Crystal and Molecular Structure of Two Calix[6]arenes: *p*-Isopropylcalix[6]arene and *p-tert*-Butylcalix[6]arene–Benzene(1 : 3) Complex

M. HALIT, D. OEHLER, M. PERRIN,* and A. THOZET
Laboratoire de Mineralogie – Cristallographie, UA 805 CNRS, Université Claude Bernard Lyon I, 43 Boulevard du 11 Novembre 1918, 69622 Villeurbanne Cedex, France

R. PERRIN, J. VICENS, and M. BOURAKHOUADAR
Laboratoire de Chimie Industrielle, Cristallographie et Chimie des matériaux, UA 805 CNRS, Université Claude Bernard Lyon I, 43 Boulevard du 11 Novembre 1918, 69622 Villeurbanne Cedex, France
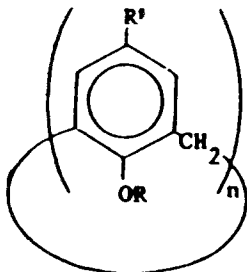
Abstract. The isopropyl derivative crystallizes from a mixture of carbon disulfide and benzene in the orthorhombic system: Space group $P2_1nb$, $a = 17.420(3)$, $b = 17.708(3)$, $c = 18.972(3)$ Å, $V = 5852(3)$ Å^3, $Z = 4$. The *t*-butyl derivative crystallizes from benzene, but the crystal is a complex (1 : 3), space group $P\bar{1}$, $a = 15.065(5)$, $b = 19.103(3)$, $c = 13.878(3)$ Å, $\alpha = 106.95(2)$, $\beta = 102.72(2)$, $\gamma = 80.61(2)°$, $V = 3703(2)$ Å^3, $Z = 2$. Refinement led to $R = 0.185$ for 1512 reflections for the isopropyl derivative, a sufficiently high number to establish the conformation of the molecule; for the *t*-butyl complex $R = 0.12$ for 7340 reflections. Intramolecular hydrogen bonds are given as well as comparison of the conformation of both compounds. The *t*-butyl groups and the benzene molecules are disordered but the isopropyl groups are not.

Key words. X-Ray crystal structure analysis, calixarene conformation.

1. Introduction

During the last few years, the calixarenes have been widely investigated, and in particular the structures of these macrocyclic compounds have been established by X-Ray diffraction methods. Several calix[4]arenes, calix[5]arenes, calix[6]arenes and even calix[8]arenes have been thoroughly investigated [1–10] and the different conformations, as well as their abilities to give complexes with solvents or cations have been compared. The present study reports the crystal structures of two calix[6]arenes with R = H, R′ = CH (CH₃)₂ (compound A) and R = H, R′ = C (CH₃)₃ (compound B).

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* Author for correspondence.

The crystal structure of a cyclic hexamer in the free phenolic form has not yet been reported. The conformation of *p-t*-butyl calix[6]arene has been mentioned [11]. It is of interest to know the two conformations since compound A does not retain solvent whereas crystals of compound B are obtained with three molecules of benzene.

2. Experimental

2.1. SYNTHESIS

The calixarenes were synthesized by the reaction of the appropriate *para*-alkylphenol and formaldehyde according to Gutsche [12, 13].

2.2. CRYSTAL DATA

Compound A. $C_{60}H_{72}O_6$: formula weight = 888. Orthorhombic, $a = 17.420(3)$, $b = 17.708(3)$; $c = 18.972(3)$ Å; $V = 5852(3)$ Å^3; $Z = 4$; $D_x = 1.01$ g cm^{-3}; $\mu = 4.34$ cm^{-1}, space group $P2_1nb$ (No. 33), or $Pmnb$ (No. 53); $P2_1nb$ chosen after calculation of the distribution of the $\langle |E|^2 - 1 \rangle$ value.

Compound B. $C_{66}H_{84}O_6 + C_6H_6$: formula weight = 1206. Triclinic, $a = 15.065(5)$, $b = 19.103(3)$, $c = 13.868(3)$ Å, $\alpha = 106.95(2)$, $\beta = 102.72(2)$, $\gamma = 80.61(2)°$, $V = 3703(2)$ Å^3; $Z = 2$; $D_x = 1.08$ g cm^{-3}; $\mu = 4.19$ cm^{-1}; space group $P\bar{1}$ (No. 2).

2.3. STRUCTURE DETERMINATION

Single crystals were obtained by slow evaporation of solutions at room temperature: a mixture of carbon disulfide-benzene for compound A; benzene for compound B. Preliminary Weissenberg photographs were taken, then an Enraf Nonius CAD–4 automatic diffractometer was used to refine lattice parameters using 25 accurately centred reflections and to collect intensities of independent reflections; one standard reflection was measured every 60 min to monitor the intensity and the same at 100 reflection intervals to control the orientation of the crystal. Crystals of compound A were of poor quality, so only 1512 independent reflections out of 11370 measured were used for refinement; for compound B, 7390 were used out of 10106 measured. Lorentz and polarisation corrections were applied, but not absorption corrections.

Structures were solved by direct methods using SHELX [14] for A, and MULTAN [15] for B. The best maps for both structures revealed only a few atoms, among them the six oxygens. Step by step, other atoms were found, those of the *para*-substituents with difficulty.

For compound A, a least-squares refinement of coordinates and isotropic thermal parameters was made by the rigid body method using SHELX [14]. Hydrogen atoms were placed in their calculated positions with C—H = 1.08 Å. Final R is 0.185 for 1512 reflection ($I > 2.5\sigma(I)$) and the final electron density map showed the highest residual peak of $0.63e$ Å^{-3}. Table I gives the final atomic coordinates and U_{iso} (numbering scheme in Figure 1) [16]. For compound B, Fourier maps showed additional peaks around some *t*-butyl groups and two of the three benzene molecules. These peaks were added with occupancy factors. The hydrogen atoms of phenol rings and methylene bridges appeared on Fourier difference maps while other hydrogens were calculated at 1.08 Å from C.

Table I.   Fractional atomic coordinates ($\times 10^4$) and U_{iso} ($\times 10^2$) with standard deviations for non-hydrogen atoms (Compound A).

Atoms	x	y	z	U_{iso}
C(37)	0395(8)	5786(5)	11532(5)	09(1)
C(38)	0465(6)	5113(8)	10281(4)	08(1)
C(39)	−0477(6)	5278(8)	9341(5)	09(1)
C(40)	−1461(8)	4913(6)	10389(4)	09(1)
C(41)	−1562(5)	5820(6)	11483(7)	11(1)
C(42)	−0531(6)	6849(6)	11751(8)	09(1)
C(1)	1279(8)	6165(5)	12460(5)	07(1)
C(2)	0898(6)	6953(6)	12449(8)	12(1)
C(3)	0082(6)	6980(6)	12848(8)	09(1)
C(4)	0062(6)	7089(6)	13575(8)	09(1)
C(5)	−0641(6)	7170(6)	13920(8)	09(1)
C(6)	−1323(6)	7143(6)	13436(8)	10(2)
C(7)	−1303(6)	7035(6)	12808(8)	08(1)
C(8)	−2096(5)	6933(6)	12463(7)	09(1)
C(9)	−2274(5)	6079(6)	12418(7)	10(1)
C(10)	−2854(5)	5946(6)	12909(7)	15(1)
C(11)	−3175(5)	5226(6)	12970(7)	14(1)
C(12)	−2916(5)	4641(6)	12539(7)	09(1)
C(13)	−2335(5)	4775(6)	12048(7)	11(1)
C(14)	−1904(8)	4274(6)	11520(4)	08(1)
C(15)	−2403(8)	4088(6)	10872(4)	09(1)
C(16)	−2900(8)	3438(6)	10750(4)	08(1)
C(17)	−3125(8)	3309(6)	10064(4)	08(1)
C(18)	−2853(8)	3738(6)	9499(4)	11(1)
C(19)	−2356(8)	4342(6)	9621(4)	14(1)
C(20)	−2019(6)	4703(8)	8949(5)	16(1)
C(21)	−1252(6)	4379(6)	8731(5)	06(1)
C(22)	−1310(6)	3733(8)	8315(5)	11(2)
C(23)	−0647(6)	3376(8)	8087(5)	09(1)
C(24)	0073(6)	3667(8)	8241(5)	09(1)
C(25)	0131(6)	4314(8)	8657(5)	11(2)
C(26)	0903(6)	4651(8)	8929(4)	08(1)
C(27)	1210(6)	4261(8)	9604(4)	08(1)
C(28)	1772(6)	3701(8)	9576(4)	10(1)
C(29)	2022(6)	3354(8)	10195(4)	14(1)
C(30)	1709(6)	3365(8)	10842(4)	14(1)
C(31)	1147(6)	4127(8)	10870(4)	08(1)
C(32)	0878(8)	4168(5)	11646(5)	07(1)
C(33)	1202(8)	4881(5)	12035(5)	08(9)
C(34)	1755(8)	4662(5)	12525(5)	12(1)
C(35)	2071(8)	5195(5)	12983(5)	10(1)
C(36)	1833(8)	5946(5)	12950(5)	07(1)
C(37)	0964(8)	5633(5)	12002(5)	10(1)
C(38)	0897(6)	4474(8)	10251(4)	07(1)
C(39)	−0532(6)	4670(8)	8902(5)	08(1)
C(40)	−2131(8)	4517(6)	10307(4)	10(1)
C(41)	−2014(5)	5494(6)	11988(7)	07(1)
C(42)	−0601(6)	6953(6)	12464(8)	08(1)
C(51)	−0727(6)	7257(6)	14723(8)	14(1)
C(52)	−0148(6)	6712(6)	15095(8)	17(0)
C(53)	−0609(6)	8111(6)	14835(8)	20(0)
C(111)	−3787(5)	4937(6)	12456(7)	17(0)

Table I. *Continued.*

Atoms	x	y	z	U_{iso}
C(112)	−4487(5)	5429(6)	13484(7)	20(0)
C(113)	−3486(5)	4737(6)	14173(7)	17(0)
C(171)	−3802(8)	2774(6)	9908(4)	17(0)
C(172)	−3640(8)	1937(6)	10073(4)	17(0)
C(173)	−4665(8)	2959(6)	9969(4)	20(0)
C(231)	−0695(6)	2666(8)	7595(5)	16(1)
C(232)	−0796(6)	2839(8)	6804(5)	20(0)
C(233)	−1330(6)	2128(8)	7860(5)	17(0)
C(291)	2565(6)	2668(8)	10140(4)	15(1)
C(292)	2402(6)	1980(8)	9652(4)	17(0)
C(293)	2423(6)	2792(8)	10257(4)	20(0)
C(351)	2727(8)	4999(5)	13503(5)	17(0)
C(352)	3517(8)	4915(5)	13184(5)	17(0)
C(353)	2692(8)	5448(5)	14183(5)	20(0)

Fig. 1.   Numbering scheme.
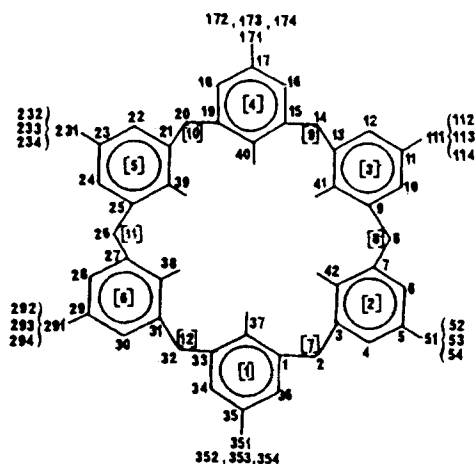
Refinement of positional parameters, anisotropic U_{ij} for carbon, and oxygen atoms except those with occupancy < 1.0 led to $R = 0.12$ with unit weight for 7340 reflections ($I > 2.5\sigma(I)$), $(\Delta/\sigma)_{av} = 0.42$ and residual density $= 0.32e$ Å^{-3}; Table II gives the final atomic coordinates and U_{eq} (with the same numbering scheme) [17]. The thermal parameters for compound B, the observed and calculated structure factors for both compounds are in supplementary Publication No. 82071 deposited at the British Library.

3. Discussion of Results

Some selected bond distances and angles as well as torsion angles are given in Table III for compound B. Unfortunately, due to the quite limited number of observed reflections, the e.s.d. values are high for compound A. Oxygen atoms are at the corners of a boat conformation hexagon. No particular disymmetry is found around the C—O bonds as

Table II.   Fractional coordinates ($\times 10^4$) and U_{eq} ($\times 10^2$) with standard deviations of non-hydrogen atoms (Compound B). Occupation factors in brackets.

Atoms	x	y	z	U_{eq}
Calix				
O(37)	9089(4)	2674(3)	8011(4)	057(2)
O(38)	9734(4)	3545(3)	9802(4)	066(3)
O(39)	11000(4)	3017(3)	11165(5)	069(3)
O(40)	11779(4)	1655(3)	10801(4)	057(2)
O(41)	10042(4)	1454(3)	10573(4)	063(3)
O(42)	8766(4)	1935(3)	9224(5)	069(3)
C(1)	7512(5)	2549(4)	7257(6)	053(3)
C(2)	7658(7)	1708(4)	7208(7)	058(4)
C(3)	7377(5)	1548(4)	8105(6)	051(3)
C(4)	6541(6)	1289(5)	7992(7)	063(4)
C(5)	6257(6)	1144(5)	8793(7)	069(4)
C(6)	6812(6)	1300(5)	9724(8)	060(4)
C(7)	7654(5)	1572(4)	9902(6)	050(4)
C(8)	8209(6)	1751(5)	10969(7)	059(4)
C(9)	8891(5)	1121(4)	11226(5)	050(3)
C(10)	8604(6)	0655(4)	11696(6)	056(4)
C(11)	9208(6)	0076(4)	11967(6)	056(3)
C(12)	10082(6)	−0003(4)	11796(6)	055(4)
C(13)	10407(5)	0445(4)	11352(6)	052(3)
C(14)	11357(7)	0356(5)	11206(8)	060(4)
C(15)	11954(6)	0918(4)	11988(6)	051(3)
C(16)	12327(7)	0842(5)	12944(8)	062(4)
C(17)	12834(5)	1325(4)	13718(6)	058(3)
C(18)	12983(5)	1959(4)	13457(6)	058(3)
C(19)	12636(5)	2069(4)	12502(6)	052(3)
C(20)	12808(5)	2788(4)	12289(7)	056(4)
C(21)	12106(5)	3437(4)	12644(6)	050(3)
C(22)	12339(6)	3950(4)	13750(6)	058(4)
C(23)	11718(5)	4536(4)	13974(6)	052(3)
C(24)	10855(6)	4575(4)	13398(6)	051(4)
C(25)	10580(5)	4076(4)	12458(6)	048(3)
C(26)	9586(6)	4103(5)	11962(7)	055(4)
C(27)	9237(5)	4535(4)	11147(6)	048(3)
C(28)	8762(5)	5235(4)	11441(6)	052(3)
C(29)	8318(4)	8614(4)	10719(6)	054(4)
C(30)	8375(5)	5278(5)	9708(4)	052(3)
C(31)	8850(5)	4590(4)	9366(6)	048(3)
C(32)	8831(6)	4243(5)	8250(5)	055(4)
C(33)	8070(5)	3745(4)	7753(6)	049(4)
C(34)	7198(6)	4016(5)	7377(7)	055(4)
C(35)	6468(5)	3611(4)	6950(6)	055(3)
C(36)	6662(6)	2846(5)	6888(6)	058(4)
C(37)	8222(5)	2984(4)	7673(6)	049(3)
C(38)	9273(5)	4243(4)	10130(6)	051(3)
C(39)	11241(5)	3520(4)	12093(5)	050(3)
C(40)	12128(5)	1557(4)	11760(6)	050(3)
C(41)	9761(5)	1000(4)	11055(6)	052(3)
C(42)	7920(5)	1681(4)	9056(6)	051(3)
C(51)	5302(8)	0840(7)	8694(8)	106(6)
C(52) [0.53]	5089(18)	0338(13)	7562(21)	100(0)

Table II.   *Continued.*

Atoms	x	y	z	U_{eq}
C(53) [0.53]	4531(18)	1368(20)	8300(20)	100(0)
C(54) [0.53]	4854(17)	1194(13)	9606(20)	100(0)
C(55) [0.47]	5662(15)	−0026(9)	8656(18)	100(0)
C(56) [0.47]	5465(15)	0226(11)	9240(16)	100(0)
C(57) [0.47]	4756(15)	0766(13)	7559(13)	100(0)
C(111)	8867(6)	−0425(5)	12515(7)	071(4)
C(112) [0.52]	7857(18)	−0611(13)	11907(19)	100(0)
C(113) [0.52]	8818(17)	−0010(13)	13632(18)	100(0)
C(114) [0.52]	9507(17)	−1142(13)	12441(18)	100(0)
C(115) [0.48]	9237(18)	−1250(14)	11927(20)	100(0)
C(116) [0.48]	7831(18)	−0032(14)	12475(21)	100(0)
C(117) [0.48]	9414(18)	−0236(14)	13656(20)	100(0)
C(171)	13232(6)	1222(5)	12786(7)	073(4)
C(172) [0.69]	13094(11)	0471(9)	14873(18)	100(0)
C(173) [0.69]	14316(12)	1231(9)	15001(13)	100(0)
C(174) [0.69]	12818(12)	1820(9)	15604(13)	100(0)
C(175) [0.31]	13713(25)	1857(21)	15571(31)	100(0)
C(176) [0.31]	12313(25)	1290(20)	15308(28)	100(0)
C(177) [0.31]	13923(25)	0559(19)	14633(28)	100(0)
C(231)	11992(6)	5060(4)	15027(6)	063(4)
C(232)	12151(9)	4614(7)	15873(10)	111(4)
C(233)	12888(8)	5371(7)	15109(10)	103(3)
C(234)	11284(10)	5711(7)	15270(10)	116(4)
C(291)	7751(5)	6373(4)	11071(7)	065(4)
C(292) [0.85]	7114(9)	6333(8)	11772(11)	100(0)
C(293) [0.85]	7196(9)	6627(7)	10172(10)	100(0)
C(294) [0.85]	8454(9)	6939(8)	11710(11)	100(0)
C(295) [0.15]	6706(25)	6250(42)	10801(52)	100(0)
C(296) [0.15]	8338(41)	6958(30)	11038(56)	100(0)
C(297) [0.15]	7560(48)	6545(40)	12180(27)	100(0)
C(351)	5501(6)	3908(5)	6536(7)	071(4)
C(352)	5414(8)	4757(7)	6757(9)	092(3)
C(353)	5267(8)	3590(6)	5392(9)	085(3)
C(354)	4787(9)	3732(8)	7049(11)	106(4)
Solvent				
C(101)	9949(8)	7452(7)	4318(9)	095(7)
C(102)	9506(10)	6961(6)	4553(10)	106(6)
C(103)	9336(9)	7090(7)	5525(12)	102(7)
C(104)	9601(10)	7684(7)	6277(9)	109(6)
C(105)	10023(13)	8166(8)	6024(11)	141(8)
C(106)	10198(9)	8058(8)	5088(11)	119(7)
C(201) [0.58]	5781(11)	2292(10)	2682(10)	120(0)
C(202) [0.58]	6620(11)	2581(10)	3068(10)	120(0)
C(203) [0.58]	7267(11)	2295(10)	3783(10)	120(0)
C(204) [0.58]	7074(11)	1721(10)	4111(10)	120(0)
C(205) [0.58]	6235(11)	1433(10)	3724(10)	120(0)
C(206) [0.58]	5588(11)	1718(10)	3010(10)	120(0)
C(301) [0.62]	7020(7)	3771(7)	10237(10)	120(0)
C(302) [0.62]	4329(7)	3369(7)	9574(10)	120(0)
C(303) [0.62]	5567(7)	3290(7)	9935(10)	120(0)
C(304) [0.62]	5496(7)	3613(7)	10960(10)	120(0)

Table II. *Continued.*

Atoms	x	y	z	U_{eq}
C(305) [0.62]	6187(7)	4014(7)	11623(10)	120(0)
C(306) [0.62]	6949(7)	4094(7)	11262(10)	120(0)
C(401) [0.42]	7020(16)	2392(12)	3392(20)	120(0)
C(402) [0.42]	7112(16)	2055(12)	4181(20)	120(0)
C(403) [0.42]	6443(16)	1630(12)	4181(20)	120(0)
C(404) [0.42]	5681(16)	1541(12)	3391(20)	120(0)
C(405) [0.42]	5589(16)	1878(12)	2602(20)	120(0)
C(406) [0.42]	6258(16)	2304(12)	2603(20)	120(0)
C(501) [0.38]	6225(13)	4337(12)	9972(16)	120(0)
C(502) [0.38]	6748(13)	3579(12)	9823(16)	120(0)
C(503) [0.38]	6167(13)	3163(12)	10027(16)	120(0)
C(504) [0.38]	5364(13)	3503(12)	10380(16)	120(0)
C(505) [0.38]	5141(13)	4677(12)	10324(16)	120(0)
C(506) [0.38]	5722(13)	4677(12)	10324(16)	120(0)

Table III. Selected bond distances (Å), bond angles (°) and torsion angles (°) for compound **B**.

C(1)—C(2)	1.57(1)		C(19)—C(20)	1.56(1)	
C(2)—C(3)	1.52(1)		C(20)—C(21)	1.53(1)	
C(7)—C(8)	1.50(1)		C(25)—C(26)	1.50(1)	
C(8)—C(9)	1.62(1)		C(26)—C(27)	1.54(1)	
C(13)—C(14)	1.49(1)		C(31)—C(32)	1.49(1)	
C(14)—C(15)	1.51(1)		C(32)—C(33)	1.52(1)	
C(37)—O(37)	1.38(1)		C(40)—O(40)	1.37(1)	
C(38)—O(38)	1.40(1)		C(41)—O(41)	1.40(1)	
C(39)—O(39)	1.38(1)		C(42)—O(42)	1.39(1)	
O(37)—O(38)	2.63(1)		O(40)—O(41)	2.64(1)	
O(38)—O(39)	2.67(1)		O(41)—O(42)	2.62(1)	
O(39)—O(40)	2.63(1)		O(42)—O(37)	2.65(1)	
C(1)—C(2)—C(3)	112.7(7)		C(19)—C(20)—C(21)	112.4(7)	
C(7)—C(8)—C(9)	114.6(7)		C(25)—C(26)—C(27)	119.3(9)	
C(13)—C(14)—C(15)	114.2(8)		C(31)—C(32)—C(33)	113.3(8)	
C(1)—C(37)—O(37)	120.1(7)		C(15)—C(40)—O(40)	119.3(7)	
C(35)—C(37)—O(37)	119.7(8)		C(19)—C(40)—O(40)	121.2(7)	
C(3)—C(42)—O(42)	121.0(8)		C(21)—C(39)—0(39)	119.0(7)	
C(7)—C(42)—O(42)	116.8(8)		C(25)—C(39)—O(39)	118.6(8)	
C(9)—C(41)—O(41)	118.9(7)		C(27)—C(38)—0(38)	119.7(7)	
C(13)—C(41)—O(41)	118.0(9)		C(31)—C(38)—O(38)	116.0(7)	

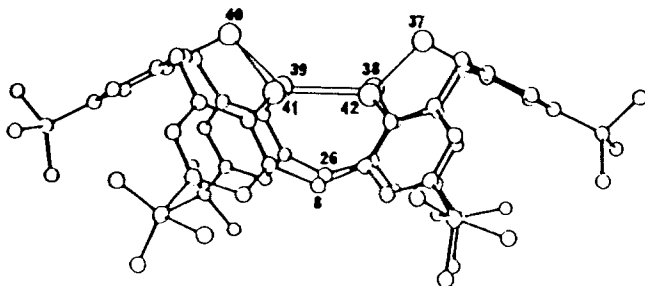|	
C(37)—C(1)—C(2)—C(3)	96(1)
C(1)—C(2)—C(3)—C(42)	−77(1)
C(42)—C(7)—C(8)—C(9)	−90(1)
C(7)—C(8)—C(9)—C(41)	89(1)
C(41)—C(13)—C(14)—C(15)	77(1)
C(13)—C(14)—C(15)—C(40)	−99(1)
C(40)—C(19)—C(20)—C(21)	94(1)
C(19)—C(20)—C(21)—C(39)	−78(1)
C(39)—C(25)—C(26)—C(27)	−93(1)
C(25)—C(26)—C(27)—C(38)	86(1)
C(38)—C(31)—C(32)—C(33)	83(1)
C(31)—C(32)—C(33)—C(37)	−93(1)

Fig. 2.   Conformation of the macrocycles (A or B) showing symmetry planes.

reported by Hirshfeld [18]; furthermore the positions of H-atoms are not well defined on difference syntheses, perhaps because hydrogen bonds are of the 'flip-flop' type. For both compounds the macrocycles possess two pseudosymmetry planes: the first is through C(8) and C(26) and the centres of O(38)—O(39) and O(41)—O(42), the second through O(37), O(40) and the centres of O(38)—O(42) and O(39)—O(41). The first plane seems to be an intersection of two cones as shown in Figure 2. These macrocycles can be described as a pitched cone as reported by several authors [11, 19–20]. The conformation of these macrocycles seems to be the same as that of the *p-t*-butyl derivative without a guest molecule [11]. The angles at the methylene bridges have values from 112.4 to 119.3° for compound B; the C—CH$_2$—C point out of the calix except for two of them at C(8) and C(26) which point inside; the signs of the torsional angles in Table III show this fact too. The same is found for compound A. Some dihedral angles have been calculated and are given in Table IV; for both compounds angles between aromatic planes are about 107° except between 2–3, and 5–6 (values around 120°–130°); dihedral angles between methylene group planes and phenol rings are also given. Thus the two compounds have the same conformation but they crystallize with one main difference: with or without solvent molecules.

The molecular packing is given in Figures 3 and 4. For compound A only Van der Waals interactions are evident with isopropyl groups, some of them near oxygen atoms. Due to the similarity of the symmetry group, this structure is probably isomorphous with *p-t*-butylcalix[6]arene published by Andreetti [11].

Table IV.   Dihedral angles (compound B). Numbering of the planes are reported in brackets in Figure 1.

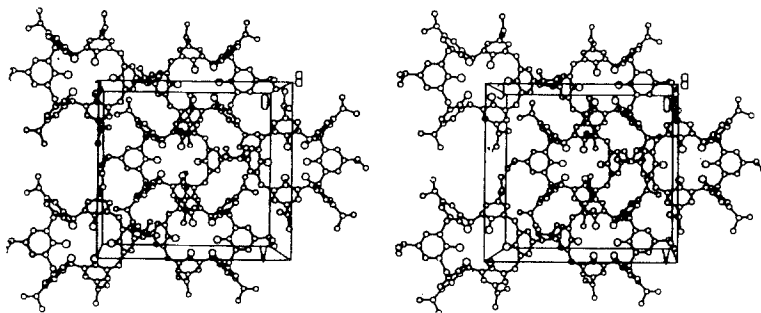| Planes	Planes	Angles	Planes	Planes	Angles
1	2	106.7(3)°	1	7	96.3(3)°
2	3	119.3(3)°	7	2	102.4(2)°
3	4	107.0(3)°	2	8	90.3(3)°
4	5	106.1(3)°	8	3	91.1(3)°
5	6	134.4(3)°	3	9	102.5(1)°
6	1	107.8(3)°	9	4	99.7(1)°
			4	10	94.8(2)°
			10	5	101.1(2)°
			5	11	91.5(1)°
			11	6	98.3(2)°
			6	12	94.5(2)°
			12	1	93.2(2)°

Fig. 3.   Stereoscopic view of the structure seen along [010] drawn by Pluto (Compound A).

Table V.   Intermolecular bonds (Compound B).

Benzene I: interactions (<4 Å) with ring 3 and *tert*-butyl of ring 4.

C(105)—C(9)	3.75	C(102)—C(174)	3.82	C(103)—C(176)	3.92
C(105)—C(10)	3.72	C(103)—C(174)	3.84	C(104)—C(176)	3.30
C(105)—C(11)	3.84	C(104)—C(174)	3.64	C(105)—C(176)	3.73
C(105)—C(12)	3.91	C(101)—C(176)	3.88	C(106)—C(176)	3.76
C(105)—C(13)	3.94	C(102)—C(176)	3.96	C(103)—C(24)	3.96
				C(103)—C(23)	4.00

Benzene III: interactions (<4 Å) with rings 1–2–6.

C(301)—C(42)	3.98	C(302)—C(1)	3.82	C(302)—C(7)	3.78
C(301)—C(27)	3.68	C(302)—C(3)	3.77	C(302)—C(35)	3.85
C(301)—C(28)	3.90	C(302)—C(4)	3.94	C(302)—C(36)	3.69
C(301)—C(38)	3.69	C(302)—C(6)	3.96	C(302)—C(42)	3.68
C(301)—C(31)	3.94	C(306)—C(27)	3.73		
C(303)—C(5)	3.99	C(306)—C(28)	3.69		
C(303)—C(6)	3.91				

Benzene III': interactions (<4 Å) with rings 1–2–6.

C(501)—C(34)	3.80	C(502)—C(1)	3.85	C(503)—C(3)	3.93
C(501)—C(35)	4.00	C(502)—C(7)	3.88	C(503)—C(4)	3.90
C(501)—C(28)	3.91	C(502)—C(33)	3.95	C(503)—C(5)	3.73
C(501)—C(29)	3.71	C(502)—C(34)	3.94	C(503)—C(6)	3.46
C(501)—C(30)	3.70	C(502)—C(35)	3.93	C(503)—C(7)	3.45
C(501)—C(31)	3.91	C(502)—C(36)	3.88	C(503)—C(42)	3.70
C(502)—C(37)	3.90	C(502)—C(42)	3.73		

Benzene II and II': interactions (<4 Å)

C(202)—C(8)	3.98	C(204)—C(113)	3.86	C(205)—C(116)	3.99
C(405)—C(54)	3.93	C(401)—C(8)	3.94	C(406)—C(8)	3.93

Benzene I: interactions (<4 Å) with other calix[6]arenes.

x, y, z + 1				x, y + 1, z	
C(101)—O(37)	3.75	C(101)—C(294)	3.76	C(102)—C(234)	3.46
		C(103)—C(234)	3.62	C(102)—C(294)	3.90

Benzene II and II': interactions (<4 Å) with other calix[6]arenes:

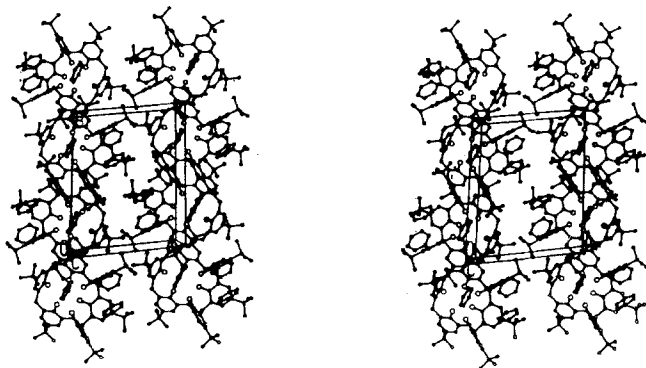| x − 1, y, z				x, y, z + 1	
C(205)—C(173)	3.83	C(204)—C(36)	3.95	C(403)—C(36)	3.77
C(403)—C(173)	3.88	C(402)—C(353)	3.96	C(403)—C(353)	3.93

Fig. 4.   Stereoscopic view of the structure seen along [001] drawn by Pluto (Compound B).

Compound B is a 1 : 3 complex with benzene. Table V shows the interactions (<4 Å) between the different benzene (I, II, III) and the calix[6]arene molecules. As mentioned previously benzene II and III are disordered in different manners: the angle between the ring planes II and II' is 17.7° while it is 74.4° between planes III and III', almost perpendicular. From Table V we see that molecule III interacts with three phenyl rings of a calixarene molecule, so this benzene is inside the half cone of the host molecule. Benzene I interacts with a ring and a t-butyl group, at the bottom of the cone, so there are some interactions with calixarene molecules translated by b or c. At least, benzene II has few interactions: some with the calix(x, y, z) and others with calix($x - 1$, y, z) and (x, y, $z + 1$). If we refer to Weber and Josel's [21] nomenclature, this compound is an intercalato cavitate, binary, monomolecular, trinuclear complex. Along the a axis, macrocycles and solvent form a column with cavities in the same direction; the next column in the b direction is antiparallel with cavities in the opposite direction.

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