Complexation of *p*-Xylene with *p*-Isopropylcalix[4]arene: Crystal Structures and Thermal Analysis of the Empty Form and the (1:1) and (2:1) Complexes

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Abstract. This paper concerns inclusion complexes of the *p*-isopropylcalix[4]arene host with *p*-xylene as guest. It is shown that from a saturated solution in *p*-xylene, the macrocycle gives a 1:1 complex; on heating, the 1:1 complex is transformed into a 2:1 complex, and then into the empty macrocycle. The compounds are studied by differential scanning calorimetry, thermogravimetry and X-ray powder diffraction; the three crystal structures are reported showing the arrangements of the macrocycles with and without their guests.

Key words. Calixarenes, inclusion complexes, crystal structures, *p*-xylene.

1. Introduction

Many of the calixarenes form complexes in the solid state [1, 2]. The tenacity with which the guest molecule is held by the calixarene varies widely among the calixarenes. Whereas the cyclic octamer loses the guest molecule after a few minutes at room temperature, the cyclic tetramer retains the solvent for many hours. In the current investigation, we were able to obtain with *p*-isopropylcalix[4]arene first the 1:1 complex with *p*-xylene, then the 2:1 complex, and finally the empty form. Here we report differential scanning calorimetry studies as well as powder diffraction results. We also describe the conformation and the structure of the three compounds obtained.

2. Experimental

2.1. DIFFERENTIAL SCANNING CALORIMETRY AND THERMOGRAVIMETRIC ANALYSES

Differential scanning calorimetry (DSC) was performed using a Perkin Elmer DSC 2 system. The loss of mass was measured on a Seteram type G70 thermobalance. DSC curves were recorded at $20°C\,min^{-1}$ while the TG curve was obtained at $3°C\,min^{-1}$.

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In order to carry out the analyses, pure p-isopropylcalix[4]arene without a solvent molecule was prepared (compound E); then, by evaporation of a saturated solution of compound E in p-xylene, crystals of compound A were obtained.

The results of the thermal analysis are shown in Figure 1 for both compounds E and A. The DSC curve of E (a) displays only a single endothermic peak near 300°C which corresponds to melting ($\Delta H = 46.37$ kJ mol^{-1}); curve (b) (compound A) is characterized by three endothermic peaks: the initial endotherm with a maximum at 78°C corresponds to the release of some guest molecules ($\Delta H = 10.94$ kJ mol^{-1}), the second endotherm at 170°C, with $\Delta H = 17.52$ kJ mol^{-1}, corresponds to the release of the remaining p-xylene molecules. This is followed by a final endotherm peak between 270 and 310°C with $\Delta H = 68.77$ kJ mol^{-1}. The TG curve (c) shows a total mass loss of 15.09% compared with a theoretical value of 15.19% for the 1:1 complex. Therefore it is clear that the first endothermic phenomenon observed on curve (b) between 52 and 83°C corresponds to the release of one of the two xylene molecules. In the same way, the second endothermic phenomenon between $157 \rightarrow 212°C$ (curve b) corresponds to the release of the remaining xylene molecules. From these data it can be concluded that the initial 1:1 complex, when heated, gives rise to a 2:1 complex between p-isopropylcalix[4]arene and p-xylene molecules, then to the pure calixarene macrocycle. The third endothermic peak corresponds to the pure calixarene. As the melting of one mole of p-isopropylcalix[4]arene requires
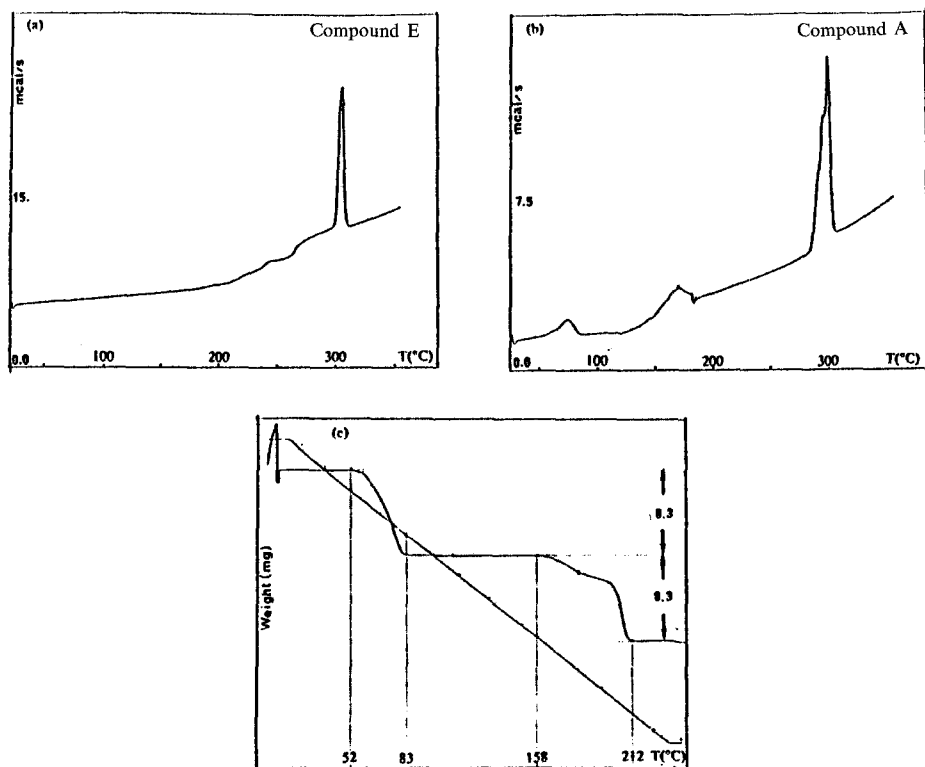

Fig. 1.   Thermal analysis curves. (a), (b) Heating rates: 20°C min^{-1}. (c) Heating rate: 3°C min^{-1}. Sample weight: 110 mg. The weight loss of each xylene molecule corresponds to 8.3 mg.

$46.37 \text{ kJ mol}^{-1}$ and we find $68.77 \text{ kJ mol}^{-1}$, the difference of $22.40 \text{ kJ mol}^{-1}$ must be explained. We suggest that the third endothermic phenomenon corresponds in fact to two distinct but related phenomena: a modification in the organization of the solid followed by melting. This modification could be a change in the configuration of the macrocycles, particularly at the isopropyl groups. From the known vaporization enthalpies of p-xylene at $25°C$ at the boiling point ($138°C$), it is possible, by considering the calorific capacity to be constant in the temperature range considered, to calculate the vaporization enthalpies of p-xylene at $60°C$ and $154°C$ (mean values for xylene release). The calculated values for half a mole are 20 kJ mol^{-1} and 17.5 kJ mol^{-1}. These values are compared to the enthalpies found when p-xylene is released from calixarenes; it can be noted that the first release is thermally much easier from the $1:1$ complex than from the liquid p-xylene: $10.94 \text{ kJ mol}^{-1}$ compared to 20 kJ mol^{-1}. Then the values are very similar: $17.52 \text{ kJ mol}^{-1}$ and 17.5 kJ mol^{-1} for the $2:1$ complex and the p-xylene. It is noted that this second release takes place at atmospheric pressure, at a mean temperature of $150°C$, close to the boiling point of p-xylene: $138°C$.

2.2. POWDER ANALYSIS BY X-RAY DIFFRACTION

X-Ray powder patterns were recorded, at room temperature, on a Siemens D500 apparatus using CuK_α radiation.

Several samples were studied:
- pure p-isopropylcalix[4]arene (compound E);
- the complex with p-xylene obtained from a saturated solution (compound A);
- compound A after heating during some days at temperatures between 70 and 100°C (compounds B_1 and B_2, depending on the number of days, larger for B_2).

Compounds E and B_2 give the same peaks, so the three different patterns are given in Figure 2 and Table I shows the d_{hkl} values for the five highest peaks.

After determination of the structures, the theoretical powder patterns were calculated by the program FINAX [3]; the data for these calculations are the cell parameters, the space group and the positional coordinates. The results with the indexation are also given in Table I. Some permutations are possible due to the preparation of powder samples and preferential orientations.

So it is established that p-isopropylcalix[4]arene gives with p-xylene a $1:1$ complex; then guest molecules are lost on heating, giving first a $2:1$ complex, then an empty form.

In order to investigate the different packings corresponding to these three compounds, the determination of the crystal structures was carried out.

2.3. CRYSTAL STRUCTURES

2.3.1. Crystallization

Single crystals of each compound were grown separately.

Crystals of A ($1:1$ complex) were obtained from a saturated solution in p-xylene at room temperature; crystals of B_1 ($2:1$ complex) were obtained from evaporation of the same solution at 85°C. Crystals of the empty form (compound E) were not obtained easily because p-isopropylcalix[4]arene likes to crystallize with a guest
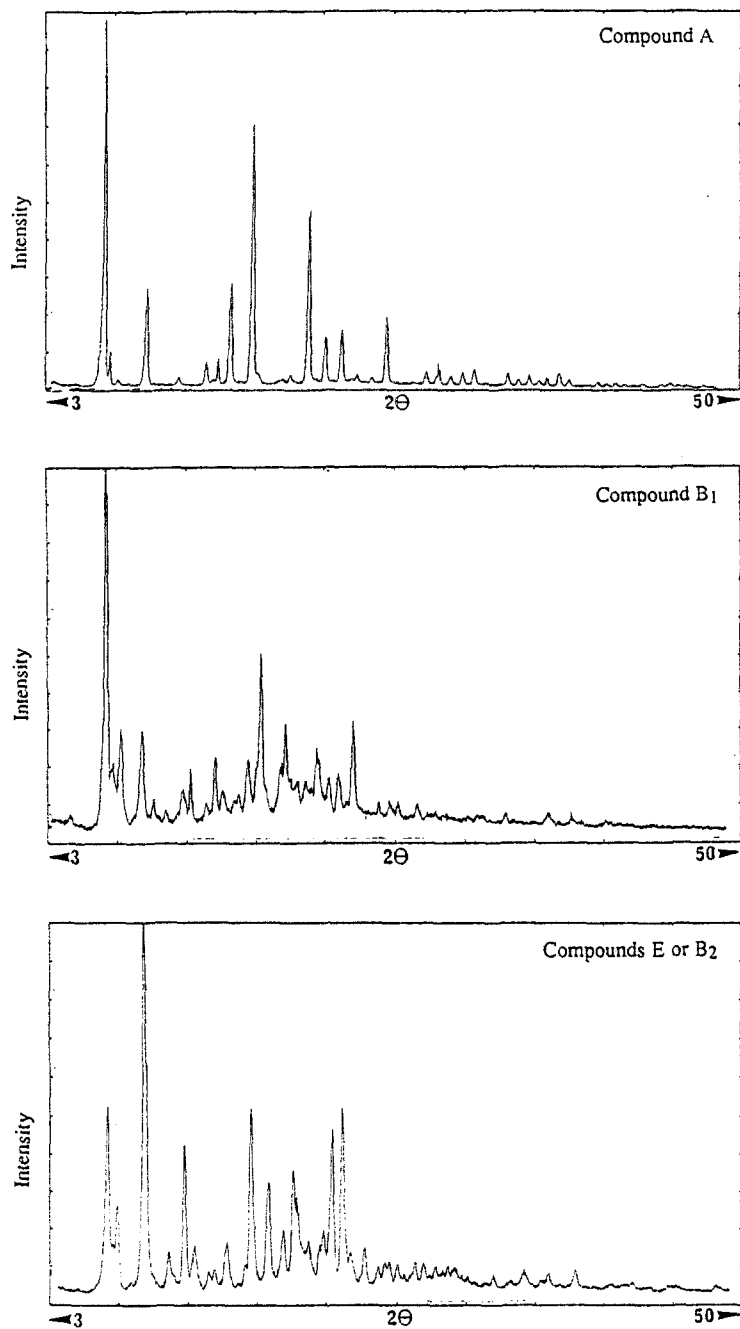
Fig. 2.   Powder diffraction patterns for the three compounds: A, B_1 and E.

Table I. Diffraction results from powders

Compounds	A		B$_1$		B$_2$ or E	
Experimental	d_{hkl}		d_{hkl}		d_{hkl}	
diagrams	12.80		12.70		9.46	
	5.23		5.07		12.93	
	4.27		3.75		5.35	
	5.73		4.63		3.90	
	9.06		11.11		4.02	
Calculated	d_{hkl}	(hkl)	d_{hkl}	(hkl)	d_{hkl}	(hkl)
diagrams	12.77	(001)	12.74	(002)	9.40	(100) or (012)
	5.21	(211)	4.64	(123)	12.91	(011)
	4.26	(221)	5.08	(122)	5.32	(113)(10$\bar{4}$)
	5.71	(201)	11.14	(101)	11.75*	(002)
	9.03	(110)	3.74	(125)	4.03	(212) (220)
				or (132)		

*This line is seen on the experimental powder diagram with a lower intensity.

molecule. Different solvents were used and crystals were finally obtained from evaporation at 65°C of a solution in molten menthol.

2.3.2. *Crystal Structure Analyses*

X-ray diffraction data were measured at 20°C on a Nonius CAD4 diffractometer. Intensity data were collected up to $\theta = 73°$ by using a $\omega - 2\theta$ scan mode with graphite monochromatized CuK_α radiation. Three standard reflections were measured every hour to control intensity variation: Lorentz and polarisation corrections were applied and absorption was corrected with the program PSI and EAC of SDP [4]. The cell constants and pertinent details of the experimental conditions are summarized in Table II.

The crystal structures were solved by direct methods with the program MULTAN [5] and refined by SHELX [6].

For compound A, the guest molecule lies on the 4 axis passing through the C—CH$_3$ bonds and there are thus two equivalent orientations in the cavity. However the guest was well positioned and the coordinates of all the carbon atoms were refined anisotropically. H atoms were refined isotropically, except those of the butyl groups, which are fixed. At the end of the refinement the value of R was 0.086.

Compound B$_1$ was different: extinctions show the space group $P4/nnc$ or $P4/n$ with very low intensities for $(h0l)$ $(h + 1 = 2n + 1)$ and for (hhl) $(l = 2n + 1)$. The two refinements were calculated giving the same reliability coefficients but a better goodness of fit in the case of $P4/n$ (1.57 instead of 2.46). The analysis of the coordinates shows that the two macrocycles have the symmetry $P4/nnc$; perhaps only the guest molecule leads to the lower symmetry $P4/n$. The structure is described with the $P4/n$ group. The carbon atoms of the macrocycle were refined anisotropically and the H atoms isotropically with B fixed. Only the carbon atoms of the solvent molecule were refined isotropically. The R value is 0.112.

The empty form E was refined anisotropically except for the H atoms. For these, the B values of the CH$_3$ groups were fixed. The final R value was 0.068 using 3897 reflections $(I > 1.5\sigma(I))$.

Table II. Summary of crystal data and experimental parameters

Compounds	A	B_1	E
Formulae	$C_{40}O_4H_{48}, C_8H_{10}$	$C_{40}O_4H_{48}, \frac{1}{2}C_8H_{10}$	$C_{40}O_4H_{48}$
Mol.Wt	$592.4 + 106.1$	$592.4 + 53.05$	592.4
a, Å	12.772(1)	12.384(3)	9.565(2)
b, Å	12.772(1)	12.384(5)	15.46(1)
c, Å	12.772(1)	25.506(3)	23.749(4)
α, °	90	90	90
β, °	90	90	98.45(2)
γ, °	90	90	90
V, Å^3	2083.5(1)	3911.8(2)	3475(2)
d_c, g cm^{-3}	1.12	1.10	1.13
μ, cm^{-1}	5.04	4.65	5.26
Z	2	4	4
$F(000)$	756	1396	1280
Space group	$P4/n$	$P4/n$	$P2_1/c$
No. of data measured	4808	8591	7673
Data used in refinement	1911	3469	3897
No. of data after merged	2097	4797	—
R int.	0.033	0.029	—
R (unit weight)	0.086	0.112	0.068
$\Delta\rho$ max, e Å^{-3}	0.15	0.30	0.26
G. of Fit	1.15	1.57	1.36

3. Results

3.1. MOLECULAR GEOMETRY

Final atomic coordinates of the three compounds are listed in Table III. The numbering scheme is given in Figure 3 for compound E. Due to the 4 symmetry the numbering scheme for the two other compounds is that of the I moiety; however we used $C(1) \rightarrow C(32)$ and $C(101) \rightarrow C(132)$ for the two independent molecules of the compound B_1. The lists of anisotropic thermal parameters as well as those of the coordinates of the H atoms have been deposited. Some characteristic covalent bond lengths, bond angles and torsion angles calculated for the three compounds are compared in Tables IV. There are no extraordinary features except that the values for the bonds $C(30)$—$C(32)$ and $C(130)$—$C(132)$ in compound B_1 are unusually short; it is noted that the two atoms $C(32)$ and $C(132)$ have large $B_{eq.}$ values and seem to be disturbed. We note the values of angles at the methylene bridges: 113.0(4)° for A, 112.2(4)° and 111.4(4)° for B_1 and 114.5(4)°, 112.3(4)°, 115.4(4)° and 112.7(3)° for E. For calix[4]arenes the mean plane of the bridging methylene groups is taken as the reference plane and the orientations of the phenyl rings with respect to this mean plane are given. The following values were calculated: 124.8(1)° for A, 124.2(1)° and 124.2(1) for B_1 and successively 126.8(2), 125.0(2), 129.5(1) and 126.1(1)° from rings $I \rightarrow IV$ for compound E. These values are in agreement with those found for calix[4]arenes [7].

O$\cdots$O intramolecular contacts are usually in the range $2.65 \rightarrow 2.67$ Å [7]. The values are similar for the present studies: 2.658(3) Å for the 1 : 1 complex, 2.671(4)
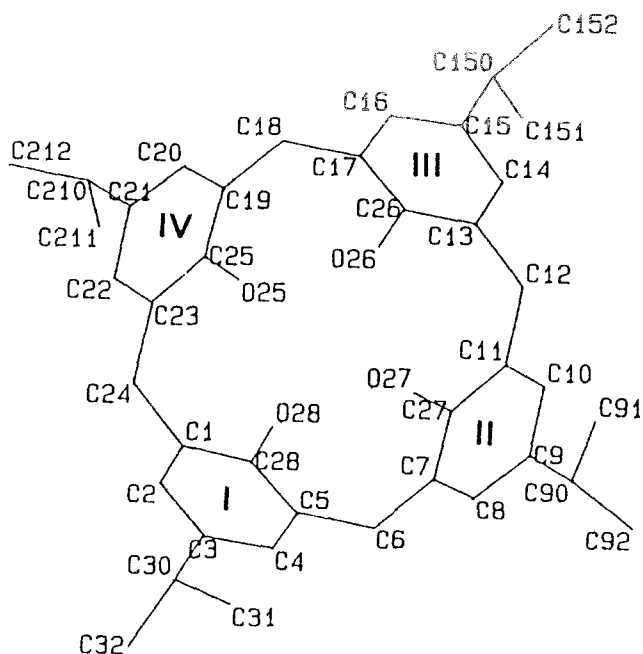
Fig. 3. Numbering scheme and conformation of compound E.

and 2.677(4) Å for the 2:1 complex. In the empty form the values are: $O(28) \cdots O(27) : 2.608(5)$, $O(27) \cdots O(26) : 2.634(4)$, $O(26) \cdots O(25) : 2.587(5)$ and $O(25) \cdots O(28) : 2.655(4)$ Å.

The dihedral angles between the benzene ring planes and the plane of the three carbons of the isopropyl groups were calculated. For compound A this angle has the value $88.1(4)°$; C(31) lies at 1.352(6) Å and C(32) at $-1.09(1)$ Å from the benzene ring plane. In the case of compound B_1 the values are 76.0(6) and 77.0(7)°. The distances of atoms C(31) and C(32) are 1.413(9) and $-0.97(1)$ Å, those of C(131) and C(132) are $-1.401(9)$ and 1.03(1) Å. The four values for compound E are 74.5(3), 72.1(4), 91.5(5) and 89.4(5)°, from I to IV. C(31), C(91), C(151) and C(211) lie at distances of $-0.558(9)$, $-0.725(9)$, $-0.962(8)$, $-1.156(8)$ Å from the ring planes I → IV. In the same manner atoms C(32), C(92), C(152) and C(212) are at distances of 1.588(9), 1.42(1), 1.505(9) and 1.363(9) Å. The conformation of the macrocycles is very similar in the three compounds. All are in the cone conformation with similar O $\cdots$ O distances and inclination angles. The main differences are found in the isopropyl groups. It is seen in Figure 3 that the C(150)—C(151)—C(152) group does not have the same orientation compared to the three others and this fact destroys the 4 symmetry of the macrocycle. It seems that the symmetry of the guest influences that of the host.

3.2. PACKING

Only the crystal structure is able to show where the solvent molecules are located in the crystals. Looking at compound A, we can see that the p-xylene molecule is

Table III. Positional parameters and their ESDs

Atom	x	y	z	B (Å²)	Atom	x	y	z	B (Å²)
Compound A									
C(1)	0.0593(2)	0.0828(2)	0.5871(2)	3.24(6)					
C(2)	0.0337(3)	0.0258(3)	0.6774(3)	3.85(7)					
C(3)	0.1015(3)	-0.0452(3)	0.7219(3)	4.14(8)					
C(4)	0.1998(3)	-0.0577(3)	0.6774(3)	3.86(7)					
C(5)	0.22294(2)	-0.0031(2)	0.5871(2)	3.23(6)					
C(28)	0.1574(2)	0.0658(2)	0.5438(2)	3.19(6)					
O(28)	0.1849(2)	0.1180(2)	0.4522(2)	3.95(5)					
C(30)	0.0679(4)	-0.1094(4)	0.8171(4)	6.2(1)					
C(31)	0.0661(5)	-0.2255(4)	0.7932(5)	9.2(2)					
C(32)	0.1340(8)	-0.0885(8)	0.9086(5)	15.9(4)					
C(24)	-0.0176(3)	0.1615(3)	0.5427(3)	3.62(7)					
C(1S)	0.2500	0.2500	1.0888(7)	7.4(8)	C(2S)	0.182(2)	0.191(2)	1.0344(8)	11.3(5)
C(3S)	0.181(1)	0.191(1)	0.9222(7)	9.7(4)	C(4S)	0.2500	0.2500	0.8689(6)	4.2(7)
C(41S)	0.2500	0.2500	0.7491(6)	6.2(6)	C(11S)	0.2500	0.2500	1.2093(7)	12(2)
Compound B₁									
C(1)	0.0506(3)	0.0810(3)	0.0492(2)	4.67(9)	C(101)	-0.0105(3)	0.2244(3)	0.4506(2)	4.72(9)
C(2)	0.0237(3)	0.0250(4)	0.0934(2)	5.6(1)	C(102)	-0.0657(3)	0.1928(4)	0.4066(2)	5.5(1)
C(3)	0.0916(4)	-0.0488(4)	0.1171(2)	6.1(1)	C(103)	-0.0485(4)	0.0922(4)	0.3828(2)	6.1(1)
C(4)	0.1923(4)	-0.0650(3)	0.0933(2)	5.6(1)	C(104)	0.0252(4)	0.0233(3)	0.4064(2)	5.5(1)
C(5)	0.2238(3)	-0.0110(3)	0.0488(2)	4.71(9)	C(105)	0.0810(3)	0.0499(3)	0.4504(2)	4.65(9)
C(28)	0.1515(3)	0.0625(3)	0.0267(2)	4.54(9)	C(128)	0.0615(3)	0.1519(3)	0.4731(2)	4.50(8)
O(28)	0.1809(2)	0.1141(2)	-0.0190(1)	5.06(6)	O(128)	0.1136(2)	0.1812(3)	0.5186(1)	5.29(7)
C(30)	0.0558(5)	-0.1099(6)	0.1643(3)	8.5(2)	C(130)	-0.1102(6)	0.0560(6)	0.3345(3)	8.9(2)
C(31)	-0.0058(9)	-0.2066(6)	0.1508(3)	15.7(4)	C(131)	-0.2079(7)	-0.003(1)	0.3481(3)	16.9(4)
C(32)	0.120(1)	-0.100(1)	0.2078(4)	26.7(8)	C(132)	-0.098(1)	0.121(1)	0.2898(4)	23.8(7)
C(6)	-0.0281(3)	0.1635(3)	0.0262(2)	5.2(1)	C(106)	0.1636(3)	-0.0276(3)	0.4742(2)	5.1(1)
C(1S)	0.2500	0.2500	0.3066(4)	5.6(2)	C(4S)	0.2500	0.2500	0.1939(4)	5.4(2)
C(11S)	0.2500	0.2500	0.3655(5)	7.8(3)	C(41S)	0.2500	0.2500	0.1333(5)	8.1(3)
C(3S)	0.1932(9)	0.1755(9)	0.2225(6)	12.2(6)	C(2S)	0.1932(9)	0.1775(9)	0.2779(6)	12.2(6)

Compound E

Atom					Atom				
C(1)	0.3343(4)	0.0664(3)	0.3675(2)	4.11(9)	C(13)	0.5535(4)	−0.3280(3)	0.3233(2)	4.4(1)
C(2)	0.3684(4)	0.1105(3)	0.4183(2)	4.4(1)	C(14)	0.6810(5)	−0.3640(3)	0.3462(2)	4.8(1)
C(3)	0.3278(4)	0.0810(3)	0.4695(2)	4.5(1)	C(15)	0.8113(5)	−0.3298(3)	0.3357(2)	5.1(1)
C(4)	0.2556(4)	0.0036(3)	0.4678(2)	4.5(1)	C(16)	0.8059(5)	−0.2563(3)	0.3024(2)	5.0(1)
C(5)	0.2169(4)	−0.0425(3)	0.4176(2)	4.3(1)	C(17)	0.6792(5)	−0.2170(3)	0.2772(2)	4.7(1)
C(28)	0.2564(4)	−0.0089(3)	0.3672(2)	4.3(1)	C(26)	0.5529(4)	−0.2554(3)	0.2881(2)	4.5(1)
O(28)	0.2141(2)	−0.0522(2)	0.3161(1)	5.29(7)	O(26)	0.4264(3)	−0.2220(2)	0.2605(1)	5.39(8)
C(30)	0.3600(5)	0.1352(3)	0.5228(2)	5.2(1)	C(150)	0.9491(5)	−0.3735(2)	0.3578(2)	5.9(1)
C(31)	0.3863(8)	0.0860(4)	0.5769(2)	7.8(2)	C(151)	0.9688(7)	−0.3871(5)	0.4211(3)	8.5(2)
C(32)	0.2440(8)	0.2036(4)	0.5245(3)	8.8(2)	C(152)	0.9628(9)	−0.4598(5)	0.3269(4)	9.9(3)
C(7)	0.2304(4)	−0.2063(3)	0.4257(2)	4.7(1)	C(19)	0.6673(5)	−0.0530(3)	0.2684(2)	4.6(1)
C(8)	0.2774(5)	−0.2384(3)	0.4797(2)	5.5(1)	C(20)	0.7891(5)	−0.0079(3)	0.2918(2)	4.8(1)
C(9)	0.3631(5)	−0.3107(3)	0.4895(2)	5.9(1)	C(21)	0.7867(4)	0.0698(3)	0.3194(2)	4.7(1)
C(10)	0.4068(5)	−0.3512(3)	0.4422(2)	5.6(1)	C(22)	0.6527(5)	0.1046(3)	0.3260(2)	4.6(1)
C(11)	0.3625(4)	−0.3217(3)	0.3873(2)	4.7(1)	C(23)	0.5288(4)	0.0613(2)	0.3040(2)	4.5(1)
C(27)	0.2756(4)	−0.2497(3)	0.3797(3)	4.6(1)	C(25)	0.5371(5)	−0.0156(3)	0.2742(2)	4.6(1)
O(27)	0.2247(3)	−0.2202(2)	0.3250(1)	5.39(8)	O(25)	0.4133(3)	−0.0557(2)	0.2492(1)	5.50(8)
C(90)	0.4068(8)	−0.3427(5)	0.5506(3)	8.4(2)	C(210)	0.9209(5)	0.1176(3)	0.3425(2)	5.2(1)
C(91)	0.5530(8)	−0.3808(4)	0.5626(2)	9.9(2)	C(211)	0.9399(7)	0.1259(3)	0.4052(3)	8.6(2)
C(92)	0.297(1)	−0.399(1)	0.5673(4)	15.5(4)	C(212)	0.9366(8)	0.2006(6)	0.3106(4)	10.4(3)
C(6)	0.1374(5)	−0.1274(3)	0.4179(2)	5.1(1)	C(18)	0.6798(6)	−0.1387(3)	0.2395(2)	5.2(1)
C(12)	0.4150(5)	−0.3670(3)	0.3372(2)	5.01(1)	C(24)	0.3868(5)	0.1013(3)	0.3137(2)	4.7(1)

Table IV. Bond distances (Å), bond angles (°) and torsion angles (°) and their ESDs

Compound A

C(3)—C(30)	1.528(6)	C(30)—C(32)	1.466(9)	C(30)—C(31)	1.513(7)		
C(1)—C(24)	1.516(4)	C(28)—O(28)	1.392(4)				
C(1S)—C(2S)	1.35(2)	C(2S)—C(3S)	1.43(1)	C(3S)—C(4S)	1.35(2)	C(4S)—C(41S)	1.53(1)

Compound B₁

C(3)—C(30)	1.488(8)	C(30)—C(31)	1.46(1)	C(30)—C(32)	1.37(1)		
C(103)—C(130)	1.519(8)	C(130)—C(131)	1.46(1)	C(130)—C(132)	1.40(1)		
C(1)—C(24)	1.529(6)	C(28)—O(28)	1.378(5)	C(101)—C(124)	1.528(6)	C(128)—O(128)	1.376(5)
C(1S)—C(11S)	1.50(1)	C(3S)—C(2S)	1.41(2)	C(4S)—C(41S)	1.54(1)		

Compound E

C(28)—O(28)	1.393(5)	C(27)—O(27)	1.396(5)	C(26)—O(26)	1.389(5)	C(25)—O(25)	1.390(5)
C(3)—C(30)	1.511(6)	C(9)—C(90)	1.532(7)	C(15)—C(150)	1.506(7)	C(21)—C(210)	1.512(6)
C(30)—C(31)	1.483(7)	C(90)—C(91)	1.51(1)	C(150)—C(151)	1.502(9)	C(210)—C(211)	1.477(8)
C(30)—C(32)	1.538(8)	C(90)—C(92)	1.47(2)	C(150)—C(152)	1.54(1)	C(210)—C(212)	1.51(1)
C(1)—C(24)	1.539(6)	C(7)—C(6)	1.506(6)	C(13)—C(12)	1.535(6)	C(19)—C(18)	1.505(6)
C(5)—C(6)	1.517(6)	C(11)—C(12)	1.528(7)	C(17)—C(18)	1.506(6)	C(23)—C(24)	1.541(6)

Compound A

C(1)—C(24)—C(23)	113.0(4)						
C(3)—C(30)—C(31)	111.7(4)	C(3)—C(30)—C(32)	112.0(5)	C(31)—C(30)—C(32)	110.4(6)		
C(1S)—C(2S)—C(3S)	121.(2)	C(11S)—C(1S)—C(2S)	121.1(7)	C(2S)—C(3S)—C(4S)	120.(1)		
C(3S)—C(4S)—C(41S)	120.4(6)						

Compound B₁

C(3)—C(30)—C(31)	112.5(6)	C(3)—C(30)—C(32)	116.0(7)	C(31)—C(30)—C(32)	124.3(8)		
C(103)—C(130)—C(131)	111.9(6)	C(103)—C(130)—C(132)	115.8(7)	C(131)—C(130)—C(132)	124.8(8)		
C(5)—C(6)—C(7)	112.2(4)	C(105)—C(106)—C(107)	111.4(3)				
C(1S)—C(2S)—C(3S)	123(1)	C(2S)—C(3S)—C(4S)	123(1)				
C(3S)—C(4S)—C(41S)	122.6(7)	C(11S)—C(1S)—C(2S)	122.7(7)				

Compound E

C(9)—C(90)—C(91)	114.9(5)	C(9)—C(90)—C(92)	110.0(6)	C(91)—C(90)—C(92)	113.6(7)
C(3)—C(30)—C(31)	115.4(4)	C(3)—C(30)—C(32)	110.2(4)	C(31)—C(30)—C(32)	111.2(5)
C(21)—C(210)—C(211)	112.3(5)	C(21)—C(210)—C(212)	112.0(4)	C(211)—C(210)—C(212)	115.1(6)
C(15)—C(150)—C(151)	112.8(5)	C(15)—C(150)—C(152)	110.8(5)	C(151)—C(150)—C(152)	110.5(6)
C(5)—C(6)—C(7)	114.5(4)	C(11)—C(12)—C(13)	112.3(4)	C(17)—C(18)—C(19)	115.4(4)
C(1)—C(24)—C(23)	112.7(3)				

Compound A

C(28)—C(1)—C(24)—C(23)	−87.9(6)	C(28)—C(5)—C(6)—C(7)	87.7(6)

Compound B₁

C(28)—C(1)—C(24)—C(23)	−88.9(5)	C(28)—C(5)—C(6)—C(7)	87.8(5)
C(128)—C(101)—C(124)—C(123)	90.4(5)	C(128)—C(105)—C(106)—C(107)	−90.4(5)

Compound E

C(27)—C(7)—C(6)—C(5)	−88.2(7)	C(27)—C(11)—C(12)—C(13)	88.3(6)
C(26)—C(13)—C(12)—C(11)	−84.8(6)	C(26)—C(17)—C(18)—C(19)	85.2(7)
C(25)—C(19)—C(18)—C(17)	−87.0(7)	C(25)—C(23)—C(24)—C(1)	87.4(6)

inside the macrocycle giving a supramolecule with $CH_3-\pi$ interactions between C(41S) and the aromatic rings (perpendicular distance between C(41S) and the benzene ring plane is 3.651(5) Å). The shorter distances between C(41S) and the macrocycle are 3.844(6) and 3.847(7) Å with C(1) and C(5).

Compound B_1 is a 2:1 complex and it is seen that two macrocycles encapsulate the p-xylene molecule. The atoms C(41S) and C(11S) lie at 3.70 Å from the benzene ring planes and at distances near 3.90 Å from atoms C(1), C(101), C(5) and C(105).

The packing of the three compounds are shown in Figure 4. Compounds A and B_1 are isomorphous with other calix[4]arenes studied by Andreetti et al. [8, 9]. The
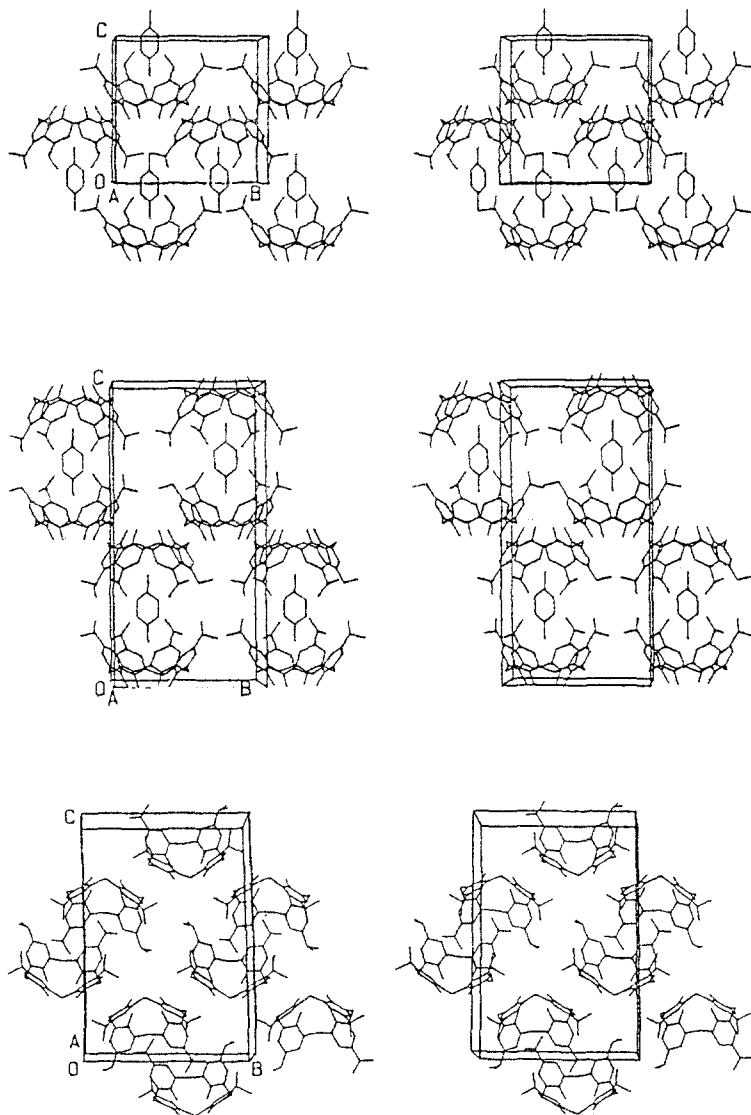

Fig. 4.   Stereoscopic views along [100] of the packing for compounds: A (top), B_1 (middle) and E (bottom).

empty form E shows that two macrocycles related by a center of symmetry are in a position such that a methyl group of the isopropyl substituent lies inside the cavity: the atom C(31)* is at distances of $-3.538(9)$ and $-3.508(6)$ Å from rings I and IV. These dimers are repeated in the crystal with van der Waals interactions.

The packing of compound A, perpendicular to the 4 axis, can be described as slices of macrocycles with the aperture alternatively up and down. A translation of one of these slices by $\frac{1}{2}\mathbf{a} + \frac{1}{2}\mathbf{b}$ gives two macrocycles face to face as in compound B_1. For a better comparison, the macrocycles have to be rotated about each other to get as close as possible.

4. Conclusions

The main conclusions of this study are summarized as follows.

p-Isopropylcalix[4]arene, pure and complexed with p-xylene (complexes 1 : 1 and 2 : 1), were obtained in the form of powders and in the form of single crystals. Powder diffraction, differential scanning calorimetry and thermogravimetric analyses show that a 1 : 1 complex is obtained from a saturated solution. On heating, this complex loses one half of these guest molecules and it is transformed into a 2 : 1 complex. Then the second half of the solvent molecules are lost leaving the empty form. The crystal structures of the three compounds were studied; they show how the guest molecule is enclosed in the macrocycles as a result of $CH_3-\pi$ interactions [2, 8, 9]. It is seen that the host macrocycle adapts its conformation with the shape and symmetry of the guest. On heating, decapsulation is an important phenomenon: it seems rather easy to lose one half of the p-xylene molecule. The rearrangement of the macrocycles is possible giving the 2 : 1 complex. At this stage, it is evident that the guest molecule is well encapsulated in a closed cage; so it will be more difficult to lose this p-xylene. However at higher temperature the guest is lost and the macrocycles re-arranged to get as close as possible with new $CH_3-\pi$ interactions. Figure 5 summarizes the phenomena of decapsulation with the rearrangement of the macrocycles as close as possible for better close packing.
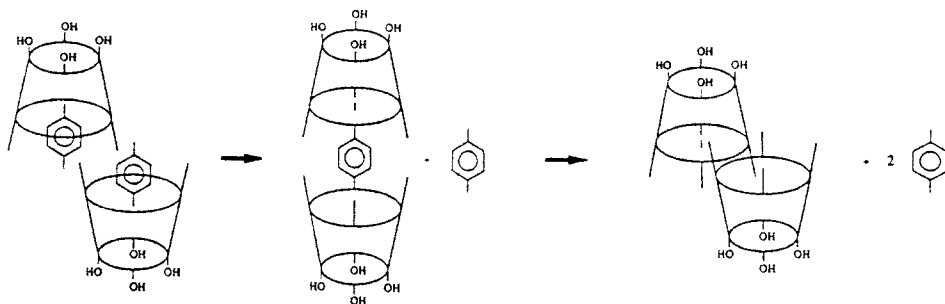

Fig. 5. Scheme of decapsulation.

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