Synthesis, X-Ray Crystal Structure and Cation Binding Properties of a Tetrahomodioxacalix[4]arene Tetraester

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Abstract. Treatment of *p-t*-butyltetrahomodioxacalix[4]arene with ethyl bromoacetate yields a tetraester derivative (**4**) whose crystal and molecular structure have been determined and whose ion binding properties have been assessed by phase transfer and stability constant measurements. Colorless transparent triclinic crystals (obtained from methoxyethanol) $C_{62}H_{84}O_{14}$, $a = 10.347(2)$, $b = 11.583(2)$, $c = 13.448(3)$ Å, $\alpha = 72.04(2)$, $\beta = 86.50(2)$, $\gamma = 81.23(2)°$, space group $P\bar{1}$, $Z = 1$, Mo K_α radiation $\lambda = 0.70930$ Å. Refinement was carried out using 2221 reflections with $I > 1.5\sigma(I)$. The complexation properties resemble those of calix[6]arene hexaester (**6**), although weaker, with a preference for the larger alkali cations. Ca^{2+} and Ba^{2+}, though not extracted, are more strongly complexed than alkali cations. Eu^{3+} is better complexed than Na^+.

1. Introduction

In the course of an extensive investigation of calixarene synthesis by base-catalysed condensation of *p*-substituted phenols with formaldehyde, Gutsche and his coworkers noted that under certain conditions the cyclic oligomers were accompanied by appreciable quantities of a related substance in which a —CH$_2$O— moiety had been incorporated into the calixarene macrocycle [1]. Gutsche established the structure of this compound as that shown in (**1**) and designated it as a dihomooxacalix[4]arene. Gutsche and Dhawan later showed how (**1**) and the homologous oxacalixarenes, *p-t*-butyltetrahomodioxacalix[4]arene (**2**), and *p-t*-butylhexahomotrioxacalix[3]-arene (**3**), could be synthesised from acyclic bis(hydroxymethylated)phenols [2]. Whereas oxacalixarene (**1**) was found to form a strong molecular complex with dichloromethane, homologue (**2**) appeared to lack significant complexing properties.

As part of a programme of synthesis of chemically modified calixarenes with ion binding affinity for metal cations [3, 4] we have converted dioxacalixarene (**2**) into tetraester (**4**). The crystal and molecular structure of (**4**) have been determined and

1

2 R = H
4 R = CH$_2$CO$_2$Et

3

5 R = CH$_2$CO$_2$Et
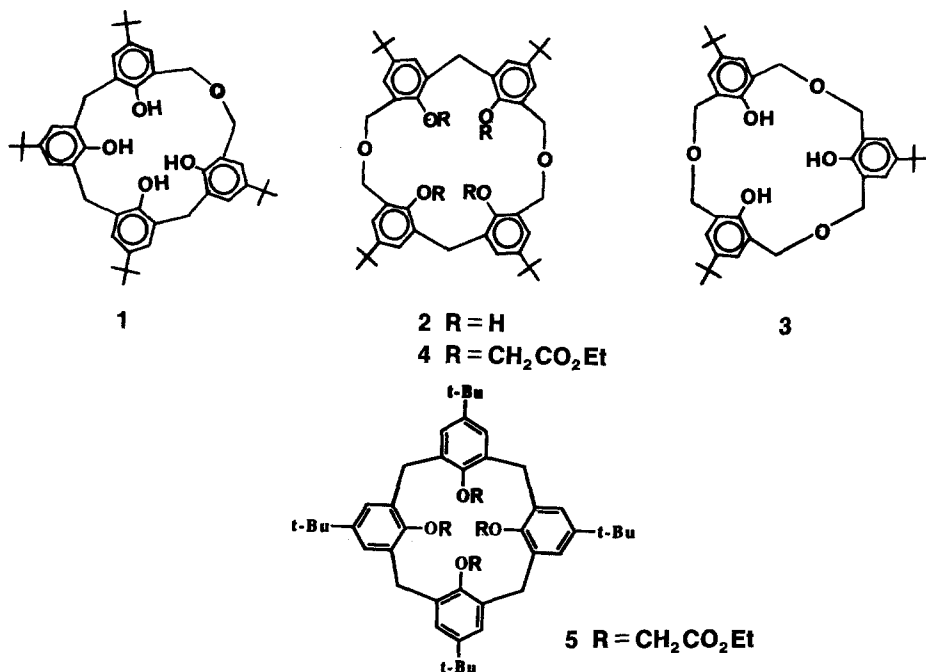
its ion binding potential towards alkali, alkaline-earth, silver and europium(III) cations has been assessed by the technique of cation extraction from aqueous solution into dichloromethane and by stability constant measurements.

2. Experimental

2.1. SYNTHESIS

p-t-Butyltetrahomodioxacalix[4]arene (2) was prepared as described by Gutsche and Dhawan and was converted into tetraester (4) by the following procedure. In a 100 mL round-bottomed flask under a nitrogen atmosphere calixarene (2) (1.4 g) was dissolved in dry acetone (50 mL) containing ethyl bromoacetate (1.4 g) and potassium carbonate (1.18 g). The mixture was heated under reflux for 5 days, then cooled and filtered. The filtrate was evaporated and the residue taken up in dichloromethane. The organic extract was washed with water, dried (MgSO$_4$), and concentrated to a solid residue which was then taken up in dichloromethane and passed through a column of alumina. Recrystallisation of the product from methoxyethanol furnished crystals of (4) (74% yield), m.p. 224–225°C, suitable for X-ray diffraction (Found: C, 70.91; H, 8.21. Calculated for C$_{62}$H$_{84}$O$_{14}$: C, 70.69; H, 8.04%).

2.2. CRYSTAL STRUCTURE DETAILS

Crystal data are given in Table I and fractional atomic coordinates in Table II. The structure was solved by direct methods, SHELX86 [5] and refined using SHELX76 [6]. The following atoms were refined anisotropically, O(1) to O(7), C(1) to C(8),

Table I. Crystal data for (4)

Formula	$C_{62}H_{84}O_{14}$
M	1053.34
Space Group	$P\bar{1}$
a (Å)	10.347(2)
b (Å)	11.583(2)
c (Å)	13.448(3)
α (°)	72.04 (2)
β (°)	86.50 (2)
γ (°)	81.23 (2)
U (Å³)	1515.1
Z	1
D_c g cm^{-3}	1.15
μ cm^{-1}	0.47
$F000$	568
Radiation Mo K$_\alpha$	
Graphite Monochromator	$\lambda = 0.7093$ Å
Diffractometer	Enraf-Nonius CAD4F
Orienting Reflections,	
Range	25, $13 < \theta < 20°$
Temperature (°C)	22
Scan Method	$\omega - 2\theta$
Data Collection Range	$2 < 2\theta < 48°$
No. unique data	4474
Total $I > 1.5 \sigma I$	2221
No of Parameters fitted	288
R^a	6.93%
R^b	7.59%
Quality-of-fit indicator^c	1.42
Largest Shift/esd, final cycle	< 0.001
Largest positive peak (e/Å³)	0.18
Largest negative peak (e/Å³)	-0.10

$^a R = [\Sigma||F_0| - |F_c||]/\Sigma|F_0|$
$^b R_w = [[\Sigma w(F_0 - F_c)^2]/[\Sigma w(F_0)^2]]^{1/2}$; $w = 1/[(\sigma F_0)^2 - 0.0025 \times F_0^2]$
^{c}Quality-of-fit $= [\Sigma w(F_0 - F_c)^2/(N_{obs} - N_{parameters})]^{1/2}$.

C(15), C(16) and C(23) to C(27). Hydrogen atoms were attached in calculated positions, with fixed thermal parameters of 0.08, to all carbons bearing hydrogens except C(29) to C(31). The Bu^t group containing these carbon atoms was disordered over two positions with equal site occupancy in each of 0.5. The carbons in one of the two orientations, C(29') to C(31'), did not refine well. The angles developed by these half carbons with the tertiary carbon, C(28), of 121°, 98° and 99° deviate from the expected values, however no better model for this disorder was found. The ORTEP program was used to obtain the drawings.

2.3. EXTRACTION STUDIES

A 2.5×10^{-4} M aqueous picrate solution (5 mL) and 5 mL of a 2.5×10^{-4}.M solution of calixarene in CH_2Cl_2 were magnetically stirred in a stoppered glass tube immersed in a thermostated water bath at $20° \pm 0.01°C$. The extraction equilibrium

Table II. Fractional atomic coordinates for (**4**) U(iso) except U(eq), U(eq) = $(U11 + U22 + U33)/3$

Atom	x	y	z	U(iso or eq)
O(1)	0.0976(4)	0.0807(4)	0.5387(3)	0.0500(2) U(eq)
O(2)	0.3243(6)	0.1767(6)	0.4467(5)	0.1050(5) U(eq)
O(3)	0.3731(5)	0.0242(5)	0.3796(5)	0.0997(5) U(eq)
O(4)	0.2514(4)	−0.2078(4)	0.7224(3)	0.0522(3) U(eq)
O(5)	0.0169(4)	0.3251(4)	0.3375(3)	0.0549(3) U(eq)
O(6)	0.0815(12)	0.3775(9)	0.1350(6)	0.2064(9) U(eq)
O(7)	0.1754(6)	0.5327(6)	0.1398(4)	0.1026(4) U(eq)
C(1)	0.1942(6)	0.0122(6)	0.4910(5)	0.0535(4) U(eq)
C(2)	0.3009(7)	0.0823(7)	0.4369(5)	0.0576(4) U(eq)
C(3)	0.4860(9)	0.0780(10)	0.3227(8)	0.1042(7) U(eq)
C(4)	0.4524(12)	0.1562(13)	0.2217(9)	0.1452(11) U(eq)
C(5)	0.0707(9)	0.4337(7)	0.2892(6)	0.0782(5) U(eq)
C(6)	0.1098(9)	0.4414(8)	0.1806(6)	0.0835(6) U(eq)
C(7)	0.2182(14)	0.5575(12)	0.0300(7)	0.1479(10) U(eq)
C(8)	0.3072(14)	0.6371(14)	0.0047(10)	0.1704(13) U(eq)
C(15)	0.1246(6)	−0.1358(5)	0.7241(5)	0.0480(4) U(eq)
C(16)	0.2425(8)	−0.3272(6)	0.7197(6)	0.0531(5) U(eq)
C(23)	0.0920(6)	0.3174(6)	0.5446(5)	0.0504(4) U(eq)
C(24)	−0.3824(7)	0.3140(7)	0.6521(5)	0.0634(5) U(eq)
C(25)	−0.3376(8)	0.2038(8)	0.7461(6)	0.0801(6) U(eq)
C(26)	−0.3986(8)	0.4289(7)	0.6859(7)	0.0767(5) U(eq)
C(27)	−0.5149(7)	0.2967(10)	0.6189(7)	0.0927(6) U(eq)
C(9)	0.1275(6)	0.0902(5)	0.6348(4)	0.043(1)
C(10)	0.1276(6)	0.2088(5)	0.6410(5)	0.043(1)
C(11)	0.1549(6)	0.2214(6)	0.7351(5)	0.048(2)
C(12)	0.1794(6)	0.1233(6)	0.8250(5)	0.050(2)
C(13)	0.1700(6)	0.0102(6)	0.8175(5)	0.055(2)
C(14)	0.1423(6)	−0.0108(6)	0.7234(5)	0.048(2)
C(17)	−0.2087(6)	0.3301(6)	0.3871(5)	0.048(2)
C(18)	−0.3060(6)	0.3263(6)	0.4641(5)	0.052(2)
C(19)	−0.2804(6)	0.3219(6)	0.5653(5)	0.048(2)
C(20)	−0.1487(6)	0.3230(5)	0.5864(5)	0.047(2)
C(21)	−0.0483(6)	0.3270(5)	0.5121(4)	0.044(1)
C(22)	−0.0797(6)	0.3312(5)	0.4134(5)	0.044(1)
C(28)	0.2090(7)	0.1444(7)	0.9280(6)	0.069(2)
C(29)	0.3244(21)	0.2112(20)	0.9169(16)	0.98(6)
C(30)	0.0767(18)	0.2146(17)	0.9639(15)	0.090(5)
C(31)	0.2294(22)	0.0278(20)	1.0195(17)	0.102(6)
C(29′)	0.2533(19)	0.2715(18)	0.9140(14)	0.083(5)
C(30′)	0.1295(23)	0.0907(22)	1.0145(18)	0.111(6)
C(31′)	0.3502(21)	0.0542(20)	0.9676(17)	0.108(6)

The t-butyl group C(29)—C(31) is disordered over two sites with 0.5 site occupancy in each.

was reached after 2 min vigorous shaking by hand, followed by 15 h magnetic stirring in the water bath. After the two phases were allowed to settle for 1 h, the absorbance, A, of the aqueous phase was measured at 355 nm, i.e. the wavelength of maximum absorption of the picrate ion (λ_{max} = 355 nm, ε = 14416 mol^{-1} L cm^{-1}). A blank experiment, without calixarene, was run under

Table III. Percentage extraction[a] of metal picrates into CH_2Cl_2 at 20°C

	Li^+	Na^+	K^+	Rb^+	Cs^+	Ag^+	Mg^{2+}	Ca^{2+}	Ba^{2+}	Eu^{3+}
(4)	2.1	3.0	16.2	16.8	12.6	–	1.5	1	1.2	–
(5)[b]	7.2	29.0	4.7	3.6	5.6	–	–	4.3	5.1	–
(6)[c]	4.7	10.4	51.3	94.1	94.6					

[a]Mean of at least 4 runs. Standard deviation σ_{n-1}, on the mean: 0.6 (Na^+, Ca^{2+}); 1.0 (Rb^+); 1.2 (K^+, Cs^+, Ba^{2+}); 1.3 (Li^+); 1.4 (Mg^{2+}).
[b]from reference [12].
[c]Data for extraction of basic metal picrates taken from reference [3].

the same conditions which yielded an absorbance, A_0, of the aqueous phase. The percentage cation extracted was calculated as the ratio $100 \times (A_0 - A)/A_0$. Measurements of the absorbance in the organic phase yielded comparable results and Table III gives the average of the results obtained from both types of measurements.

The alkali picrates were prepared by stepwise addition of a 2×10^{-2} M aqueous picric acid solution to a 0.15 M aqueous solution of metal hydroxide, until neutralisation was reached as measured by potentiometry with a glass electrode. After precipitation, the picrates were filtered off and recrystallized from water. The alkaline-earth picrates were obtained from hot aqueous solutions of picric acid in the presence of an excess of metal carbonate. After filtration of the carbonate in excess, the solution was cooled to 0°C and allowed to stand until precipitation was complete. The picrates were recrystallized from water [8]. All recrystallized picrates were rapidly washed with ethanol, then ether, and dried under vacuum during 24 h. The picrates were sheltered from air humidity and light before use.

2.4. STABILITY CONSTANT DETERMINATIONS

As shown in Figure 1 the stepwise addition of a cation salt to a 2×10^{-4} M solution of (4) in acetonitrile induced spectral changes in the wavelength range 250–300 nm, significant enough to be exploited by a multi-wavelength numerical treatment of the data by the computer program Letagrop Spefo [9], which yielded the stability constants of the complexes.

For each cation, several solutions were prepared with a ligand concentration of 1.87×10^{-4} M in acetonitrile, (Merck, Uvasol), varying concentrations of cations salts (cation to ligand molar ratio, R, up to 60 when necessary), and a constant ionic strength 10^{-2} M in Et_4NClO_4 (Fluka, purum, recrystallized twice from acetone and dried under vacuum at 50°C for 24 h). The spectra were recorded for each solution between 250 and 300 nm, with a Shimadzu-240 spectrophotometer equipped with a cell compartment thermostated at 25 ± 0.01°C.

The cation salts were perchlorates ($LiClO_4$ Fluka purum; $NaClO_4$ Merck p.a.; $KClO_4$ Prolabo normapur; $AgClO_4$ Fluka puriss.; $Mg(ClO_4)_2 \cdot H_2O$ Merck; Ca $(ClO_4)_2 \cdot 6 H_2O$ Alfa and $Ba(ClO_4)_2$ Prolabo), or nitrates ($RbNO_3$ and $CsNO_3$ Fluka purum). The hydrated salts were dried under vacuum before use. The europium salt was $Eu(CF_3SO_3)_3$ prepared as published elsewhere [10]. The kinetics of approach to equilibrium was checked in all cases: only with Ca^{2+} and Eu^{3+}, 2h and 3 days respectively were necessary for establishment of equilibria. For each
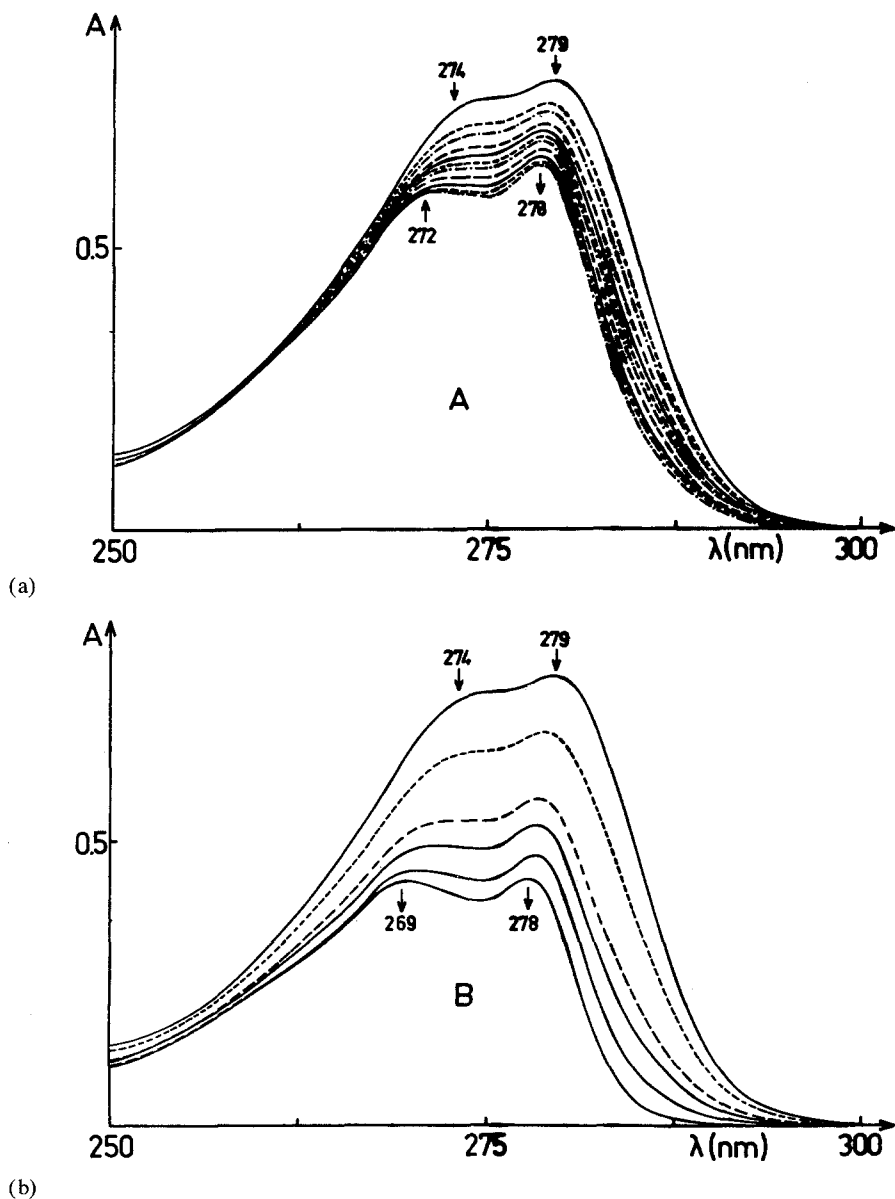
(a)

(b)

Fig. 1. Absorbances, at 25°C, of solutions of (4) (1.87×10^{-4} M) in acetonitrile (ionic strength 10^{-2} M in Et_4NClO_4) containing different amounts of: 1(a) : $KClO_4$ – Cation to ligand molar ratio R successively equal to 0 (upper curve); 0.48; 0.66; 1.0; 1.33; 1.66; 2.0; 2.66; 3.8; 5.6; 9.9. 1(b): $BaClO_4$ – R successively equal to 0 (upper curve); 0.29; 0.59; 0.73; 0.88; 1.03 (lower curve, unchanged for $R = 1.2$ and 2.4).

cation, the experiments were repeated from 2 to 4 times, and a minimum of 50 experimental data points was interpreted for each run. The data listed in Table IV are the mean of the results of the different runs.

In all cases, the experimental data could be entirely described by assuming the presence of mononuclear 1 : 1 complexes only.

Table IV. Logarithms of the stability constants (β)[a] for cation complexes in acetonitrile, at 25°C; ionic strength $= 10^{-2}$ M Et_4NClO_4.

	Li^+	Na^+	K^+	Rb^+	Cs^+	Ag^+	Mg^{2+}	Ca^{2+}	Ba^{2+}	Eu^{3+}
(4)	3.2	3.5	3.9	3.9	4.0	< 1	2.2	> 6	> 6	4.5
(5)	6.4[b]	5.8[b]	4.5[b]	1.9[b]	2.8[b]	2.5[c]	–	–	–	–
(6)	3.7[b]	3.5[b]	5.1[b]	4.8[b]	4.3[b]	4.2[c]	–	–	–	–

[a]Mean of minimum of two experiments. Standard deviation σ_{n-1} on the mean: 0.05 (Rb^+, Cs^+) or 0.1 (Li^+, Na^+, K^+, Mg^{2+}, Eu^{3+}).
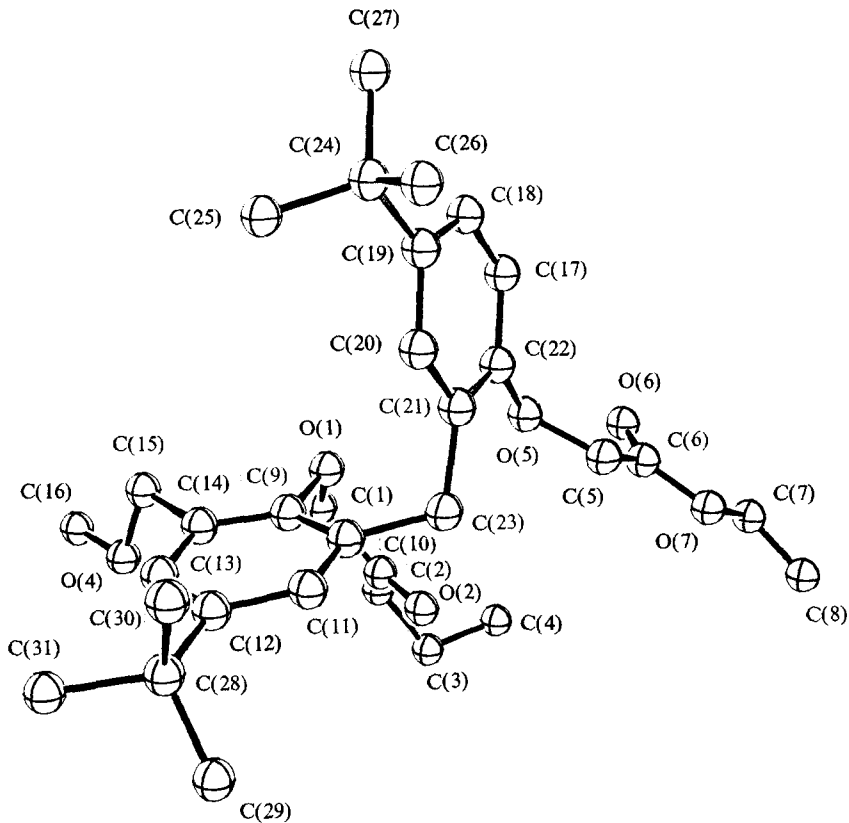[b]from reference [3].
[c]from reference [4].

Fig. 2A. A view of the asymmetric unit with hydrogen atoms omitted for clarity.

3. Results and Discussion

3.1. MOLECULAR GEOMETRY AND CRYSTAL STRUCTURE

Tetraester (4) possesses an irregular cavity defined by the conformations of the four pendant ester functions and the macrocyclic ring. The X-ray crystal structure reveals that the repeat (asymmetric) unit is one half molecule, Figure 2A and 2B. Full molecules are generated from these half molecules by inversion centres, Figure 2C.
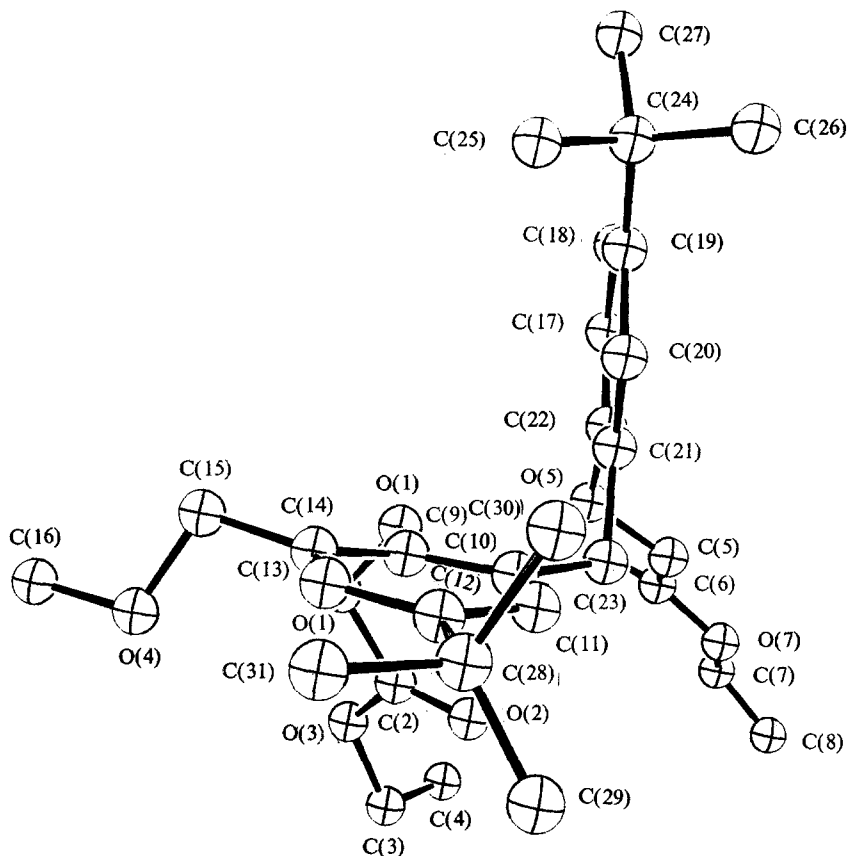
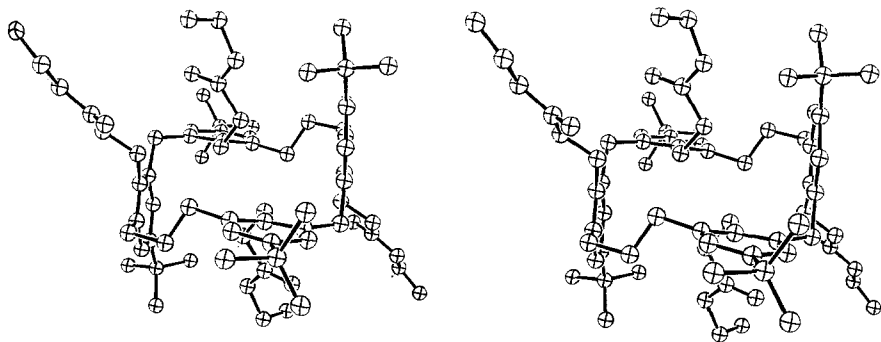Fig. 2B. The asymmetric unit oriented as in Figure 2C.

Fig. 2C. Stereo pair of whole molecules.

Two adjacent ester groups are *cis*, but the inversion symmetry places the other two *cis* ester groups in the *anti* position on the opposite face of the macroring. It is helpful in visualising the molecular conformation of (**4**) to compare it with that of the *p-t*-butylcalix[4]arene ester (**5**) whose crystal structure is also available [3]. Constitutionally, the two molecules differ only by two CH$_2$O groups in the

macroring. In solution and in the solid state tetraester (**5**) adopts a distorted cone conformation in which the four ester groups are mutually *syn* with respect to the macroring, defining a central cavity with a 3.10–3.28 Å separation between adjacent phenolate oxygen atoms. The molecular conformation may be defined by the angles which the four aromatic rings (A)–(D) make with the macroring CH_2 groups: A (138°), B (94°), C (136°), and D (92°). Rings B and D are thus essentially parallel (interplanar angle 2°), while rings A and C are almost normal to one another (interplanar angle 94°). In contrast, expanding the macroring of (**5**) by two distal CH_2O groups has a major effect on the molecular conformation in that the inversion symmetry requires that (**4**) adopts the 1,2-alternate arrangement shown in Figure 2.

In this arrangement the ester groups are above and below the general plane of the macroring. The cavity adopts an approximate right angled parallelepiped shape, i.e. the shape of a brick. The body diagonal of 7.5 Å is defined by the phenolic oxygen O(5) and its symmetry related partner. The sides of the cavity are defined by the planes of the aromatic rings. The rings on opposite faces are close to parallel with interplanar angles of less than 0.05° while adjacent phenyl rings define an interplanar angle of 83°. Other distances across the cavity are defined by O(1) and O(4) and their symmetry related partners are O(1)···O(1) 3.36 Å and O(4)···O(4) 8.017 Å. The view down the cavity, Figure 2, clearly shows the way in which the inclusion of the extra O—CH_2 groups gives the cavity a rectangular opening. Interestingly, tetraester (**4**) has more in common conformationally with its carbocyclic hexaester counterpart (**6**), which also possesses inversion symmetry, though the cavity dimensions of the latter are larger.

3.2. COMPLEXATION PROPERTIES OF TETRAESTER (**4**)

Two aspects of the complexation properties of tetraester (**4**) towards a selection of metal cations were examined experimentally. The cations chosen were the monovalent alkali and silver(I) cations, for which information is already available concerning their complexation by other calixarene esters [3, 4], divalent alkaline-earth cations, and one trivalent lanthanide cation. Firstly, we applied Pedersen's technique [11] of picrate extraction as a convenient, semi-quantitative means of assessing ion transfer ability from aqueous solution into a non-polar organic solvent. Secondly, we determined the stoichiometry and the stability constants, β, of the complexes of the same set of cations by UV absorption spectrophotometry. Application of both techniques as applied to calixarene esters is already described elsewhere [3], the only difference in the former being that neutral picrates were used instead of alkaline picrate solutions (see experimental section for details).

The results obtained with calixarene ester (**4**) in dichloromethane and metal picrate in neutral aqueous solution at 20°C are collected in Table III which also includes, for comparison, the corresponding values for tetraester (**5**) and hexaester (**6**) in basic medium. The stability constants β of the 1:1 ML complexes, equal to the concentration ratios [ML]/[M][L] with M = cation, L = Ligand, could not be obtained in hydroxylic solvents due to solubility limitations and consequently were measured in acetonitrile which can be assumed to be totally dissociating; the values of log β are listed in Table IV.

4. Conclusions

The main conclusions of these studies are:

(i) *In the alkali series*: dioxacalix[4]arene tetraester (**4**) does have extracting and complexing properties, lower than those of the tetraester (**5**) for Li^+ and Na^+, but higher for K^+ (in extraction only), Rb^+ and Cs^+, and overall lower than those of the hexaester (**6**) for all cations. The behaviour of (**4**) resembles that of hexaester (**6**) in its preference for the larger alkali cations. The extraction selectivity is in favour of K^+ and Rb^+, with a slight decrease for Cs^+. Although β slightly increases from Na^+ to K^+, the complexation selectivity of (**4**) is rather poor $(\beta(K^+)/\beta(Na^+) = 2.5)$. However, in both extraction and complexation, there is very little differentiation between the three larger alkali cations. This behaviour is consistent with the larger cavity present in (**4**) compared with that of (**5**).

(ii) The low stability constant of the softer Ag^+ complex $(\log \beta < 1)$ did not allow the use of Ag^+ as an auxiliary cation in competitive potentiometry measurements, as could be done in solvent methanol for tetraester (**5**) [3, 4].

(iii) *In the alkaline earth series*: all cations are essentially not extracted by (**4**) although the complexing power of (**4**) towards Ca^{2+} and Ba^{2+} (as defined by β which is expressed in units independent of the cation charge) is definitely much higher $(\log \beta > 6)$ than towards any of the alkali cations $(\log \beta \leqslant 4)$. The reason why the stability constants of Ca^{2+} and Ba^{2+} can only be estimated by a lower limit lies in the fact that the spectrophotometric method is unable to provide stability constants of 1:1 complexes higher than 6 log units. It must be emphasized however that a drop in the percentage cation extracted, P, when going from a monovalent to a divalent cation does not inevitably imply a drop in the extraction equilibrium constant K_e which is related differently to P in both cases: under the experimental conditions used in this work, and neglecting the activity coefficients of the cation and picrate ions, K_e is equal to $P/c^2(1 - P)^3$ for monovalent cations (with $c =$ analytical initial concentration of calixarene in $CH_2Cl_2 =$ analytical initial concentration of cation in the aqueous phase), whereas K_e is equal to $P/4c^3(1 - P)^4$ for divalent cations. In the present case, K_e ranges between 5 and $50 \times 10^5 \, mol^{-3}$ for alkali cations, and between 1.7 and $2.5 \times 10^8 \, mol^{-4}$ for alkaline-earth cations. Such a comparison of K_e values for differently charged cations is however meaningless due to the different units of K_e. This is the reason why we chose to present the extraction power of (**4**) as P values which are comparable useful experiment data, whatever the cation charge. The low extractability of the doubly charged ML^{2+} complex is of course responsible for the drop in percentage cation extracted by (**4**) in spite of an increase in stability constants in going from the monovalent alkali cations to the divalent alkaline-earth cations. The results for Na^+ and Ca^{2+}, two ions of about the same ionic radius of 1 Å, show that the influence of the charge, at constant ionic size within both series, consists of an increase of at least 2 log units in the stability constants.

(iv) The triply charged europium cation has about the same ionic radius as Na^+ and Ca^{2+}: whereas it is slightly better complexed than Na^+, it is not as well complexed as Ca^{2+}.

Acknowledgements

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