

Cation Complexation by Chemically Modified Calixarenes. Part 6.† Alkali and Silver(I) Cation Complexation by *p*-*tert*-Butylcalix[5]arene Derivatives and X-Ray Structure Determination of a Pentaester

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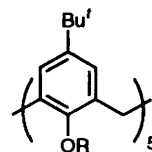
The preparation of two *p*-*tert*-butylcalix[5]arene esters and a *p*-*tert*-butylcalix[5]arene carboxylic acid are reported. The cone conformation in solution at 20 °C has been established for all three compounds by ¹H NMR spectroscopy. Crystals of pentaethyl ester **2** were studied by X-ray diffraction and the molecule was found to possess a distorted cone conformation in the solid state. Crystals of **2** are triclinic, space group P $\bar{1}$, with two molecules in a cell of dimensions $a = 11.656(2)$, $b = 14.912(3)$, $c = 23.044(5)$ Å; $\alpha = 79.23(2)$, $\beta = 78.31(2)$, $\gamma = 67.52(2)$ °. The structure was solved by direct methods and refined by least squares to $R = 0.084$ for 6967 reflections. One phenolic ring (B) is tilted inwards at the upper rim of the cone; the others are tilted outwards, but by varying amounts. The pendant side-chains also adopt very different conformations, resulting in a range of inter-chain O...O distances around the cavity, from 3.35 Å upwards. The binding properties of the esters towards alkali cations have been assessed by picrate extraction experiments and stability constant determinations. The main conclusions are: (a) both pentamer esters are much more effective in extraction than either their tetramer or hexamer counterparts; (b) the nature of the alkoxy residue in the ester influences the extent of extraction, the *tert*-butyl ester being more effective than the ethyl ester; (c) extraction favours the larger cations with little discrimination between K⁺, Rb⁺, and Cs⁺; (d) the trends in extraction are mirrored in stability constants with the *tert*-butyl derivative forming the stronger complexes.

The calixarene series of [1_{*n*}]metacyclophanes, produced by condensation of *p*-substituted phenols with formaldehyde, currently extends from $n = 4$ to 14.¹ The most accessible and therefore the most extensively studied members of the series are those with $n = 4$, 6 and 8,¹⁻⁴ for which well tested synthetic procedures are now available. Procedures for producing the smaller, odd-membered calixarenes, $n = 5$ ⁵ and 7⁶ are also available, but yields tend to be very low. The *p*-*tert*-butyl-pentamer **1** can be produced in 10–12% yield in a one-pot procedure employing tetralin as the solvent.⁷

Earlier work with calix[4], [6] and [8]arenes had established that the phenolic functions could be alkylated with alkyl bromoacetates to form alkyl calixarene acetates with significant ion binding potential for (mainly) alkali metal cations.⁸⁻¹³ Subsequent work extended the series to include calixarene ketones,^{10,14} amides,¹⁵⁻¹⁸ thioamides,¹⁹ and calixcrowns,²⁰ calixspherands,²¹ and carboxylic acids,²² also with ion binding properties. The principal findings of these studies were (a) tetramer esters, ketones and amides show a clear preference for Na⁺, the *p*-*tert*-butylcalix[4]arene tetraethyl ester having a selectivity factor for Na⁺ over K⁺ in stability constant of 400 in methanol; (b) the hexamer series, reflecting the larger receptor volume relative to the tetramers, favours the larger cations K⁺, Rb⁺, Cs⁺ over Na⁺, with a preference for Cs⁺; (c) the octamer series is characterised by low extraction activity and low levels of discrimination among the alkali cations.

It became a matter of interest to determine what position pentamer derivatives occupy on this spectrum of complexation behaviour. Accordingly, two pentaesters were prepared from *p*-

tert-butylcalix[5]arene **1**,⁷ the ethyl derivative **2** and the *tert*-butyl derivative **3**. Treatment of **1** with ethyl bromoacetate and *tert*-butyl bromoacetate in acetone containing potassium carbonate furnished the esters **2** and **3**, respectively, in high yield. In each case the material isolated directly from the reaction mixture was in fact largely the K⁺ complex of the pentaester. Prolonged treatment with warm water was necessary to release each ligand. Excessive treatment with hot water, however, led to hydrolysis to the pentaacid **4**, a compound more conveniently obtained by treating either ester with sodium hydroxide in ethanol. Esters **2** and **3** were isolated as crystalline solids. Apart from differences associated with the alkoxy residue, the two esters have identical ¹H NMR spectra. The aromatic, methyleneoxy and *p*-*tert*-butyl protons appear as singlets with an AB system for the bridging methylene protons, a pattern reminiscent of a calix[4]arene in a stable cone conformation. These data suggest that these two pentaesters, when prepared by the above procedure, also possess a cone-like conformation



- 1**: R = H
2: R = CH₂CO₂Et
3: R = CH₂CO₂Bu'
4: R = CH₂CO₂H

† For Part 5 see ref. 22.

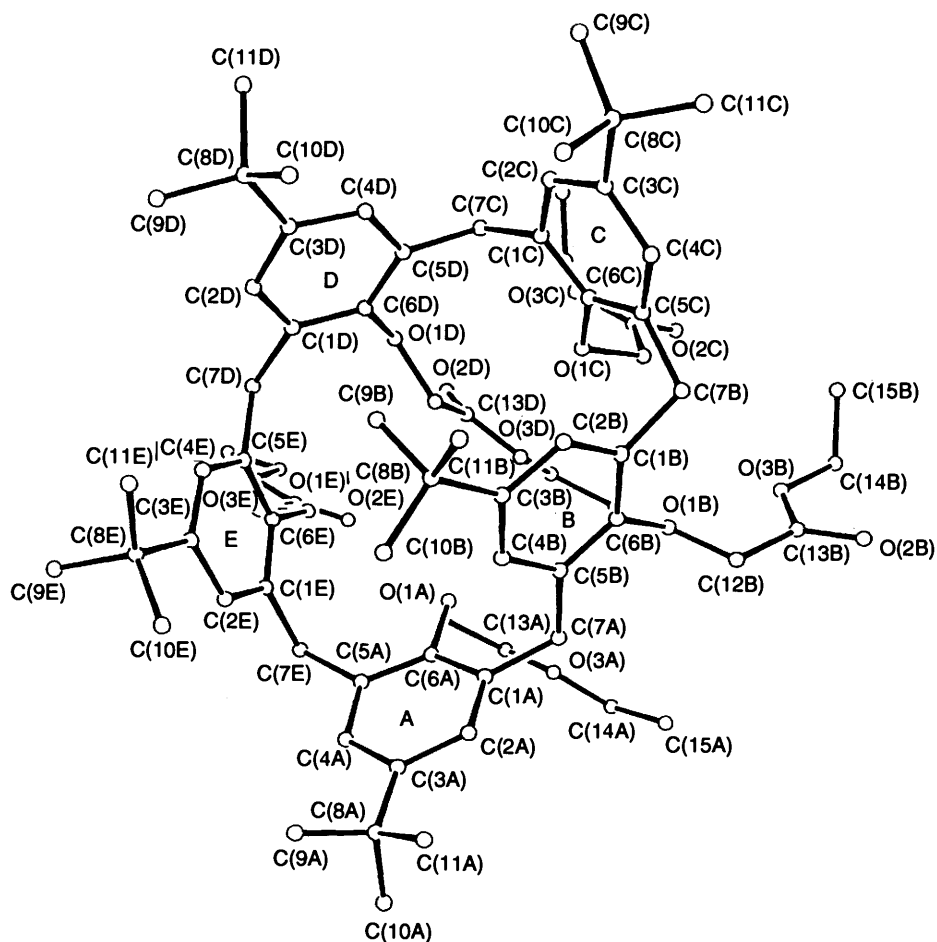


Fig. 1 A view of 2 from the upper rim

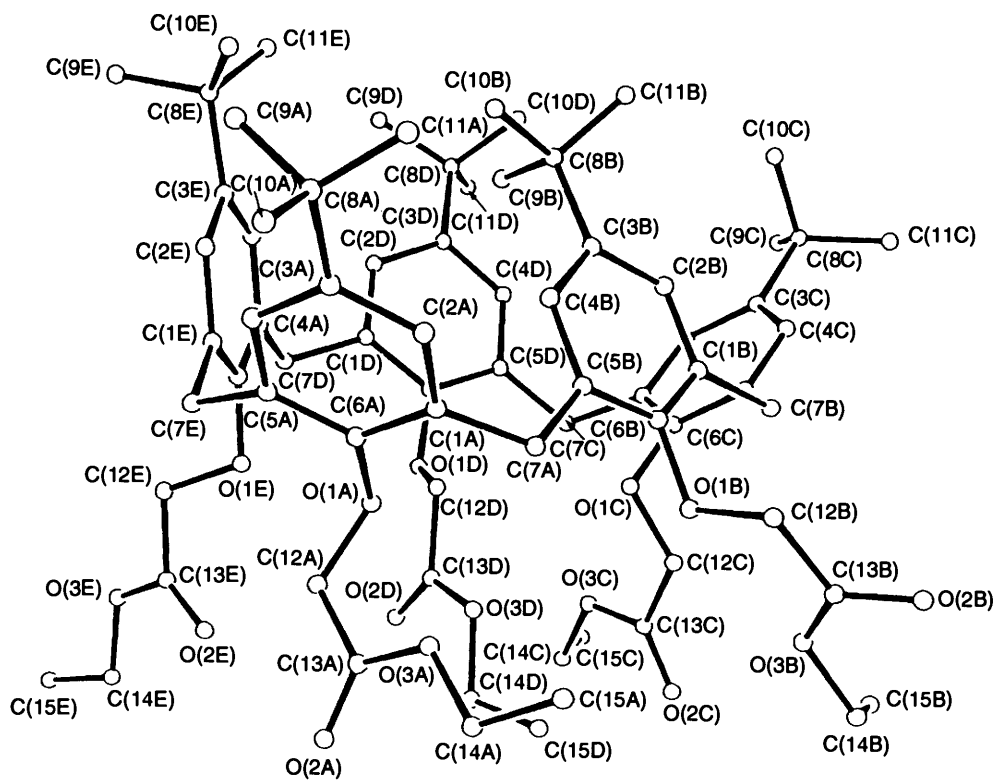


Fig. 2 A side view of 2

Table 1 Selected side-chain torsion angles ($^{\circ}$) for **2**

	A	B	C	D	E
C6–O1–C12–C13	–87.4	–145.6	–107.9	–172.0	–178.9
O1–C12–C13–O3	+15.4	–7.7	+3.1	+160.2	–155.3
C12–C13–O3–C14	+175.1	–176.9	+178.5	+177.7	+179.7
C13–O3–C14–C15	+173.8	–121.6	–115.0	+168.2	+171.3

Table 2 Percentage cation extraction^a from an aqueous neutral alkali picrate solution (2.5×10^{-4} mol dm⁻³) into dichloromethane by *p*-tert-butylcalix[n]arene esters of varying degrees of condensation (2.5×10^{-4} mol dm⁻³), at 20 $^{\circ}$ C

Cations	Li ⁺	Na ⁺	K ⁺	Rb ⁺	Cs ⁺
<i>n</i> = 5, R = CH ₂ CO ₂ Et	8	33	47	51	51
<i>n</i> = 5, R = CH ₂ CO ₂ Bu ^t	25	69	74	72	68
<i>n</i> = 4, R = CH ₂ CO ₂ Et ^c	7	29	5	4	6
<i>n</i> = 4, R = CH ₂ CO ₂ Bu ^t ^d	<i>b</i>	56	9	<i>b</i>	<i>b</i>
<i>n</i> = 6, R = CH ₂ CO ₂ Et ^e	1	3	18	16	33

^a The standard deviation σ_{N-1} on the mean value of at least $N = 3$ independent series (of 6 experiments each) range between 0.1 and 1. ^b Not measured. ^c From ref. 16. ^d From ref. 13. ^e From ref. 19.

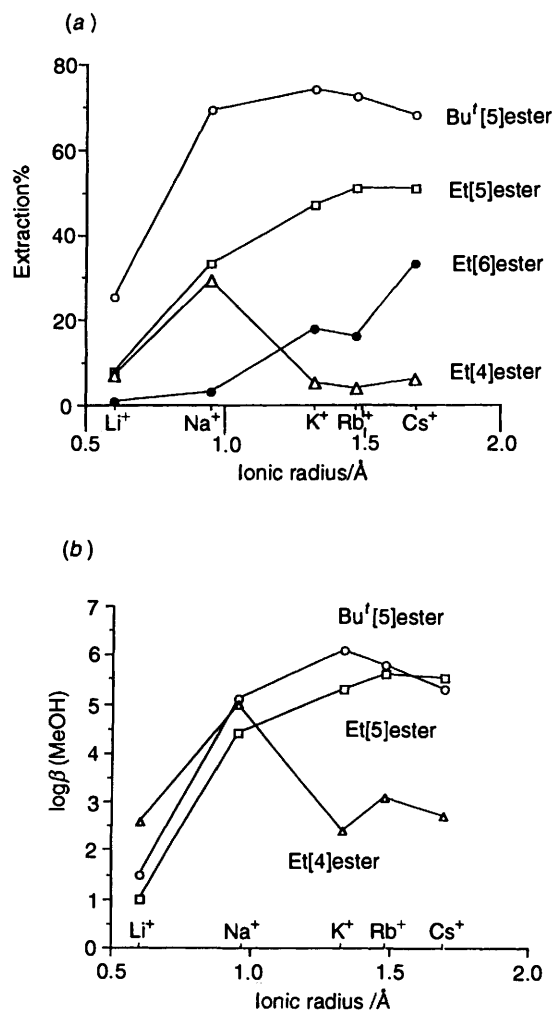
Table 3 Log β values^a for alkali and silver cations complexation in MeOH, $T = 25$ $^{\circ}$ C, $I = 0.1$ mol dm⁻³ Et₄NCl^e or Et₄NClO₄^f

Cations	Li ⁺	Na ⁺	K ⁺	Rb ⁺	Cs ⁺	Ag ⁺
<i>n</i> = 5, R = CH ₂ CO ₂ Et	1.0 ^e	4.4 ^e	5.3 ^f	5.6 ^f	5.5 ^f	4.0 ^e
<i>n</i> = 5, R = CH ₂ CO ₂ Bu ^t	1.5 ^e	5.1 ^f	6.1 ^f	5.8 ^f	5.3 ^f	4.3 ^f
<i>n</i> = 4, R = CH ₂ CO ₂ Et ^c	2.6	5.0	2.4	3.1	2.7	4.0
<i>n</i> = 4, R = CH ₂ CO ₂ Bu ^t ^d	<i>b</i>	4.7	4.0	<i>b</i>	<i>b</i>	<i>b</i>

^a The standard deviation σ_{N-1} on the mean value of at least $N = 3$ independent runs is usually ≤ 0.1 log units except for the systems Li⁺/Bu^t ester ($\sigma_{N-1} = 0.3$) and K⁺/Bu^t ester ($\sigma_{N-1} = 0.2$). ^b Not measured. ^c From ref. 11. ^d From ref. 13. ^e Spectrophotometric determination. ^f Potentiometric determination.

Relatively little is known about the conformations accessible to calix[5]arenes, unlike calix[4]arenes for which four stable conformations (cone, partial cone, 1,2-alternate, 1,3-alternate) are now well established.¹ X-Ray diffraction studies of the parent pentamer²³ and its *p*-tert-butyl²⁴ and *p*-(1,1,3,3-tetramethylbutyl)²⁵ counterparts show that all three compounds possess cone conformations in the crystalline state; there are no published crystallographic data for chemically modified calix[5]arenes. We have used X-ray diffraction to probe the solid-state conformation of the pentaethyl ester **2**. The molecule possesses a distorted cone (Figs. 1 and 2) in the solid state. It has no crystallographically-imposed symmetry and does not approximate to any regular geometrical arrangement. The conformation is best described by the angles that the five aromatic rings (A–E) make with the mean plane of the five macrocyclic ring methylene groups: 130.8 $^{\circ}$ (A), 60.2 $^{\circ}$ (B), 132.3 $^{\circ}$ (C), 116.5 $^{\circ}$ (D) and 96.6 $^{\circ}$ (E). [The methylene carbons deviate considerably from co-planarity, with individual atoms as much as 0.43 Å from the mean plane, but this mean plane is almost parallel (1.3 $^{\circ}$) to the mean plane of the five phenolic oxygens which are almost coplanar (maximum deviation from plane is 0.11 Å).] Thus, ring B tilts inwards at the upper rim while the four other rings tilt outwards, as is normal, but by very different amounts.

The conformations of the pendant side-chains are also very different. Only chains D and E approximate to full extension (defined as all 180 $^{\circ}$ torsion angles between C6 and C15) but, whereas E has the ethoxy oxygen (O3) directed away from the

**Fig. 3** (a) Percentage alkali cation extraction by calixarene esters in Table 2; (b) logarithms of the stability constants β for the calixarene esters in Table 3

cavity, D has O3 directed into the cavity. This necessarily means that the phenolic O1 lone pairs on D are directed away from the cavity and could not be co-ordinated in this conformation. Side-chains A–C have a torsion angle close to 0 $^{\circ}$ ($\pm 15^{\circ}$) for the O1–C12–C13–O3 sequence and at least one torsion angle close to 90 $^{\circ}$ (Table 1).

The pentaester cavity is enclosed by a distorted pentagonal pyramid comprising the five co-planar phenolic oxygens (O1A–E) and O3D. O...O distances in this polygon vary between 3.4 and 4.7 Å. However, because of the conformations of the side chains, not all lone pairs on these atoms point into the cavity and thus this arrangement does not represent a co-ordination sphere. Small conformational changes could lead to fluxionality and an averaging which makes the molecule symmetrical in solution, as noted below. There are no unusual bond lengths and no short intermolecular contacts. Some of the *tert*-butyl carbons [and the terminal chain atom C(15C)] are probably slightly disordered as their thermal parameters are large.

Attempts to refine them as disordered atoms, partitioned between two sites, however, proved unsuccessful.

The binding properties of both esters **2** and **3** towards alkali cations have been assessed by picrate extraction experiments and stability constant measurements; the latter were also extended to silver ion. For all cations investigated, the experimental data could be interpreted with good accuracy by assuming the formation of 1:1 complexes only. The results of both sets of measurements and some earlier comparative data for the calix[4]arene and calix[6]arene analogues are summarised in Tables 2 and 3 and shown graphically in Fig. 3.

The data indicate that both the ethyl and *tert*-butyl pentaesters have high extraction levels, significantly higher than those of corresponding tetraesters. Among all the calixarene esters that we have studied thus far, the pentamers are the best extractants for all the alkali cations. For pentamers and tetramers the *tert*-butyl derivatives are more effective than the ethyl derivatives. Although the calix[5] and calix[4] ethyl esters are both in the cone conformation, they display quite different selectivity patterns as shown in Fig. 3(a): whereas the tetramer shows a sharp peak selectivity for Na⁺, the pentamer has a preference for the larger cations K⁺, Rb⁺ and Cs⁺, with little discrimination between them; the same trends are exhibited by the *tert*-butyl derivatives with, however, a very slight selectivity for potassium.

In extraction, in addition to the different parameters which govern the binding abilities and selectivities, *i.e.* the number of donor sites, the size of the hydrophilic cavity, the flexibility and conformation of the receptor and the extent of preorganisation, the lipophilic properties play an important role. In the present case it is assumed that the larger pentamer has a greater lipophilicity than the tetramer, *e.g.* lower solubility in methanol. It is therefore more appropriate to discuss the binding properties in terms of the stability constants in a single homogeneous medium, where differences in lipophilicity are not relevant. However, the discussion must be confined to the stability constants ($\log \beta$) for pentamers and tetramers in methanol since the hexamer derivatives are insoluble in this medium. The $\log \beta$ data in Table 3 show that the *tert*-butyl derivative **3** is a stronger binder than the ethyl derivative **2**, as was found in extraction; the selectivity patterns shown in Fig. 3(a) and (b) are quite similar in both extraction and in complexation. The same applies to the *tert*-butyl derivative for which there is a slight selectivity for K⁺ ($\beta_{\text{K}^+}/\beta_{\text{Na}^+} = 10$).

Although the extraction values for the pentaethyl ester are all higher than those for the tetraethyl ester, this is not so with the stability constants. The values of $\log \beta$ for the Li⁺ and Na⁺ complexes are lower with the pentamer than with the tetramer, whereas they are higher for the larger K⁺, Rb⁺ and Cs⁺ cations. Considering that both series of compounds are all in the cone conformation, the stabilities of their complexes are expected to be mainly controlled by the number of donor sites (factor 1) and the match between the cation size and the cavity size of the receptor (factor 2). On going from the tetramer to the pentamer one would expect factor 1 to increase $\log \beta$ provided of course that all the donor sites are involved in binding. This is not the trend observed suggesting that factor 2 may be unfavourable and predominant. Thus, the cavity size of the pentamer seems to be too large for Na⁺ while better adapted to the larger cations and hence both factors co-operate so as to increase the stability constants of their complexes. X-Ray diffraction studies of a tetramer amide and its complexes show that the binding sites are the phenolic oxygens and the carbonyl oxygens and that in the K⁺ complex¹⁷ (but not the Li⁺ complex)²⁶ all four podands are simultaneously engaged with the cation, *i.e.* 8-fold coordination and 4-fold symmetry. We presume that tetramer esters bind alkali cations in much the same way as the tetramer amides and the close correspondence between the ¹H NMR

spectral changes which occur on complexation in the two series supports this view. Although we have isolated crystalline complexes of the pentamer esters and alkali cations, none has been of sufficient quality for X-ray diffraction. However, a ¹H NMR study of the complexation of K⁺ and Cs⁺ by the penta *tert*-butyl ester showed that uptake of the cation in CDCl₃ solution produces the same type of spectral changes that occur with the tetraester. Whereas the pentaester, like the tetraester, in the solid state exists as a distorted cone, in solution there is an averaging molecular motion in the system which makes each molecule symmetrical; on the NMR timescale the Cs⁺ and K⁺ complexes are also symmetrical.

Table 3 also shows that Ag⁺ is equally well complexed by the ethyl pentamer and the ethyl tetramer ($\log \beta = 4.0$). Here again the *tert*-butyl substituent enhances the stability of the Ag⁺ complex ($\log \beta = 4.3$).

Experimental

Penta-tert-butylpentakis(ethoxycarbonylmethoxy)calix[5]-arene.—*p-tert*-Butylcalix[5]arene (1.0 g, 1.233×10^{-3} mol) was dissolved in dry acetone (100 cm³) containing potassium carbonate (1.28 g) and ethyl bromoacetate (1.37 cm³, 100% molar excess) and the mixture was heated under reflux for 5 days when TLC analysis (eluent 3:2 dichloromethane–hexane) showed the absence of calixarene. The cooled mixture was filtered and the solid residue was washed with dichloromethane. The combined organic solutions were concentrated to an oil which contained residual ethyl bromoacetate. The oil was triturated with a small volume of cold ethanol and allowed to stand for 24 h, whereupon a solid formed. Filtration yielded a material which was found by ¹H NMR analysis to be a mixture of the pentaester and its K⁺ complex. (*J*-Values are given in Hz.) The solid was suspended in water at 40 °C for 12 h and stirred vigorously following which the cooled mixture was extracted (3 × 50 cm³) with dichloromethane. The combined extracts were washed with water and dried. Removal of the solvent at reduced pressure furnished the pentaester which was crystallised from ethanol–dichloromethane to yield the pure compound (1.21 g, 79%), m.p. 146–148 °C (Found: C, 72.95; H, 8.2. C₇₅H₁₀₀O₁₅ requires C, 72.55; H, 8.12%); δ_{H} (CDCl₃) 1.01 (s, 45 H, Bu^t), 1.31 (t, 15 H, Me of Et), 3.35 (d, 5 H, H_B of ArCH₂Ar, *J* 14.0), 4.22 (q, 10 H, CH₂ of Et), 4.62 (s, 10 H, OCH₂), 4.81 (d, 5 H, H_A of ArCH₂Ar, *J* 14.0), 6.87 (s, 10 H, ArH).

Penta-tert-butyl-pentakis(tert-butoxycarbonylmethoxy)-calix[5]arene.—The procedure described above for the pentaethyl ester was repeated with *tert*-butyl bromoacetate as the electrophile and the same molar proportions to afford the penta *tert*-butyl ester after decomplexation with warm water. Crystallisation from ethanol–dichloromethane gave crystals, m.p. 211–212 °C (83% yield) (Found: C, 73.65; H, 8.85. C₈₅H₁₂₀O₁₅ requires C, 73.88; H, 8.75%); δ_{H} (CDCl₃) 1.00 (s, 45 H, Bu^t), 1.45 (s, 45 H, OBU^t), 3.35 (d, 5 H, H_B of ArCH₂Ar, *J* 14.6), 4.57 (s, 10 H, OCH₂), 4.77 (d, 5 H, H_A of ArCH₂Ar, *J* 14.6), 6.86 (s, 10 H, ArH).

Penta-tert-butyl-pentakis(carboxymethoxy)calix[5]arene.—The penta *tert*-butyl ester (0.43 g, 3.11×10^{-4} mol) was suspended in ethanol (50 cm³) and water (20 cm³) containing sodium hydroxide (0.18 g). The mixture was heated under reflux for 18 h, then was cooled, diluted with water (15 cm³) and filtered. The precipitate was suspended in 50% sulfuric acid and the mixture was stirred vigorously for several hours to effect protonation of the carboxylate salt. The suspension was then filtered and the solid washed several times with cold water to

afford, after drying, the crude pentaacid (0.33 g, 96%). Crystallisation from aqueous ethanol furnished the analytically pure acid (0.28 g, 82%) as a white powder, m.p. 220–222 °C (Found: C, 67.6; H, 8.15. $C_{65}H_{80}O_{15}$ 5EtOH, requires C, 67.64; H, 8.34%).

Physicochemical Studies.—The extraction of alkali picrates from an aqueous solution (2.5×10^{-4} mol dm⁻³) into a 2.5×10^{-4} mol dm⁻³ solution of calixarene in dichloromethane, at 20 °C, was monitored spectrophotometrically in the aqueous phase, at 355 nm. The stability constants were determined at 25 °C by UV absorption spectrophotometry or, for $\log \beta > 5$, by competition potentiometry using Ag⁺ as auxiliary cation. The concentrations of the ligand solutions were 10^{-4} mol dm⁻³ in spectrophotometry and 2.5×10^{-4} mol dm⁻³ in potentiometry. The ionic strength *I* was maintained constant at 0.01 mol dm⁻³ with Et₄NCl and Et₄NClO₄, respectively. The details of the experimental procedures, the nature and the origin of the chemicals used, as well as the methods of interpretation of the data, have already been described.¹⁶

X-Ray Crystal Structure Analysis of 2.— $C_{75}H_{100}O_{15}$, *M* = 1241.62, triclinic, *a* = 11.656(2), *b* = 14.912(3), *c* = 23.044(5) Å, α = 79.23(2), β = 78.31(2), γ = 67.52(2)°, *U* = 3597(2) Å³, *Z* = 2, $\lambda(\text{Mo-K}\alpha)$ = 0.710 73 Å, *D_c* = 1.15 g, cm⁻³, *F*(000) = 1340, space group P $\bar{1}$. Crystals, grown from ethanol, were colourless prisms, size 0.6 × 0.2 × 1.25 mm, $\mu(\text{Mo-K}\alpha)$ = 0.7 cm⁻¹.

Accurate cell dimensions were determined by least squares treatment of the setting angles of 25 reflections (with $5 < 2\theta < 22^\circ$). Data were collected on a Siemens P3/V2000 diffractometer, using graphite-monochromated Mo-K α radiation, with ω -scan, scan width 1.0° + α_1/α_2 splitting, scan speed 5–15° min⁻¹, scan range $3 < 2\theta < 55^\circ$. Intensities of three standard reflections, measured after every 100 reflections, showed no decay. A total of 13 097 reflections were measured, of which 10 839 had *I* > 0. The structure was solved by the direct methods of SHELXS86 and refined by blocked least squares (SHELX76), allowing anisotropic vibrations for non-hydrogen atoms. Hydrogen atoms were included at positions calculated from the geometry of the molecule (C–H = 1.08 Å) with common isotropic temperature factors for methyl methylene and aromatic hydrogens, which refined to final values of 0.17(1), 0.11(1) and 0.05(1) Å², respectively.

In the final cycles the 6967 data with $I > 2\sigma(I)$ gave *R* = 0.084, *R_w* = 0.087, with weighting scheme $w = 2.52/[\sigma^2(F_o) + 0.00084 F_o^2]$. The maximum residual electron density was 0.36 eÅ⁻³. The molecule is shown in Figs. 1 and 2. Atomic coordinates and all derived results have been deposited with the Director, Cambridge Crystallographic Data Centre.*

References

- 1 C. D. Gutsche, *Calixarenes*, vol. 1 in *Monographs in Supramolecular Chemistry*, ed. J. F. Stoddart, Royal Society of Chemistry, 1989.
- 2 *Topics in Inclusion Phenomena, Calixarenes, A Versatile Class of Macrocyclic Compounds*, eds. V. Böhmer and J. Vicens, Kluwer Academic Publishers, 1990.
- 3 C. D. Gutsche and M. Iqbal, *Org. Synth.*, 1989, **69**, 234.
- 4 M. A. McKervey and V. Böhmer, *Chem. Brit.*, 1992, 724.
- 5 A. Ninagawa and H. Matsuda, *Makromol. Chem. Rapid Commun.*, 1982, **3**, 65.
- 6 Y. Nakamoto and S. Ishida, *Makromol. Chem. Rapid Commun.*, 1982, **3**, 705.
- 7 D. R. Stewart and C. D. Gutsche, *Org. Prep. Proc. Intl.*, in the press.
- 8 M. A. McKervey, E. M. Seward, G. Ferguson, B. L. Ruhl and S. J. Harris, *J. Chem. Soc., Chem. Commun.*, 1985, 388.
- 9 S. K. Chang and I. Cho, *Chem. Lett.*, 1984, 477; *J. Chem. Soc., Perkin Trans. 1*, 1986, 211.
- 10 M. J. Schwing-Weill and M. A. McKervey, ref. 2, pp. 149–172.
- 11 F. Arnaud-Neu, E. M. Collins, M. Deasy, G. Ferguson, S. J. Harris, B. Kaitner, A. J. Lough, M. A. McKervey, E. Marquis, B. L. Ruhl, M. J. Schwing-Weill and E. M. Seward, *J. Am. Chem. Soc.*, 1989, **111**, 8681.
- 12 A. Arduini, A. Pochini, S. Reverberi, R. Ungaro, G. D. Andreotti and F. Ugozzoli, *Tetrahedron*, 1986, **42**, 2089.
- 13 F. Arnaud-Neu, G. Barrett, S. Cremin, M. Deasy, G. Ferguson, S. J. Harris, A. J. Lough, L. Guerra, M. A. McKervey, M. J. Schwing-Weill and P. Schwinte, *J. Chem. Soc., Perkin Trans. 2*, 1992, 1119.
- 14 G. Ferguson, B. Kaitner, M. A. McKervey and E. M. Seward, *J. Chem. Soc., Chem. Commun.*, 1987, 584.
- 15 G. Calestani, F. Ugozzoli, A. Arduini, E. Ghidini and R. Ungaro, *J. Chem. Soc., Chem. Commun.*, 1987, 344.
- 16 F. Arnaud-Neu, M. J. Schwing-Weill, K. Ziat, S. Cremin, S. J. Harris and M. A. McKervey, *New J. Chem.*, 1991, **15**, 33.
- 17 A. Arduini, E. Ghidini, A. Pochini, R. Ungaro, G. D. Andreotti, G. Calestani and F. Ugozzoli, *J. Incl. Phenom.*, 1988, 119.
- 18 S. K. Chang and I. Cho, *Chem. Lett.*, 1987, 947.
- 19 F. Arnaud-Neu, M. A. McKervey and M. J. Schwing-Weill, *J. Phys. Org. Chem.*, 1992, **5**, 496.
- 20 R. Ungaro and A. Pochini, ref. 2, pp. 127–147; C. Alfieri, E. Dradi, A. Pochini, R. Ungaro and G. D. Andreotti, *J. Chem. Soc., Chem. Commun.*, 1983, 1075; E. Ghidini, F. Ugozzoli, R. Ungaro, S. Harkema, A. Abu El-Fadl and D. N. Reinhoudt, *J. Am. Chem. Soc.*, 1990, **112**, 6979.
- 21 D. N. Reinhoudt, P. J. Dijkstra, P. J. A. in't Veld, K. E. Bugge, S. Harkema, R. Ungaro and E. Ghidini, *J. Am. Chem. Soc.*, 1987, **109**, 4761.
- 22 F. Arnaud-Neu, G. Barrett, S. J. Harris, M. A. McKervey, M. Owens, M.-J. Schwing-Weill and P. Schwinte, *Inorg. Chem.*, in the press.
- 23 M. Coruzzi, G. D. Andreotti, V. Bocchi, A. Pochini and R. Ungaro, *J. Chem. Soc., Perkin Trans. 2*, 1982, 1133.
- 24 R. K. Juneja, K. D. Robinson, G. W. Orr, R. H. Dubois, K. A. Belmore, J. L. Atwood, J. M. Ripmeester and C. I. Ratcliffe, *J. Incl. Phenom. Molec. Recogn.*, 1992, **13**, 93.
- 25 M. Perrin and S. Lecocq, *J. Incl. Phenom.*, 1991, **11**, 171.
- 26 Unpublished results.

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