Supramolecular Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713649759

all-Homocalixarenes: Large hydrocarbon rings with numerous ligand-arms as selective host compounds

Jürgen Schmitz[a]; Fritz Vögtle[a]; Martin Nieger[b]; Karsten Gloe[c]; Holger Stephan[c]; Olaf Heitzsch[c]; Hans-Jürgen Buschmann[d]
[a] Institut für Organische Chemie und Biochemie der Universität Bonn, [b] Institut für Anorganische Chemie der Universität Bonn, Bonn, Germany [c] Institut für Anorganische Chemie der TU Dresden, Dresden, Germany [d] Deutsches Textilforschungszentrum Nord-West e. V., Krefeld, Germany

To cite this Article Schmitz, Jürgen , Vögtle, Fritz , Nieger, Martin , Gloe, Karsten , Stephan, Holger , Heitzsch, Olaf and Buschmann, Hans-Jürgen(1994) '*all*-Homocalixarenes: Large hydrocarbon rings with numerous ligand-arms as selective host compounds', Supramolecular Chemistry, 4: 2, 115 — 119
To link to this Article: DOI: 10.1080/10610279408029870
URL: http://dx.doi.org/10.1080/10610279408029870

SUPRAMOLECULAR CHEMISTRY, Vol. 4, pp. 115–119
Reprints available directly from the publisher
Photocopying permitted by license only

all-Homocalixarenes: Large hydrocarbon rings with numerous ligand-arms as selective host compounds

JÜRGEN SCHMITZ[a], FRITZ VÖGTLE*[a], MARTIN NIEGER[b], KARSTEN GLOE[c], HOLGER STEPHAN[c], OLAF HEITZSCH[c], and HANS-JÜRGEN BUSCHMANN[d]

Institut für Organische Chemie und Biochemie der Universität Bonn[a], Institut für Anorganische Chemie der Universität Bonn[b], Gerhard-Domagk-Straße 1, D-53121 Bonn, Germany

Institut für Anorganische Chemie der TU Dresden[c], Mommsenstraße 13, D-01062 Dresden, Germany

Deutsches Textilforschungszentrum Nord-West e.V.[d], Frankenring 2, D-47798 Krefeld, Germany

Keywords: Carbocycles, homocalixarenes, large rings, macrocycles, [2$_n$]metacyclophanes.

(Received June 2, 1993)

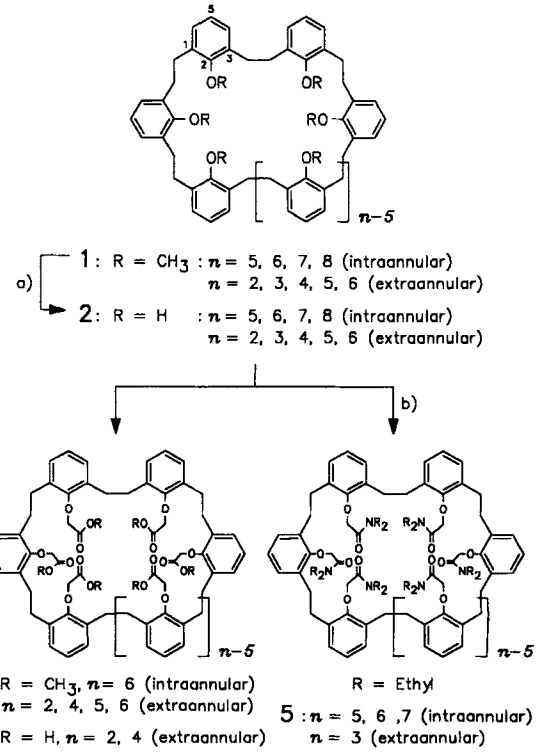
A new type of carbomacrocyclic ligand and host compounds is described allowing conversion of functional groups to ligand-arms with many coordination sites. As an example, the hexameric amido-substituted *all*-homocalixarene 5(n = 6) is described: synthesis, X-ray-structural analysis and ligand qualities in liquid-liquid extraction studies combined with determination of Log K-values are explained. Peak-selectivity with regard to Ba^{2+} and formation of 1:1-complexes in extraction experiments are proven, the influence of solvents is discussed.

INTRODUCTION

Recently we reported on the first preparation of methoxy-substituted, many-membered hydrocarbon rings (cf. **1**)[1]. This type of host compound now turned out to allow not only modification of ring size (10 to 80 ring members) and also the number of methoxy groups but almost any variation of functional groups to yield ligand-arms with many coordination sites (cf. **3**, **4**). This renders access to a new independent family of ligand and host compounds with some specific advantages.[2]

NEW HOMOCALIXARENES AND THEIR PROPERTIES

Cleavage of the methoxy protection-groups in **1** led to a series of oligophenols **2** [dimer (n = 2) to hexamer[3] (n = 6, extraannularly substituted) and pentamer to octamer



Scheme 1 Isolated all-homocalixarenes. Intraannular: OR-substituents in 2-position (as shown); extraannular: OR-substituents (not shown) in 5-position. a) BBr_3 in CH_2Cl_2; 93% yield (n = 6, intraannular), b) $BrCH_2C(O)NR_2/K_2CO_3/KI$ in acetone; 80% yield (n = 6, intraannular).

*Corresponding author.

(intraannularly substituted)] in very good yields (scheme 1). The polyphenols **2** exhibit strongly differing solubilities, e. g. pentamer and octamer[4] with intraannular hydroxy groups show good solubility in tri- or dichloromethane[5] in contrast to the hexameric polyphenol being soluble only in DMSO and the heptameric one requiring acetone as solvent.

Some selected oligophenols **2** were functionalized to homocalixarenes **3** with $OCH_2C(O)OCH_3$-groups in very good yields (dimer, tetramer, pentamer and hexamer with extraannular $OCH_2C(O)OCH_3$-functions and hexamer with intraannular ones[6] (scheme 1)[7]. Two oligoesters were converted to the homocalixarenes **4** with free oxaacetic acid substituents.

We report here in particular on the structure and on the cation selectivities obtained by liquid-liquid extraction experiments of the hexamer **5** (n = 6) with intraannular $OCH_2C(O)N(C_2H_5)_2$-groups as an example for the interesting properties of properly substituted *all*-homocalixarenes **5**. This host compound was obtained from the hexaphenol **2** (n = 6) in crystalline form (yield 80%; mp. 146 - 149°C).

Figure 1 shows the results of the x-ray-structural analysis of the hexaamide **5**. The molecule has a centre of inversion within the macroring (crystallographic C_i-symmetry). Two benzene rings (C3-C4-C5-C6-C7-C8 and C3b-C4b-C5b-C6b-C7b-C8b) are *syn*-oriented with regard to one of the neighbouring benzene rings, so that a three-dimensional cavity is formed. The amido-substituents do not project into the cavity presumably because of steric hindrance but are bent out of the macrocycle due to conformational flexibility of the cyclophane. All C=O-groups of the amido-functions project into the same direction, clockwise in figure 1. Two amido-groups (at O1 and O1b) are oriented above and two (opposite) below the centre of the macroring-plane. The two remaining substituents connected to benzene rings (C3a-C4a-C5a-C6a-C7a-C8a and the opposite thereof) without *syn*-type conformation to neighbouring benzene rings are found within the cyclophane ring-plane. As a consequence the following orientation of the amido-groups is present: above, below, within, below, above and within the middle ring-plane. The homocalixarene molecules are connected with embeded water-molecules by hydrogen bridges within the crystal to form long cords.

Due to introduction of amido groups into the molecule the selectivity shall adjust favourably for alkaline earth metal ions. To examine the host properties of the hexaamide **5** (n = 6) liquid-liquid extraction studies were performed to investigate the phase transfer of various metal ions from aqueous to different lipophilic phases (figure 2)[8]:

Ba^{2+} ions are extracted with a pronounced peak selectivity in contrast to other bivalent cations (smaller alkaline earth metal ions such as Sr^{2+} and Ca^{2+}; Co^{2+}, Zn^{2+} and Hg^{2+}) and monovalent cations (alkali ions such as Na^+ and Cs^+; Tl^+ and Ag^+, not represented in figure 2). High extractabilities are obtained in case of toluene as solvent. Changing to trichloromethane the extraction efficiency decreases drastically probably due to blocking of amido-oxygen atoms by hydrogen bonding to solvent molecules[9]. A strong interaction between amido groups and trichloromethane has been proven using infrared

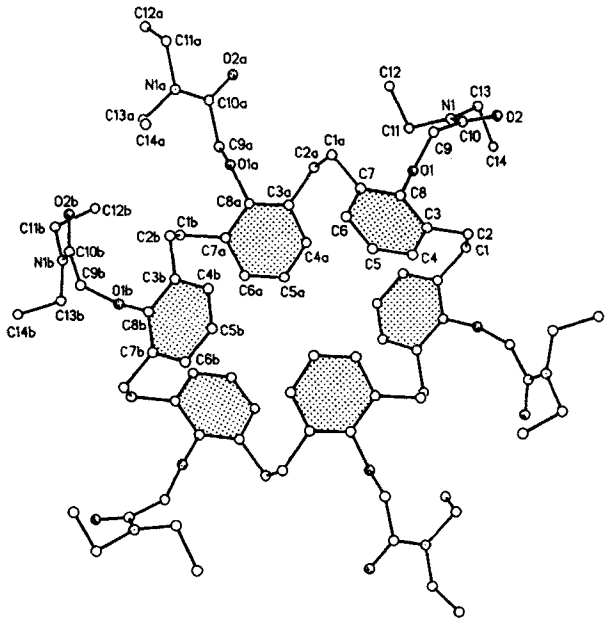


Figure 1 Structure of hexaamide **5** (n = 6) in the crystal.

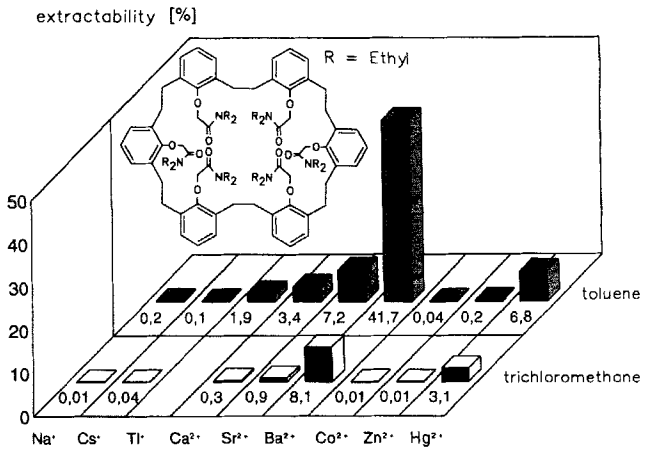


Figure 2 Extractability of metal ions with the hexameric amido-substituted homocalixarene **5** (n = 6) {[$M(NO_3)_n$] = 1.10^{-4} M; [picric acid] = 5.10^{-3} M; pH = 5.2 (NaOAc/HCl-buffer); [ligand] = 1.10^{-3} M in trichloromethane or toluene}.

spectroscopy.[10] Because of the distinct lipophilicity caused by the large carbocyclic cyclophane ring hexaamide **5** (n = 6) is well soluble in unpolar solvents like toluene, so that an increase in extraction efficiency is achieved without loss of peak selectivity for Ba^{2+}.[11]

The composition of host-guest complexes is important, especially in regard of a high separation efficiency. A single, well-defined complex stoichiometry seems to be favourable[13]. Slope analyses of the straight lines shown in the Log D_M - Log c_L diagram in figure 3 indicate the exceptional formation of 1:1-complexes for all cations with the amido-substituted homocalixarene **5** (n = 6)[14] (D_M = quotient of concentrations of the cation M in organic and aqueous phase, resp.; c_L = concentration of ligand **5** in the organic solvent).[20]

Determination of complex formation constants of the homocalixarene **5** (n = 6) with different cations in aqueous solution was performed as described in literature.[21] The increase of solubility of ligand **5** in water at 25° C was measured using UV spectroscopy as function of rising salt concentrations (chlorides of metal ions are employed). As the measurements were carried out at differing salt concentrations, the influence of ionic strength was corrected by using the extended Debye-Hückel equation. The results of liquid-liquid extraction investigations are confirmed qualitatively (table 1). Hexaamide **5** (n = 6) gives the highest Log K-values for Ba^{2+} in contrast to Na^+, K^+ and Ca^{2+} (Sr^{2+}: complex formation not detectable).

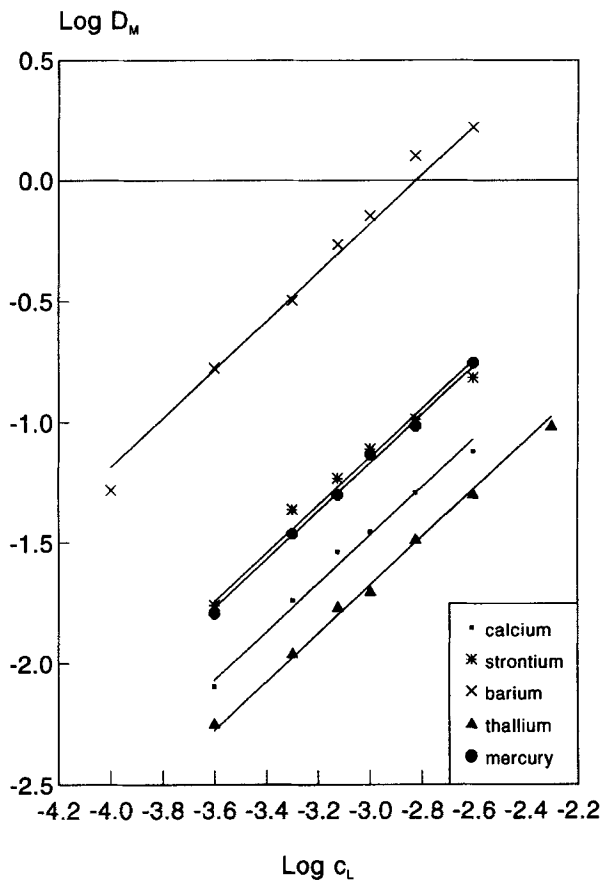


Figure 3 Extraction of Ca^{2+}, Sr^{2+}, Ba^{2+}, Hg^{2+} and Tl^+ with the hexaamide **5** (n = 6) {[$M(NO_3)_n$] = 1.10^{-4} M; [picric acid] = 5.10^{-3} M; pH = 5.2 (NaOAc/HCl-buffer); [ligand] = 1.10^{-4} – 5.10^{-3} M in toluene}.

CONCLUSION

The number of homocalixarene ring members (corresponding to size of cavity) and functional groups are variable in a wide range. Intra- and extraannular substituents can be introduced without any danger of cleavage of the carbocyclic macroring[22] in case of eventual drastic reaction conditions. Endo-receptor-abilities and complexation selectivities can be tailored for certain guests. Selectivity for Ba^{2+}-ions are exemplified for the case of oligoamides. *all*-Homocalixarenes are expected to induce an interesting competing development in comparison to the calixarenes. These two ligand and anchor group classes are expected to complement each other in future because of differing solubilities, conformational flexibilities, accessible ring-sizes and numbers of donor centres. In the future learning processes can be transferred from one host system to the other.[23]

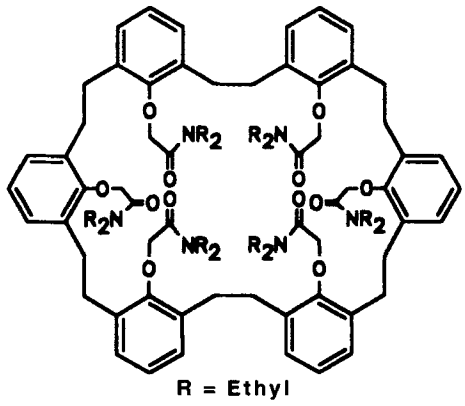


Table 1

cation	Na^+	K^+	Ca^{2+}	Sr^{2+}	Ba^{2+}
Log K	1.96	1.38	1.07	n.d.	2.47

Table 1 Complex formation constants of hexaamide **5** (n = 6) with Na^+, K^+, Ca^{2+} and Ba^{2+} (Sr^{2+} not detectable) in water determined UV-spectroscopically as increase of solubility of **5** in water as function of rising $M^{n+}Cl^-_n$-concentrations (Δ = ±0.08)

EXPERIMENTAL SECTION

^{1}H- und ^{13}C-NMR: WM-250 (250 bzw 62.90 MHz), Bruker Physik AG. FAB-MS: Concept 1 H, Kratos. IR:

Table 2

Atom	*x*	*y*	*z*	*U(eq)*
C(1)	3742(7)	2320(2)	5717(2)	57(2)
C(2)	5426(7)	2224(2)	5372(2)	61(2)
C(3)	5722(6)	2694(2)	4934(2)	52(2)
C(4)	7083(7)	3111(3)	4976(2)	69(2)
C(5)	7359(8)	3539(3)	4574(3)	77(2)
C(6)	6206(8)	3568(2)	4121(2)	67(2)
C(7)	4789(7)	3168(2)	4062(2)	51(2)
C(8)	4579(6)	2726(2)	4475(2)	45(1)
O(1)	3150(4)	2329(1)	4438(1)	49(1)
C(9)	3474(8)	1776(2)	4142(2)	60(2)
C(10)	2369(10)	1259(2)	4363(2)	67(2)
O(2)	3189(8)	796(2)	4505(2)	120(2)
N(1)	575(9)	1323(2)	4397(2)	86(2)
C(11)	-503(9)	1874(3)	4231(3)	90(3)
C(12)	-1319(12)	1807(5)	3709(4)	172(6)
C(13)	-448(15)	821(3)	4621(4)	159(5)
C(14)	-794(16)	881(4)	5213(4)	184(6)
C(1A)	3469(7)	3220(2)	3586(2)	55(2)
C(2A)	1708(7)	3520(2)	3734(2)	50(2)
C(3A)	1958(6)	4167(2)	3929(2)	41(1)
C(4A)	2322(7)	4282(2)	4480(2)	49(2)
C(5A)	2692(7)	4865(2)	4665(2)	52(2)
C(6A)	2693(6)	5338(2)	4303(2)	48(1)
C(7A)	2332(6)	5251(2)	3746(2)	42(1)
C(8A)	1987(6)	4661(2)	3572(2)	38(1)
O(1A)	1723(4)	4559(1)	3010(1)	46(1)
C(9A)	-129(7)	4546(2)	2837(2)	56(2)
C(10A)	-242(8)	4277(2)	2269(2)	61(2)
O(2A)	-832(5)	3755(2)	2209(1)	72(1)
N(1A)	355(8)	4602(2)	1842(2)	83(2)
C(11A)	321(10)	4323(3)	1276(2)	87(3)
C(12A)	-1416(14)	4468(4)	1006(4)	149(5)
C(13A)	1089(14)	5226(3)	1874(2)	106(4)
C(14A)	3158(15)	5233(4)	1819(3)	139(5)
C(1B)	2395(7)	5773(2)	3353(2)	54(2)
C(2B)	4264(7)	5887(2)	3134(2)	55(2)
C(3B)	5551(6)	6164(2)	3541(2)	48(1)
C(4B)	6999(8)	5839(2)	3770(2)	61(2)
C(5B)	8176(7)	6103(3)	4138(2)	63(2)
C(6B)	7932(7)	6694(2)	4297(2)	58(2)
C(7B)	6524(6)	7043(2)	4096(2)	48(2)
C(8B)	5364(6)	6763(2)	3710(2)	44(1)
O(1B)	3890(4)	7099(1)	3514(1)	43(1)
C(9B)	4119(6)	7381(2)	2986(2)	51(2)
C(10B)	2455(7)	7269(2)	2642(2)	49(2)
O(2B)	2574(5)	6947(2)	2224(1)	67(1)
N(1B)	898(5)	7512(2)	2796(2)	54(1)
C(11B)	-721(8)	7342(2)	2483(2)	69(2)
C(12B)	-1279(8)	6715(3)	2613(2)	76(2)
C(13B)	720(8)	7929(2)	3265(2)	66(2)
C(14B)	539(9)	8575(3)	3086(3)	89(3)
O(1W)	6079(30)	353(8)	4887(8)	435(10)

Table 2 Atomic coordinates ($\cdot 10^4$) and equivalent isotropic displacement coefficients ($Å^2 \cdot 10^3$) of **5** ($n = 6$); equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor

SP 1100 infrared spectrometer, Pye Unicam Ltd. FT-IR: spectrometer modell 1600, Perkin-Elmer. - Melting points: Kofler-Mikroskop-Heiztisch, Reichert. - DC: SiO_2 $60F_{254}$, Merck. - Measurement of γ-radiation: scintillation counter Cobra II, Canberra-Packard; β-radiation: liquid scintillation counter Tricarb 2500, Canberra-Packard. - Temperature dependence of extraction: shaking water bath SWB 20, Haake. - Na-22, Cs-137, Tl-204, Ca-45, Sr-85, Ba-133, Ag-110, Co-60, Zn-65 and Hg-203: Isocommerz.

Synthesis of 8,16,24,32,40,48-Hexahydroxy-[2$_6$]metacyclophane (2):

In an argon-atmosphere 20 ml of a solution of 370 mg (0.46 mmol) 8,16,24,32,40,48-hexamethoxy[2_6]metacyclophane (**1**, $n = 6$)[11] in dried dichloromethane are added dropwise to 11.0 ml (11.0 mmol) 1.0 M-solution of borontribromide in dichloromethane within 6 h at room temperature. After stirring over night the solution is cooled in an ice-bath and an excess of water is added dropwise. The colorless solid is filtered, washed with water and dried in vacuo to yield 309 mg (93%) pure hexaphenol **2** ($n = 6$).

$R_f = 0.28$ (CH_2Cl_2); mp.: 250–253°C; ^{1}H-NMR (250 MHz, DMSO-d^6/$TMS_{int.}$): $\delta = 2.82$ (s, 24H; CH_2), 6.80 (t, ^3J(H,H) = 7.5 Hz, 6H; aromat. 5-H), 7.11 (d, ^3J(H,H) = 7.5 Hz, 12H; aromat. 4-H), 8.35 (s, br, 6H; OH); ^{13}C-NMR [62.90 MHz, DMSO-d^6/$TMS_{int.}$; DEPT (spinecho)]: $\delta = 30.95$ (CH_2), 119.90 (aromat. C-5), 127.56 (aromat. C-4), 128.95 (aromat. C-3), 152.30 (aromat. C-8); IR (KBr) $\tilde{\nu} = 670$ cm^{-1} (w), 755 (s), 800 (w), 1090 (m), 1205 (s), 1230 (s), 1475 (s), 2910 (w), 2990 (w), 3490 (s, br); FABMS: *m/z* (%) = 720 (100) [M$^+$], 721 (99) [M$^+$+H].

Synthesis of 8,16,24,32,40,48-Hexakis[(N,N-diethylcarbamoyl)methoxy][2$_6$]metacyclophane (5):

In an argon-atmosphere 340 mg (1.75 mmol) 2-bromo-*N,N*-diethylacetamide are added to a mixture of 50 mg (0.069 mmol) hexaphenol **2** ($n = 6$), 68 mg (0.50 mmol) powdered K_2CO_3 and 83 mg (0.50 mmol) KI in 50 ml dried acetone. The mixture is heated at reflux for 71 h. The solvent and excess alkylation reagent are removed in vacuo. The residue is dissolved in 100 ml trichloromethane and washed with saturated $NaHCO_3$-solution (three times) and with water. After drying with $MgSO_4$ the trichloromethane is evaporated. The remaining yellow oil is recrystallized from a dichloromethane/petroleum ether(40/60)-mixture to yield 78 mg (80%) crystalline compound **5** (n = 6).

$R_f = 0.65$ (CH_2Cl_2:ethanol = 10:1); mp.: 146 – 149°C; ^{1}H-NMR (250 MHz, $CDCl_3$/$TMS_{int.}$): $\delta = 1.22$ (m, 36H; CH_3), 3.04 (s, 24H; CH_2), 3.31–3.51 (m, 24H; NCH_2), 4.52 (s, 12H; OCH_2), 6.33 ("s", 18 H; arene-H); ^{13}C-NMR [62.90 MHz, $CDCl_3$/$TMS_{int.}$; DEPT (spinecho)]: $\delta = 13.03$ (CH_3), 14.59 (CH_3), 31.05 (CH_2), 40.26 (NCH_2), 41.41 (NCH_2), 72.21 (OCH_2), 123.50 (aromat. C-5), 130.07 (aromat. C-4), 133.68 (aromat. C-3), 156.06 (aromat. C-8), 167.31 (C=O); FT-IR (KBr) $\tilde{\nu}$

= 774 cm^{-1} (w), 1020 (w), 1085 (w), 1189 (m), 1461 (s), 1640 (s), 2931 (w); FABMS: *m/z* (%) = 1398 (22) [M^+], 1399 (100) [M^++H], 1298 (13) [M^+-$C_5H_{10}NO$], 1284 (23) [M^+-$C_6H_{12}NO$], 1171 (7) [M^+-2 × $C_6H_{12}NO$+H].

The extraction studies were carried out in buffer solutions to avoid superimposition caused by protonation-equilibrium [Na^+, Tl^+, Ca^{2+}, Sr^{2+}, Ba^{2+}, Co^{2+}, Zn^{2+} and Hg^{2+}: metal nitrate/picric acid-buffer (NaOAc/HCl; pH = 5.2) in water/ligand in toluene (trichloromethane); Tl^+ and Ag^+: 4-morpholinoethanesulfonic acid/NaOH-buffer (pH = 5.5)]. Micro-reaction vials (volume 2 cm^3) were used at a temperature of 25±1°C. The phase ratio $V_{(org)}$:$V_{(aq)}$ was 1:1 (0.5 cm^3 for each). The shaking time was 30 min. All samples were centrifuged after extraction. The determination of concentrations was carried out radiometrically in both phases.

Data Collection:

$C_{84}H_{114}N_6O_{12} - 2\,H_2O$, M_r = 1435.8; colorless plates obtained by diffusion of petroleum ether (40/60) into a solution of hexaamide 5 in trichloromethane; crystal dimensions: 0.20 × 0.25 × 0.35 mm. Intensity data were collected on Enraf Nonius CAD4 diffractometer with $Cu_{K\alpha}$ (λ =1.54178 Å) radiation, using the 2θ/ω scan technique in the 2θ-range 5° – 149°. 8193 unique reflections were measured [4209 with $|F| > 3\sigma(F)$]. The correction for extinction and absorption[24] were applied. SHELXTL-Plus[25] was used for solution refinement (table 2)

Crystal data:

monoclinic, $P2_1/n$, a = 7.475(2) Å, b = 21.967(3) Å, c = 24.472(4) Å, β = 91.25(2)°; V = 4017(1) $Å^3$; Z = 2; $\rho_{calc.}$=1.19 g cm^{-3}; μ ($Cu_{K\alpha}$) = 0.64 mm^{-1}; $F(000)$ = 1552; T = 193 K; R = 0.079 [R_w = 0.086, $w^{-1} = \sigma^2(F) + 0.0015F^2$].

ACKNOWLEDGEMENTS

This work has been supported by the *Bundesminister für Forschung und Technologie* (Projekt Nr. NT 2057 4). We thank *Dr. D. Tiebes* and *Dr. K. Wagemann* (DECHEMA) for cooperation. We are greatful to *Prof. K. Cammann* (Münster) for exchange of informations. We are obliged to *Dr. S. Schuth* and *Dr. G. Eckhardt* for recording FAB-mass spectra.

REFERENCES AND NOTES

1 Vögtle, F., Schmitz, J., Nieger, M.; *Chem. Ber.*, **1992**, *125*, 2523–2531: M. Nieger, J. Schmitz, F. Vögtle, *Chem. Ber.* **1992**, *125*, 2523-2531; J. Schmitz, F. Vögtle, M. Nieger, K. Gloe, H. Stephan, O. Heitzsch, H.-J. Buschmann, W. Hesse, K. Cammann, *Chem. Ber.* **1993**, *126*, 2483-2491; see also; F. Vögtle, G. Brodesser, M. Nieger, K. Rissanen, *Recl. Trav. Chim. Pays-Bas* **1993**, *112*, 325-329, G. Brodesser, F. Vögtle, *J. Incl. Phenom.* **1994**, in press.

2 Use of middle-pressure-liquid-chromatography (MPLC) shortened considerably the required time for separation of mixture of products obtained in the series of [2_n]metacyclophanes with intraannular methoxy groups in contrast to our former procedure[1]: 24 hours of chromatography is sufficient to obtain comparable yields and purities.

3 Hexamer means the molecule is containing six benzene rings (n = 6).

4 An X-ray-structural analysis was performed of the octameric hydroxy-compound **2** (n = 8).

5 Phenols derived from calixarenes generally exhibit low solubility in spite of their *tert*-butyl groups.

6 These compounds had already been examined with regard to their host-properties, details will be communicated later.

7 X-ray-structural analyses were performed of extraannular tetrameric ester **3** (n = 4) and intraannular hexameric ester **3** (n = 6).

8 Gloe, K., Mühl, P.; *Isotopenpraxis*, **1983**, *19*, 257–260.

9 Stephan, H., Gloe, K., Beger, J., Mühl, P.; *Solv. Extr. Ion Exch.*, **1991**, *9*, 435.

10 Güggi, M. Dissertation 5866, ETH Zürich **1977**.

11 Ligands of ethertetralactame-structure described by *Cazaux* et al.[12] exhibit selectivity for Ba^{2+}-cations in contrast to smaller alkaline earth and alkali metal ions too, but they are not very lipophilic. The selectivity decreases, if the lipophilicity and the ring size, resp., are increased. The ring enlargement caused by simultaneous introduction of oxyethylene units leads to more pronounced extraction of alkali metal ions.

12 Pigot, T., Duriez, M.Ch., Picard, C., Cazaux, L., Tisnes, P.; *Tetrahedron*, **1992**, *48*, 4359–4368.

13 Gloe, K., Müh', P., Beger, J.; *Z. Chem* **1988**, *28*, 1–14.

14 Tetralactames described by *Cazaux* et al[12] form 1:1- to 1:2-complexes with alkaline earth metal ions in polar media. Open-chain diamides[15, 16] used in ion-selective electrodes show a high preference for alkaline earth over alkali metal ions[17, 18, 19]. In solution they form different complexes with 1:1-, 1:2- and 1:3-stoichiometry (cation: ligand).

15 Simon, W., Pretsch, E., Morf, W.E., Amman, D., Oesch, U., Dinten, O.; *Analyst*, **1984**, *109*, 207.

16 Läubli, M.W., Dinten, O., Pretsch, E., Simon, W., Vögtle, F., Bongardt, F., Kleiner, T.; *Anal. Chem.*, **1985**, *57*, 2756–2758.

17 Kirsch, N.N.L., Funck, R.J.J. Simon, W.; *Helv. Chim. Acta.*, **1978**, *61*, 2019–2039.

18 Borowitz, I.J., Lin, W., Wun, T., Bittman, R., Weiss, L., Diakiw, V., Borowitz, G.B.; *Tetrahedron*, **1977**, *33*, 1697–1705.

19 Stephan, H., Gloe, K., Beger, J., Mühl, P.; *Solv. Extr. Ion Exch.*, **1991**, *9*, 459.

20 First measurements of influence of temperature in extraction of Ba^{2+}-cations show a decrease of extraction efficiency with increasing temperature, so that total extraction process is exothermic.

21 a) Buschmann, H.J., Cleve, E., Schollmeyer, E.; *Inorg. Chim. Acta*, **1992**, *193*, 93–97; b) Weber, E., Piel, M., Buschmann, H.J., Cleve, E.; *Chem. Ber.*, **1992**, *125*, 2483–2485.

22 Cleavage of calixarenes to phenol and formaldehyde can occur not rarely.

23 Parts of this work were reported at the occasion of lectures at Nijmegen, Holland (17.02.1993); at the "Bienal del grupo de quimica organica", Real Sociedad Espanola de Quimica, Palma de Mallorca (12.04.1993), at the "International Symposium on Metal Ions in Solution" Malelane Lodge, Transvaal, South Africa (20. – 23.04.93) and at the Ohio States University, USA (29.04.93).

24 Walker, N., Stuart, D.; *Acta Cryst.*, **1983**, *A 39*, 158–166.

25 Sheldrick, G.M. SHELXTL-PLUS **1989**, Siemens Analytical X-ray Instruments, Inc., Madison, Wisconsin, USA.