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p-tert-Butylcalix[5]arene: A New Synthetic Pathway and Crystal Structure of the *N*,*N*-Dimethylformamide Complex

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Abstract. The formation of *p-tert*-butylcalix[5]arene by the opening of *p-tert*-butyldihomooxacalix arene and the addition of a monomer has been studied. Various facets, including the effects of bases and the nature of the monomer added to the *p-tert*-butyldihomooxacalix[4]arene, have been investigated. *p-tert*-Butylcalix[5]arene can be prepared in yields up to 30%. The structure of its 1 : 2 complex with DMF has been determined by X-ray crystallography. Crystals are triclinic, space group $P\bar{1}$, a = 1428.2(3) pm, b = 1837.3(3) pm, c = 1276.1(2) pm, α = 108.98(1)°, β = 105.02(2)°, γ = 95.21(1)°, Z = 2, D_c = 1.059 kg m^{-3}, final R value = 0.087. The macrocycle adopts a cone conformation, one guest enclosed inside the cavity, the other one outside.

Key words: *p-tert*-Butylcalix[5]arene, synthesis, complexation, crystal structure.

Supplementary Data relating to this article have been deposited with the British Library as Supplementary Publication No. SUP 82222 (154 pages).

1. Introduction

Hitherto *p-tert*-butylcalix[5]arene has been prepared from *p-tert*-butylphenol and formaldehyde and isolated from a mixture of calixarenes. In 1981 Ninagawa and Matsuda [1] isolated it in ca. 6% yield. Subsequently, Stewart and Gutsche [2] improved the yield to 15%: a slurry of *p-tert*-butylphenol, *p*-formaldehyde and KOH in tetralin was stirred and heated up to 80–85°C for 1.5 h; the temperature was then rapidly increased to 180–185°C for 10 min and maintained at 160–165°C for 3 h. After several separations, *p-tert*-butylcalix[5]arene was obtained. A similar procedure was later published by Shinkai [3] in which comparable yields were reported.

Recent studies dealing with the mechanisms of formation of calixarenes [4, 5] have shown that cyclisation occurs via hemi- or pseudocalixarenes, formed by addition reactions of monomers and linear oligomers. Under these conditions, one-

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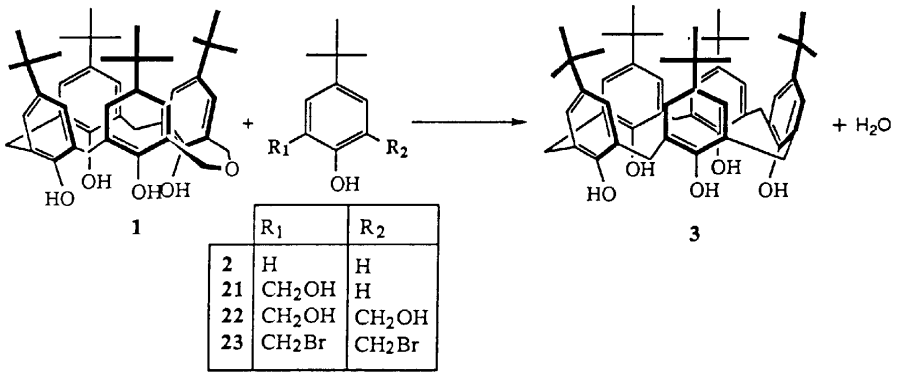

	R_1	R_2
2	H	H
21	CH_2OH	H
22	CH_2OH	CH_2OH
23	CH_2Br	CH_2Br

Scheme 1.

step reactions preferentially lead to even-numbered calixarenes. In order to prepare the odd-numbered calixarenes, an alternative to the Gutsche reaction pathway was studied in our laboratory.

In the first part of this work, we describe a new synthetic pathway to *p-tert*-butylcalix[5]arene **3**, involving the addition of different monomers **2**–**21**–**22**–**23**, to *p-tert*-butyldihomooxacalix[4]arene **1** in the presence of different bases, as depicted in Scheme 1.

Employing the same procedures and using a compound other than *p-tert*-butylphenol for reaction component **2**, we have tried to obtain new calix[5]arenes with four *p-tert*-butylphenol groups and one alkylphenol moiety. This is described in the second part of this work.

Calixarenes are able to form complexes with several small organic molecules in the solid state. Six X-ray crystal structures of differently substituted calix[5]arenes have been reported. One is of the empty form of *p*-(1,1,3,3-tetramethylbutyl)calix[5] arene [6]. The five other structures are of complexes: calix[5]arene–acetone 1 : 2 [7] (one guest is inside the cavity formed by the macrocycle and the other outside); *p*-(1,1,3,3-tetramethylbutyl)calix[5]arene–toluene 1 : 1 [6]; *p-tert*-butylcalix[5]arene–tetralin 1 : 1 [8] (the guest being inside the cavity); *p-tert*-butylcalix[5]arene–*n*-hexane 1 : 0.3 [9] and *p-tert*-butylcalix[5]arene–ethylacetate [10] where the *tert*-butyl groups from one macrocycle are located in the cavity of a neighbouring calixarene.

In the third part, we describe the structure of a new complex of *p-tert*-butylcalix-[5]arene with *N*,*N*,-dimethylformamide.

2. Synthesis of *p-tert*-Butylcalix[5]arene

2.1. Experimental

The analysis of the products was carried out by isolation and by HPLC methods [11]. Compound **1** was prepared as previously described [12] and easily obtained

in a one step reaction in quantities larger than 15 g. Compounds **2**, **21**, **22** and **23** were synthesized in our laboratory.

A mixture of 1.6 g (2.35 mmol) of **1**, 0.354 g (2.35 mmol) of **2** and 30 mL of tetralin were stirred in a three-necked flask equipped with a mechanical stirrer, a Dean-Stark trap fitted with a condenser, and a nitrogen inlet. The turbid mixture was heated to 190°C by means of a heating mantle. When the mixture became clear, at about 60°C, 100 mL of 4N potassium hydroxide (0.4 mmol) was added. During this time, the reaction mixture turned to a light yellow. The heat was increased rapidly. During this heating period, the color of the reaction mixture changed from yellow to orange and finally to a dark red-brown. The reaction mixture was held at 180–190°C for 4 h and then allowed to cool to room temperature.

When cooled, the reaction mixture was analysed by HPLC, showing a 32% yield of **3**. The solution was evaporated to dryness in vacuo and the dark brown gummy residue was stirred vigorously with 40 mL of $CHCl_3$ and 20 mL of 1N hydrochloric acid for 20 min. The chloroform layer was washed three times with 40 mL of water, dried, and the solvent removed in vacuo.

The new residue was triturated by refluxing for 30 min with 40 mL of acetone and hot filtered to leave 200 mg of a white powder (a mixture of the *p-tert*-butylcalix[4]arene, *p-tert*-butylcalix[6]arene and *p-tert*-butylcalix[8]arene). The filtrate was concentrated to 25–30 mL and was placed in a freezer at −30°C. After some hours, 403 mg of **3**, as diamond-shaped crystals, was collected by filtration. The filtrate was again concentrated and placed in the freezer. After some days, a new precipitate gave 126 mg of **3**. After further concentration a final 43 mg of **3** was obtained by crystallisation. The total yield was 572 mg of *p-tert*-butylcalix[5]arene. ^{1}H-NMR (200 MHz, $CDCl_3$, relative to TMS): δ_H 1.25 (45H, s, —$C(CH_3)_3$), 3.4–4.3 (10H, br. s, Ar—CH_2—Ar), 7.2 (10H, s, Ar—H), 8.65 (5H, s, —OH). TLC analysis was carried out on silica gel plates with the eluant shown below, which allowed the various calixarenes to be detected as separate spots. The bracketed numbers represent the calix[n]arenes with n = 4–8. R_f values with hexane/acetone (9.5 : 0.5): [4] = 0.59, [5] = 0.64, [6] = 0.39, [7] = 0.31, [8] = 0.29.

2.2. RESULTS AND DISCUSSION

Using tetralin as solvent, **1** and **2** as reactants, and a reaction temperature of 180–190°C, the effect of the bases NaOH, LiOH, KOH, $KOC(CH_3)_3$, CsOH and RbOH was studied. The data in Figure 1 show the influence of these bases on the reaction.

The change in the yields of the cyclic pentamer according to the different bases was noticeable. The lowest yield was obtained with NaOH (11.3%) and the best yield reached 32% (HPLC yield) with KOH. The cation seems to play an important part in the cyclization of the phenolic oligomers. The somewhat greater yield of *p-tert*-butylcalix[5]arene in the presence of K^+ suggests that a template effect may be operating.

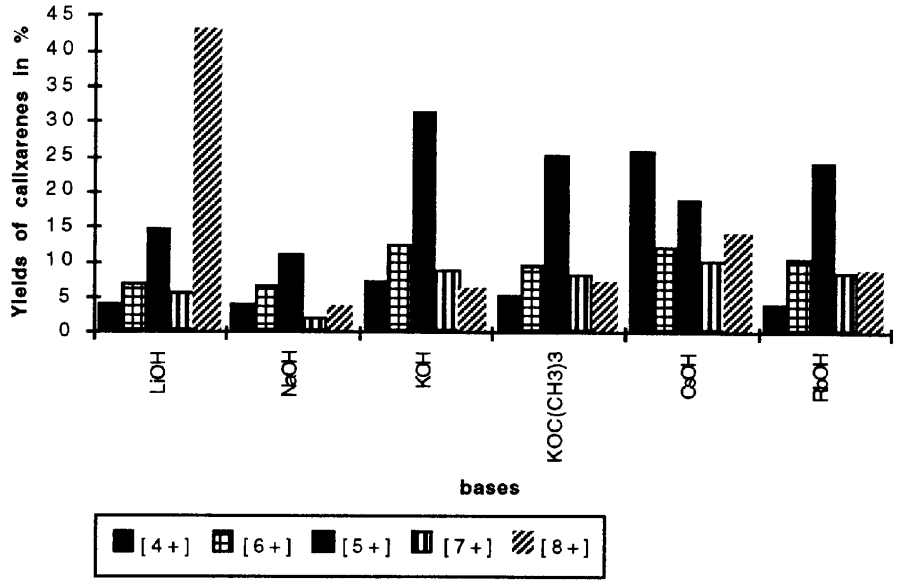

Figure 1. Yields of calixarenes as a function of the base; $[n+]$: p-*tert*-butylcalix[n]arene.

As a function of the nature of the added monomer, significant differences in the yields of the calixarene were observed (Figure 2). We note that p-*tert*-butylphenol is the best monomer for the production of p-*tert*-butylcalix[5]arene in this addition reaction.

3. Synthesis of Alkylcalixarenes

3.1. EXPERIMENTAL

The experimental conditions used were the same as above. 3,4-Dimethylphenol, p-isopropylphenol, p-(1,1,3,3)-tetramethylbutylphenol, phenol, 3-methylphenol and 4-methylphenol were used as component **2**.

Using 3,4-dimethylphenol, the corresponding calixarene (4,5 dimethyl-11,17,23,29-tetra-*tert*-butylcalix[5]arene) was isolated by column chromatography using petroleum ether/acetone (9/1) as eluant to yield 1.35% of the desired product. ^{1}H-NMR (200 MHz, $CDCl_3$, relative to TMS) δ_H 1.28, 1.26, 1.25, 1.24 (each 9H; each s; Ar—C(CH_3)$_3$), 2.18 (3H; s; Ar—CH_3), 2.38 (3H; s; Ar—CH_3), 3.89 (10H; br.; Ar—CH_2—Ar), 7.18–6.99 (9H; m; Ar—H), 8.71 (1H; s; Ar—OH), 8.84 (1H; s; Ar—OH), 8.89 (2H; s; Ar—OH), 8.99 (1H; s; Ar—OH) and one molecule of tetrahydronaphthalene per molecule of calixarene. ^{13}C-NMR (50.32 MHz, $CDCl_3$, relative to TMS) δ_C 16.74 (Ar—$\underline{C}H_3$), 20.35 (Ar—$\underline{C}H_3$), 23.2 (Ar—$\underline{C}H_2$—Ar), 29.37 (Ar—$\underline{C}H_2$—Ar), 31.43–31.92 (Ar—C($\underline{C}H_3$)$_3$), 33.90 (Ar—$\underline{C}$(CH_3)$_3$), 125.00–130.00 ($\underline{C}H_{Ar}$), 134.75—148.8 ($\underline{C}_{Ar}$). MS (FAB +) : 789.7 $[M + Li]^+$. Crys-

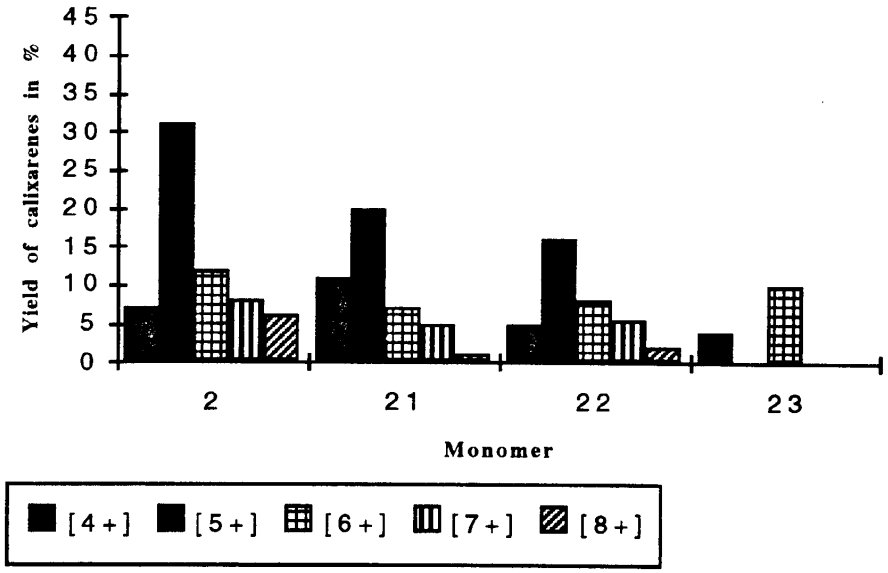

Figure 2. Yields of calixarenes as a function of the monomer. [n+]: *p-tert*-butylcalix[n]arene. **2**: *p-tert*-butylphenol, **21**: 2-hydroxymethyl-*p-tert*-butylphenol, **22**, 2,6-dihydroxymethyl-*p-tert*-butylphenol, **23**: 2,6-dibromomethyl-*p-tert*-butylphenol.

Table I. Mass spectrometry of alkylcalix[5]arenes

Compounds	MS (ES)
4-methyl-11,17,23,29-tetra-*tert*-butylcalix[5]arene	767.6 $[M - H]^-$
5-methyl-11,17,23,29-tetra-*tert*-butylcalix[5]arene	794.4 $[M + Na]^+$
5-isopropyl-11,17,23,29-tetra-*tert*-butylcalix[5]arene	795.6 $[M - H]^-$
11,17,23,29-tetra-*tert*-butylcalix[5]arene	753.5 $[M - H]^-$
5-(1,1,3,3)tetramethylbutyl-11,17,23,29-tetra-*tert*-butylcalix[5]arene	865.6 $[M - H]^-$

tallized from tetralin: $C_{53}H_{66}O_5 + C_{10}H_{12}$. *Analysis found* C, 82.50; H, 9.01; O, 8.36. *Calc.* for C, 82.67; H, 8.59; O, 8.74.

In the other cases, mixtures of calixarenes were obtained, the corresponding alkylcalixarenes were identified in the mixture by HPLC and MS (Table I).

4. Structure of the *p-tert*-Butylcalix[5]arene–*N,N*-dimethyIformamide Complex

4.1. EXPERIMENTAL

Crystals suitable for X-ray determination were grown by slow evaporation of a saturated solution in N,N-dimethylformamide.

A crystal of dimensions 0.3 × 0.3 × 0.7 mm^3 was sealed in a Lindemann capillary and used for data collection on a Nonius CAD4 diffractometer using

Table II. Crystallographic data.

$C_{55}O_5H_{70}$, $C_6O_2N_2H_{14}$		
M = 957.344 g mol^{-1}		
Triclinic		
Space group $P\bar{1}$		
a = 1428.2(3) pm	b = 1837.3(3) pm	c = 1276.1(2) pm
α = 108.98(1)°	β = 105.02(2)°	γ = 95.21(1)°
V = 3001(1) × 10^6 pm^3		
Z = 2		
D_c = 1.059 kg m^{-3}		
F(000) = 2600		
CuK_α radiation:	λ = 154.056 pm	μ = 5045 m^{-1}
T = 293 K		

CuK$_\alpha$ radiation. Accurate unit cell dimensions were obtained by a least-squares fit of 25 reflections ($10 < \theta < 48°$).

Intensity data were collected up to θ = 73°. Three standard reflections were measured every hour to determine intensity variation (−11.2% in 200 h). Lorentz polarization and absorption corrections were applied using programs of the SDP system [13] (T_{min} = 0.788, T_{max} = 0.999, average transmission 0.900). 13156 reflections were measured, 11845 considered as unique, 9553 used in the refinement.

The structure was solved by MULTAN [14] and refined by SHELXL-93 [15]. From direct methods, the first E-map revealed the non-H atoms of the five phenolic moieties but only some of the carbon atoms of the *tert*-butyl groups. Some cycles of difference Fourier synthesis showed the positions of the remaining atoms and of two N,N-dimethylformamide molecules. The structure was refined by least-squares methods with anisotropic temperature factors for all non-H atoms. Hydrogen atoms were calculated at theoretical positions and introduced in structure factor calculations with isotropic temperature factors. Two *tert*-butyl groups (B and E) are disordered over two orientations. The final R value was 0.087 (with $F > 4\sigma(F)$). The maximum and the minimum residual electron density was, respectively, 0.20×10^{-6} and -0.18×10^{-6} e pm^{-3}.

The crystallographic data are collected in Table II. Final atomic coordinates and thermal parameters of the non-H atoms are given in Table III. Large thermal parameters have been found for non-H atoms of methyl groups and guest molecules. This is often the case for this type of macrocycle [9, 10]. Bond distances and bond angles are in good agreement with other calix[5]arenes and have been deposited as supplementary data.

Table III. Positional and thermal parameters

Atom	x	y	z	B_{eq}
O(1A)	−0.0726(2)	0.0076(2)	−0.2476(3)	6.01(9)
C(1A)	−0.0476(2)	0.0641(2)	−0.2903(3)	4.09(9)
C(2A)	0.0318(2)	0.0640(2)	−0.3340(2)	4.04(7)
C(3A)	0.0587(2)	0.1275(2)	−0.3639(3)	4.05(7)
C(4A)	0.0073(3)	0.1885(2)	−0.3565(3)	4.29(8)
C(40A)	0.0377(4)	0.2599(3)	−0.3872(4)	5.6(1)
C(41A)	−0.0437(7)	0.2601(5)	−0.4917(7)	9.4(2)
C(42A)	0.1299(7)	0.2544(6)	−0.424(1)	10.4(4)
C(43A)	0.0527(9)	0.3334(4)	−0.2862(8)	10.1(3)
C(5A)	−0.0772(2)	0.1820(2)	−0.3225(3)	4.40(8)
C(6A)	−0.1058(2)	0.1212(2)	−0.2891(3)	4.05(7)
C(7A)	−0.1980(2)	0.1182(2)	−0.2519(3)	4.78(9)
O(1B)	−0.1049(2)	0.1136(1)	−0.0231(2)	4.86(6)
C(1B)	−0.1435(2)	0.1784(2)	−0.0321(3)	4.09(8)
C(2B)	−0.1874(2)	0.1836(2)	−0.1393(3)	4.40(8)
C(3B)	−0.2187(3)	0.2536(3)	−0.1408(4)	5.2(1)
C(4B)	−0.2075(4)	0.3167(3)	−0.0411(5)	6.3(1)
C(40B)	−0.2362(7)	0.3951(4)	−0.0446(7)	9.4(2)
C(41B)	−0.179(2)	0.4256(9)	−0.107(2)	10.4(3)
C(42B)	−0.209(2)	0.4590(7)	0.075(2)	10.3(3)
C(43B)	−0.344(2)	0.386(1)	−0.058(2)	12.0(4)
C(44B)	−0.279(1)	0.3914(7)	−0.170(1)	11.6(3)
C(45B)	−0.138(1)	0.4518(8)	−0.011(2)	10.7(3)
C(46B)	−0.297(2)	0.4224(9)	0.022(2)	10.7(3)
C(5B)	−0.1684(3)	0.3073(2)	0.0650(4)	5.4(1)
C(6B)	−0.1365(2)	0.2389(2)	0.0713(3)	4.37(8)
C(7B)	−0.0947(3)	0.2322(2)	0.1882(3)	4.54(9)
O(1C)	0.0492(2)	0.1294(1)	0.1894(2)	4.96(6)
C(1C)	0.0812(2)	0.2092(2)	0.2472(3)	3.81(7)
C(2C)	0.0156(2)	0.2604(2)	0.2423(3)	4.08(8)
C(3C)	0.0542(3)	0.3408(2)	0.2957(3)	4.78(9)
C(4C)	0.1535(3)	0.3705(2)	0.3556(4)	5.16(9)
C(40C)	0.1929(5)	0.4593(3)	0.4165(6)	7.6(1)
C(41C)	0.2895(7)	0.4808(4)	0.397(1)	10.8(2)
C(42C)	0.208(1)	0.4805(5)	0.545(1)	13.0(3)
C(43C)	0.1238(8)	0.5065(4)	0.368(1)	11.5(2)
C(5C)	0.2148(3)	0.3172(2)	0.3667(3)	4.63(8)
C(6C)	0.1800(2)	0.2362(2)	0.3153(3)	3.92(7)
C(7C)	0.2459(2)	0.1808(2)	0.3446(3)	4.24(7)
O(1D)	0.1989(2)	0.0592(1)	0.1149(2)	4.42(5)
C(1D)	0.2951(2)	0.0988(2)	0.1719(3)	3.74(7)
C(2D)	0.3205(2)	0.1598(2)	0.2795(3)	4.31(7)
C(3D)	0.4186(3)	0.1969(2)	0.3323(4)	5.73(9)
C(4D)	0.4921(3)	0.1761(3)	0.2820(5)	6.5(1)

Table III. Continued

Atom	x	y	z	B_{eq}
C(40D)	0.6005(4)	0.2168(5)	0.3478(8)	10.5(2)
C(41D)	0.6691(4)	0.1837(7)	0.283(1)	12.5(3)
C(42D)	0.6063(8)	0.3030(6)	0.365(2)	20.3(5)
C(43D)	0.6295(7)	0.224(1)	0.469(1)	18.8(4)
C(5D)	0.4648(3)	0.1138(3)	0.1767(4)	5.7(1)
C(6D)	0.3668(2)	0.0742(2)	0.1199(3)	4.16(7)
C(7D)	0.3416(2)	0.0042(2)	0.0080(3)	4.05(7)
O(1E)	0.1390(2)	−0.0133(1)	−0.1325(2)	4.52(6)
C(1E)	0.2151(2)	0.0095(2)	−0.1694(3)	3.71(7)
C(2E)	0.3138(2)	0.0230(2)	−0.1023(3)	3.92(7)
C(3E)	0.3857(3)	0.0521(3)	−0.1399(4)	5.3(1)
C(4E)	0.3655(4)	0.0638(4)	−0.2452(7)	7.6(2)
C(40E)	0.4475(5)	0.0992(6)	−0.2843(8)	9.4(2)
C(41E)	0.528(1)	0.057(1)	−0.281(2)	10.6(3)
C(42E)	0.406(1)	0.099(1)	−0.411(2)	11.0(3)
C(43E)	0.494(1)	0.180(2)	−0.198(2)	12.0(3)
C(44E)	0.480(2)	0.028(1)	−0.358(3)	11.5(4)
C(45E)	0.546(1)	0.133(2)	−0.177(2)	11.1(4)
C(46E)	0.422(1)	0.160(1)	−0.317(2)	10.6(3)
C(5E)	0.2675(3)	0.0424(3)	−0.3141(4)	5.6(1)
C(6E)	0.1919(3)	0.0163(2)	−0.2782(3)	4.34(8)
C(7E)	0.0869 (3)	−0.0034(2)	−0.3548(3)	4.64(8)
O(600)	0.288(2)	0.3952(6)	0.048(3)	21.0(9)
C(600)	0.230(2)	0.349(1)	0.039(3)	17.1(6)
N(600)	0.2138(9)	0.2743(4)	0.0005(6)	9.9(2)
C(601)	0.141(1)	0.2119(7)	−0.021(1)	12.0(3)
C(602)	0.299(2)	0.244(1)	−0.015(4)	17.0(1)
O(700)	0.445(1)	0.338(1)	0.590(1)	20.2(5)
C(700)	0.474(2)	0.402(1)	0.651(2)	15.9(5)
N(700)	0.4536(6)	0.4405(7)	0.7371(9)	10.9(2)
C(701)	0.479(2)	0.518(1)	0.815(2)	17.3(6)
C(702)	0.389(1)	0.406(1)	0.790(2)	13.6(4)

Table IV. Intramolecular and intermolecular O···O distances in pm ($i = -x, -y, -z$).

O(1A)···O(1E)	311.7(4)	O(1A)···O(1C^{i})	287.0(5)
O(1A)···O(1B)	307.1(4)	O(1A)···O(1D^{i})	318.8(5)
O(1B)···O(1C)	292.4(4)	O(1B)···O(1D^{i})	304.0(3)
O(1C)···O(1D)	281.0(4)	O(1B)···O(1E^{i})	320.7(4)
O(1D)···O(1E)	285.2(3)	O(1C)···O(1E^{i})	304.0(3)

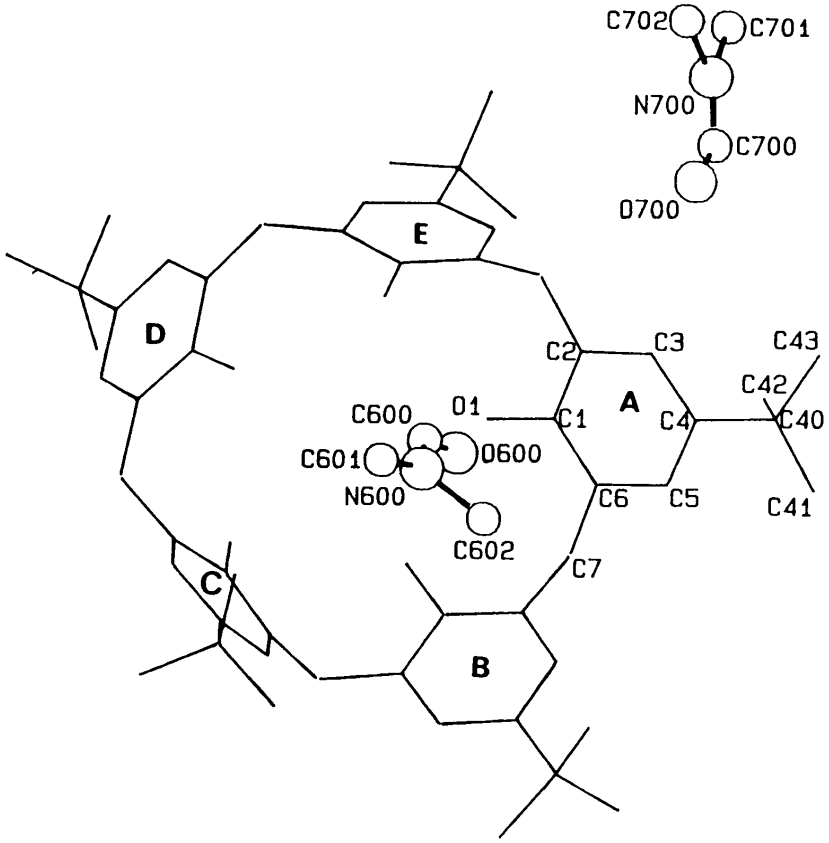

Figure 3. Numbering scheme.

4.2. RESULTS AND DISCUSSION

Figure 3 shows the numbering scheme of the calixarene and N,N-dimethylformamide molecules. The title product adopts a cone conformation, as do other calix[5] or calix[4]arenes with free OH groups. The angles between the phenyl rings and the mean plane defined by the methylene bridges are, respectively: 105.9(1), 137.7(1), 120.6(1), 141.3(1) and 129.5(1)°. The cone is therefore distorted from a regular pentagonal shape.

Intramolecular and intermolecular O· · ·O distances are given in Table IV. These values show interactions between OH groups of one molecule and those of two neighbouring molecules. The H atoms of hydroxyl groups could not be located. The intramolecular O· · ·O distances are larger than those found for other calix[5]arenes (268.0(8)–288(1) pm).

The cyclic pentamer crystallises with two N,N-dimethylformamide molecules. Generally, when calixarenes form complexes with N,N-dimethylformamide, the guest molecule is held to the host by a hydrogen bond between the O atom of

Table V. Distances between C(601), C(602) and the C atoms of rings A and E in pm.

	C(1)	C(2)	C(3)	C(4)	C(5)	C(6)	Average
C(601)···A	377(1)	384(1)	394(1)	407(1)	411(1)	398(1)	395
C(602)···E	402(2)	388(2)	383(2)	402(3)	426(3)	426(3)	404

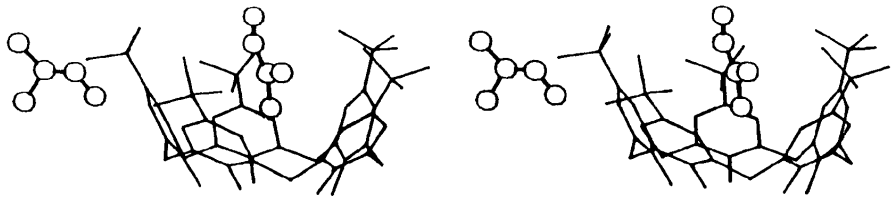

Figure 4. Conformation of the *p-tert*-butylcalix[5]arene and guest positions.

the N,N-dimethylformamide molecule and an OH group of the calixarene molecule. The guest molecule thus lies outside the macrocycle cavity as in the following complexes: p-cumylcalix[6]arene–N,N-dimethylformamide 1 : 2.5 [16], 3,5-dimethylcalix[4]arene–N,N-dimethylformamide 1 : 1 [17], and p-tetrakis-(phenylazo)calix[4]arene–N,N-dimethylformamide 1 : 1 [18]. Concerning the title complex, one guest molecule is entirely inserted in the macrocycle cavity with the methyl groups directed towards the inside (Figure 4). The distances between C(601) and C(602) respectively with the C atoms of the aromatic rings A and E (Table V) correspond to $CH_3 \cdots \pi$ interactions. The other N,N-dimethylformamide molecule lies in the interhost space.

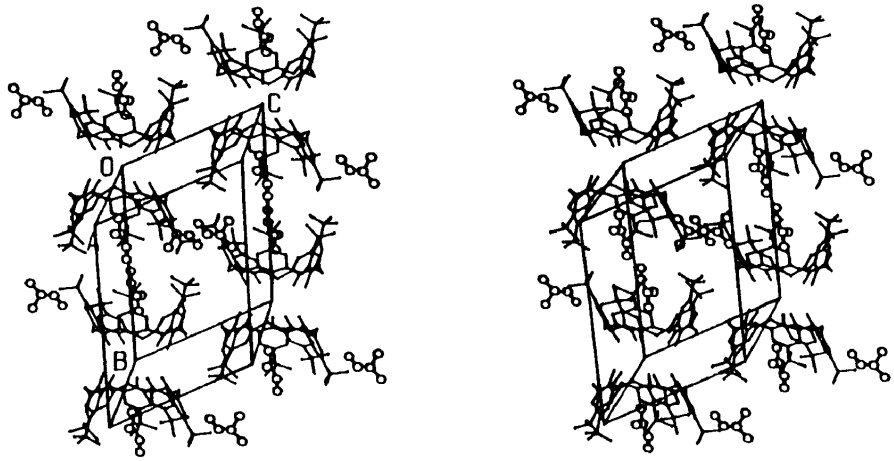

Figure 5. Packing of the title complex.

A stereoview of the packing is given in Figure 5. We can see the repetition of a group of two calix[5]arenes which are held together by O—H· · ·O intermolecular bonds.

5. Conclusion

An alternative synthesis of *p-tert*-butylcalix[5]arene was established using *p-tert*-butyldihomooxacalix[4]arene and *p-tert*-butylphenol as reagents. The reaction was carried out with KOH as base. The yield of isolated cyclic pentamer was 30%. Using this procedure with 3,4-dimethylphenol as component **2**, a nonsymmetric calix[5]arene was obtained and isolated in low yield.

p-tert-Butylcalix[5]arene crystallizes with two *N*,*N*-dimethylformamide molecules to give a new type of complex for calixarenes with five phenolic units. In fact, the guest molecules are located both inside and outside the cavity. It is also the first case in which the *p-tert*-butylcalix[5]arene molecules are held together by hydrogen bonds between their hydroxyl groups.

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