A Series of Calix[4]arenes, Having Two Opposite Para Positions Connected by an Aliphatic Chain

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Abstract: A series of bridged calix[4]arenes having two opposite phenolic units connected by an aliphatic chain were synthesized by condensation of suitable α,ω-(p-hydroxyphenyl)alkanes with 2,6-bisbromomethylated phenols. With $TiCl_4$ as a catalyst in dioxane at 100 °C, the yields of pure products were in the range of 2%–20%. The length of the connecting chain was varied between $n = 5$ and 16 carbon atoms. The unconnected phenolic units were substituted in the para position by methyl, octyl, dodecyl, octadecyl, *tert*-butyl, cyclohexyl, phenyl, and chloro groups. The temperature independence of the AB pattern found for the benzylic methylene groups in the ^{1}H NMR spectra proves that the cone conformation is fixed in these compounds. This was confirmed by X-ray analysis for compounds with $n = 6$, 8, and 16, which also revealed a distortion of the ideal cone conformation with shorter connecting chains. This is in accord with the weaker intramolecular hydrogen bonds found by IR and ^{1}H NMR spectra. Ion transport experiments with Cs^+ ions show a sharp maximum of the transport ability for $n = 8$, suggesting complexation of the Cs^+ ions inside the cavity.

Cyclic structures were first postulated by Zinke[1] for the condensation products of para-substituted phenols with formaldehyde obtained under alkaline conditions. Later, several cyclic oligomers consisting of four to seven phenolic units linked via methylene groups were synthesized by Kämmerer and Happel[2] using a stepwise procedure first described by Hayes and Hunter.[3] However, these compounds did not become popular until Gutsche[4] elaborated simple conditions for the preparation of larger quantities of these oligomers. He also coined the name "calixarenes",[5] which is now generally accepted.

During the last decade the interest in calixarenes has increased continuously,[6] mainly because they are regarded as host molecules of a potentially large variety. Inclusion of neutral molecules[7,8] or cations,[9] or both,[10] has been reported for calixarenes or suitable derivatives thereof in the solid state. Remarkable selectivities for the complexation of cations also have been found in solution for some derivatives.[6,11-13] Furthermore, calixarenes are able to act as ion carrier molecules in the proton-coupled ion transport through

Scheme I
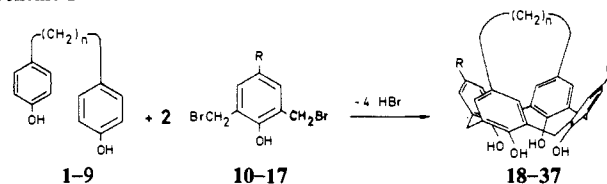
1, $n = 5$; **2**, $n = 6$; **3**, $n = 7$; **4**, $n = 8$; **5**, $n = 9$; **6**, $n = 10$; **7**, $n = 12$; **8**, $n = 14$; **9**, $n = 16$; **10**, R = CH_3; **11**, R = C_8H_{17}; **12**, R = $C_{12}H_{25}$; **13**, R = $C_{18}H_{37}$; **14**, R = $C(CH_3)_3$; **15**, R = C_6H_{11}; **16**, R = C_6H_5; **17**, R = Cl; **18**, R = CH_3, $n = 5$; **19**, R = CH_3, $n = 6$; **20**, R = CH_3, $n = 7$; **21**, R = CH_3, $n = 8$; **22**, R = CH_3, $n = 9$; **23**, R = CH_3, $n = 10$; **24**, R = CH_3, $n = 12$; **25**, R = CH_3, $n = 14$; **26**, R = CH_3, $n = 16$; **27**, R = $C(CH_3)_3$, $n = 6$; **28**, R = $C(CH_3)_3$, $n = 8$; **29**, R = $C(CH_3)_3$, $n = 12$; **30**, R = $C(CH_3)_3$, $n = 16$; **31**, R = C_8H_{17}, $n = 8$; **32**, R = $C_{12}H_{25}$, $n = 8$; **33**, R = C_6H_{11}, $n = 8$; **34**, R = C_6H_5, $n = 8$; **35**, R = Cl, $n = 8$; **36**, R = Cl, $n = 12$; **37**, R = $C_{18}H_{37}$, $n = 16$

liquid membranes,[14] and examples of enzyme-like catalysis have also been reported recently.[15]

The name calixarene, referring to a somewhat rigid, cuplike molecule, is more appropriate for calix[4]arenes (and calix[5]-arenes), while the higher oligomers are more flexible cyclic molecules. Indeed free calix[4]arenes always exist in the so-called cone conformation, which is stabilized by a cyclic array of intramolecular hydrogen bonds and thus, is favored over other possible conformations such as the partial cone, or the 1,2- or 1,3-alternate.[6] For the solid state this was shown for several examples by X-ray analysis.[7] In solution it follows from the AB-type pattern found in the ^{1}H NMR spectra for the benzylic methylene protons at lower temperatures.[16,17] At higher temperatures, however, a sharp singlet for the methylene protons indicates an interconversion of the two opposite cone conformations, which becomes rapid on the NMR time scale.

The cone conformation of calix[4]arenes may be fixed by the introduction of suitable substituents at the phenolic hydroxy

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groups,[8,9,12] which means, however, that the cyclic array of intramolecular hydrogen bonds has disappeared or at least is interrupted.   We were interested in the design of preorganized calixarene molecules with a fixed cone conformation, but having still the complete system of free OH groups. Fixation of the cone conformation seemed possible by the connection of two opposite para positions by an aliphatic chain[18] (compare Scheme I). Variation of the chain length *n* then would have the following effects.   For greater chain lengths (*n* > 8), the flexibility of the calixarene part is influenced in a precisely controlled manner.[19] Shortening of the chain (*n* < 8) results in well-defined distortions of the cone conformation, especially affecting the phenolic O–O distances, the relative angles between aromatic ring planes, and thus the shape and volume of the cavity.

It is the purpose of this paper to describe the synthesis and some properties of those compounds that to our knowledge represent the first molecules having a fixed cone conformation and simultaneously the complete cyclic array of hydroxy groups.[20]

Synthesis. All the bridged calix[4]arenes (**18–37**) described[21] were obtained by the reaction outlined in Scheme I. The α,ω-(*p*-hydroxyphenyl)alkanes (**1–9**) are easily available by Friedel–Crafts acylation of anisole with α,ω-diacid chlorides, followed by simultaneous reduction and demthylation.[22] Bis(bromomethyl)phenols (**10–17**) were obtained either by direct bromomethylation or via the corresponding bishydroxymethylated phenols.

The formation of a bridged calixarene in this manner, e.g., **21** from **4** and **10**, requires two inter- and two intramolecular condensation steps. Consequently, we first conducted reactions under very dilute conditions with continuous addition of the reactants, using different solvents (acetic acid, dioxane) and different catalysts ($ZnCl_2$, BF_3Et_2O, $TiCl_4$). Optimization of the reaction conditions, which was carried out for the synthesis of **21**, however, led to a more convenient batch procedure with a moderate concentration of 0.01 M for **4**. Accordingly, nearly all further reactions were conducted under similar conditions in boiling dioxane, using $TiCl_4$ as catalyst in a ratio of "diphenol"/"(bromomethyl)phenol"/$TiCl_4$ of 1:2:4.8. However, most probably the optimum concentration is different for the preparation of different compounds, e.g., the yield of **18** was increased from 5% to 14% when the concentration was increased from 0.01 to 0.015 M, while a similar increase of the concentration led to smaller yields of **28**. The reaction time (in the range of 30–144 h) was adjusted according to intermediate analysis of the reaction mixture by TLC.

It may be anticipated that $TiCl_4$ not only acts as a Lewis acid and Friedel–Crafts catalyst but also as a template for the cyclization reaction. There are several examples known for complexation between titanium and calix[4]- or calix[6]arenes (or their derivatives) in the solid state.[23-25] The common feature of all these complexes is that three adjacent phenolic units of the calixarene are bound to the Ti via their oxygen atoms, as could
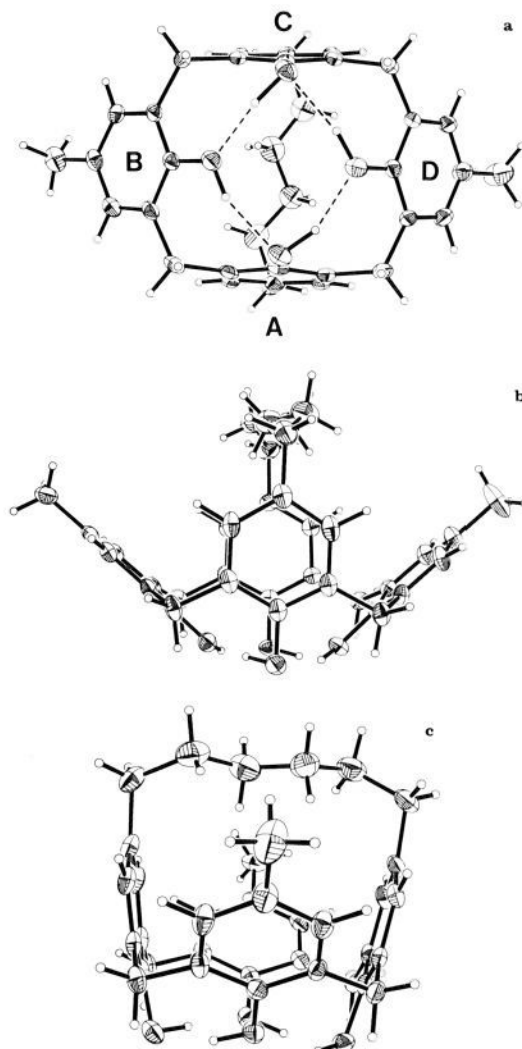

Figure 1. Molecular conformation of compound **19**, with *n* = 6 and R = CH_3, seen from different directions turned by 90°. Hydrogen bonds are indicated by dotted lines in a.

be shown by X-ray analysis. Of course, a similar prearrangement of the phenolic units would be helpful for the closure of the calix[4]arene ring.

The yields of pure products, which are easily isolated by flash chromatography,[26] varied between 2% and 20%. Obviously, the yield is influenced by the substituent R as well as by the chain length *n*. There is a maximum for *n* = 8, if compounds with R = CH_3 are compared, but **21** (with R = CH_3 and *n* ≈ 8) was the compound taken for the optimization. The already mentioned example of **18** suggests that better yields for other compounds may be obtained too, if the most favorable conditions are found for the special case.

In spite of the comparably good yield of **18**, the preparation of a shorter bridged compound with *n* = 4 was not successful under the conditions applied, while the synthesis of compounds having longer bridges (*n* > 16) seems possible.

X-ray Analysis. For three compounds, **19**, **27**, and **30**, the molecular structure was confirmed by single-crystal X-ray analysis, in addition to the crystal structures of **21** and **34**, which have been reported already.[27] Single crystals were obtained from acetone. With the exception of **30**, no inclusion of solvent was observed in the crystal lattice. For **30**, however, the ¹H NMR spectrum and a comparison of the measured and calculated densities sug-

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(19) Differences in the flexibility are reflected for instance by the photo-CIDNP spectra of these compounds; see: Böhmer, V.; Goldmann, H.; Kaptein, R.; Zetta, L. *J. Chem. Soc., Chem. Commun.* **1987**, 1358.

(20) Gutsche has mentioned an example in which two adjacent phenolic units of a calix[4]arene are additionally connected (see ref 6), but this was not described in detail up to now.

(21) The application of a systematic nomenclature to those compounds leads to very lengthy expressions, e.g. compound **21** becomes 7,19-dimethyl-hexacyclo[11.11.8.1³,²³.1⁵,⁹.1¹¹,¹⁵.1¹⁷,²¹]hexatriaconta-1(24),2,5(36),6,8,11-(33),12,14,17(34),18,20,23(35)-dodecaene-33,34,35,36-tetrol. If the nomenclature proposed by Gutsche for calixarenes is combined with the IUPAC nomenclature (rule A-34) the same compound is called 11,23-dimethyl-5,17-octano-25,26,27,28-tetrahydroxycalix[4]arene. This nomenclature is used here throughout the Experimental Section.

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Table I. Crystallographic Data of the X-ray Structure Determination

	compound		
	19	**27**	**30**
formula	$C_{36}H_{38}O_4$	$C_{42}H_{50}O_4$	$C_{52}H_{70}O_4$
mol wt	534.66	618.82	759.08
cryst size, mm³	0.5 × 0.5 × 0.3	0.3 × 0.3 × 0.2	0.5 × 0.4 × 0.1
lattice type	orthorhombic	monoclinic	monoclinic
space group	$P2_12_12_1$	$P2_1/n$	$P2_1/c$
a, Å	9.364	13.299	16.764
b, Å	17.909	18.512	35.435
c, Å	18.125	14.851	17.009
α, deg	90	90	90
β, deg	90	94.6	97.13
γ, deg	90	90	90
Z	4	4	8
V, Å³	3039.6	3644.4	10 025.7
d_{calcd}, g cm⁻³	1.168	1.128	1.111[a]
d_{measd}, g cm⁻³	1.17	1.13	1.08
no. of measd reflcns	7807	6676	14 142
no. of unique reflcns	7371	6207	13 111
no. of obsd reflcns, >1σ(F)	6411	4112	5404
final R_w, %	3.8	4.7	b

[a] Calculated with one molecule of acetone. [b] Not all atoms could be found.

gested the inclusion of one molecule of acetone per molecule, although its exact position in the crystal lattice could not be found. The determination of the structure of **30** was complicated by two factors: The asymmetric unit contains 2 molecules, leading to the determination of 252 atoms (without included solvent), and the *tert*-butyl groups as well as the aliphatic chain are disordered. Nevertheless, the conformation of the calixarene part of the molecule was well-defined.

All parameters of the X-ray structure determination of **19, 27,** and **30** are collected in Table I. In general, the conformation of all compounds corresponds to the cone conformation of calix[4]arenes, although the partial cone or the 1,3-alternate conformation would be also possible for the calixarene moiety, since the joining of two opposite para positions only excludes the 1,2-alternate conformation. Thus, the whole molecule has a basketlike shape, the oxygen atoms forming the bottom and the oligo-methylene chain the handle.[28] As an example, Figure 1 illustrates the molecular conformation of **19,** seen from different directions.

The cone conformation of the bridged calixarenes is more or less distorted, as compared with the "ideal" 4-fold symmetry found, for instance, for *tert*-butylcalix[4]arene.[7a] This is mainly due to the bridging aliphatic chain (a short chain necessarily forces together the para positions of the phenolic rings A and C), but packing effects also play a certain role. The conformational differences of all five compounds are best demonstrated by the data collected in Table II. The different atoms in the following discussion refer to the phenolic rings A–D, where the aliphatic chain connects the para position of A and C.

In all cases the benzylic methylene carbons C(A/B), C(B/C), C(C/D), and C(D/A) lie very nearly within one plane. The strongest deviation of methylene carbons from the calculated best plane is found for **33** with a value of 0.079 Å. Therefore, it is reasonable to refer to this plane in the description of the molecular conformation. As shown by nearly equal diagonal distances and by angles close to 90°, the methylene carbons form a regular square in all compounds. Table II shows that the distances C(A/B)–C(C/D) and C(B/C)–C(D/A) differ usually by less than 0.1 Å and that the angles C(C/D)–C(D/A)–C(A/B), C(D/A)–C(A/B)–C(B/C), and so on, are between 88.6 and 90.8°.

Two other quadrangles that, however, are not planar can be regarded as describing differences in the shape of the different molecules: the quadrangle of the oxygen atoms and that of the

C-atoms attached to the para positions. All O–O distances between adjacent oxygens are in accordance with those expected for intramolecular hydrogen bonds. Their average is slightly higher for the compounds with n = 6 (2.78–2.82 Å) than for n = 8 (2.65–2.73 Å) or n = 16 (2.62–2.69 Å). A strong increase for the distance O(A)–O(C) and a decrease for the other diagonal O(B)–O(D) is observed for shorter chains. This is necessarily accompanied by increasing values for the angles O(A)–O(B)–O(C) and O(C)–O(D)–O(A) and decreasing values for the angles O(B)–O(C)–O(D) and O(D)–O(A)–O(B). Just the opposite deformation of the "ideal" regular square is observed for the carbon atoms C(A), C(B), C(C), and C(D) that are attached to the para positions. For shorter connecting chains, diagonal C(B)–C(D) is much longer than C(A)–C(C), and the angles at C(C) and C(A) are higher than those at C(B) and C(D). For the longest chain of 16 carbon atoms, these squares come close to regular squares although slight but significant deviations are still present.

Thus, the differences in the conformations of the bridged calixarenes may be described by rotation of the phenolic units around axes through both ortho methylene carbons as fix points or hinges. The shorter the bridging chain, the more are the rings A and C pulled into the cavity, and consequently, to keep bond distances and bond angles close to usual values, the rings B and D are forced out of the cavity, which can be seen easily from Figure 1.

Spectra. Due to their "macrobicyclic" structure the bridged calixarenes show very simple electron impact mass spectra. Up to M = 870 (compound **32**), the molecular ion is found with a relative intensity of 100% and little fragmentation is observed. Even for **37** with a molar mass of 1150, the molecular ion can still be detected.

The most characteristic region in the ¹H NMR spectra of calix[4]arenes is that of the benzylic methylene protons. A sharp singlet at higher temperatures indicates a flexible molecule, while the two doublets (AB-type pattern) found at lower temperature show that now the interconversion of the two opposite conformations is slow on the NMR time scale. The coalescence temperature is slightly different for different compounds and different solvents.

In contrast to "free" calix[4]arenes, all the bridged compounds **18–37** show a stable AB system in different solvents for all available temperatures. Two examples are given in Table III showing no indication of any conformational change. Slight variations in the chemical shift may be explained by solvation differences.

For compounds with R = CH₃ and different chain length n, the chemical shift may be regarded as a function of n. Here again only a very slight trend to higher field is found for the signals of both protons of the methylene groups for decreasing chain length. Therefore it is concluded that, independent of the chain length, all bridged compounds in all solvents and all measured temperatures have the same general conformation for the calixarene part of the molecule. This is obviously the cone conformation, which was found for five examples in the solid state. The existence of the 1,3-alternate conformation, which might be assumed for shorter chains, e.g., n = 5, instead of the cone conformation, would also lead to two nonidentical methylene protons. However, this should be reflected in a stronger difference in their chemical shift in comparison to compounds with a longer chain.

The increasing distortion of the calixarene part, which is necessarily caused by the shortening of the connecting chain and which was proved by the X-ray analysis, is also found in solution. It is especially demonstrated by the resonance of the hydroxy protons. A high-field shift for decreasing n, especially for n < 9, shows the weakening of the intramolecular hydrogen bonds. Furthermore, the signal splits into two singlets for short chains, indicating the nonequivalence of the OH protons. (For **21** this splitting is found only at low temperatures.) While the singlet of the aromatic protons of the unconnected phenolic rings shows only a slight downfield shift, a distinct high-field shift is found for decreasing n for the aromatic protons of the connected phenolic rings. This is obviously caused by the ring current of the unconnected phenolic units.

(28) In an extension of Gutsche's proposal, these compounds may be named arrichoarenes, Greek arrichos, "basket with a handle"; see also 6c.

Table II. Comparison of the Shape of the Calixarene Part of Different Bridged Calixarenes, As Determined by X-ray Analysis[a]

	19 (6/CH₃)	27 (6/tBu)	21a (8/CH₃)	21b	33 (8/cHex)	30a (16/tBu)	30b
	Quadrangle of Benzylic Methylene Carbons						
C(A/B)-C(B/C)	5.006	5.013	5.022	5.082	5.056	5.042	5.083
C(B/C)-C(C/D)	5.078	5.118	5.094	5.094	5.102	5.044	5.251
C(C/D)-C(D/A)	5.026	5.000	5.101	5.094	5.076	5.093	5.097
C(D/A)-C(A/B)	5.105	5.110	5.161	5.144	5.124	5.062	5.280
C(A/B)-C(C/D)	7.169	7.143	7.166	7.228	7.172	7.152	7.227
C(B/C)-C(D/A)	7.125	7.169	7.244	7.205	7.216	7.160	7.369
C(A/B)-C(B/C)-C(C/D)	90.6	89.7	90.2	90.5	89.8	90.3	89.5
C(B/C)-C(C/D)-C(D/A)	89.7	90.2	90.5	90.0	90.3	89.9	90.8
C(C/D)-C(D/A)-C(A/B)	90.1	89.9	88.6	89.8	89.4	89.5	89.0
C(D/A)-C(A/B)-C(B/C)	89.6	90.2	90.7	89.6	90.3	90.2	90.6
	Quadrangle of Oxygen Atoms						
O(A)-O(B)	2.758	2.868	2.630	2.625	2.683	2.644	2.724
O(B)-O(C)	2.777	2.835	2.692	2.681	2.779	2.668	2.629
O(C)-O(D)	2.819	2.775	2.723	2.679	2.732	2.576	2.685
O(D)-O(A)	2.762	2.805	2.665	2.627	2.711	2.583	2.706
O(A)-O(C)	4.318	4.461	4.029	3.902	4.089	3.799	3.917
O(B)-O(D)	3.449	3.392	3.503	3.558	3.589	3.596	3.664
O(D)-O(A)-O(B)	77.3	73.4	82.8	86.2	83.4	86.9	84.9
O(A)-O(B)-O(C)	102.6	102.9	98.4	94.7	96.9	91.3	94.0
O(B)-O(C)-O(D)	76.1	74.4	80.6	84.0	81.9	86.6	87.2
O(C)-O(D)-O(A)	101.4	106.1	96.8	94.7	97.4	94.9	93.2
	Quadrangle of Carbon Atoms Attached to Para Positions						
C(A)-C(B)	6.623	7.018	6.705	6.934	6.723	7.289	7.007
C(B)-C(C)	6.889	7.106	7.278	7.364	6.624	7.422	7.054
C(C)-C(D)	6.876	6.910	7.283	7.434	7.123	7.295	7.252
C(D)-C(A)	6.953	6.802	6.773	6.753	6.623	6.971	7.244
C(A)-C(C)	6.246	6.110	8.202	8.412	8.063	9.465	9.172
C(B)-C(D)	11.812	12.054	11.212	11.328	10.795	10.924	10.843
C(D)-C(A)-C(B)	120.9	121.4	112.6	111.7	108.0	100.0	99.1
C(A)-C(B)-C(C)	55.0	51.3	71.7	72.0	74.3	80.1	81.4
C(B)-C(C)-C(D)	118.2	118.6	100.7	99.9	103.4	95.8	98.6
C(C)-C(D)-C(A)	53.7	52.9	71.3	72.5	71.7	83.1	78.5
	Inclination Relative to the Plane of Benzylic Methylene Carbons						
ring A	101.9	99.9	115.9	119.8	114.0	121.8	116.9
ring B	139.1	139.2	133.7	132.0	130.8	129.6	133.4
ring C	98.9	97.5	107.6	108.4	108.1	118.7	122.0
ring D	136.6	142.1	130.7	133.0	128.5	127.2	124.4

[a] For three characteristic quadrangles (see text) distances (Å) and angles (deg) are given. The different shape is characterized further by the inclination of the phenolic rings relative to the plane of the benzylic methylene carbons.

Table III. Chemical Shifts (δ) and Coupling Constants (Hertz) of the Methylene Protons for Compounds 19 and 21 in Different Solvents at Different Temperatures

	T, °C					
solvent	−48	31	55	82	122	182
			19			
CDCl₃	4.14	4.12	4.12			
	3.38	3.32	3.31			
J_{AB}	14.0	14.2	14.2			
nitrobenzene-d_5		4.11		4.14	4.16	4.19
		3.22		3.34	3.37	3.40
J_{AB}		14.1		14.1	14.2	14.1

	T, °C					
solvent	−63	−43	27	67	97	117	162
			21			
CHCl₃	4.17	4.16	4.15	4.15			
	3.41	3.39	3.35	3.33			
J_{AB}	13.8	13.9	13.8	13.9			
pyridine-d_5		4.80	4.53	4.43	4.38		
		3.60	3.46	3.42	3.40		
J_{AB}		13.5	13.3	13.5	13.5		
DMSO-d_6				4.15		4.15	4.16
				3.27		3.27	3.28
J_{AB}				13.3		13.6	13.8

These NMR spectral data are in accordance with an increasing OH-stretching frequency found for the compounds with shorter connecting chains, indicating also weaker hydrogen bonds.

Ion Transport Experiments. Izatt et al. have demonstrated the ability of calixarenes to transport cations from an alkaline source phase through a liquid membrane to a neutral receiving phase.[14] The comparison of different alkali cations revealed that the highest efficiency for this proton-coupled ion transport was always observed for Cs⁺ ions (p-tert-butylcalix[8]arene showed the highest absolute transport rate, while p-tert-butylcalix[4]arene was most

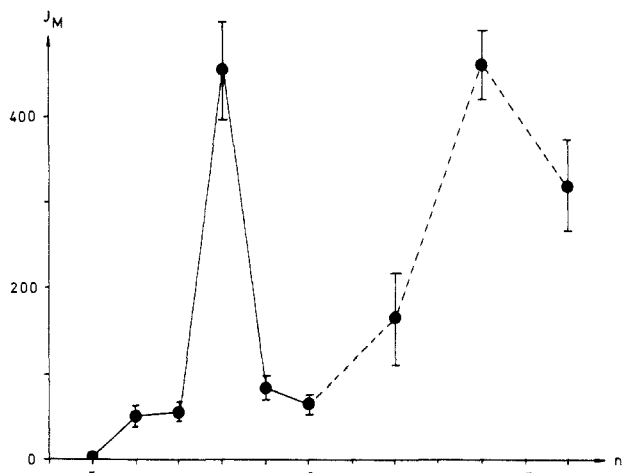*Calix[4]arene Syntheses*

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Figure 2. Plot of Cs^+ flux (J_M, 10^8 mol s^{-1} m^{-2}) as a function of the chain length n. Membrane: 0.001 M of a bridged calix[4]arene (R = CH_3) in CH_2Cl_2/CCl_4 25:75 (v/v); source phase, 1 M CsOH; T, 25 °C. Dotted lines are used on the right side to indicate the absence of compounds with n = 11, 13, and 15.

selective). The exact structure of the phenolate Cs^+ ion complex formed in the organic phase is still subject to debate. The cation may be surrounded by the oxygen atoms or it may be situated in the cavity after loss of its hydration shell, which would best explain the preference for the weakly hydrated Cs^+ ion.

We have carried out ion transport experiments with Cs^+ ions, using the bridged calixarenes **18–26** as carrier molecules. The experimental device was constructed in close analogy to that described by Izatt, and the experimental procedure also closely followed his prescription. A transport rate of $(437 \pm 83) \times 10^{-8}$ mol s^{-1} m^{-2} found for *p-tert*-butylcalix[4]arene [$(260 \pm 90) \times 10^{-8}$ mol s^{-1} m^{-2} was reported by Izatt] justifies a comparison of the results.

In Figure 2 the transport rate is plotted versus the number of carbon atoms in the connecting chain. A sharp maximum is observed for n = 8, corresponding to the value for *p-tert*-butylcalix[4]arene. This value is reached again for molecules with longer chains (n = 14, 16). In our opinion these results cannot be understood by complexation via Cs^+–oxygen interactions. The slight distortion of the cyclic array of hydroxy groups in compounds with n < 8 shown by X-ray analysis and ^1H NMR spectra at least could account for the low transport rates of the compounds with short bridges, although the large difference for n = 7 and n = 8 remains surprising. For n > 8 however, the geometrical arrangement of the OH groups is obviously undisturbed as in free calixarenes, and differences in the complexation ability would not be expected if the cation is held near the phenoxide group.

If the Cs^+ ion is thought to be inside the cavity, surrounded by the partly negatively charged aromatic residues, it may be that any slight deviation of its ideal size relationship with the cavity for n = 8 leads to a sharp decrease in the transport ability. For n < 8, this deviation may be caused by the smaller distance between the phenolic rings A and C, connected by the aliphatic chain. For n = 9, 10, and 12, preferred conformations of the chain may interfer with the complexation of Cs^+ in the cavity, and thus the transport rate for unbridged calixarenes is obtained again only for long chains.

It must be underlined that the transport rate is influenced by many factors,[29] e.g., by the rates of complexation and decomplexation, and that the structure of a complex cannot be derived from these measurements. If any conclusion should be drawn, however, it is in favor of complexation inside the cavity. Experiments are in progress to construct bridged calixarenes with additional donor groups in the bridge to support cation complexation within the cavity.

Experimental Section

X-Ray Studies. The crystallographic data together with the characteristic criteria of the least-squares refinement for the three compounds **19, 27,** and **30** are given in Table I. The crystals were sealed in Lindemann glass capillary tubes; 25 reflections with 2θ > 10° (for compounds **27** and **30**), respectively, 2θ > 20° (for compound **19**) were used for the cell refinement; one standard reflection; reflections with $I > \sigma(I)$ were used for structure analysis, Nicolet R 3 computer-controlled diffractometer; $2\theta/\theta$ scan; $2\theta_{max}$ = 56°; [λ(Mo Kα) = 0.7107 Å, T = 295 K] speed of measurement 3–20 ° min^{-1}; no correction for absorption or extinction. The phase problem was solved by direct methods. The least-squares parameter refinement was performed by the cascade method.[31] All non-hydrogen atoms in compounds **19** and **27** could be refined with anisotropic temperature coefficients. In compound **30** it was not possible to determine all the atoms of the connecting aliphatic chain and of the *tert*-butyl groups unambigously. For the two other compounds, however, we succeeded in determining the hydrogen position on the oxygen atoms from a difference Fourier synthesis of the electron density. The coordinates of the other hydrogen atoms resulted from a model with idealized geometry (C–H, 0.96 Å). All calculations were performed with a Nova 3/12 computer and SHELXTL.[31] The scattering factors were taken from ref 32.

Ion Transport. The experimental device was constructed exactly as described by Izatt, and the experiments were carried out in close analogy (source phase 0.8 mL of 1 M CsOH solution, receiving phase 5 mL of water, membrane phase 10^{-3} M carrier in CH_2Cl_2/CCl_4 25/75, 24 h at 25 °C, 114 rpm). The Cs^+ ion concentration in the receiving phase was determined three times for each experiment by atomic emission spectroscopy at 852.1 nm with a Perkin-Elmer AAS 2280. The values reported for the ion flux in Figure 2 are the average of six independent transport experiments. Experiments performed in which no carrier was present in the membrane showed cation fluxes to be less than 3 × 10^8 mol s^{-1} m^{-2}.

Spectral Data. ^1H NMR spectra were recorded on a Bruker AC 200 (200 MHz), using 2.5 × 10^{-3} M solutions in $CDCl_3$. Chemical shifts are reported as δ values relative to tetramethylsilane as an internal standard. IR spectra were recorded from KBr pellets (2 mg of substance/200 mg of KBr) on a Perkin-Elmer 597. Electron impact mass spectra were recorded on a CH 7 A Varian MAT, at 70 eV. Besides the molecular ion, only the most characteristic peaks are reported.

Preparations. α,ω-(*p*-Hydroxyphenyl)alkanes were prepared starting with dicarboxylic acid dichlorides by Friedel–Crafts acylation of anisole, followed by Wolff–Kishner reduction and ether cleavage as described elsewhere. Bis(bromomethyl)phenols were prepared either by direct bromomethylation or via the corresponding bishydroxymethylated phenols.

The melting points reported are uncorrected. Values higher than 200 °C were determined in sealed capillary tubes under argon and all other melting points in the usual way.

All compounds were checked for purity by thin-layer chromatography on silica gel plates of 0.25-mm thickness (E. Merck, 70–230 mesh ASTM). For flash chromatography, silica gel (E. Merck, 230–400 mesh ASTM) was used in columns of 15–40 mm in diameter filled to a height of ~20 cm.

The values of the elemental analyses of bridged calixarenes sometimes show deviations somewhat greater than the usual experimental error, the total sum of C, H, and O being less than 100%. This phenomenon, which is often observed in calixarene chemistry, cannot be explained entirely by solvent inclusion, since the deviation was also found for those samples where X-ray analysis and ^1H NMR spectra proved the compound to be free of solvent.

General Procedure for the Preparation of Bridged Calix[4]arenes. A solution of 5 mmol of the α,ω-(*p*-hydroxyphenyl)alkane, 10 mmol of the para-substituted 2,6-bis(bromomethyl)phenol, and 24 mmol $TiCl_4$ in 500 mL of dry dioxane was heated with stirring under argon to 100 °C (bath temperature) for 30–144 h. After the reaction was complete (the disappearance of the diphenol was controlled by TLC), the dark red solution was evaporated; the residue was dissolved in 150–200 mL of CH_2Cl_2, and, after the addition of 50 g of silica gel, the resultant mixture was evaporated again. The silica gel was extracted for 24 h with CH_2Cl_2 in a Soxhlet apparatus. This procedure, which removes most of the oligomeric and polymeric byproducts and the titanium complexes, was usually repeated. The crude product thus obtained was separated and purified by

(29) Behr, J.-P.; Kirch, M.; Lehn, J.-M. *J. Am. Chem. Soc.* **1985**, *107*, 241.

(30) Detailed FT-IR studies in solution are in progress; the principal results are shown already by the measurements with KBr pellets.

(31) Sheldrick, G. M. *SHELXTL, An Integrated System for Solving, Refining and Displaying Crystal Structures from Diffraction Data*; University of Göttingen: Göttingen, 1983.

(32) *International Tables for X-Ray Crystallography*; Kynoch: Birmingham, 1974; Vol. IV.

flash chromatography with different solvents. Further details are given for the individual compounds.

11,23-Dimethyl-5,17-pentano-25,26,27,28-tetrahydroxycalix[4]arene (18): 1.92 g (7.5 mmol) of **1**, 4.41 g (15 mmol) of **10**, 6.84 g (36 mmol) of TiCl$_4$, 120 h. Purification by flash chromatography with CHCl$_3$ and CCl$_4$ and recrystallization from acetone gave 510 mg (13.1%) of colorless crystals: mp 268 °C; ^{1}H NMR (CDCl$_3$, 200 MHz) δ 6.93 (s, 2 H, ArOH), 6.91 (s, 4 H, ArH), 6.87 (s, 2 H, ArOH), 6.27 (s, 4 H, ArH), 4.10 (d, 4 H, ArCH_AH$_B$Ar, J_{AB} = 14.4 Hz), 3.27 (d, 4 H, ArCH$_A$$H_B$Ar, J_{AB} = 14.4 Hz), 2.31 (s, 6 H, CH_3), 2.17 (br t, 4 H, ArCH_2), 0.94 (m, 4 H, CH_2), -0.51 (m, 2 H, CH_2); mass spectrum, *m/e* 520 (M$^+$, 100), 502 (18), 260 (16), 133 (13), 121 (15); IR (KBr) 3410 (ν_{OH}), 3010, 2920, 2850 (ν_{CH}), 1600 ($\nu_{C=C}$), 1475, 1445 (ν_{CH}) cm^{-1}. Anal. Calcd for C$_{35}$H$_{36}$O$_4$: C, 80.74; H, 6.97; O, 12.29. Found: C, 80.47; H, 7.01; O, 12.10.

11,23-Dimethyl-5,17-hexano-25,26,27,28-tetrahydroxycalix[4]arene (19): 1.35 g (5 mmol) of **2**, 2.94 g (10 mmol) of **10**, 4.56 g (24 mmol) of TiCl$_4$, 72 h. Purification by flash chromatography (CH$_2$Cl$_2$/CCl$_4$, 1:1) and recrystallization from acetone and methanol gave 244 mg (9.1%) of colorless crystals: mp 268–270 °C; ^{1}H NMR (CDCl$_3$, 200 MHz) δ 7.89 (s, 2 H, ArOH), 7.73 (s, 2 H, ArOH), 6.91 (s, 4 H, ArH), 6.42 (s, 4 H, ArH), 4.11 (d, 4 H, ArCH_AH$_B$Ar, J_{AB} = 14.2 Hz), 3.31 (d, 4 H, Ar-CH$_A$$H_B$Ar, J_{AB} = 14.2 Hz), 2.29 (s, 6 H, CH_3), 2.12 (m, 4 H, ArCH_2), 0.90 (m, 4 H, CH_2), 0.05 (m, 4 H, CH_2); mass spectrum, *m/e* 534 (M$^+$, 100), 516 (10), 267 (14), 121 (11); IR (KBr) 3340 (ν_{OH}), 3010, 2920, 2850 (ν_{CH}), 1610 ($\nu_{C=C}$), 1480, 1450 (ν_{CH}) cm^{-1}. Anal. Calcd for C$_{36}$H$_{38}$O$_4$: C, 80.87; H, 7.16. Found: C, 80.22; H, 7.12.

11,23-Dimethyl-5,17-heptano-25,26,27,28-tetrahydroxycalix[4]arene (20): 2.13 g (7.5 mmol) of **3**, 4.41 g (15 mmol) of **10**, 6.84 g (36 mmol) of TiCl$_4$, 96 h. Purification by flash chromatography with CHCl$_3$ and CCl$_4$ and recrystallization from acetone gave 510 mg (12.4%) of colorless crystals: mp 270 °C; ^{1}H NMR (CDCl$_3$, 200 MHz) δ 8.65 (s, 2 H, ArOH), 8.47 (s, 2 H, ArOH), 6.89 (s, 4 H, ArH), 6.53 (s, 4 H, ArH), 4.13 (d, 4 H, ArCH_AH$_B$Ar, J_{AB} = 14.0 Hz), 3.33 (d, 4 H, ArCH$_A$$H_B$Ar, J_{AB} = 14.0 Hz), 2.26 (t, 4 H, ArCH_2), 2.24 (s, 6 H, CH_3), 1.02 (m, 4 H, CH_2), 0.41 (m, 2 H, CH_2), -0.13 (m, 4 H, CH_2); mass spectrum, *m/e* 548 (M$^+$, 100), 530 (7), 274 (12), 133 (15), 121 (19); IR (KBr) 3250 (ν_{OH}), 3010, 2920, 2850 (ν_{CH}), 1600 ($\nu_{C=C}$), 1480, 1450 (ν_{CH}) cm^{-1}. Anal. Calcd for C$_{37}$H$_{40}$O$_4$: C, 80.99; H, 7.35; O, 11.66. Found: C, 80.39; H, 7.39; O, 10.90.

11,23-Dimethyl-5,17-octano-25,26,27,28-tetrahydroxycalix[4]arene (21): 1.49 g (5 mmol) of **4**, 2.94 g (10 mmol) of **10**, 4 g (21 mmol) of TiCl$_4$, 30 h. Purification by flash chromatography (CH$_2$Cl$_2$) and recrystallization from acetone gave 565 mg (20.1%) of colorless crystals: mp 278–280 °C; ^{1}H NMR (CDCl$_3$, 200 MHz) δ 9.11 (br s, 2 H, ArOH), 9.00 (br s, 2 H, ArOH), 6.88 (s, 4 H, ArH), 6.61 (s, 4 H, ArH), 4.15 (d, 4 H, ArCH_AH$_B$Ar, J_{AB} = 13.8 Hz), 3.35 (d, 4 H, ArCH$_A$$H_B$Ar, J_{AB} = 13.8 Hz), 2.35 (br t, 4 H, ArCH_2), 2.22 (s, 6 H, CH_3), 1.13 (m, 4 H, CH_2), 0.48 (m, 4 H, CH_2), 0.08 (m, 4 H, CH_2); mass spectrum, *m/e* 562 (M$^+$, 100), 544 (8), 281 (10), 121 (12); IR (KBr) 3250 (ν_{OH}), 3010, 2920, 2850 (ν_{CH}), 1610 ($\nu_{C=C}$), 1485, 1460 (ν_{CH}) cm^{-1}. Anal. Calcd for C$_{38}$H$_{42}$O$_4$: C, 81.10; H, 7.52. Found: C, 81.07; H, 7.43.

11,23-Dimethyl-5,17-nonano-25,26,27,28-tetrahydroxycalix[4]arene (22): 1.56 g (5 mmol) of **5**, 2.94 g (10 mmol) of **10**, 4 g (21 mmol) of TiCl$_4$, 100 h. Purification by flash chromatography with CH$_2$Cl$_2$ and CHCl$_3$/CCl$_4$ (1:3) and recrystallization from acetone gave 268 mg (9.3%): mp 349–351 °C; ^{1}H NMR (CDCl$_3$, 200 MHz) δ 9.53 (s, 4 H, ArOH), 6.85 (s, 4 H, ArH), 6.72 (s, 4 H, ArH), 4.13 (d, 4 H, Ar-CH$_A$H$_B$Ar, J_{AB} = 13.8 Hz), 3.37 (d, 4 H, ArCH$_A$$H_B$Ar, J_{AB} = 13.8 Hz), 2.36 (br t, 4 H, ArCH_2), 2.16 (s, 6 H, CH_3), 1.25 (m, 4 H, CH_2), 0.51 (m, 4 H, CH_2), 0.20 (m, 4 H, CH_2), 0.02 (m, 2 H, CH_2); mass spectrum, *m/e* 576 (M$^+$, 100), 558 (8), 288 (11), 121 (11); IR (KBr) 3210 (ν_{OH}), 3010, 2930, 2850 (ν_{CH}), 1610 ($\nu_{C=C}$), 1480, 1460 (ν_{CH}) cm^{-1}. Anal. Calcd for C$_{39}$H$_{44}$O$_4$: C, 81.21; H, 7.69. Found: C, 80.92; H, 7.80.

11,23-Dimethyl-5,17-decano-25,26,27,28-tetrahydroxycalix[4]arene (23): 1.63 g (5 mmol) of **6**, 2.94 g (10 mmol) of **10**, 4.56 g (24 mmol) of TiCl$_4$, 52 h. Purification by flash chromatography (CH$_2$Cl$_2$) and recrystallization from acetone gave 253 mg (8.6%) of a white, microcrystalline product: mp 340–342 °C; ^{1}H NMR (CDCl$_3$, 200 MHz) δ 9.72 (s, 4 H, ArOH), 6.82 (s, 4 H, ArH), 6.75 (s, 4 H, ArH), 4.18 (d, 4 H, ArCH_AH$_B$Ar, J_{AB} = 13.7 Hz), 3.37 (d, 4 H, ArCH$_A$$H_B$Ar, J_{AB} = 13.7 Hz), 2.42 (br t, 4 H, ArCH_2), 2.12 (s, 6 H, CH_3), 1.25 (m, 4 H, CH_2), 0.57 (m, 8 H, CH_2), 0.34 (m, 4 H, CH_2); mass spectrum, *m/e* 590 (M$^+$, 100), 572 (9), 295 (5), 135 (23), 133 (20), 121 (38); IR (KBr) 3190 (ν_{OH}), 3010, 2925, 2850 (ν_{CH}), 1610 ($\nu_{C=C}$), 1480, 1460 (ν_{CH}) cm^{-1}. Anal. Calcd for C$_{40}$H$_{46}$O$_4$: C, 81.32; H, 7.85. Found: C, 78.63, 78.81; H, 7.62, 7.97.

11,23-Dimethyl-5,17-dodecano-25,26,27,28-tetrahydroxycalix[4]arene (24): 2.66 g (7.5 mmol) of **7**, 4.41 g (15 mmol) of **10**, 6.84 g (36 mmol) of TiCl$_4$, 120 h. Purification by flash chromatography with CH$_2$Cl$_2$ and

recrystallization from acetone gave 113 mg (2.4%) of colorless crystals: mp 343–344 °C dec; ^{1}H NMR (CDCl$_3$, 200 MHz) δ 10.00 (s, 4 H, ArOH), 6.82 (s, 4 H, ArH), 6.81 (s, 4 H, ArH), 4.24 (d, 4 H, ArCH_AH$_B$Ar, J_{AB} = 13.8 Hz), 3.40 (d, 4 H, ArCH$_A$$H_B$Ar, J_{AB} = 13.8 Hz), 2.45 (br t, 4 H, ArCH_2), 2.10 (s, 6 H, CH_3), 1.41 (m, 4 H, CH_2), 0.91 (m, 8 H, CH_2), 0.69 (m, 4 H, CH_2), 0.40 (m, 4 H, CH_2); mass spectrum, *m/e* 618 (M$^+$, 100), 600 (5), 309 (5), 135 (14), 133 (10), 121 (20); IR (KBr) 3165 (ν_{OH}), 3010, 2930, 2850 (ν_{CH}), 1610 ($\nu_{C=C}$), 1480, 1460 (ν_{CH}) cm^{-1}. Anal. Calcd for C$_{42}$H$_{50}$O$_4$: C, 81.51; H, 8.14. Found: C, 79.78, 79.41; H, 8.22, 8.24.

11,23-Dimethyl-5,17-tetradecano-25,26,27,28-tetrahydroxycalix[4]arene (25): 1.91 g (5 mmol) of **8**, 2.94 g (10 mmol) of **10**, 4 g (21 mmol) of TiCl$_4$, 41 h. Purification by flash chromatography (CH$_2$Cl$_2$) and recrystallization from acetone and ethanol gave 298 mg (9.2%) of a microcrystalline product: mp 338–339 °C; ^{1}H NMR (CDCl$_3$, 200 MHz) δ 10.19 (s, 4 H, ArOH), 6.83 (s, 4 H, ArH), 6.82 (s, 4 H, ArH), 4.19 (d, 4 H, ArCH_AH$_B$Ar, J_{AB} = 13.8 Hz), 3.41 (d, 4 H, ArCH$_A$$H_B$Ar, J_{AB} = 13.8 Hz), 2.41 (br t, 4 H, ArCH_2), 2.10 (s, 6 H, CH_3), 1.33–1.09 (m, 24 H, CH_2); mass spectrum, *m/e* 646 (M$^+$, 100), 628 (10), 323 (3), 135 (23), 133 (14), 121 (30); IR (KBr) 3165 (ν_{OH}), 3010, 2930, 2850 (ν_{CH}), 1610 ($\nu_{C=C}$), 1480, 1460 (ν_{CH}) cm^{-1}. Anal. Calcd for C$_{44}$H$_{54}$O$_4$: C, 81.69; H, 8.41. Found: C, 77.38, 77.36; H, 7.89, 7.85.

11,23-Dimethyl-5,17-hexadecano-25,26,27,28-tetrahydroxycalix[4]arene (26): 2.05 g (5 mmol) of **9**, 2.94 g (10 mmol) of **10**, 4.56 g (24 mmol) of TiCl$_4$, 96 h. Purification by flash chromatography with CH$_2$Cl$_2$, CCl$_4$, and CHCl$_3$/CCl$_4$ (1:4) and recrystallization from acetone gave 94 mg (2.8%) of colorless crystals: mp 333–334 °C dec; ^{1}H NMR (CDCl$_3$, 200 MHz) δ 10.18 (s, 4 H, ArOH), 6.87 (s, 4 H, ArH), 6.81 (s, 4 H, ArH), 4.20 (d, 4 H, ArCH_AH$_B$Ar, J_{AB} = 13.8 Hz), 3.41 (d, 4 H, ArCH$_A$$H_B$Ar, J_{AB} = 13.8 Hz), 2.44 (br t, 4 H, ArCH_2), 2.10 (s, 6 H, CH_3), 1.44–1.13 (m, 28 H, CH_2); mass spectrum, *m/e* 674 (M$^+$, 100), 656 (10), 337 (3), 135 (30), 133 (19), 121 (40); IR (KBr) 3180 (ν_{OH}), 3010, 2930, 2850 (ν_{CH}), 1610 ($\nu_{C=C}$), 1480, 1460 (ν_{CH}) cm^{-1}. Anal. Calcd for C$_{46}$H$_{58}$O$_4$: C, 81.86; H, 8.66; O, 9.48. Found: C, 80.94; H, 8.73; O, 9.06.

11,23-Di-*tert*-butyl-5,17-hexano-25,26,27,28-tetrahydroxycalix[4]arene (27): 2.03 g (7.5 mmol) of **2**, 5.04 g (15 mmol) of **14**, 6.84 g (36 mmol) of TiCl$_4$, 98 h. Purification by flash chromatography with CH$_2$Cl$_2$, CH$_2$Cl$_2$/CCl$_4$ (1:2), and CH$_2$Cl$_2$/CCl$_4$ (1:2) and recrystallization from acetone gave 492 mg (10.6%) of colorless crystals: mp 314–316 °C; ^{1}H NMR (CDCl$_3$, 200 MHz) δ 7.98 (s, 2 H, ArOH), 7.82 (s, 2 H, ArOH), 7.11 (s, 4 H, ArH), 6.41 (s, 4 H, ArH), 4.15 (d, 4 H, ArCH_AH$_B$Ar, J_{AB} = 14.1 Hz), 3.35 (d, 4 H, ArCH$_A$$H_B$Ar, J_{AB} = 14.1 Hz), 2.09 (m, 4 H, ArCH_2), 1.32 (s, 18 H, C$_4$H$_9$), 0.83 (m, 4 H, CH_2), -0.06 (m, 4 H, CH_2); mass spectrum, *m/e* 618 (M$^+$, 100), 600 (8), 562 (17), 506 (7), 121 (11); IR (KBr) 3470, 3350 (ν_{OH}), 3010, 2950, 2920, 2850 (ν_{CH}), 1610 ($\nu_{C=C}$), 1485, 1475, 1450 (ν_{CH}) cm^{-1}. Anal. Calcd for C$_{42}$H$_{50}$O$_4$: C, 81.51; H, 8.14. Found: C, 81.48; H, 8.13.

11,23-Di-*tert*-butyl-5,17-octano-25,26,27,28-tetrahydroxycalix[4]arene (28): 1.49 g (5 mmol) of **4**, 3.36 g (10 mmol) of **14**, 4.56 g (24 mmol) of TiCl$_4$, 30 h. Purification by flash chromatography with CHCl$_3$ and CCl$_4$ and recrystallization from acetone gave 235 mg (7.3%) of colorless crystals: mp 378–380 °C; ^{1}H NMR (CDCl$_3$, 200 MHz) δ 9.17 (br s, 2 H, ArOH), 9.06 (br s, 2 H, ArOH), 7.08 (s, 4 H, ArH), 6.63 (s, 4 H, ArH), 4.19 (d, 4 H, ArCH_AH$_B$Ar, J_{AB} = 13.7 Hz), 3.39 (d, 4 H, Ar-CH$_A$$H_B$Ar, J_{AB} = 13.7 Hz), 2.33 (br t, 4 H, ArCH_2), 1.26 (s, 18 H, C$_4$H$_9$), 1.10 (m, 4 H, CH_2), 0.46 (m, 4 H, CH_2), -0.01 (m, 4 H, CH_2); mass spectrum, *m/e* 646 (M$^+$, 100), 628 (2), 590 (11), 534 (14), 308 (14); IR (KBr) 3240 (ν_{OH}), 3020, 2960, 2920, 2850 (ν_{CH}), 1600 ($\nu_{C=C}$), 1480, 1490 (ν_{CH}) cm^{-1}. Anal. Calcd for C$_{44}$H$_{54}$O$_4$: C, 81.69; H, 8.41. Found: C, 81.85; H, 8.67.

11,23-Di-*tert*-butyl-5,17-dodecano-25,26,27,28-tetrahydroxycalix[4]arene (29): 2.66 g (7.5 mmol) of **7**, 5.04 g (15 mmol) of **14**, 6.84 g (36 mmol) of TiCl$_4$, 72 h. Purification by flash chromatography with CH$_2$Cl$_2$ and CH$_2$Cl$_2$/CCl$_4$ (1:4) and recrystallization from acetone gave 199 mg (3.8%) of slightly yellow crystals: mp 329–330 °C; ^{1}H NMR (CDCl$_3$, 200 MHz) δ 10.01 (s, 4 H, ArOH), 7.00 (s, 4 H, ArH), 6.82 (s, 4 H, ArH), 4.23 (d, 4 H, ArCH_AH$_B$Ar, J_{AB} = 12.9 Hz), 3.45 (d, 4 H, Ar-CH$_A$$H_B$Ar, J_{AB} = 12.9 Hz), 2.44 (br t, 4 H, ArCH_2), 1.34 (m, 4 H, CH_2), 1.16 (s, 18 H, C$_4$H$_9$), 0.89 (m, 8 H, CH_2), 0.64 (m, 8 H, CH_2); mass spectrum, *m/e* 702 (M$^+$, 100), 684 (3), 646 (14), 590 (4), 161 (11), 147 (11), 121 (18); IR (KBr) 3170 (ν_{OH}), 3020, 2930, 2850 (ν_{CH}), 1610 ($\nu_{C=C}$), 1480, 1460 (ν_{CH}) cm^{-1}. Anal. Calcd for C$_{48}$H$_{62}$O$_4$: C, 82.01; H, 8.89. Found: C, 80.08, 80.16; H, 8.72, 8.75.

11,23-Di-*tert*-butyl-5,17-hexadecano-25,26,27,28-tetrahydroxycalix[4]arene (30): 3.08 g (7.5 mmol) of **9**, 5.04 g (15 mmol) of **14**, 6.84 g (36 mmol) of TiCl$_4$, 72 h. Purification by flash chromatography with CH$_2$Cl$_2$ and CH$_2$Cl$_2$/CCl$_4$ (1:4) and recrystallization from acetone gave 430 mg (7.6%) of colorless crystals: mp 337–338 °C; ^{1}H NMR (CDCl$_3$, 200 MHz) δ 10.36 (s, 4 H, ArOH), 7.04 (s, 4 H, ArH), 6.86 (s, 4 H,

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ArH), 4.24 (d, 4 H, ArCH$_A$H$_B$Ar, J$_{AB}$ = 13.9 Hz), 3.46 (d, 4 H, Ar-CH$_A$H$_B$Ar, J$_{AB}$ = 13.9 Hz), 2.43 (m, 4 H, ArCH$_2$), 1.43 (m, 4 H, CH$_2$), 1.22, 1.10 (s, m, 42 H, C$_4$H$_9$, (CH$_2$)$_{12}$); mass spectrum, m/e 758 (M$^+$, 100), 740 (4), 700 (14), 643 (7), 121 (19); IR (KBr) 3200 (ν_{OH}), 3010, 2925, 2850 (ν_{CH}), 1600 ($\nu_{C=C}$), 1480, 1475 (ν_{CH}) cm^{-1}. Anal. Calcd for C$_{52}$H$_{70}$O$_4$: C, 82.27; H, 9.29. Found: C, 81.24; H, 8.16.

11,23-Dioctyl-5,17-octano-25,26,27,28-tetrahydroxycalix[4]arene (31): 1.49 g (5 mmol) of 4, 3.92 g (10 mmol) of 11, 4.56 g (24 mmol) of TiCl$_4$, 68 h. Purification by flash chromatography with CHCl$_3$, CH$_2$Cl$_2$, and CHCl$_3$/CCl$_4$ (1:1) and recrystallization from acetone gave 275 mg (7.3%) of colorless needles: mp 101–102 °C; ^{1}H NMR (CDCl$_3$, 200 MHz) δ 9.17 (br s, 2 H, ArOH), 9.04 (br s, 2 H, ArOH) 6.88 (s, 4 H, ArH), 6.62 (s, 4 H, ArH), 4.16 (d, 4 H, ArCH$_A$H$_B$Ar, J$_{AB}$ = 13.8 Hz), 3.37 (d, 4 H, ArCH$_A$H$_B$Ar, J$_{AB}$ = 13.8 Hz), 2.46 (t, 4 H, ArCH$_2$), 2.33 (br t, 4 H, ArCH$_2$), 1.47 (m, 4 H, CH$_2$), 1.26 (br m, 20 H, (CH$_2$)$_5$CH$_3$), 1.12 (m, 4 H, CH$_2$), 0.87 (t, 6 H, CH$_3$), 0.49 (m, 4 H, CH$_2$), 0.05 (m, 4 H, CH$_2$); mass spectrum, m/e 758 (M$^+$, 100), 740 (4), 379 (5), 135 (12), 133 (7), 121 (20); IR (KBr) 3210 (ν_{OH}), 3000, 2920, 2840 (ν_{CH}), 1610 ($\nu_{C=C}$), 1480, 1460 (ν_{CH}) cm^{-1}. Anal. Calcd for C$_{52}$H$_{70}$O$_4$: C, 82.27; H, 9.29. Found C, 82.49; H, 9.21.

11,23-Didodecyl-5,17-octano-25,26,27,28-tetrahydroxycalix[4]arene (32): 1.49 g (5 mmol) of 4, 4.48 g (10 mmol) of 12, 4.56 g (24 mmol) of TiCl$_4$, 49 h. Purification by flash chromatography with CCl$_4$ and CH$_2$Cl$_2$/CCl$_4$ (1:2) and recrystallization from ethanol gave 313 mg (7.2%) of colorless needles: mp 59 °C; ^{1}H NMR (CDCl$_3$, 200 MHz) δ 9.15 (br s, 2 H, ArOH), 9.04 (br s, 2 H, ArOH) 6.88 (s, 4 H, ArH), 6.62 (s, 4 H, ArH), 4.16 (d, 4 H, ArCH$_A$H$_B$Ar, J$_{AB}$ = 13.8 Hz), 3.36 (d, 4 H, ArCH$_A$H$_B$Ar, J$_{AB}$ = 13.8 Hz), 2.46 (t, 4 H, ArCH$_2$), 2.33 (br t, 4 H, ArCH$_2$), 1.47 (m, 4 H, CH$_2$), 1.25 (br m, 36 H, (CH$_2$)$_9$CH$_3$), 1.12 (m, 4 H, CH$_2$), 0.87 (t, 6 H, CH$_3$), 0.49 (m, 4 H, CH$_2$), 0.05 (m, 4 H, CH$_2$); mass spectrum, m/e 870 (M$^+$, 100), 852 (3), 435 (3), 135 (22), 121 (29); IR (KBr) 3250 (ν_{OH}), 3010, 2920, 2850 (ν_{CH}), 1610 ($\nu_{C=C}$), 1480, 1460 (ν_{CH}) cm^{-1}. Anal. Calcd for C$_{60}$H$_{86}$O$_4$: C, 82.71; H, 9.95; O, 7.34. Found: C, 82.59; H, 9.98; O, 6.40.

11,23-Dicyclohexyl-5,17-octano-25,26,27,28-tetrahydroxycalix[4]arene (33): 1.49 g (5 mmol) of 4, 3.62 g (10 mmol) of 15, 4.56 g (24 mmol) of TiCl$_4$, 96 h. Purification by flash chromatography (CH$_2$Cl$_2$) and recrystallization from acetone gave 140 mg (4.0%) of colorless crystals: mp 266–268 °C. ^{1}H NMR (CDCl$_3$, 200 MHz) δ 9.14 (br s, 2 H, ArOH), 9.04 (br s, 2 H, ArOH), 6.90 (s, 4 H, ArH), 6.62 (s, 4 H, ArH), 4.16 (d, 4 H, ArCH$_A$H$_B$Ar, J$_{AB}$ = 13.8 Hz), 3.37 (d, 4 H, ArCH$_A$H$_B$Ar, J$_{AB}$ = 13.8 Hz), 2.34 (m, 4 H + 2 H, ArCH$_2$ + ArCH), 1.76 (m, 10 H, cyclohexyl), 1.33 (m, 10 H, cyclohexyl), 1.11 (m, 4 H, CH$_2$), 0.44 (m, 4 H, CH$_2$), 0.01 (m, 4 H, CH$_2$); mass spectrum, m/e 698 (M$^+$, 100), 680 (5), 615 (20), 533 (2), 121 (11); IR (KBr) 3250 (ν_{OH}), 3010, 2920, 2850 (ν_{CH}), 1610 ($\nu_{C=C}$), 1480, 1460 (ν_{CH}) cm^{-1}. Anal. Calcd for C$_{48}$H$_{58}$O$_4$: C, 82.48; H, 8.36. Found: C, 82.69; H, 8.34.

11,23-Diphenyl-5,17-octano-25,26,27,28-tetrahydroxycalix[4]arene (34): 1.49 g (5 mmol) of 4, 3.56 g (10 mmol) of 16, 4.56 g (24 mmol) of TiCl$_4$, 98 h. Purification by flash chromatography with CH$_2$Cl$_2$, CH$_2$Cl$_2$/CCl$_4$ (1:3), and CHCl$_3$/CCl$_4$ (1:2) and recrystallization from ethanol gave 60 mg (1.7%) of yellowish prisms: mp 256 °C; ^{1}H NMR (CDCl$_3$, 200 MHz) δ 9.40 (br s, 2 H, ArOH), 8.92 (br s, 2 H, ArOH), 7.52–7.25 (m, 10 H, phenyl), 7.31 (s, 4 H, ArH), 6.68 (s, 4 H, ArH), 4.25 (d, 4 H, ArCH$_A$H$_B$Ar, J$_{AB}$ = 14.0 Hz), 3.50 (d, 4 H, ArCH$_A$H$_B$Ar, J$_{AB}$ = 14.0 Hz), 2.33 (br t, 4 H, ArCH$_2$), 1.09 (m, 4 H, CH$_2$), 0.40 (m, 4 H, CH$_2$), 0.05 (m, 4 H, CH$_2$); mass spectrum, m/e 686 (M$^+$, 100), 668 (6), 343 (16); IR (KBr) 3240 (ν_{OH}), 3020, 2920, 2850 (ν_{CH}), 1600 ($\nu_{C=C}$), 1475, 1455 (ν_{CH}). Anal. Calcd for C$_{48}$H$_{46}$O$_4$: C, 83.93; H, 6.75; O, 9.32. Found: C, 83.49; H, 6.83; O, 9.20.

11,23-Dichloro-5,17-octano-25,26,27,28-tetrahydroxycalix[4]arene (35): 2.24 g (7.5 mmol) of 4, 4.72 g (15 mmol) of 17, 6.84 g (36 mmol)

of TiCl$_4$, 120 h. Purification by flash chromatography with CH$_2$Cl$_2$ and CH$_2$Cl$_2$/CCl$_4$ (1:3) and recrystallization from acetone gave 507 mg (11.2%) of slightly yellow crystals: mp 291–292 °C; ^{1}H NMR (CDCl$_3$, 200 MHz) δ 9.31 (br s, 2 H, ArOH), 8.67 (br s, 2 H, ArOH), 7.08 (s, 4 H, ArH), 6.61 (s, 4 H, ArH), 4.13 (d, 4 H, ArCH$_A$H$_B$Ar, J$_{AB}$ = 14.0 Hz), 3.36 (d, 4 H, ArCH$_A$H$_B$Ar, J$_{AB}$ = 14.0 Hz), 2.35 (br t, 4 H, ArCH$_2$), 1.16 (m, 4 H, CH$_2$), 0.38 (m, 4 H, CH$_2$), 0.12 (m, 4 H, CH$_2$); mass spectrum, m/e 606/604/602 (M$^+$, 15/69/100), 304/302 (2/7); IR (KBr) 3240 (ν_{OH}), 3000, 2920, 2840 (ν_{CH}), 1610 ($\nu_{C=C}$), 1470, 1425 (ν_{CH}) cm^{-1}. Anal. Calcd for C$_{36}$H$_{36}$Cl$_2$O$_4$: C, 71.64; H, 6.01; Cl, 11.75. Found: C, 71.60; H, 5.97; Cl, 11.5.

11,23-Dichloro-5,17-dodecano-25,26,27,28-tetrahydroxycalix[4]arene (36): 2.66 g (7.5 mmol) of 7, 4.72 g (15 mmol) of 17, 6.84 g (36 mmol) of TiCl$_4$, 120 h. Purification by flash chromatography with CHCl$_3$ and CHCl$_3$/CCl$_4$ (1:10) and recrystallization from acetone gave 169 mg (3.4%) of colorless crystals: mp 337–339 °C; ^{1}H NMR (CDCl$_3$, 200 MHz) δ 9.82 (s, 4 H, ArOH), 6.97 (s, 4 H, ArH), 6.82 (s, 4 H, ArH), 4.18 (d, 4 H, ArCH$_A$H$_B$Ar, J$_{AB}$ = 14.0 Hz), 3.41 (d, 4 H, ArCH$_A$H$_B$Ar, J$_{AB}$ = 14.0 Hz), 2.45 (br t, 4 H, ArCH$_2$), 1.41 (m, 4 H, CH$_2$), 0.90 (m, 4 H, CH$_2$), 0.71 (m, 4 H, CH$_2$), 0.37 (m, 4 H, CH$_2$); mass spectrum, m/e 662/660/658 (M$^+$, 16/73/100), 121 (30); IR (KBr) 3200 (ν_{OH}), 3020, 2930, 2850, (ν_{CH}), 1610 ($\nu_{C=C}$), 1460, 1450 (ν_{CH}) cm^{-1}. Anal. Calcd for C$_{40}$H$_{44}$Cl$_2$O$_4$: C, 73.83; H, 6.72; Cl, 10.75. Found: C, 72.58; H, 6.70; Cl, 11.0.

11,23-Dioctadecyl-5,17-hexadecano-25,26,27,28-tetrahydroxycalix[4]arene (37): 2.05 g (5 mmol) of 9, 5.32 g (10 mmol) of 17, 4.56 g (24 mmol) of TiCl$_4$, 144 h. Purification by flash chromatography with CH$_2$Cl$_2$ and CCl$_4$ and recrystallization from acetone gave 116 mg (2.0%) of colorless needles: mp 134–135 °C; ^{1}H NMR (CDCl$_3$, 200 MHz) δ 10.23 (s, 4 H, ArOH), 6.86 (s, 4 H, ArH), 6.81 (s, 4 H, ArH), 4.20 (d, 4 H, ArCH$_A$H$_B$Ar, J$_{AB}$ = 13.8 Hz), 3.43 (d, 4 H, ArCH$_A$H$_B$Ar, J$_{AB}$ = 13.8 Hz), 2.43 (t, 4 H, ArCH$_2$), 2.34 (t, 4 H, ArCH$_2$), 1.46 (m, 4 H, CH$_2$), 1.25, 1.13 (2 m, 88 H, CH$_2$), 0.87 (t, 6 H, CH$_3$); mass spectrum, m/e 1151 (M$^+$, 3), 361 (28), 347 (18), 121 (100); IR (KBr) 3400, 3120 (ν_{OH}), 3000, 2920, 2845 (ν_{CH}), 1600 ($\nu_{C=C}$), 1475, 1460 (ν_{CH}) cm^{-1}. Anal. Calcd for C$_{80}$H$_{126}$O$_4$: C, 83.42; H, 11.02. Found: C, 82.90; H, 11.04.

Supplementary Material Available: Tables of atomic coordinates, anisotropic and isotropic thermal parameters, bond distances, bond angles, and torsion angles for 19, 27, and 30 (53 pages). Ordering information is given on any current masthead page.