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Molecular Inclusion in Calixarenes. XVIII.† Crystal and Molecular Structure of the *p-tert*-Butylcalix[7]arene 1 : 3 Pyridine Complex/Clathrate

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Abstract. The structure of the *p-tert*-butylcalix[7]arene 1:3 pyridine complex/clathrate ($C_{77}H_{98}O_7 \cdot 3\,C_5H_5N$) has been determined by X-ray crystallography. The crystal data are as follows: monoclinic, space group $P2_1/c$, $a = 37.790(4)$, $b = 9.423(2)$, $c = 29.075(4)$ Å; $\beta = 112.74(2)°$; $V = 8285(3)$ Å^3; $Z = 4$; $D_{\text{calc}} = 1.10\ \text{g·cm}^{-3}$. The host *p-tert*-butylcalix[7]arene links one pyridine molecule through a hydrogen bond between one of the seven hydroxy groups and the nitrogen of the pyridine. Two other guest molecules have been found in the crystal lattice, so the title compound may be defined as a complex/clathrate hybrid. The unambiguous conformation of the macrocycle is described by an alternative method, which avoids the use of dihedral angles (and the ambiguities in their values).

Key words. Inclusion compounds, crystal structure *p-tert*-butylcalix[7]arene, complex, clathrate, pyridine, conformation, hydrogen bonding.

Supplementary Data relating this article are deposited with the British Library as supplementary publication No. 82100 (43 pages).

1. Introduction

Due to their ability to form inclusion complexes with neutral molecules and metal cations, the calix[*n*]arenes (**I**), are attracting increasing interest as building blocks in *host–guest* or *supramolecular* chemistry. Until now, even-membered calixarenes [$n = 4, 6, 8$] have been mainly studied [1–3], and a variety of molecules derived from them have been synthesized and characterized by X-ray diffraction studies [4]. Among odd-membered calix[*n*]arenes, only the structure of the pentamer [5] has been established. Here we report the crystal and molecular structure, obtained by X-ray diffraction, of the *p-tert*-butylcalix[7]arene ($R_1 = H$, $R_2 = Bu^t$) which represents the second odd-membered calixarene studied to date.

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† Part XVII. Ref. [2].

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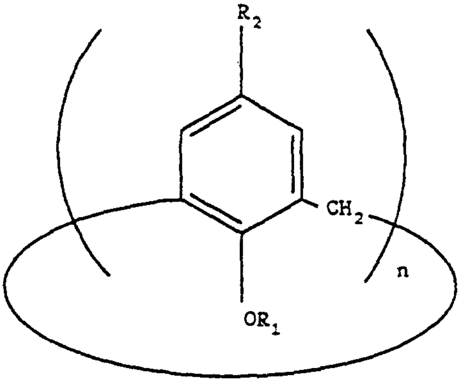
As is normally done when the structure of a calixarene is reported, the conformation of the macrocycle is described by the dihedral angles formed by the planes of the phenolic rings with respect to a reference plane in the molecule. This approach may be a source of some ambiguities and a new method to describe the molecular conformation of calix[*n*]arenes is here proposed; it is based on some of the torsion angles which involves the methylene bridges and gives a non equivocal picture of the arrangement of the phenolic rings around the macrocycle.

(I)



2. Experimental

2.1. PREPARATION OF CRYSTALLINE SAMPLES

Transparent yellow crystals for X-ray analysis were obtained by slow evaporation of a pyridine solution of the amorphous powder obtained from the one-step synthesis described elsewhere [6].

2.2. X-RAY DATA COLLECTION, STRUCTURE DETERMINATION AND REFINEMENT

The X-ray measurements were performed at room temperature on a SIEMENS AED single crystal diffractometer using Ni filtered CuK_α radiation. The lattice parameters were calculated from $30(\theta, \chi, \phi)_{hkl}$ reflections in the range $25° < \theta < 35°$. The systematic data collection, in the range $3° < \theta < 70°$, was performed in the $\theta - 2\theta$ step scanning mode (scan speed $3 - 12° \text{ min}^{-1}$) using scan widths from $(\theta - 0.60)$ to $(\theta + 0.60 + \Delta\lambda/\lambda \text{ tg}\theta)°$; $\Delta\lambda$ being $\lambda_{\alpha 2} - \lambda_{\alpha 1} = 0.142$ Å. A total of $16232 \pm h,k,l$ reflections were collected. The intensities I_{hkl} were determined by the analysis of the reflection profiles [7] and corrected for Lorenz and polarization effects.

The 6173 observed reflections with $I_{hkl} > 2\sigma(I_{hkl})$ (6011 unique: internal $R = 0.05$) were used in the refinement of the structure. One standard reflection checked every 100 reflections showed no significant variations.

The structure was solved by direct methods using MULTAN80 [8], then it was refined using the SHELX76 [9] package of crystallographic computer programs by several cycles of blocked full-matrix least squares methods (734 parameters).

Parameters refined were: the overall scale factor, the atomic coordinates, the anisotropic thermal parameters for all the non-hydrogen atoms of the *p-tert*-butylcalix[7]arene with the exception of the carbon atoms of four of the seven *p-tert*-butyl groups which are disordered and for which isotropic temperature factors were assumed. Anisotropic temperature factors were assigned also to the C and N atoms of one of the three molecules of pyridine (linked by a hydrogen bond to the phenolic unit A). From the ΔF map only hydrogen H(1A), responsible for the H-bond, was revealed, the other hydrogens atoms were placed in their calculated positions with the geometrical constraint C—H = 1.08 Å. The hydrogens of the two clathrated molecules of pyridine, for which it was impossible to establish unambiguously the position of the N atoms, were not taken into account.

The final R value was 0.096, $R_w = 0.105$ $w = 1.689\,[\sigma^2(F_0) + 0.002551\,F_0^2]^{-1}$. The highest residual peak in the final ΔF map was 0.48 e Å^{-3}.

The scattering factors were taken from the literature [10]. Geometrical calculations were obtained by PARST [11]. The drawings were executed by PLUTO in the CRYSRULER package [12].

The correction for absorption effects was applied at the end of the isotropic refinement using the program ABSORB [13]. The maximum and minimum values of the absorption coefficient in the polar angles of the incident and diffracted beams were 1.17 and 0.72.

2.3. CRYSTAL DATA

Molecular formula $C_{77}H_{98}O_7 \cdot 3\,C_5H_5N$; molecular weight 1372.92 g mol^{-1}; monoclinic $P2_1/c$; $a = 37.790(4)$, $b = 9.423(2)$, $c = 29.075(4)$ Å; $\beta = 112.74(2)$°; $V = 8285(3)$ Å^3; $Z = 4$; $D_{\text{calc}} = 1.10$ g cm^{-3}; F(000) = 2968; $\lambda = 1.54178$ Å; $\mu(\text{Cu}K_\alpha) = 5.00$ cm^{-1}.

3. Results and Discussion

Table I reports the fractional atomic coordinates. Bond distances and bond angles are reported in Tables II and III respectively. Lists of atomic coordinates for the hydrogens, thermal parameters, and structure factors have been deposited.

Perspective views of the host molecule and its three associated pyridine guest molecules are shown in Figure 1(a) and (b). (The atomic numbering scheme is shown in Figure 3). The host molecule links the pyridine molecule M, by the hydrogen bond through the hydroxyl group at the phenolic units A and the nitrogen atoms of the pyridine. The geometrical parameters of this interaction are: donor—H, O(1A)—H(1A) 1.42(8), donor···acceptor O(1A)···N(6M) 2.632(8) Å, H···acceptor H(1A)···N(6M) 1.26(8) Å, donor—H···acceptor 159(6)°. Two other guest molecules (I and L) have been found in the crystal lattice, so the title compound may be classified as a *complex/clathrate hybrid.*

The conformation of the host *p-tert*-butylcalix[7]arene is determined by the strong intramolecular H bonding system between the hydroxyl groups. However, the analysis of the intramolecular O···O contacts (see Table IV) shows that the

Table I. Fractional atomic coordinates.

Atom	*x*/*y*	*y*/*b*	*z*/*c*
O(1A)	0.1298(1)	−0.1065(5)	0.7033(2)
H(1A)	0.1249(24)	0.0423(90)	0.6953(28)
C(1A)	0.0958(2)	−0.1922(7)	0.7018(3)
C(2A)	0.0945(2)	−0.2445(7)	0.7462(3)
C(3A)	0.0579(2)	−0.3260(7)	0.7443(3)
C(4A)	0.0233(2)	−0.3575(7)	0.6997(3)
C(5A)	0.0272(2)	−0.3134(7)	0.6558(3)
C(6A)	0.0628(2)	−0.2328(7)	0.6560(3)
C(7A)	−0.0176(2)	−0.4413(8)	0.6969(3)
C(8A)	−0.0590(3)	−0.3519(13)	0.6701(5)
C(9A)	−0.0172(3)	−0.4709(12)	0.7492(4)
C(10A)	−0.0201(4)	−0.5821(11)	0.6716(5)
C(20A)	0.1320(3)	−0.2169(9)	0.7959(3)
O(1B)	0.2054(1)	−0.1547(5)	0.7683(2)
C(1B)	0.2056(2)	−0.2825(7)	0.7915(3)
C(2B)	0.2410(2)	−0.3744(8)	0.8008(3)
C(3B)	0.2411(2)	−0.5021(8)	0.8250(3)
C(4B)	0.2075(2)	−0.5410(8)	0.8401(3)
C(5B)	0.1724(2)	−0.4470(7)	0.8298(2)
C(6B)	0.1709(2)	−0.3164(7)	0.8059(3)
C(7B)	0.2099(3)	−0.6807(8)	0.8673(3)
C(8B)	0.2031(4)	−0.8036(10)	0.8312(4)
C(9B)	0.1773(3)	−0.6852(11)	0.8936(4)
C(10B)	0.2563(3)	−0.7000(10)	0.9082(3)
C(20B)	0.2792(2)	−0.3355(8)	0.7853(3)
O(1C)	0.2818(2)	−0.0245(5)	0.7935(2)
C(1C)	0.3154(2)	−0.1067(9)	0.8268(3)
C(2C)	0.3500(2)	−0.0309(8)	0.8623(3)
C(3C)	0.3847(3)	−0.1097(10)	0.8967(3)
C(4C)	0.3861(2)	−0.2563(10)	0.8952(3)
C(5C)	0.3514(2)	−0.3255(9)	0.8588(3)
C(6C)	0.3158(2)	−0.2528(8)	0.8248(3)
C(7C)	0.4261(3)	−0.3416(11)	0.9338(4)
C(8C)	0.4579(7)	−0.3737(26)	0.9046(9)
C(9C)	0.4111(8)	−0.4842(26)	0.9483(10)
C(10C)	0.4505(10)	−0.2566(34)	0.9795(11)
C(20C)	0.3503(3)	0.1315(8)	0.8641(3)
O(1D)	0.2925(1)	0.2500(5)	0.7687(2)
C(1D)	0.3373(2)	0.2614(8)	0.7822(3)
C(2D)	0.3533(2)	0.3326(7)	0.7517(3)
C(3D)	0.3992(3)	0.3443(8)	0.7653(3)
C(4D)	0.4289(2)	0.2750(8)	0.8068(3)
C(5D)	0.4116(2)	0.2070(8)	0.8383(3)
C(6D)	0.3663(2)	0.2024(7)	0.8267(3)
C(7D)	0.4783(2)	0.2723(11)	0.8183(4)
C(8D)	0.4869(4)	0.1377(15)	0.7942(6)
C(9D)	0.4936(3)	0.4019(15)	0.7987(6)
C(10D)	0.5071(3)	0.2702(18)	0.8750(4)
C(20D)	0.3232(3)	0.4088(8)	0.7040(3)
O(1E)	0.2473(2)	0.2577(5)	0.6382(2)
C(1E)	0.2837(2)	0.2671(7)	0.6247(3)
C(2E)	0.2815(2)	0.2106(7)	0.5795(3)

Table I. (continued)

Atom	x/y	y/b	z/c
C(3E)	0.3189(2)	0.2146(7)	0.5681(3)
C(4E)	0.3570(2)	0.2827(8)	0.5986(3)
C(5E)	0.3574(3)	0.3458(8)	0.6424(3)
C(6E)	0.3216(2)	0.3411(7)	0.6563(3)
C(7E)	0.3994(3)	0.2821(12)	0.5865(4)
C(8E)	0.4169(5)	0.4354(20)	0.5882(7)
C(9E)	0.4345(7)	0.2016(26)	0.6296(9)
C(10E)	0.3906(8)	0.2144(31)	0.5364(10)
C(20E)	0.2395(2)	0.1405(7)	0.5426(3)
O(1F)	0.2192(2)	−0.0159(5)	0.6136(2)
C(1F)	0.2306(2)	−0.0957(8)	0.5796(3)
C(2F)	0.2326(2)	−0.2418(8)	0.5818(3)
C(3F)	0.2461(2)	−0.3111(8)	0.5481(3)
C(4F)	0.2570(2)	−0.2437(8)	0.5129(3)
C(5F)	0.2543(2)	−0.0959(8)	0.5118(3)
C(6F)	0.2407(2)	−0.0184(8)	0.5443(3)
C(7F)	0.2704(3)	−0.3221(9)	0.4747(3)
C(8F)	0.2837(6)	−0.2279(19)	0.4410(7)
C(9F)	0.2216(7)	−0.3922(24)	0.4331(7)
C(10F)	0.3020(9)	−0.4380(27)	0.4969(8)
C(20F)	0.2214(2)	−0.3288(8)	0.6201(3)
O(1G)	0.1604(2)	−0.1445(5)	0.6380(2)
C(1G)	0.1431(2)	−0.2692(7)	0.6113(3)
C(2G)	0.0990(2)	−0.2978(7)	0.5962(3)
C(3G)	0.0832(2)	−0.4238(8)	0.5702(3)
C(4G)	0.1107(2)	−0.5189(8)	0.5585(3)
C(5G)	0.1553(2)	−0.4846(8)	0.5756(3)
C(6G)	0.1729(2)	−0.3608(7)	0.6022(3)
C(7G)	0.0928(3)	−0.6568(9)	0.5280(3)
C(8G)	0.1152(4)	−0.7883(14)	0.5633(5)
C(9G)	0.1100(4)	−0.6661(14)	0.4839(5)
C(10G)	0.0432(5)	−0.6632(16)	0.5036(7)
C(20G)	0.0671(2)	−0.1995(7)	0.6073(3)
C(1M)	0.1748(3)	0.2061(8)	0.6986(3)
C(2M)	0.1872(3)	0.3492(10)	0.7000(3)
C(3M)	0.1555(3)	0.4522(9)	0.6987(3)
C(4M)	0.1159(3)	0.4076(10)	0.6976(3)
C(5M)	0.1068(3)	0.2657(11)	0.6976(3)
N(6M)	0.1355(2)	0.1711(7)	0.6979(2)
C(1I)	0.6041(3)	0.1990(10)	0.7996(4)
C(2I)	0.5991(4)	0.2525(14)	0.7565(5)
C(3I)	0.6181(5)	0.3858(16)	0.7515(6)
C(4I)	0.6414(5)	0.4504(17)	0.7974(7)
C(5I)	0.6490(4)	0.3910(16)	0.8430(6)
C(6I)	0.6292(4)	0.2587(14)	0.8427(5)
C(1L)	0.0462(4)	−0.0335(13)	0.3937(5)
C(2L)	0.0308(4)	−0.0878(15)	0.4264(6)
C(3L)	0.0634(6)	−0.1604(16)	0.4648(6)
C(4L)	0.1036(5)	−0.1831(14)	0.4695(5)
C(5L)	0.1163(5)	−0.1265(16)	0.4287(6)
C(6L)	0.0836(5)	−0.0569(14)	0.3907(5)

Table II. Selected bond distances (Ångstrom)

O(1A)—C(1A)	1.367(8)	C(2E)—C(3E)	1.39(1)
C(1A)—C(2A)	1.40(1)	C(2E)—C(20E)	1.530(8)
C(1A)—C(6A)	1.406(9)	C(3E)—C(4E)	1.379(9)
C(2A)—C(3A)	1.41(1)	C(4E)—C(5E)	1.40(1)
C(2A)—C(20A)	1.51(1)	C(4E)—C(7E)	1.56(1)
C(3A)—C(4A)	1.385(9)	C(5E)—C(6E)	1.38(1)
C(4A)—C(5A)	1.39(1)	C(20E)—C(6F)	1.50(1)
C(4A)—C(7A)	1.53(1)	O(1F)—C(1F)	1.40(1)
C(5A)—C(6A)	1.39(1)	C(1F)—C(2F)	1.38(1)
C(6A)—C(20G)	1.51(1)	C(1F)—C(6F)	1.40(1)
C(20A)—C(6B)	1.52(1)	C(2F)—C(3F)	1.38(1)
O(1B)—C(1B)	1.379(9)	C(2F)—C(20F)	1.54(1)
C(1B)—C(2B)	1.39(1)	C(3F)—C(4F)	1.36(1)
C(1B)—C(6B)	1.39(1)	C(4F)—C(5F)	1.40(1)
C(2B)—C(3B)	1.39(1)	C(4F)—C(7F)	1.53(1)
C(2B)—C(20B)	1.53(1)	C(5F)—C(6F)	1.40(1)
C(3B)—C(4B)	1.38(1)	C(20F)—C(6G)	1.500(9)
C(4B)—C(5B)	1.390(9)	O(1G)—C(1G)	1.402(8)
C(4B)—C(7B)	1.52(1)	C(1G)—C(2G)	1.366(9)
C(5B)—C(6B)	1.40(1)	C(1G)—C(6G)	1.40(1)
C(20B)—C(6C)	1.517(9)	C(2G)—C(3G)	1.40(1)
O(1C)—C(1C)	1.388(8)	C(2G)—C(20G)	1.52(1)
C(1C)—C(2C)	1.399(9)	C(3G)—C(4G)	1.40(1)
C(1C)—C(6C)	1.38(1)	C(4G)—C(5G)	1.389(9)
C(2C)—C(3C)	1.40(1)	C(4G)—C(7G)	1.55(1)
C(2C)—C(20C)	1.53(1)	C(5G)—C(6G)	1.40(1)
C(3C)—C(4C)	1.38(1)	C(1M)—C(2M)	1.40(1)
C(4C)—C(5C)	1.38(1)	C(1M)—N(6M)	1.32(1)
C(4C)—C(7C)	1.57(1)	C(2M)—C(3M)	1.41(1)
C(5C)—C(6C)	1.384(9)	C(3M)—C(4M)	1.35(1)
C(20C)—C(6D)	1.53(1)	C(4M)—C(5M)	1.37(1)
O(1D)—C(1D)	1.370(7)	C(5M)—N(6M)	1.29(1)
C(1D)—C(2D)	1.37(1)	C(1I)—C(2I)	1.30(2)
C(1D)—C(6D)	1.391(9)	C(1I)—C(6I)	1.33(2)
C(2D)—C(3D)	1.40(1)	C(2I)—C(3I)	1.43(2)
C(2D)—C(20D)	1.53(1)	C(3I)—C(4I)	1.40(2)
C(3D)—C(4D)	1.39(1)	C(4I)—C(5I)	1.37(3)
C(4D)—C(5D)	1.40(1)	C(5I)—C(6I)	1.40(2)
C(4D)—C(7D)	1.52(1)	C(1L)—C(2L)	1.34(2)
C(5D)—C(6D)	1.391(9)	C(1L)—C(6L)	1.28(2)
C(20D)—C(6E)	1.51(1)	C(2L)—C(3L)	1.39(2)
O(1E)—C(1E)	1.40(1)	C(3L)—C(4L)	1.29(3)
C(1E)—C(2E)	1.39(1)	C(4L)—C(5L)	1.50(3)
C(1E)—C(6E)	1.411(8)	C(5L)—C(6L)	1.37(2)

intramolecular H bonding is not cyclic as observed in the *p-tert*-butylcalix[*n*]arenes with $n = 4$, 5, 6 and 8, because the complexation of the pyridine subtracts the hydrogen atoms H(1A) to the circular array of hydrogen bonds. The remaining six intramolecular H bonds (O(1A)···O(1B), O(1B)···O(1C), O(1C)···O(1D) and O(1A)···O(1G), O(1G)···O(1F), O(1F)···O(1E)) leave O(1D)···O(1E) at 3.500(8) Å and strongly determine the conformation of the macrocycle. As shown in Figure

Table III. Selected bond angles (degrees) (e.s.d. following Cruickshank, *Internat. Tables*, II, 1959, p. 331).

O(1A)—C(1A)—C(6A)	120.8(7)	C(3D)—C(4D)—C(5D)	117.2(7)
O(1A)—C(1A)—C(2A)	119.7(7)	C(5D)—C(4D)—C(7D)	120.8(7)
C(2A)—C(1A)—C(6A)	119.5(7)	C(4D)—C(5D)—C(6D)	121.3(7)
C(1A)—C(2A)—C(20A)	121.2(7)	C(1D)—C(6D)—C(5D)	119.7(7)
C(1A)—C(2A)—C(3A)	119.1(7)	C(20C)—C(6D)—C(5D)	117.9(7)
C(3A)—C(2A)—C(20A)	119.8(7)	C(20C)—C(6D)—C(1D)	122.4(7)
C(2A)—C(3A)—C(4A)	122.1(7)	C(2D)—C(20D)—C(6E)	114.5(6)
C(3A)—C(4A)—C(7A)	122.9(7)	O(1E)—C(1E)—C(6E)	118.8(7)
C(3A)—C(4A)—C(5A)	117.5(7)	O(1E)—C(1E)—C(2E)	120.2(7)
C(5A)—C(4A)—C(7A)	119.6(7)	C(2E)—C(1E)—C(6E)	120.9(8)
C(4A)—C(5A)—C(6A)	122.2(7)	C(1E)—C(2E)—C(20E)	122.0(7)
C(1A)—C(6A)—C(5A)	119.3(7)	C(1E)—C(2E)—C(3E)	119.1(7)
C(5A)—C(6A)—C(20G)	119.5(7)	C(3E)—C(2E)—C(20E)	118.9(7)
C(1A)—C(6A)—C(20G)	121.0(7)	C(2E)—C(3E)—C(4E)	121.5(7)
C(2A)—C(20A)—C(6B)	112.9(6)	C(3E)—C(4E)—C(7E)	121.2(7)
O(1B)—C(1B)—C(6B)	119.8(6)	C(3E)—C(4E)—C(5E)	118.9(8)
O(1B)—C(1B)—C(2B)	119.0(6)	C(5E)—C(4E)—C(7E)	120.7(8)
C(2B)—C(1B)—C(6B)	121.1(7)	C(4E)—C(5E)—C(6E)	122.8(7)
C(1B)—C(2B)—C(20B)	120.7(7)	C(1E)—C(6E)—C(5E)	117.3(7)
C(1B)—C(2B)—C(3B)	118.4(7)	C(20D)—C(6E)—C(5E)	121.6(7)
C(3B)—C(2B)—C(20B)	120.9(7)	C(20D)—C(6E)—C(1E)	121.1(7)
C(2B)—C(3B)—C(4B)	122.8(7)	C(2E)—C(20E)—C(6F)	113.8(6)
C(3B)—C(4B)—C(7B)	120.4(7)	O(1F)—C(1F)—C(6F)	116.2(7)
C(3B)—C(4B)—C(5B)	117.2(7)	O(1F)—C(1F)—C(2F)	121.6(7)
C(5B)—C(4B)—C(7B)	122.4(7)	C(2F)—C(1F)—C(6F)	122.3(7)
C(4B)—C(5B)—C(6B)	122.2(7)	C(1F)—C(2F)—C(20F)	123.1(7)
C(1B)—C(6B)—C(5B)	118.2(7)	C(1F)—C(2F)—C(3F)	117.4(7)
C(20A)—C(6B)—C(5B)	120.1(7)	C(3F)—C(2F)—C(20F)	119.5(7)
C(20A)—C(6B)—C(1B)	121.6(7)	C(2F)—C(3F)—C(4F)	124.0(7)
C(2B)—C(20B)—C(6C)	113.5(6)	C(3F)—C(4F)—C(7F)	123.4(7)
O(1C)—C(1C)—C(6C)	123.1(7)	C(3F)—C(4F)—C(5F)	116.7(7)
O(1C)—C(1C)—C(2C)	115.4(7)	C(5F)—C(4F)—C(7F)	119.9(7)
C(2C)—C(1C)—C(6C)	121.5(7)	C(4F)—C(5F)—C(6F)	122.7(7)
C(1C)—C(2C)—C(20C)	121.9(7)	C(1F)—C(6F)—C(5F)	116.9(7)
C(1C)—C(2C)—C(3C)	117.3(7)	C(20E)—C(6F)—C(5F)	120.8(7)
C(3C)—C(2C)—C(20C)	120.8(7)	C(20E)—C(6F)—C(1F)	122.3(7)
C(2C)—C(3C)—C(4C)	122.3(8)	C(2F)—C(20F)—C(6G)	112.0(7)
C(3C)—C(4C)—C(7C)	121.0(8)	O(1G)—C(1G)—C(6G)	117.2(7)
C(3C)—C(4C)—C(5C)	117.9(8)	O(1G)—C(1G)—C(2G)	119.7(6)
C(5C)—C(4C)—C(7C)	121.1(8)	C(2G)—C(1G)—C(6G)	123.1(7)
C(4C)—C(5C)—C(6C)	122.1(8)	C(1G)—C(2G)—C(29G)	122.7(6)
C(1C)—C(6C)—C(5C)	118.9(7)	C(1G)—C(2G)—C(3G)	117.9(7)
C(20B)—C(6C)—C(5C)	119.2(7)	C(3G)—C(2G)—C(20G)	119.4(6)
C(20B)—C(6C)—C(1C)	121.8(7)	C(2G)—C(3G)—C(4G)	122.4(7)
C(2C)—C(20C)—C(6D)	114.3(6)	C(3G)—C(4G)—C(7G)	122.4(7)
O(1D)—C(1D)—C(6D)	120.4(7)	C(3G)—C(4G)—C(5G)	116.8(7)
O(1D)—C(1D)—C(2D)	119.3(7)	C(5G)—C(4G)—C(7G)	120.8(7)
C(2D)—C(1D)—C(6D)	120.2(7)	C(4G)—C(5G)—C(6G)	123.1(7)
C(1D)—C(2D)—C(20D)	122.8(7)	C(1G)—C(6G)—C(5G)	116.7(7)
C(1D)—C(2D)—C(3D)	119.6(7)	C(20F)—C(6G)—C(5G)	121.1(7)
C(3D)—C(2D)—C(20D)	117.6(7)	C(20F)—C(6G)—C(1G)	122.2(6)
C(2D)—C(3D)—C(4D)	121.6(8)	C(6A)—C(20G)—C(2G)	113.2(6)
C(3D)—C(4D)—C(7D)	121.9(8)	C(2M)—C(1M)—N(6M)	120.6(8)

Table III. (continued)

C(1M)—C(2M)—C(3M)	117.2(9)	C(4I)—C(5I)—C(6I)	116(1)
C(2M)—C(3M)—C(4M)	118.5(8)	C(1I)—C(6I)—C(5I)	120(1)
C(3M)—C(4M)—C(5M)	121(1)	C(2L)—C(1L)—C(6L)	128(1)
C(4M)—C(5M)—N(6M)	121(1)	C(1L)—C(2L)—C(3L)	112(1)
C(1M)—N(6M)—C(5M)	122.0(8)	C(2L)—C(3L)—C(4L)	127(2)
C(2I)—C(1I)—C(6I)	123(1)	C(3L)—C(4L)—C(5L)	116(1)
C(1I)—C(2I)—C(3I)	123(1)	C(4L)—C(5L)—C(6L)	116(2)
C(2I)—C(3I)—C(4I)	113(1)	C(1L)—C(6L)—C(5L)	120(2)
C(3I)—C(4I)—C(5I)	125(2)		

Table IV. Intramolecular O···O contacts (Å).

O(1A)···O(1B)	2.510(5)	O(1E)···O(1F)	2.738(7)
O(1B)···O(1C)	2.627(7)	O(1F)···O(1G)	2.60(1)
O(1C)···O(1D)	2.744(7)	O(1G)···O(1A)	2.430(9)
O(1D)···O(1E)	3.500(8)		

1(a) and 1(b) the structure of the *p-tert*-butylcalix[7]arene host molecule may be described as a combination of a tetrameric and of a trimeric substructure.

The tetrameric substructure, formed by the four phenolic rings (C–D–E–F), is blocked in a distorted cone conformation by the two intramolecular hydrogen bonds O(1C)···O(1D) 2.744(7) Å and O(1E)···O(1F) 2.738(7) Å, and shows the two long contacts: O(1C)···O(1F) 4.825(8) Å and O(1D)···O(1E) 3.500(8) Å. The trimeric substructure, is formed by the phenolic units A–B–G and it is blocked by the two intramolecular H bonds O(1A)···O(1B) 2.510(5) Å and O(1A)···O(1G) 2.430(9) Å. The tetrameric and the trimeric substructures are linked together through the two methylene bridges C(20B) and C(20G). The dihedral angle (90.8(2)°) between the weighted least squares plane through O(1C)—O(1D)—O(1E)—O(1F) and the plane containing O(1A)—O(1B)—O(1G), shows that the two intramolecular cavities of the tetrameric and trimeric substructures point their axes in two mutually perpendicular directions.

It may be interesting to inquire how the pure *p-tert*-butylcalix[7]arene differs from the observed structure of the complex. On the basis of a three-dimenisonal model it seems reasonable to hypothesize that the conformation of the pure *p-tert*-butylcalix[7]arene is again describable by a combination of a trimeric and of a tetrameric subunit. The trimeric one is quite similar to that observed in the complex, whereas in the tetrameric subunit the two phenolic units D and E have to be reoriented to bring O(1D)···O(1E) at a distance of the order of 2.5 ~ 2.8 Å to form the seventh intramolecular hydrogen bond. This geometrical condition may be obtained by rotations of the phenolic units D and E, around their methylene bridges, to bring the two phenolic oxygens D and E more inside the cavity of the tetrameric subunit. As a consequence, the intramolecular cavity of the tetrameric subunit is enlarged in the pure *p-tert*-butylcalix[7]arene. The reciprocal orientation of the two intramolecular cavities is only slightly affected by this process.

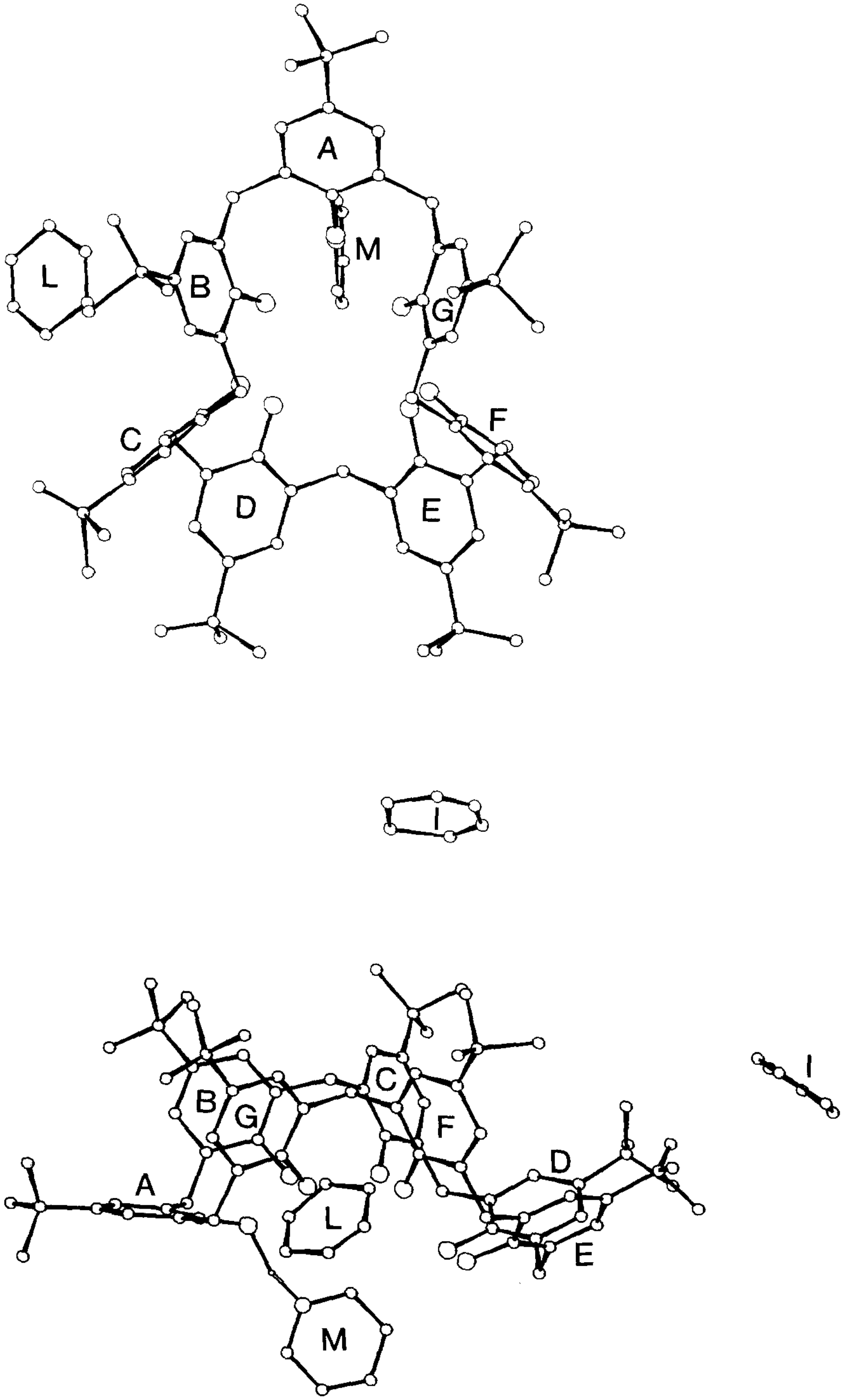


Fig. 1(a) and 1(b). Perspective view of the *p-tert*-butylcalix[7]arene host molecule and its three associated pyridine molecules.

It is also interesting to note that, in any case, calix[*n*]arenes with *n* up to 7 still maintain a cone conformation (or a combination of cone conformations as in the present case), whereas as shown by Gutsche [3] in the *p*-*tert*-butylcalix[8]arene the cone conformation is destroyed and the macrocycle resembles an undulated loop. In this sense, the seven membered calixarenes probably represent the upper limit for the existence of calix[*n*]arenes with intramolecular cavities available for complexation of neutral molecules.

The molecular symmetry may be referred to the pseudo-mirror plane *m* which passes through C(4A)—C(1A)—O(1A) and C(20A) and the plane of the pyridine molecule M. The dihedral angles formed by the pseudo-mirror plane *m* and the weighted least-squares planes through the phenolic rings are: *m*—A 85.2(7)°, *m*—B 26.9(2)°, *m*—C 49.9(2)°, *m*—D 32.0(2)°, *m*—E 27.0(2)°, *m*—F 51.4(2)°, *m*—G 31.7(2)°.

Although extensively used, the description of the conformation of calixarenes by the dihedral angles between the planes of the phenolic rings and a reference plane found in the molecule, contains some ambiguities. The first one is intrinsic, and arises from the impossibility to make an unequivocal choice of a 'positive' side on

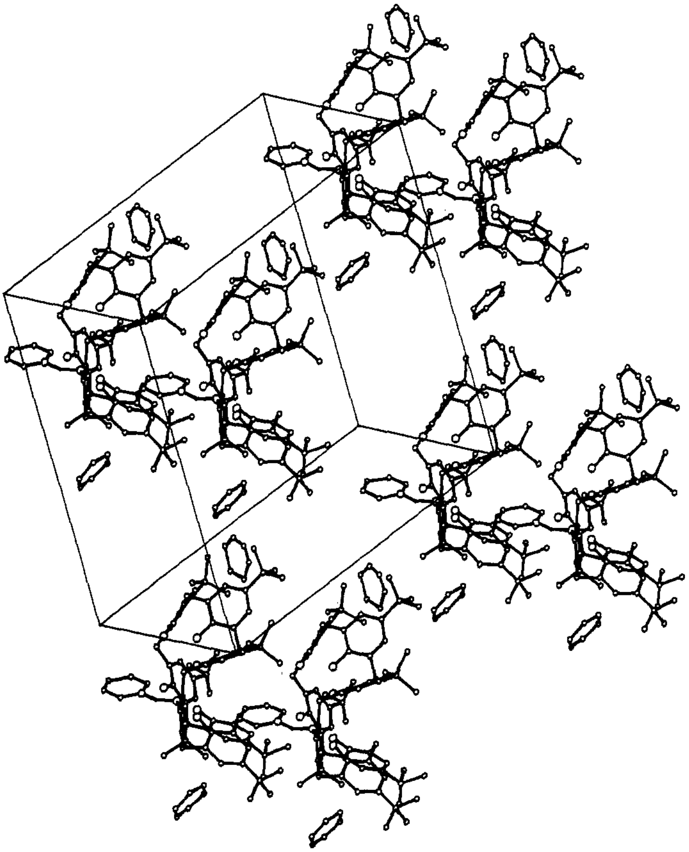


Fig. 2. Crystal structure of the *p*-*tert*-butylcalix[7]arene 1 : 3 pyridine complex/clathrate.

any of the planes. So any given dihedral angle could be given as α or as $180 - \alpha°$. Another ambiguity is related to the fact that, even supposed correctly given, the dihedral angles formed by the phenolic rings with respect to a reference plane give only a partial picture of the arrangement of the phenolic rings around the macrocycle. To obtain a complete description of the conformation of the macrocycle it is necessary to give also the dihedral angles between adjacent phenolic units, with the ambiguities on the values described above.

However, the correct values of the dihedral angles may be deduced by looking at the structures of simple calixarenes up to calix[5]arenes. But in the largest calix[6,7,8]arenes these problems become more serious.

With the aim of giving a simple and unambiguous rule to describe the conformation of the *p-tert*-butylcalix[7]arene here reported, and more generally with the aim of deriving general parameters to describe the conformation of calix[*n*]arenes, we have concentrated on the mechanisms which allow the conformation to change in order to form, for example, a cyclic H-bond between the phenolic OH groups. We can imagine a start from two adjacent, phenolic units A and B, with B lying in the same plane as A on its right side as shown in Figure 3. The two oxygens are separated by an O···O contact of 4.94 Å (having taken C(1A)—O(1A) = C(1B)—O(1B) = 1.38 Å, C(1A)—C(2A) = C(1B)—C(2B) = 1.40 Å and C(2A)—C(20A) = C(20A)—C(6B) = 1.54 Å). The shortening of the O···O distance (which has to reach a value of 2.4–2.8 Å) due to the hydrogen bond may be realized in two steps: the methylene bridge C(20A) and the calixarene unit B have to rotate ϕ degrees rigidly around the bond C(2A)—C(20A) and then the calixarene unit B has to be rotated χ degrees around C(20A)—C(6B). The conformation of the molecule is reached by repeating this mechanism $n - 1$ times for two adjacent phenolic units.

The signs of the conformational angles ϕ and χ are imposed by the condition of the cyclic periodicity after n calixarene units, which also determine the dimensions

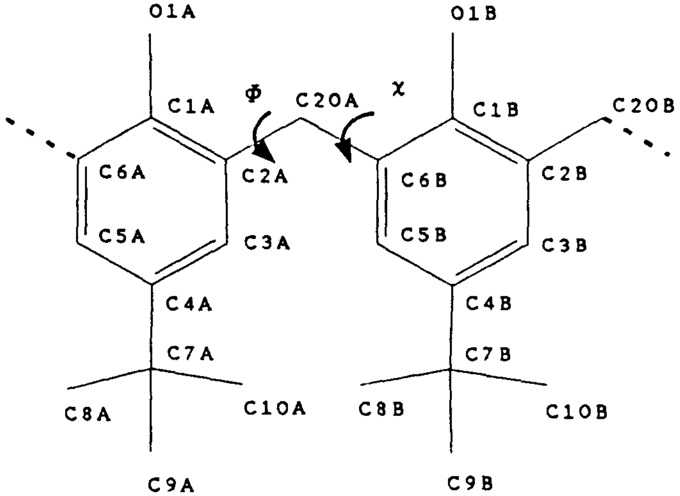


Fig. 3. Atomic numbering scheme in the *p-tert*-butylcalix[7]arene host molecule. The two conformational angles ϕ = C(3)—C(2)—C(20)—C(6′) and χ = C(2)—C(20)—C(6′)C(5′) are illustrated.

(diameter) of the macroring. Although in principle $n - 1$ pairs of conformational angles ϕ and χ are enough to describe a calix[n]arene conformation, in practice, the arbitrary choice of the 'first' phenolic unit suggests that, in general, the conformation of a calix[n]arene is completely defined by giving the n pairs of ϕ and χ. In the *p-tert*-butylcalix[4]arene and in the calix[5]arene the conformation is obtained with all the pairs of conformational angles $\phi > 0$ and $\chi > 0$. This arrangement brings all the hydrogens of the methylene bridges outside of the macroring.

But in calix[7]arenes no more than four adjacent phenolic units may be arranged with the pairs $\phi > 0$ and $\chi < 0$ without preventing the periodicity of the conformation. So it is necessary that the fifth calixarene unit is taken with values of $\phi < 0$ and $\chi > 0$ (this brings the hydrogens of the CH_2 bridge inside the macroring). Then the trimeric subunit with all the $\phi > 0$ and $\chi < 0$ may be obtained. Finally another change of sign in the pair of the conformational angles is required, in correspondence of the seventh CH_2 bridge, to close the macroring.

The values of the conformational angles ϕ and χ are determined by the length of the intramolecular O···O contacts that have to reach to the minimum of the total potential energy U of the molecule

$$U = \sum_{ij} \frac{q_i q_j}{r_{ij}} + \Sigma ij \frac{B_{ij}}{r_{ij}^{12}} - \frac{A_{ij}}{r_{ij}^{6}} + U_{\text{H bonds}}$$

where q_i, q_j are the residual atomic charge, A_{ij} and B_{ij} are the van der Waals coefficients and r_{ij} the interatomic distance between the two atoms i and j.

To avoid any ambiguity in calculating the values and the signs of the conformational angles we have taken as ϕ and χ the two torsion angles C(3)—C(2)—C(20)—C(6′) and C(2)—C(20)—C(6′)—C(5′) (′ labels the atoms in the adjacent phenolic unit) calculated as described in Ref. [14].

The values of χ and ϕ, reported in Table V, shows that ϕ and χ, which are always + and − respectively, change their signs in correspondence of the linking B–C and F–G. This corresponds to the change of the orientation of the tetrameric and the trimeric subunits already discussed. The smallest (in their absolute values) of the conformational angles $\phi = 72.2(9)$ and $\chi = -70(1)°$ reveal the presence of the longest cyclic intramolecular O···O contact: O(1D)···O(1E) 3.500(8) Å.

The molecular packing, which is shown in Figure 2, results from stacks of calixarene units which point the complexed pyridine molecule of one *p-tert*-butylcalix[7]arene inside the cavity of the trimeric subunit of another *p-tert*-butyl-

Table V. Conformational parameters ϕ and χ(°).

	ϕ	χ
A–B	98.5(9)	−89.0(9)
B–C	−90.8(9)	92.6(9)
C–D	98.9(9)	−78.5(9)
D–E	72(1)	−70(1)
E–F	77.5(9)	−94.2(9)
F–G	−94.4(9)	91.1(9)
G–A	89.2(9)	−98.5(9)

calix[7]arene host molecule. The other two molecules of pyridine I and L are blocked in the crystal lattice by the steric barriers offered by the nearest neighbour host molecules. However the orientation of the pyridine molecule I, which is almost parallel to the plane of the methyl groups of the $\mathrm{Bu^t}$ attached to the calixarene units D and E, seem to suggest a certain degree of cooperation of attractive $\mathrm{CH_3} \cdots \pi$ interaction between the methyl groups at D and E and the aromatic moiety at the pyridine (the shortest contact is C(8D)···C(1I) 3.83(2) Å) but the absence of the atomic coordinates of the methyl H atoms, prevents any further consideration.

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