 : 1 stoichiometry (unambiguously confirmed by Job plot procedure) is formed in all cases except for compound **4** where complexation of the sodium cation in two distinct positions has been detected. The influence of anions as well as the solvents used on the sodium complexation of **2** was examined. No chiral recognition of the ion-pair formed from the sodium cation and (chiral) anion has been found for **2**.

## EXPERIMENTAL

NMR spectra in $CDCl_3$, $(CD_3)_2SO$, $DCON(CD_3)_2$, and $D_2O$ were measured on a Gemini 2000 (300HC Varian) instrument ($^1$H at 300.075 MHz, $^{13}$C at 75.46 MHz). TMS was used as an internal standard. Majority of measurements were performed at 303 K. Assignment of signals was confirmed by 2D homonuclear and heteronuclear correlated spectra ($^1$H-$^1$H COSY,

$m^1H$-$^{13}C$ HETCOR). Chemical shifts are given in ppm (δ-scale), coupling constants (*J*) in Hz. It was proved by dilution experiments, that NMR spectra of **1**, **2**, **4**, are concentration independent in the $10^{-4}$–$10^{-2}$ mol $l^{-1}$ range; this points to the intramolecular hydrogen bonding in these compounds. Mass spectra were recorded on a ZAB-EQ (VG Analytical) instrument using the EI (70 eV) or FAB (Xe, 8 kV) techniques. IR spectra (ν in $cm^{-1}$) were obtained on a Nicolet 750 FT IR spectrometer. Optical rotations were determined on a JASCO DIP370 digital polarimeter. Specific optical rotations [α] are given in deg $cm^3$ $g^{-1}$ $dm^{-1}$. Thin-layer chromatography (TLC) was carried out on Polygram SIL-G/$UV_{254}$ (Macherey–Nagel) plates. The method of addition of the solid salts to a solution of calixarene was used for the determination of complexation properties of calixarenes.

The stoichiometry of complexes and the complexation constants were calculated using the program OPIUM (Kývala M.) freely available at http://www.natur.cuni.cz/~kyvala/opium.html.

(+)-5,11,17,23-Tetra-*tert*-butyl-25,27-bis{[*N*-((*R*)-1-phenylethyl)carbamoyl]methoxy}-26,28-calix[4]arene (**1a**) and
(–)-5,11,17,23-Tetra-*tert*-butyl-25,27-bis{[*N*-((*S*)-1-phenylethyl)carbamoyl]methoxy}-26,28-calix[4]arene (**1b**)

Solution of acid chloride[56] **12** (2.5 g, 3.1 mmol) in benzene (20 ml) was added dropwise to a solution of (*R*)-(1-phenylethyl)amine (0.77 g, 6.3 mmol) in benzene (20 ml) and triethylamine (1 ml, 6 mmol) maintaining temperature at 20 °C overnight. The reaction was monitored by TLC (silica gel G, $CHCl_3$–EtOH–$Et_3N$ 100 : 10 : 1, $R_F$ 0.3). The thick reaction mixture was diluted with chloroform (20 ml) and washed with water (40 ml), 1 M HCl (20 ml) and again with water (20 ml). The organic phase was dried with anhydrous magnesium sulfate, evaporated to dryness and crystallized from methanol giving 1.7 g (56%) of **1a**, m.p. 287 °C, $[\alpha]_D^{27}$ –37.5 (*c* 0.639, $CHCl_3$).

Using the same procedure, diamide **1b** was prepared from (*S*)-(1-phenylethyl)amine (1.96 g, 65%), m.p. 290 °C, $[\alpha]_D^{27}$ +37.8 (*c* 0.619, $CHCl_3$). IR ($CHCl_3$): 3 325 (OH), 2 966 (NH), 1 669 (C=O). For $C_{64}H_{78}N_2O_6$ (971.3) calculated: 79.13% C, 8.11% H, 2.88% N; found: 79.45% C, 8.06% H, 3.04% N.

(+)-5,11,17,23-Tetra-*tert*-butyl-25,26,27,28-tetrakis{[*N*-((*R*)-1-phenylethyl)carbamoyl]-methoxy}calix[4]arene (**2a**) and
(–)-5,11,17,23-Tetra-*tert*-butyl-25,26,27,28-tetrakis{[*N*-((*S*)-1-phenylethyl)carbamoyl]-methoxy}calix[4]arene (**2b**)

Solution of acid chloride[29] **13** (0.50 g, 0.525 mmol) in benzene (10 ml) was added dropwise to a solution of (*R*)-(1-phenylethyl)amine (0.26 g, 2.16 mmol) in benzene (20 ml) with triethylamine (0.3 ml, 2.15 mmol) maintaining temperature at 20 °C. The reaction was stirred at 20 °C for 2 h (monitored by TLC, silica gel G, benzene–acetone 10 : 1, $R_F$ 0.3). The thick reaction mixture was diluted with chloroform (10 ml) and washed with water (20 ml), dried with anhydrous magnesium sulfate, evaporated and crystallized from toluene or methanol giving 0.48 g (72%) of **2a**, m.p. 322–325 °C, $[\alpha]_D^{27}$ 35.6 (*c* 0.381, $CH_2Cl_2$).

The same method was used for the synthesis of **2b** from (*S*)-(1-phenylethyl)amine giving 0.45 g (68%), m.p. 320–324 °C, $[\alpha]_D^{27}$ –35.4 (*c* 0.379, $CH_2Cl_2$).

**2a**. IR ($CHCl_3$): 2 966 (NH), 1 656 (C=O). For $C_{84}H_{100}N_4O_8$ (1 293.7) calculated: 77.98% C, 7.81% H, 4.33% N; found: 77.83% C, 7.83% H, 4.19% N.

(+)-5,11,17,23-Tetra-*tert*-butyl-25,26,27,28-tetrakis({*N*-[(*S*)-1-(methoxycarbonyl)-2-phenylethyl]carbamoyl}methoxy)calix[4]arene (**7**)

Methyl L-phenylalaninate hydrochloride (455 mg, 0.0021 mol) was suspended in dichloromethane (10 ml) and treated with 4-(dimethylamino)pyridine (643 mg, 0.0052 mol). Acyl chloride **13** (500 mg, 0.525 mmol) in dichloromethane (15 ml) was added dropwise with stirring at ambient temperature and the reaction was monitored by TLC (silica gel Merck G, dichloromethane–methanol 20 : 1). The reaction was quenched by addition of 1 M Hcl (30 ml), phases were separated and the organic layer was washed with water (25 ml), dried with anhydrous magnesium sulfate and evaporated giving 368 mg (46%) of practically pure **7**, further purified by crystallization from methanol–heptane. M.p. 105–108 °C, $R_F$ 0.5 (dichloromethane–methanol 20 : 1), $[\alpha]_D$ +23.8 (*c* 0.147, $CH_2Cl_2$). IR ($CHCl_3$): 1 671 (C=O), 1 743 (C=O), 3 348 (NH). $^1$H NMR: 7.71 d, 4 H, *J* = 8.3 (4 × NH); 7.21 d, 12 H, *J* = 6.5 (arom.); 7.09 d, 8 H, *J* = 7.2 (arom.); 6.74 s, 8 H (arom.); 4.93 q, 4 H, *J* = 7.5 (4 × NHCH); 4.61 q, 8 H, *J* = 7.4 (4 × $OCH_2CO$); 4.48 d, 4 H, *J* = 14.2 (4 × $ArCH_2Ar$); 3.56 s, 12 H (4 × $CH_3$); 3.11 d, 8 H, *J* = 6.9 (4 × $CH_2Ph$); 1.08 s, 36 H (4 × *t*-Bu). For $C_{92}H_{108}N_4O_{16}$ (1 525.9) calculated: 72.42% C, 7.13% H, 3.67% N; found: 72.32% C, 7.55% H, 3.58% N.

5,11,17,23-Tetra-*tert*-butyl-25,26,27,28-tetrakis({*N*-[(methoxycarbonyl)methyl]carbamoyl}-methoxy)calix[4]arene (**4**)

Methyl glycinate hydrochloride (0.75 g, 8.4 mmol) in dichloromethane (15 ml) was treated with 4-(dimethylamino)pyridine (2.75 g, 21 mmol). Acyl chloride **13** (2 g, 2.1 mmol) in dichloromethane (15 ml) was added dropwise with stirring at ambient temperature and the course of reaction was monitored by TLC (silica gel Merck G, dichloromethane–methanol 10 : 1). The reaction was quenched by addition of 1 M HCl (20 ml), phases were separated, the organic layer was washed with water (20 ml), dried and evaporated. The residue was subjected to flash chromatography (silica gel, $CH_2Cl_2$–MeOH 10 : 1) to yield 1.7 g (74%) of practically pure **4**. M.p. 229–233 °C, $R_F$ 0.5 (dichloromethane–methanol 10 : 1). $^1$H NMR: 7.92 t, 4 H, *J* = 5.4 (4 × NH); 6.84 s, 8 H (arom.); 4.59 s, 8 H (4 × $OCH_2CO$); 4.56 d, 4 H, *J* = 15.1 (4 × $CH_2$); 4.15 d, 8 H, *J* = 5.7 (4 × $NHCH_2CO$); 3.75 s, 12 H (4 × $CH_3$); 3.32 d, 4 H, *J* = 13.1 (4 × $CH_2$); 1.09 s, 36 H (4 × *t*-Bu). For $C_{64}H_{84}N_4O_{16}$ (1 165.4) calculated: 65.96% C, 7.28% H, 4.81% N; found: 66.04% C, 7.45% H, 4.58% N.

5,11,17,23-Tetra-*tert*-butyl-25,26,27,28-tetrakis{[*N*-(carboxymethyl)carbamoyl]methoxy}-calix[4]arene (**5**)

Tetraester **4** (200 mg, 0.172 mmol) was added to a solution of potassium hydroxide (92 mg, 0.0017 mol) in methanol (8 ml) and the reaction mixture was stirred for 12 h (disappearance of the ester was monitored by TLC). Methanol was evaporated, residual salts were dissolved in water (10 ml), acidified with 1 M HCl to pH 1, the resulting solid was extracted with dichloromethane (2 × 10 ml), organic phases were combined, dried with anhydrous $MgSO_4$ and evaporated to yield 106 mg (56%) of pure acid **5**. M.p. 155–156 °C. IR (KBr): 1 666 (C=O), 1 735 (C=O), 3 390 (NH, OH assoc.). MS, *m/z* (%): 1 110 ($M^+$ + 1, 100), 995 (55), 612 (52), 337 (45), 556 (25), 759 (20), 880 (19). $^1$H NMR ($CD_3COCD_3$ ): 8.31 t, 4 H (4 × NH); 7.01 s, 8 H (arom.); 4.76 d, 4 H, *J* = 12.7 (4 × $CH_2$); 4.65 s, 8 H (4 × $OCH_2CO$); 4.17 d, 8 H, *J* = 5.9 (4 × $NHCH_2CO$); 3.38 d, 4 H, *J* = 12.6 (4 × $CH_2$); 1.16 s, 36 H (4 × *t*-Bu). For

$C_{60}H_{76}N_4O_{16}$ (1 109.3) calculated: 64.97% C, 6.91% H, 5.05% N; found: 65.06% C, 6.80% H, 4.92% N.

5,11,17,23-Tetra-*tert*-butyl-25,26,27,28-tetrakis{*N*-[(*N*-propylcarbamoyl)methyl]carbamoyl}-methoxy)calix[4]arene (**6**)

Compound **5** (70 mg, 0.063 mmol) and *N*,*N*′-carbonyldiimidazole (40 mg, 0.25 mmol) were dissolved in dry THF (5 ml). The progress of reaction was monitored by TLC (silica gel Merck G, $CH_2Cl_2$–MeOH 10 : 1). The resulting solution was directly treated with propylamine (0.021 ml, 0.25 mmol). Reaction mixture was stirred at ambient temperature overnight (monitored by TLC – the same condition), evaporated *in vacuo*, dissolved in dichloromethane (20 ml), washed successively with 1 M HCl (5 ml) and water (5 ml), dried with anhydrous $MgSO_4$ and evaporated to yield 44 mg (55%) of **6**. M.p. 126–131 °C, $R_F$ 0.5 (dichloromethane–methanol 10 : 1). $^1$H NMR: 8.19 t, 4 H, $J$ = 4.6 (4 × NH); 6.90 t, 4 H, $J$ = 4.7 (4 × NH); 6.80 s, 8 H (arom.); 4.46 d, 4 H, $J$ = 12.5 (4 × $ArCH_2Ar$); 4.45 s, 8 H (4 × $OCH_2CO$); 3.91 d, 8 H, $J$ = 5.7 (4 × $NHCH_2CO$); 3.17 d, 4 H, $J$ = 12.9 (4 × $ArCH_2Ar$); 3.04 q, 8 H, $J$ = 6.4 (4 × $NHCH_2$); 1.34–1.42 m, 8 H (4 × $NHCH_2CH_2CH_3$); 0.99 s, 36 H (4 × *t*-Bu); 0.78 t, 12 H, $J$ = 7.3 (4 × $CH_3$). MS, *m*/*z* (%): 1 274 ($M^+$ + 1, 15), 57 (100), 115 (28), 612 (18), 1 119 (10). For $C_{72}H_{104}N_8O_{16}$ (1 273.7) calculated: 67.90% C, 8.23% H, 8.80% N; found: 67.71% C, 8.34% H, 8.50% N.

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