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Synthesis of calix[4]arenes modified with germanium-containing side chains on the upper rim

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With the expectation to prepare a new type of heteroditopic host, a series of calix[4]arenes modified with germanium-containing side chains at the upper rim was prepared. Compounds 1 and 2 bear two or four triethylgermyl moieties respectively, and compounds 3 and 4 bear two or four trimethylgermyl moieties respectively. For 1 and 2, the hydroxy groups at the lower rim are either tosylated (series a) or kept free (series b). For reference, a carbon analog of 3, compound 5, was also prepared. Unfortunately, all calixarenes prepared failed to show any appreciable cation transport property, indicating that the structure designed, i.e. a calixarene with germanium-containing side chains at the upper rim, cannot meet the requirement for an appropriate heteroditopic host. Copyright © 2004 John Wiley & Sons, Ltd.

KEYWORDS: calixarene; heteroditopic host; organogermanium compound; ^{1}H NMR spectra; ^{13}C NMR spectra; cation transport; H-tube test

INTRODUCTION

Calixarenes, especially calix[4]arenes, have been thoroughly investigated and their ability to complex with cations under certain conditions has been well studied.[1,2] During the course of an investigation of the synthesis, structure and properties of cyclic organo-germanium compounds, it was found that macrocyclic species, such as 1,8-dimethyl-1,8-dihalo-1,8-digermacyclotetradecanes, possess anion transport capability.[3]

It was anticipated that a heteroditopic host[4,5] with novel properties may be obtained by combining the cation-capturing capability of calixarenes and anion-capturing capability of germanium moieties.

With this in mind, it was hypothesized that an appropriate host, such as a calixarene or a crown ether, modified with a side chain containing Lewis acidic germanium, would enhance the cation transporting properties of the substrate. In a previous communication,[6] the synthesis of 5,17-bis[2-(triethylgermylpropanoyloxy)ethyl]-25,26,27,28-tetrakis(*p*-toluenesulfonyl)calix[4]arene (**1a**) was reported. However, this compound did not show any ability to capture and/or transport cations. The presence of bulky *p*-toluenesulfonyl(tosyl) moieties and/or ethyl groups bonded to germanium might inhibit cations from sitting in the cavity of the calixarene. Furthermore, the anion-capturing ability of the germanium moieties might be insufficient.

In order to make calixarenes modified with germanium better ditopic hosts, we modified compound **1a** in the following way.

First, we prepared 5,17-bis[2-(triethylgermylpropanoyloxy)ethyl]-25,26,27,28-tetrahydroxycalix[4]arene (**1b**) by removing tosyl groups from **1a**. We also prepared 5,11,17,23-tetrakis[2-(triethylgermylpropanoyloxy)ethyl]-25,26,27,28-tetrakis(*p*-toluenesulfonyl)oxycalix[4]arene (**2a**) and 5,11,17,23-tetrakis[2-(triethylgermylpropanoyloxy)ethyl]-25,26,27,28-tetrahydroxycalix[4]arene (**2b**), which have four germanium moieties.

Trimethyl germyl derivatives, 5,17-bis[2-(trimethylgermylpropanoyloxy)ethyl]-25,26,27,28-tetrahydroxycalix[4]arene (**3**) and 5,11,17,23-tetrakis[2-(trimethylgermylpropanoyloxy)-ethyl]-25,26,27,28-tetrahydroxycalix[4]arene (**4**) were prepared to make the anion more easily accessible to germanium atom(s). We also synthesized a carbon analog of these germanium-containing compounds, namely 5,17-bis[(4,4-dimethylpentanoyloxy)ethyl]-25,26,27,28-hydroxycalix[4]arene (**5**). The structures of the calixarenes prepared in this study, together with some of the

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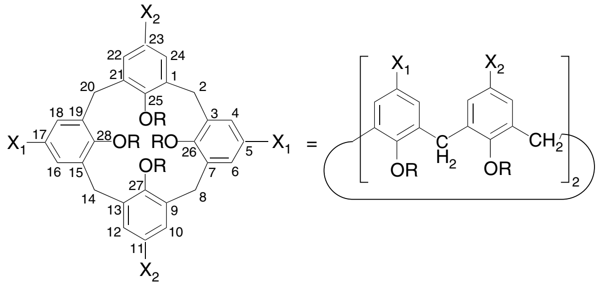
Table 1. Calix[4]arenes prepared in this study



Compound	R[a]	X_1	X_2
1a	Ts	$CH_2CH_2OCOCH_2CH_2Ge(C_2H_5)_3$	H
1b	H	$CH_2CH_2OCOCH_2CH_2Ge(C_2H_5)_3$	H
2a	Ts	$CH_2CH_2OCOCH_2CH_2Ge(C_2H_5)_3$	$CH_2CH_2OCOCH_2CH_2Ge(C_2H_5)_3$
2b	H	$CH_2CH_2OCOCH_2CH_2Ge(C_2H_5)_3$	$CH_2CH_2OCOCH_2CH_2Ge(C_2H_5)_3$
3	H	$CH_2CH_2OCOCH_2CH_2Ge(CH_3)_3$	H
4	H	$CH_2CH_2OCOCH_2CH_2Ge(CH_3)_3$	$CH_2CH_2OCOCH_2CH_2Ge(CH_3)_3$
5	H	$CH_2CH_2OCOCH_2CH_2C(CH_3)_3$	H
6a	Ts	CH_2CH_2OH	H
6b	H	CH_2CH_2OH	H
7a	Ts	CH_2CH_2OH	CH_2CH_2OH
7b	H	CH_2CH_2OH	CH_2CH_2OH

[a] Ts = *p*-$CH_3C_6H_5SO_2$−.

calixarenes **6** and **7** necessary for preparing **1**–**5**, are given in Table 1.

It was anticipated that the germanium atom in the triethyl- or trimethyl-germyl moieties is not Lewis acidic enough to capture anions. Substitution of halogen(s) on germanium will certainly enhance its Lewis acidity, as was proved elsewhere.[3] Our preliminary attempts to introduce halogen(s) into the germanium atom in the side chain of calixarenes was not successful.

RESULTS AND DISCUSSION

Synthesis

The preparation of 5,17-bis(2-hydroxyethyl)-25,26,27,28-tetrakis-(*p*-toluenesulfonyloxy)calix[4]arene (**6a**) has been described previously.[6] 5,17-Bis-(2-hydroxyethyl)-25,26,27,28-tetrahydroxycalix[4]arene (**6b**) was prepared by the hydrolysis of **6a** with 50% NaOH in EtOH.

The preparation of the other intermediates, 5,11,17,23-tetrakis(2-hydroxyethyl)-25,26,27,28-tetrahydroxycalix[4]-arene (**7b**) and 5,11,17,23-tetrakis(2-hydroxyethyl)-25,26,27,28-tetrakis(*p*-toluenesulfonyloxy)calix[4]arene (**7a**), have been described elsewhere.[7] Trimethylgermylpropanoyl chloride (**9**) was prepared in a similar manner to that of triethylgermylpropanoyl chloride (**8**).[8]

The structures of these new calixarene derivatives were confirmed by elemental analysis and ^1H and ^{13}C NMR spectroscopy, all of which were consistent with the assigned structure.

^1H and ^{13}C NMR spectra

A complete assignment of the ^1H and ^{13}C NMR spectra of the prepared calixarenes **1**–**5** was carried out with the aid of conventional techniques together with difference NOE, and ^1H–^{13}C COSY, HMQC and HMBC. The data for other calix[4]arene derivatives previously reported by us were also taken into consideration.[9]

Table 2 summarizes the ^1H and ^{13}C NMR chemical shifts of calixarenes **1b**, **2a**, **2b**, **3**, **4** and **5**. The numbering of these compounds is given in Fig. 1.

There is one peak that characterizes these calixarenes: the Ar–CH_2–Ar methylene resonance, which is susceptible to conformational change among the cone, partial-cone, 1,2-alternate and 1,3-alternate. This conformational change is effectively analyzed by variable-temperature NMR measurements of the methylene protons, which appeared as a pair of doublets if the conformation was frozen in the cone conformer.[1]

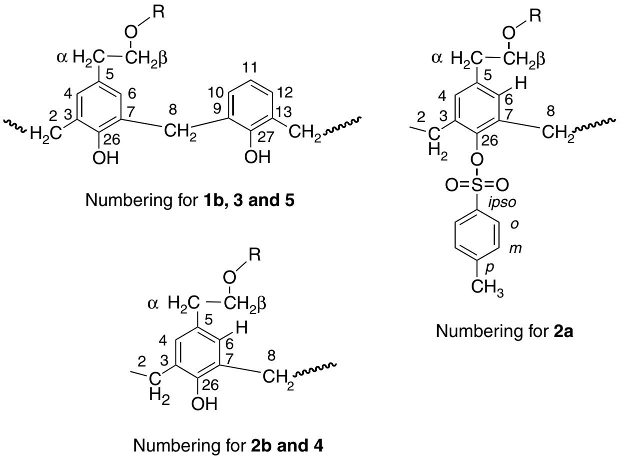
The relevant proton resonances for **2a** (and **1a**), which are frozen in the cone conformation, form a well-defined doublet of doubles at *ca* δ 2.4 and 3.5. For **1b**, **2b**, **3**, **4** and **5**, i.e. hydroxycalixarenes, the proton chemical shifts are uniformly at *ca* δ 3.4 and 4.2; at room temperature, broadening of this characteristic doublet of doublets takes place.

Table 2. ^{1}H and ^{13}C NMR chemical shifts for **1b**, **2a**, **2b**, **3**, **4** and **5**[a,b]

	1b	**2a**	**2b**	**3**	**4**	**5**
2(8)	3.49b, 4.24b (31.8)	2.36d, 3.49d (31.2)	3.44b, 4.21b (31.8)	3.49b, 4.24b (31.8)	3.44b, 4.21b (31.8)	3.49b, 4.24b (31.7)
3(7)	– (128.2 or 128.3)	– (135.7)	– (128.0)	– (128.2 or 128.3)	– (128.2)	– (128.2 or 128.3)
4(6)	6.89s (129.4)	6.31s (129.2)	6.88s (129.2)	6.89s (129.4)	6.89s (129.4)	6.89s (129.4)
5	– (131.4)	– (135.0)	– (131.2)	– (131.1)	– (131.3)	– (131.4)
26	– (147.4)	– (144.0)	– (147.3)	– (147.4)	– (147.5)	– (147.4)
9(13)	– (128.2 or 128.3)	equal to 3(7)	equal to 3(7)	– (128.2 or 128.3)	equal to 3(7)	– (128.2 or 128.3)
10(12)	7.04d (129.4)	equal to 4(6)	equal to 4(6)	7.04d (129.0)	equal to 4(6)	7.04d (129.0)
11	6.73t (122.2)	equal to 5	equal to 5	6.73t (122.2)	equal to 5	6.72t (122.2)
27	– (148.8)	equal to 26	equal to 26	– (148.8)	equal to 26	– (148.6)
α	2.69t (34.3)	2.71t (34.4)	2.73t (34.3)	2.71t (34.3)	2.73t (34.3)	2.69t (34.2)
β	4.17t (64.9)	4.18t (64.5)	4.18t (64.3)	4.17t (64.8)	4.18t (64.9)	4.17t (64.7)
R						
C=O	– (175.1)	– (174.8)	– (174.8)	– (174.9)	– (174.9)	– (174.1)
$\mathrm{CO}\mathit{CH_2}\mathrm{CH_2}$	2.31t (30.0)	2.30t (30.0)	2.32t (30.1)	2.32t (30.0)	2.34t (30.0)	2.25t (30.1)
$\mathrm{COCH_2}\mathit{CH_2}$	1.00t (6.5)	0.99t (6.5)	1.00t (6.5)	0.98t (11.6)	0.98t (11.6)	1.52t (38.6)
$\mathrm{Ge}\mathit{CH_2}\mathrm{CH_3}$	0.72q (3.8)	0.74q (3.8)	0.72q (3.8)	—(–)	—(–)	—(–)
$\mathrm{GeCH_2}\mathit{CH_3}$	1.01t (8.9)	1.02t (8.9)	1.01t (8.9)	—(–)	—(–)	—(–)
$\mathrm{GeCH_3}$	—(–)		—(–)	0.12 (–2.6)	0.12 (–2.5)	—(–)
$\mathit{C}\mathrm{CH_3}$	—(–)		—(–)	—(–)	—(–)	– (30.3)
$\mathrm{C}\mathit{CH_3}$	—(–)		—(–)	—(–)	—(–)	0.87 (29.0)
Tosyl						
ipso	—(–)	– (132.6)	—(–)	—(–)	—(–)	—(–)
o	—(–)	7.75d (129.6)	—(–)	—(–)	—(–)	—(–)
m	—(–)	7.34d (129.7)	—(–)	—(–)	—(–)	—(–)
p	—(–)	– (144.8)	—(–)	—(–)	—(–)	—(–)
$\mathrm{CH_3}$		2.48s (21.3)				

[a] Values in parentheses are for ^{13}C NMR data.

[b] – and (–) indicate no relevant nuclei at this position.



Numbering for **1b, 3 and 5**

Numbering for **2a**

Numbering for **2b and 4**

Figure 1. Numbering of calixarenes.

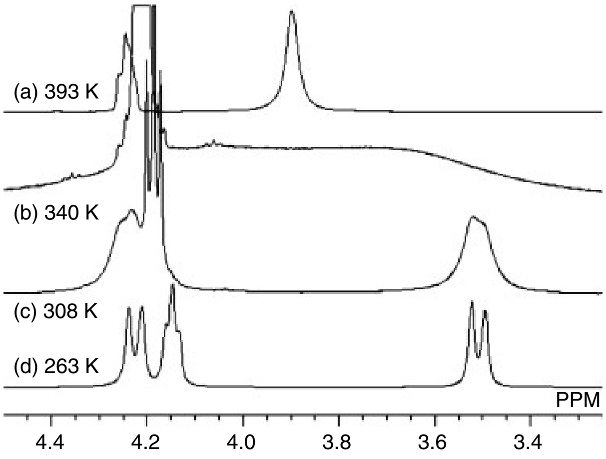


Figure 2. ^{1}H NMR spectra of **1b**.

Figure 2 shows the variable-temperature ^{1}H NMR spectra of the CH_2 resonance of **1b**, showing the coalescence at *ca* 340 K (Fig. 2(b)). The free energy of activation was estimated by the coalescence temperature method[10] to be 64.6 kJ mol^{-1}. This value is in agreement with the values previously reported for conformational inversion of a variety of calix[4]arenes.[11]

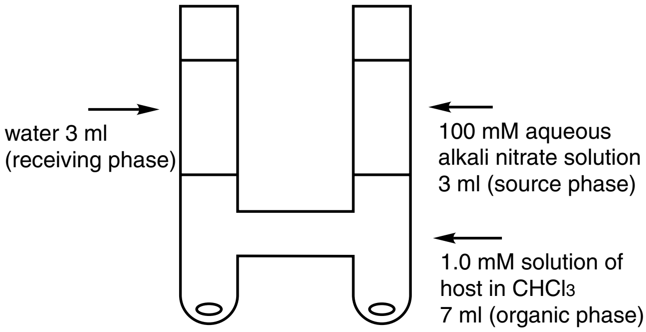


Figure 3. Cation transport measurement by H-tube method.

Cation transport experiment

Cation transport experiments of the calixarenes **1b**, **2a**, **2b**, **3**, **4** and **5** were conducted using an H-tube test as described by Izatt *et al*[12] (Fig. 3). A chloroform solution of the host was added to the bottom of the H-tube and an aqueous nitrate solution (100 mmol dm^{-3}; 3 ml) of Li$^+$, Na$^+$, K$^+$, Rb$^+$, Cs$^+$ or Ag$^+$ was added to the right arm of the H-tube (source phase). Pure H_2O was added to the left arm of the H-tube (receiving phase). A small magnetic bar was stirred in the bottom of each arm, and the whole apparatus was kept at 25 °C for 24 h. The amount of cations in the receiving arm was measured by atomic absorption spectroscopy. A blank test was also performed, where no host was dissolved in the organic layer. Virtually no cations were detected in the H_2O in the receiving arm.

CONCLUSION

Several calix[4]arenes modified with side chains containing germanium on the upper rim, viz. **1b, 2a, 2b, 3** and **4**, were prepared, and the structures of these calixarenes were confirmed by a detailed analysis of their respective ^{1}H and ^{13}C NMR spectra.

The cation transport experiment using an H-tube test revealed that calixarenes **1b, 2a, 2b, 3** and **4** did not exhibit any cation transport properties. Since one of the carbon analogs of germanium-containing calixarene, **5**, also failed to show cation transporting ability, these experiments were inconclusive as to the effect of incorporating germanium into calixarenes. It had been anticipated that including germanium would enhance the cation transport properties of these hosts because of the Lewis acidity of the germanium.

EXPERIMENTAL

General

IR spectra were determined with a JASCO FT/IR-300 spectrometer. ^{1}H NMR spectra were measured with a JEOL ECP 500 spectrometer operating at 500 MHz, and the chemical shifts were reported in δ (ppm) with tetramethylsilane (TMS) as the internal standard. ^{13}C NMR spectra were determined using the same spectrometer operating at 125 MHz and the chemical shifts were also reported in δ (ppm) with TMS as the internal standard. Elemental analyses were carried out with Perkin–Elmer Series II CHNS/O elemental analyzer or at the Microanalytical Laboratory, Department of Chemistry, Faculty of Science, the University of Tokyo. Atomic absorption spectra were determined with a Hitachi 12–8100 polarized Zeeman atomic absorption spectrometer.

5,11,17,23-Tetrakis[2-(triethylgermylpropanoyloxy)ethyl]-25,26,27,28-tetrakis(*p*-toluenesulfonyl)calix[4]arene (2a)

A $CHCl_3$ (5 ml) solution of **7a** (0.54 g, 0.44 mmol) was added to a $CHCl_3$ (2.5 ml) solution of triethylgermylpropanoyl chloride (**8**; 0.82 g, 8.92 mmol) over 10 min under reflux. Further $CHCl_3$ (5 ml) was added, and the reflux was continued for 85 h. The solvent was removed *in vacuo* to afford a viscous yellow oily material, which was purified by column chromatography (silica gel; toluene:ethyl acetate, 6 : 1) to give a colourless powder of 5,11,17,23-tetrakis-[2-(triethylgermylpropanoyloxy) ethyl]-25,26,27,28-tetrakis(*p*-toluenesulfonyl)calix[4]arene (**2a**; 0.83 g, 95%). An analytically pure sample was obtained by recrystallization from 2-propanol; m.p.: 125–129 °C. Anal. Found: C, 57.72, H, 6.28. Calc. for $C_{100}H_{136}Ge_4O_{20}S_4$: C, 57.83; H, 6.60%.

5,17-Bis[2-(triethylgermylpropanoyloxy)ethyl]-25,26,27,28-tetrahydroxycalix[4]arene (1b)

To a refluxing mixture of **6b** (0.54 g, 1.05 mmol) in $ClCH_2CH_2Cl$ (25 ml) was added a $ClCH_2CH_2Cl$ (10 ml) solution of **8** (0.6 g, 2.38 mmol) over 20 min. This mixture was refluxed for a further 65 h. The solvent was removed *in vacuo* to afford a viscous yellow oily material, which was purified by column chromatography (silica gel; toluene:$CHCl_3$, 2 : 1) to give a colorless powder of 5,17-bis-[2-(triethylgermylpropanoyloxy)ethyl]-25,26,27,28-tetrahydroxycalix[4]arene (**1b**). Recrystallization from ethanol gave analytically pure thin plates, m.p.: 95–98 °C. Anal. Found: C, 63.61, H, 7.36. Calc. for $C_{50}H_{68}Ge_2O_8$: C, 63.73; H, 7.27%.

5,11,17,23-Tetrakis[2-(triethylgermylpropanoyloxy)ethyl]-25,26,27,28-tetrahydroxycalix[4]arene (2b)

A $ClCH_2CH_2Cl$ (7 ml) solution of **8** (0.42 g, 1.67 mmol) was added over 20 min to a refluxing mixture of **7b** (0.22 g, 0.37 mmol) in $ClCH_2CH_2Cl$ (20 ml) and the mixture was refluxed for a further 48 h. The solvent was removed *in vacuo* to afford a viscous yellow oily material, which was purified by means of column chromatography (silica gel; CH_2Cl_2:ethyl acetate, 1 : 1) followed by crystallization from $CHCl_3$–CH_3OH–C_2H_5OH to afford a colorless powder of 5,11,17,23-tetrakis[2-(triethylgermylpropanoyloxy)ethyl]-25,26,27,28-tetrahydroxycalix[4]arene (**2b**; 0.15 g, 28%). The structure was confirmed by spectroscopic data.

5,17-Bis-[2-(trimethylgermylpropanoyloxy)ethyl]-25,26,27,28-tetrahydroxycalix[4]arene (3)

A $ClCH_2CH_2Cl$ (10 ml) solution of trimethylgermylpropanoyl chloride (**9**; 0.82 g, 3.92 mmol) was added over 5 min to a $ClCH_2CH_2Cl$ (20 ml) solution of **6b** (0.87 g, 1.70 mmol) under reflux. The reflux was continued for 24 h, and the solvent was then removed *in vacuo*. The residue was treated with ethanol to afford crystals that were purified by column chromatography (silica gel; benzene:$CHCl_3$, 2 : 1). Recrystallization from ethanol afforded colorless needles of 5,17-bis-[2-(trimethylgermylpropanoyloxy)ethyl]-25,26,27,28-tetrahydroxycalix[4]arene (**3**; 0.99 g, 68%); m.p.: 134–136 °C. Anal. Found: C, 61.42, H, 6.63. Calc. for $C_{44}H_{56}Ge_2O_8$: C, 61.59; H, 6.58%.

5,11,17,23-Tetrakis[2-(trimethylgermylpropanoyloxy)ethyl]-25,26,27,28-tetrahydroxycalix[4]arene (4)

A $ClCH_2CH_2Cl$ (10 ml) solution of **9** (1.98 g, 9.46 mmol) was added in 5 min to a refluxing $ClCH_2CH_2Cl$ (20 ml) solution of **7b** (1.22 g, 2.03 mmol). The reflux was continued for 24 h, and the solvent was then removed *in vacuo*. The residue was treated with ethanol to afford crystals that were purified by column chromatography (silica gel; benzene:$CHCl_3$, 1 : 5). Recrystallization from CH_2Cl_2–CH_3OH afforded 5,11,17,23-tetrakis[2-(trimethylgermylpropanoyloxy)ethyl]-25,26,27,28-tetrahydroxycalix[4]arene (**4**; 0.75 g, 28%), m.p. 135–137 °C. Calcd for $C_{60}H_{56}O_{12}Ge_4$: C, 55.79; H, 6.87. Found: C, 55.62, H, 6.66.

5,17-Bis[2-(4,4-dimethylpentanoyloxy)ethyl]-25,26,27,28-tetrahydroxycalix[4]arene (5)

4,4-Dimethylpentanoic acid was prepared by the method described by Whitesides *et al.*;[13] b.p.: 90 °C (32 mmHg). IR (CCl_4): 1711 cm^{-1} (C=O). ^1H NMR ($CDCl_3$, 400 MHz) δ 2.33 (m, 2H, $CH_2C\mathit{H}_2CO$), 1.57 (m, 2H, $C\mathit{H}_2CH_2CO$), 0.91 (s, 9H, CH_3). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 179.9, 38.3 (CH_2CH_2CO), 30.0 (CCH_2CH_2CO), 29.7 (CH_2CH_2CO), 28.9 (CH_3).

4,4-Dimethylpentanoyl chloride (**10**) was prepared from 4,4-dimethylpentanoic acid and thionyl chloride by the same method of Whitesides *et al.*[13] as a colorless liquid in 63% yield; b.p.: 83–85 °C (70 mmHg). IR: 1801 cm^{-1} (C=O). ^1H NMR ($CDCl_3$, 400 MHz) δ 2.86 (m, 2H, $CH_2C\mathit{H}_2CO$), 1.64 (m, 2H, $C\mathit{H}_2CH_2CO$), 0.92 (s, 9H, CH_3). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 174.2, 43.4 (CH_2CH_2CO), 38.4 (CH_2CH_2CO), 30.1 (CCH_2CH_2CO), 28.9 (CH_3).

A $ClCH_2CH_2Cl$ (10 ml) solution of **10** (0.36 g, 2.42 mmol) was added in 80 min to a solution of $ClCH_2CH_2Cl$ (10 ml) solution of **6b** (0.54 g, 1.05 mmol) under constant reflux. The reflux was continued for 44 h. Ethanol (0.08 g, 1.74 mmol) was added and the mixture stirred for 1 h at room temperature. The solvent was removed *in vacuo*. The residue was purified by column chromatography (silica gel; benzene:$CHCl_3$, 2 : 1). Recrystallization from ethanol afforded colorless needles of 5,17-bis[2-(3,3-dimethylbutanoyloxy)ethyl]-25,26,27,28-tetrahydroxycalix-[4]arene (**5**; 0.47 g, 60%). EI-MS: 736 (M^+); calc. for $C_{46}H_{56}O_8$, 736.93.

5,17-Bis(2-hydroxyethyl)-25,26,27,28-tetrahydroxycalix[4]arene (6b)

50% NaOH in EtOH (100 ml) was added to **6a** (1.30 g, 1.15 mmol) in EtOH (100 ml) under reflux. Reflux was continued for 8 h, and the mixture was left at room temperature for 1 day. Acetic acid (10 ml) was added to neutralize the mixture, which was then poured into ice-water and stirred. The precipitate was collected and recrystallized from CH_3CN to afford **6b** (0.32 g, 72%) as a faintly pink powder; m.p.: >300 °C. Anal. Found: C, 74.73, H, 6.07. Calc. for $C_{32}H_{32}O_6$: C, 74.98; H, 6.29%.

Acknowledgements

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REFERENCES

1. Gutsche CD. *Calixarenes*. Royal Society of Chemistry: Cambridge, 1989.
2. McKervey MA, Schwing-Weill M-J, Arnaud-Neu F. In *Comprehensive Supramolecular Chemistry*, vol. 1, Gokel GW (ed). Pergamon: 1996; 537–603.
3. Aoyagi S, Tanaka K, Takeuchi Y. *J. Chem. Soc. Perkin Trans. 2* 1994; 1549.
4. Kemmer M, Ghys L, Gielen M, Biesemans M, Tiekink ERT, Willem R. *J. Organometal. Chem.* 1999; **582**: 195.
5. Kemmer M, Biesemans M, Gielen M, Martins JC, Gramlich V, Willem R. *Chem. Eur. J.* 2001; **7**: 4686.
6. Takeuchi Y, Sakurai T, Tanaka K. *Main Group Met. Chem.* 2000; **23**: 311.
7. Gutsche CD, Levine JA, Sujeeth PK. *J. Org. Chem.* 1985; **50**: 5802.
8. Kakimoto N, Akiba M, Takada T. *Synthesis* 1985; **3**: 272.
9. Sakurai T, Takeuchi Y. *Heteroat. Chem.* 2003; **14**: 365.
10. Harris RK. *Nuclear Magnetic Resonance Spectroscopy*. Pitman: 1983; 188.
11. Gutsche CD, Bauer LJ. *J. Am. Chem. Soc.* 1985; **107**: 6052.
12. Izatt SR, Hawkins RT, Christensen JJ, Izatt RM. *J. Am. Chem. Soc.* 1985; **107**: 63.
13. Whitesides GM, Sevenair JP, Goetz RW. *J. Am. Chem. Soc.* 1967; **89**: 1135.