Crystal and Molecular Structure of a Crown-Bridged *p-t*-butyl-Calix[4]arene (1 : 1) Pyridine Complex. Host-Guest Interaction Model Based on Molecular Mechanics Analysis [1]

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Abstract. The crystal and molecular structure of a crowned *p-t*-butyl-calix[4]arene (1:1) pyridine complex is reported. Colourless transparent prismatic crystals (obtained from pyridine) $C_{54}H_{74}O_8 \cdot C_5H_5N$, $a = 13.486(4)$, $b = 15.193(4)$, $c = 16.432(5)$ Å, $\beta = 116.44(4)°$, space group $P2_1$, $Z = 2$, $D_{calc} = 1.02$ g cm^{-3}, CuK_α radiation $\lambda = 1.5418$ Å $\mu(CuK_\alpha) = 4.99$ cm^{-1}. Refinement was carried out using 1702 reflections with $I > 3\sigma(I)$ to R 0.12. The macrocycle shows a distorted cone conformation which defines an intramolecular apolar cavity whose elliptical aperture is 11.5×8.6 Å calculated as distances between the two opposite central C atoms of the Bu^t groups. A molecule of pyridine is included in this cavity, whereas the intermolecular cavities of the host lattice remain empty. The influence of the guest molecule on the conformation of the calixarene-crown is discussed. Potential energy calculations are performed in order to understand the nature of the host-guest interactions responsible for the stabilisation of the complex. Evidence for stabilizing CH_3-π interactions are obtained from the calculations.

Key words. Bridged calixarene, inclusion compounds, pyridine complex, molecular mechanics, X-ray, macrobicyclic compounds, weak host-guest interactions, CH_3-π interactions.

1. Introduction

Several concave macrocyclic host molecules have been synthesized with the aim of obtaining well defined cavities for the selective inclusion of neutral guest species [2].

Among them *p-t*-butyl-calix[4]arene (**1**) has shown an ability to form intramolecular inclusion complexes with aromatic compounds [3, 4, 5]. On the basis of the results obtained we hypothesized that these complexes are stabilized, in the solid state, by weak intermolecular CH_3-π interactions [4, 5, 6].

For this purpose we have undertaken a systematic search for other solid state and solution complexes between calix[4]arene derivatives and neutral molecules with the aim of obtaining further information on the role of this weak interaction in host-guest chemistry.

We report in this paper the X-ray crystal and molecular structure of the 1 : 1 pyridine complex of a crown-bridged *p-t*-butyl-calix[4]arene (**2**) together with results of potential energy calculations on the inclusion complex.

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R = Bu^t n = 4

(1)   (2)
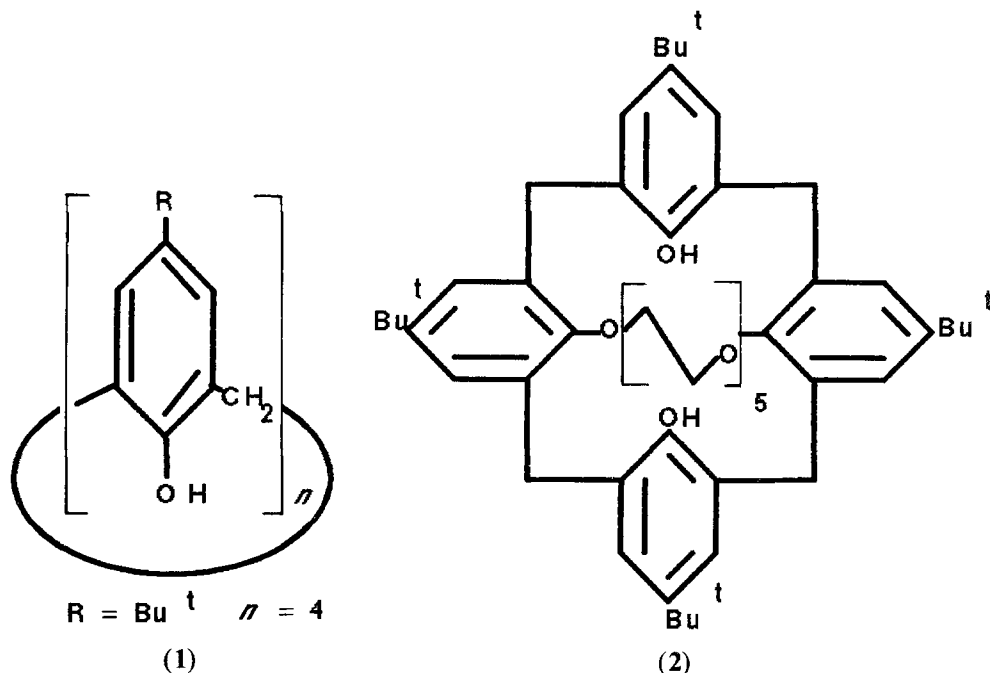
2. Experimental

A preliminary communication of the synthesis of host (2) has been reported [7] and experimental details will be reported elsewhere. Colourless crystals of the complex were obtained by slow evaporation of a pyridine solution of compound (2).

2.1. CRYSTAL DATA

$C_{54}H_{74}O_8 \cdot C_5H_5N$, $M = 930.3$, Monoclinic, $a = 13.486(4)$, $b = 15.193(4)$, $c = 16.432(5)$ Å, $\beta = 116.44(4)°$, $U = 3015(2)$ Å^3, $Z = 2$, $D_{calc} = 1.02$ g cm^{-3}, Space Group $P2_1$ (2nd setting) from structure analysis, CuK_α radiation $\lambda = 1.5418$ Å, $\mu(\text{Cu}K_\alpha) = 4.99$ cm^{-1}. $F(000) = 1008$. Absent spectra $0k0$ $k \neq 2n$ define possible space groups C_{2h} No. 11 or C_2 No. 4; the latter was assigned from structure analysis.

2.2. STRUCTURE DETERMINATION

Lattice parameters were determined from 28 $(\theta, \chi, \phi)_{hkl}$ collected on a Siemens AED single crystal diffractometer on line to a General Automation Jumbo 220 minicomputer [8]. A crystal specimen of dimensions 0.5 × 0.6 × 0.5 mm suitable for X-ray analysis was used for data collection.

A total of 5985 reflections were collected at room temperature using the $\theta - 2\theta$ step scanning mode in the range $3° < \theta < 70°$ using nickel filtered CuK_α radiation. The method described in [9] was used to calculate the intensities I_{hkl} from profile analysis.

One standard reflection collected every $50I_{hkl}$ measurements showed no significant fluctuation in intensity. 1702 Significant reflections with $I > 3\sigma(I)$ [(I) based on counting statistics] have been retained as observed and used in the structure refinement.

The structure was solved and refined using the SHELX package of crystallographic computer programs [10]. From direct methods the analysis of the E-map computed with the most consistent set of signs, led to the approximate positions of about 80% of the scattering power. Successive cycles of least-squares refinements with isotropic temperature factors followed by difference $F_0 - F_c$ Fourier maps made it possible to complete the structure.

Afterwards the atom parameters were refined using anisotropic temperature factors with cycles of full matrix least squares blocked to 216 variables and applying to the carbon atoms of the *t*-butyl groups the geometrical constraints C—C = 1.54 Å.

The positions of the 79 hydrogen atoms were all calculated with C—H = 1.08 Å. Nevertheless, due to the upper limit in the total number of atoms imposed by the SHELX program, only 24 hydrogen atoms (none of them belonging to methylene groups) were introduced in the last cycle and excluded from the refinement but used only in the F_c calculation.

The refinement process was stopped at $R = 0.12$; the final difference electron-density map did not show residual peaks $> 0.47e$ Å^{-3} and plots of $\Delta|F|$ as a function of scattering angle, magnitude of F_0 and Miller indices reveal a linear trend.

The method of Walker and Stuart [11] was applied to account for absorption effects [12]. The absorption coefficients calculated in the polar angles of the incident and diffracted beams range from 1.29 to 0.75 while the absorption corrections in the scattering angles range from 1.15 to 0.87.

The calculations were performed on the GOULD 32/77 of Centro di Studio per la Strutturistica Diffractometrica del C.N.R. Parma.

3. Results and Discussion

3.1. MOLECULAR GEOMETRY AND CRYSTAL STRUCTURE

The macrobicyclic compound (**2**), obtained by bridging two opposite phenolic OH groups of the *p-t*-butyl-calix[4]arene (**1**) with a polyethereal chain possesses a hydrophilic cavity suitable for complexing cations and a lipophilic one for the inclusion of neutral molecules.

The X-ray crystal structure of the pyridine 1:1 complex (Figures 1, 2) shows the guest inside the apolar cavity, whereas the intermolecular voids of the crystal lattice are empty.

The atomic fractional coordinates are shown in Table I; bond distances, bond angles and selected torsion angles are reported in Table II. As shown in Figures 1(a) and 1(b), the molecule exhibits a distorted cone conformation, which can be referred to the mean plane of the macrocycle passing through the 4 methylene bridges C(11A), C(11B), C(11C), C(11D).

The dihedral angles that the phenyl rings B and D, carrying the OH groups, form with this plane are 43.5(4)° and 39.4(5)° respectively, while the phenyl rings A and C carrying the crown moiety form dihedral angles of 72.5(5)° and 69.0(6)°.

A comparison with the corresponding dihedral angles found in the empty form [7], 46.9(9), 49.5(10), 86.2(8), 86.9(9)° shows that the guest mainly influences the inclination, with respect to the plane of the macrocycle, of the two phenyl rings bridged with the polyethereal chain, while the two phenyl rings carrying the OH groups seem to be unaffected. So, passing from the empty form to the complex, the two opposite, crown-bridged, phenyl rings are pushed from the bottom part bearing the *t*-butyl groups towards the exterior of the macroring and allow the guest molecule of pyridine to be inside the intramolecular cavity.

With this behaviour, the elliptical aperture of the intramolecular apolar cavity shows a reduction in its minor axis. This is shown by calculating the two principal axes of the elliptical aperture of the calix as distances between two opposite central C atoms of the *t*-butyl groups that are C(7B)—C(7D) = 11.54(4) Å and C(7A)—C(7C) = 8.62(2) Å, while in the empty form they are 11.71(4) Å and 5.69(2) Å respectively.

The calix deformation induced by the guest molecule of pyridine influences also the crown conformation. This can be described from the torsion angles O—C—C—O; they range from 56.2(2) to 61(3)° (with the exception of two that are 18(4) and 91(2)°), average value 58(2)°, showing practically a *gauche* conformation and deviates significantly from the mean value of 76(1)° observed in the empty form.

The torsion angles C—O—C—C range from 167(3) to 176(3)°, average value 173(3)°, with the exception of one 77(3)°, showing practically a *trans* conformation. The average values do not deviate significantly from those observed in the empty form.

These arrangements of the torsion angles fold the crown chain in such a way that its projection on the mean plane of the macrocycle lies outside the macroring (see Figure 1(b)). The dihedral angle formed by the mean plane through the crown and the mean plane of the macrocycle is 27.0(3)° which is significantly lower than the value calculated in the empty form: 41.5(1)°.

The mean plane passing through the pyridine is perpendicular the mean plane of the macroring (see Figure 1-b) and is almost perpendicular to the line O(1A)—O(1C). Due to the reciprocal orientation of the phenyl rings, the OH groups are able to form weak
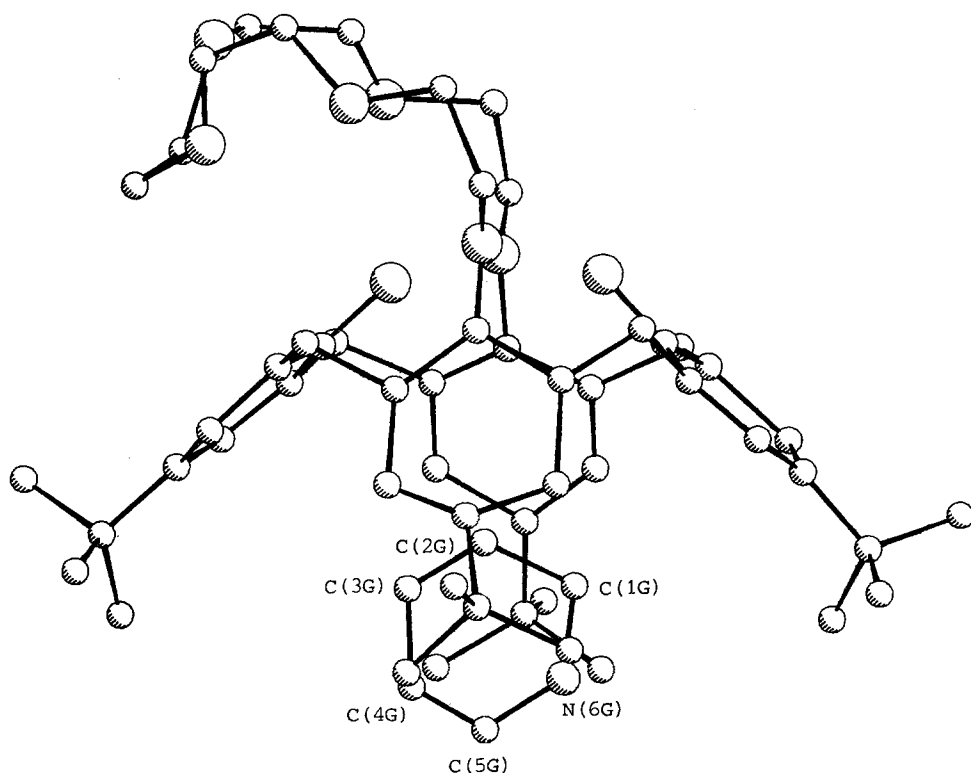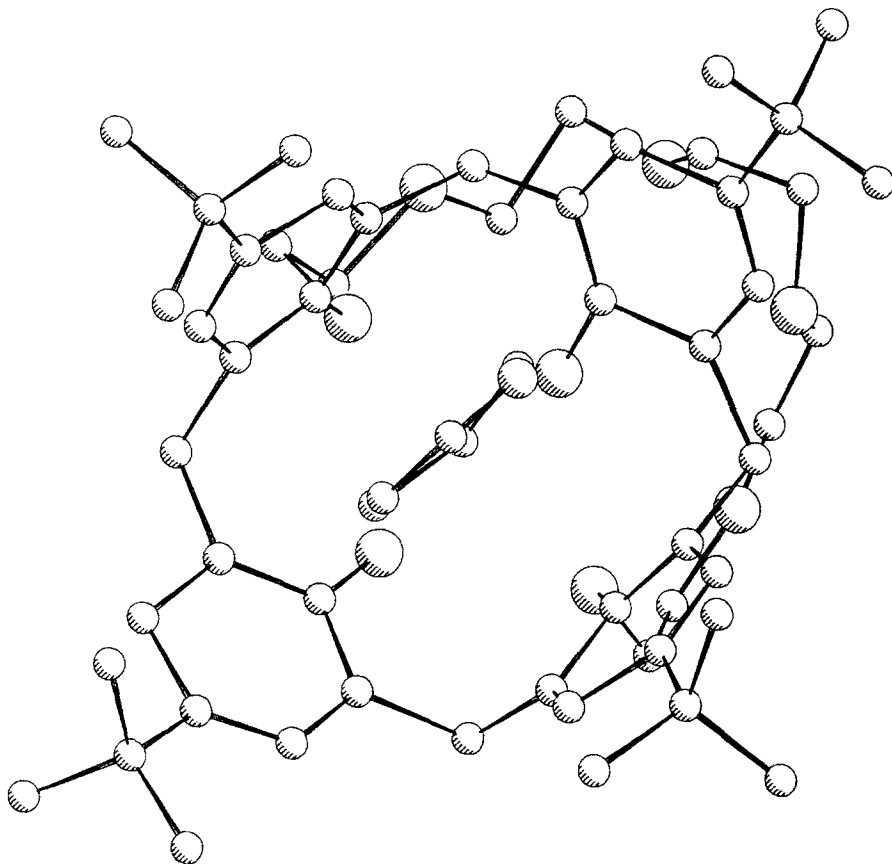

Fig. 1. (a).

Fig. 1. (a) Perspective view of the complex. The pyridine guest molecule is denoted by labelled atoms. (b) View perpendicular to the mean molecular plane.

intramolecular hydrogen bonds, and the O· · ·O contacts of the oxygens of the calix[4]arene moiety range from 2.77(2) to 2.98(2) Å with an average shortening of 0.16 Å with respect to the values observed in the empty form. So the inclusion of the pyridine molecule favours the conformation which can form intramolecular hydrogen bonds. Finally the molecular packing (Figure 2) is compatible with usual van der Waals contacts, and gives a calculated density of 1.02 g cm^{-3} which is lower than the corresponding one (1.108 g cm^{-3}) calculated for the empty form.

3.2. POTENTIAL ENERGY CALCULATIONS

In order to clarify the nature of the host-guest interactions we have undertaken the calculation of the potential energy of the title compound by molecular mechanics techniques.

In our approach both the host and the guest are treated as rigid bodies and the potential energy of the system is calculated as a function of the rigid rotations φ of the guest around the three axes of the pyridine molecule passing through C(1G)—C(4G), C(2G)—C(5G), C(3G)—N(6G) respectively. The host remains at rest as depicted in Figure 1(b) and is considered to have $\varphi = 0$, the orientation observed in the crystal structure.

Table I. Atomic coordinates.

Atom	x/a	y/b	z/c	Atom	x/a	y/b	z/c
C(1A)	0.5407(18)	0.3755(16)	0.2694(15)	O(1C)	0.6331(11)	0.0440(9)	0.2795(9)
C(2A)	0.4499(16)	0.3827(14)	0.1771(13)	C(11C)	0.4760(17)	0.0319(16)	0.0960(14)
C(3A)	0.3397(18)	0.4189(16)	0.1615(16)	C(1D)	0.4691(14)	0.1851(16)	0.0949(12)
C(4A)	0.3221(15)	0.4357(13)	0.2282(13)	C(2D)	0.4159(17)	0.1140(15)	0.0499(14)
C(5A)	0.3908(16)	0.4118(14)	0.3216(13)	C(3D)	0.3262(17)	0.1186(17)	−0.0269(15)
C(6A)	0.5142(17)	0.3870(14)	0.3504(14)	C(4D)	0.2813(13)	0.2046(18)	−0.0711(12)
C(7A)	0.2176(15)	0.4860(13)	0.2238(12)	C(5D)	0.3366(17)	0.2752(16)	−0.0265(15)
C(8A)	0.2398(19)	0.5838(14)	0.2129(16)	C(6D)	0.4306(17)	0.2754(16)	0.0562(15)
C(9A)	0.1146(20)	0.4557(17)	0.1381(13)	C(7D)	0.1760(12)	0.1982(12)	−0.1620(10)
C(10A)	0.1948(20)	0.4755(17)	0.3071(13)	C(8D	0.0862(17)	0.1359(14)	−0.1611(17)
O(1A)	0.6461(12)	0.3473(10)	0.2887(10)	C(9D)	0.2132(18)	0.1651(16)	−0.2327(15)
C(11A)	0.5978(19)	0.3657(18)	0.4355(16)	C(10D)	0.1266(17)	0.2912(11)	−0.1886(16)
C(1B)	0.5841(14)	0.1984(0)	0.4403(12)	O(1D)	0.5680(10)	0.2014(15)	0.1773(8)
C(2B)	0.5508(17)	0.2768(17)	0.4636(16)	C(11D)	0.4706(20)	0.3677(19)	0.0946(17)
C(3B)	0.4996(15)	0.2733(12)	0.5190(12)	C(1G)	0.2677(18)	0.1929(22)	0.2989(16)
C(4B)	0.4758(14)	0.1988(20)	0.5511(11)	C(2G)	0.2913(16)	0.2030(21)	0.2217(15)
C(5B)	0.5147(21)	0.1211(20)	0.5329(19)	C(3G)	0.2124(17)	0.1930(22)	0.1322(14)
C(6B)	0.5673(16)	0.1169(15)	0.4708(14)	C(4G)	0.0930′(17)	0.2071(20)	0.1211(15)
C(7B)	0.4058(11)	0.1888(12)	0.6002(9)	C(5G)	0.0690(17)	0.1996(22)	0.1900(16)
C(8B)	0.3558(17)	0.2778(11)	0.6081(14)	N(6G)	0.1558(17)	0.1927(21)	0.2724(14)
C(9B)	0.4761(15)	0.1519(13)	0.6963(11)	C(1*)	0.7195(17)	0.4148(15)	0.3087(15)
C(10B)	0.3101(17)	0.1242(14)	0.5472(15)	C(2*)	0.8133(18)	0.3925(17)	0.2816(16)
O(1B)	0.6462(10)	0.2023(14)	0.3914(8)	O(3*)	0.7672(19)	0.3777(18)	0.1866(16)
C(11B)	0.5813(16)	0.0285(14)	0.4391(13)	C(4*)	0.8289(23)	0.3457(23)	0.1362(22)
C(1C)	0.5230(14)	0.0188(12)	0.2651(12)	C(5*)	0.7684(21)	0.3159(19)	0.0433(18)
C(2C)	0.5005(15)	0.0074(13)	0.3373(12)	O(6*)	0.6685(17)	0.2991(16)	0.0259(14)
C(3C)	0.4085(15)	−0.0266(13)	0.3241(13)	C(7*)	0.6120(21)	0.2263(21)	−0.0498(20)
C(4C)	0.3208(17)	−0.0408(16)	0.2420(15)	C(14*)	0.7072(18)	−0.0355(17)	0.2929(15)
C(5C)	0.3562(14)	−0.0234(12)	0.1666(11)	C(13*)	0.8013(20)	0.0063(19)	0.2958(17)
C(6C)	0.4553(16)	0.0031(14)	0.1818(13)	O(12*)	0.7751(13)	0.0044(12)	0.1909(11)
C(7C)	0.2098(11)	−0.0812(9)	0.2201(8)	C(11*)	0.8409(18)	0.0618(16)	0.1734(15)
C(8C)	0.1699(15)	−0.0476(12)	0.2894(9)	C(10*)	0.8182(19)	0.0492(18)	0.0750(17)
C(9C)	0.2294(17)	−0.1812(10)	0.2323(13)	O(9*)	0.7903(18)	0.1300(16)	0.0416(15)
C(10C)	0.1183(14)	−0.0620(12)	0.1234(8)	C(8*)	0.6569(21)	0.1438(20)	−0.0044(19)

We started the calculations introducing van der Waals attractive interactions using the Lennard-Jones expression:

$$U_{vdw} = \sum_{ij} \frac{B_{ij}}{r_{ij}^{12}} - \frac{A_{ij}}{r_{ij}^6} \tag{1}$$

where the subscripts i and j run on the atoms of the guest and the host respectively and the constants A_{ij} and B_{ij} are derived from the literature [13].

The electrostatic contribution (2) was also added

$$U_{el} = \sum_{ij} \frac{q_i q_j}{r_{ij}} \tag{2}$$

where the charges q_i, q_j were calculated, according to ref. [13], by dividing the bond and group dipolar moments often found in macromolecules by the observed bond lengths r_{ij}.

Table II.   Bond distances (Å), bond angles (°) and selected torsion angles (°).

Bond distances (Å) concerning the phenyl rings

	A	B	C	D
C(1A)—C(2A)	1.47(2)	1.39(3)	1.36(3)	1.33(3)
C(1A)—C(6A)	1.53(4)	1.39(3)	1.29(2)	1.50(3)
C(1A)—O(1A)	1.38(3)	1.40(3)	1.45(2)	1.44(2)
C(2A)—C(3A)	1.50(3)	1.37(4)	1.27(3)	1.30(2)
C(3A)—C(4A)	1.25(4)	1.35(3)	1.36(2)	1.49(3)
C(4A)—C(5A)	1.44(3)	1.38(4)	1.54(4)	1.33(3)
C(4A)—C(7A)	1.58(3)	1.50(3)	1.51(3)	1.54(3)
C(5A)—C(6A)	1.56(3)	1.48(4)	1.31(3)	1.39(3)
C(6A)—C(11A)	1.39(3)	1.48(3)	1.61(4)	1.53(4)
C(7A)—C(8A)	1.54(3)	1.54(3)	1.55(3)	1.54(3)
C(7A)—C(9A)	1.54(2)	1.54(2)	1.54(2)	1.54(3)
C(7A)—C(10A)	1.54(4)	1.54(2)	1.54(2)	1.54(2)
C(11A)—C(2B)	1.64(4)	1.57(2)	1.50(3)	1.52(4)

Bond distances (Å) concerning the guest

C(1G)—C(2G)	1.45(4)	C(3G)—C(4G)	1.55(3)
C(1G)—N(6G)	1.37(3)	C(4G)—C(5G)	1.31(4)
C(2G)—C(3G)	1.39(3)	C(5G)—N(6G)	1.34(3)

Bond distances (Å) concerning the crown

O(1A)—C(1*)	1.36(3)	O(1C)—C(14*)	1.52(3)
C(1*)—C(2*)	1.55(4)	C(14*)—C(13*)	1.40(4)
C(2*)—O(3*)	1.42(3)	C(13*)—O(12*)	1.60(3)
O(3*)—C(4*)	1.49(5)	O(12*)—C(11*)	1.36(3)
C(4*)—C(5*)	1.45(4)	C(11*)—C(10*)	1.52(4)
C(5*)—O(6*)	1.27(4)	C(10*)—O(9*)	1.33(4)
O(6*)—C(7*)	1.58(4)	O(9*)—C(8*)	1.63(3)
C(7*)—C(8*)	1.45(4)		

Bond angles (°) concerning the phenyl units

	A	B	C	D
C(6A)—C(1A)—O(1A)	117(2)	119(1)	114(2)	104(2)
C(2A)—C(1A)—O(1A)	124(2)	118(1)	120(2)	135(2)
C(2A)—C(1A)—C(6A)	119(2)	123(1)	125(2)	121(2)
C(1A)—C(2A)—C(3A)	121(2)	118(2)	119(2)	122(2)
C(1A)—C(2A)—C(11D)	121(2)	115(2)	126(2)	111(2)
C(3A)—C(2A)—C(11D)	118(2)	126(2)	115(2)	126(2)
C(2A)—C(3A)—C(4A)	119(2)	125(2)	126(2)	121(2)
C(3A)—C(4A)—C(7A)	125(2)	128(2)	129(2)	115(2)
C(3A)—C(4A)—C(5A)	127(2)	117(2)	109(2)	116(2)
C(5A)—C(4A)—C(7A)	108(2)	115(2)	121(2)	130(2)
C(4A)—C(5A)—C(6A)	118(2)	122(2)	124(2)	126(2)
C(1A)—C(6A)—C(5A)	113(2)	114(2)	116(2)	114(2)
C(5A)—C(6A)—C(11A)	130(2)	117(2)	118(2)	114(2)
C(1A)—C(6A)—C(11A)	117(2)	128(2)	124(2)	132(2)
C(4A)—C(7A)—C(10A)	116(2)	109(1)	115(1)	108(2)
C(4A)—C(7A)—C(9A)	109(2)	110(1)	106(2)	106(2)
C(4A)—C(7A)—C(8A)	105(2)	111(2)	109(1)	115(2)
C(9A)—C(7A)—C(10A)	109(2)	109(1)	109(1)	109(2)
C(8A)—C(7A)—C(10A)	109(2)	109(2)	108(1)	109(2)
C(8A)—C(7A)—C(9A)	109(2)	109(1)	109(1)	109(2)
C(6A)—C(11A)—C(2B)	103(2)	115(2)	114(2)	110(2)

Table II. *(continued)*

Bond angles (°) concerning the crowns

C(1A)—O(1A)—C(1*)	113(2)	C(1C)—O(1C)—C(14*)	112(2)
O(1A)—C(1*)—C(2*)	111(2)	O(1C)—C(14*)—C(13*)	110(2)
C(1*)—C(2*)—O(3*)	110(2)	C(14*)—C(13*)—O(12*)	101(2)
C(2*)—O(3*)—C(4*)	126(2)	C(13*)—O(12*)—C(11*)	111(2)
O(3*)—C(4*)—C(5*)	120(3)	O(12*)—C(11*)—C(10*)	108(2)
C(4*)—C(5*)—O(6*)	110(3)	C(11*)—C(10*)—O(9*)	102(2)
C(5*)—O(6*)—C(7*)	114(2)	C(10*)—O(9*)—C(8*)	111(2)
O(6*)—C(7*)—C(8*)	105(2)	C(7*)—C(8*)—O(9*)	118(2)

Bond angles (°) concerning the guest

C (2G)—C(1G)—N(6G)	111(2)	C(3G)—C(4G)—C(5G)	122(2)
C(1G)—C(2G)—C(3G)	124(2)	C(4G)—C(5G)—N(6G)	116(2)
C(2G)—C(3G)—C(4G)	112(2)	C(1G)—N(6G)—C(5G)	131(2)

Torsion angles (°) concerning the methylene bridging atoms

	A	B	C	D
C(1A)—C(6A)—C(11A)—C(2B)	−111.(2)	−64(3)	−100(3)	−65(3)
C(6A)—C(11A)—C(2B)—C(1B)	93(2)	94(2)	80(2)	102(3)

Torsion angles (°) concerning the *tert*-butyl groups

C(3A)—C(4A)—C(7A)—C(8A)	−77(3)	2(3)	41(3)	46(2)
C(3A)—C(4A)—C(7A)—C(9A)	39(3)	−118(2)	−77(3)	−74(2)
C(3A)—C(4A)—C(7A)—C(10A)	162(2)	122(2)	162(2)	168(2)
C(5A)—C(4A)—C(7A)—C(8A)	104(2)	−174(2)	−150(2)	−133(2)
C(5A)—C(4A)—C(7A)—C(9A)	−140(2)	65(2)	65(2)	106(3)
C(5A)—C(4A)—C(7A)—C(10A)	−17(2)	−54(3)	−28(3)	−11(3)

Torsion angles (°) concerning the guest

C(2G)—C(1G)—N(6G)—C(5G)	1(4)	C(2G)—C(3G)—C(4G)—C(5G)	−21(4)
N(6G)—C(1G)—C(2G)—C(3G)	−14(4)	C(3G)—C(4G)—C(5G)—N(6G)	10(4)
C(1G)—C(2G)—C(3G)—C(4G)	23(4)	C(4G)—C(5G)—N(6G)—C(1G)	1(4)

Torsion angles (°) concerning the crowns

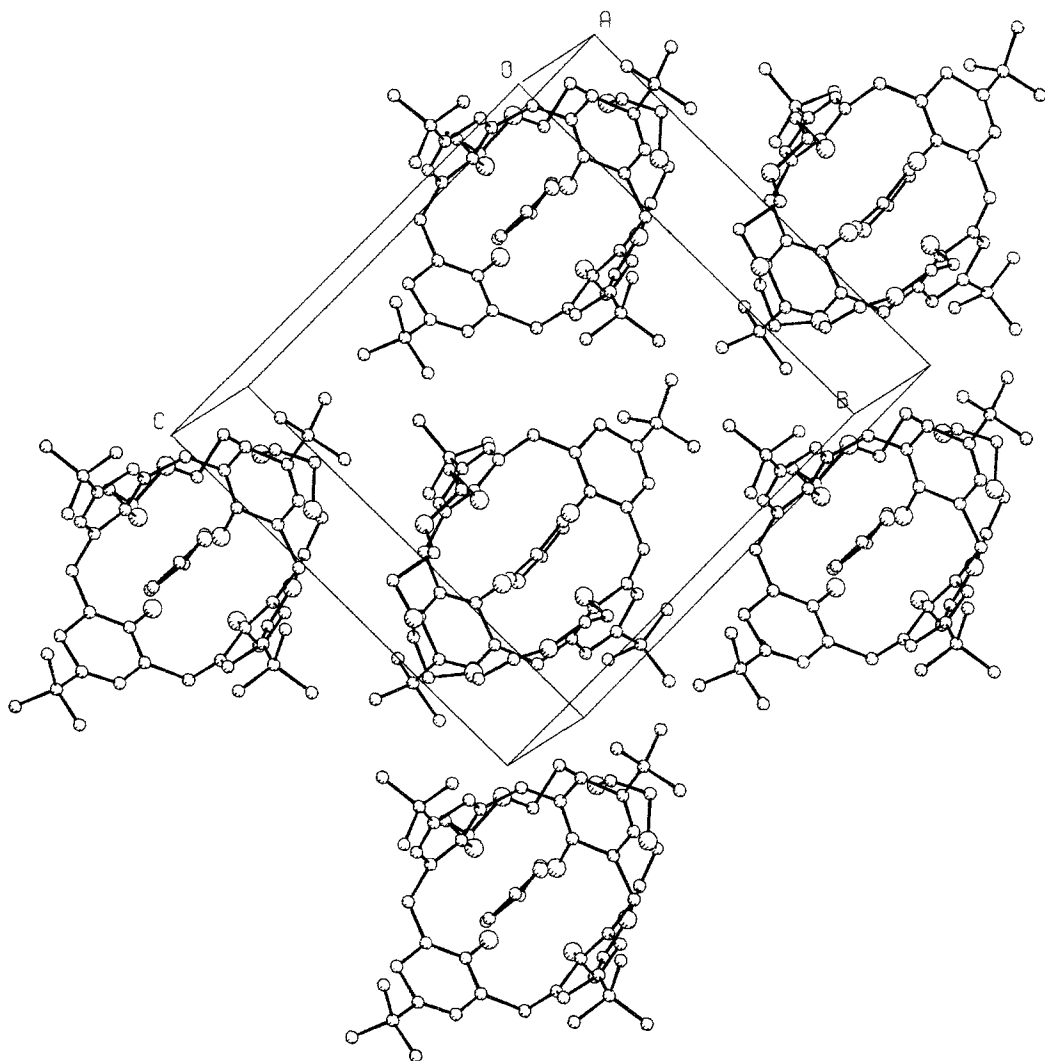|	
O(1A)—C(1*)—C(2*)—O(3*)	−61(3)
C(1*)—C(2*)—O(3*)—C(4*)	−173(3)
C(2*)—O(3*)—C(4*)—C(5*)	167(3)
O(3*)—C(4*)—C(5*)—O(6*)	−18(4)
C(4*)—C(5*)—O(6*)—C(7*)	−152(3)
C(5*)—O(6*)—C(7*)—C(8*)	77(3)
O(6*)—C(7*)—C(8*)—O(9*)	−57(3)
O(1C)—C(14*)—C(13*)—O(12*)	−91(2)
C(14*)—C(13*)—O(12*)—C(11*)	164(2)
C(13*)—O(12*)—C(11*)—C(10*)	175(2)
O(12*)—C(11*)—C(10*)—O(9*)	124(2)
C(11*)—C(10*)—O(9*)—C(8*)	−94(2)
C(10*)—O(9*)—C(8*)—C(7*)	−176(3)

Fig. 2. Perspective view of the molecular packing.

The calculations were extended to the lattice taking into account the contribution of the shell of fifth neighbour cells surrounding the reference one.

The contributions of the lattice to the total potential energy resulted in only 10% of the contribution given by the complex unit to be taken as the origin for each φ value.

The results of the calculations of the potential energy of the system, performed at intervals of 5° up to a maximum of $\pm 90°$ around the axes of the pyridine are depicted in Figure 3(1).

This shows that with the contributions (1) + (2) only, the potential energy exhibits a minimum at $-30°$ and disagrees with the model obtained from the X-ray analysis.

A question can arise from the rotational indetermination of the H atoms of the methyl groups, whose positions were calculated, but several calculations of the total potential energy (1) + (2) taking into account the rotations of the CH_3 groups around the C—C bond, at intervals of 5°, gave similar trends to those shown in Figure 3(1).
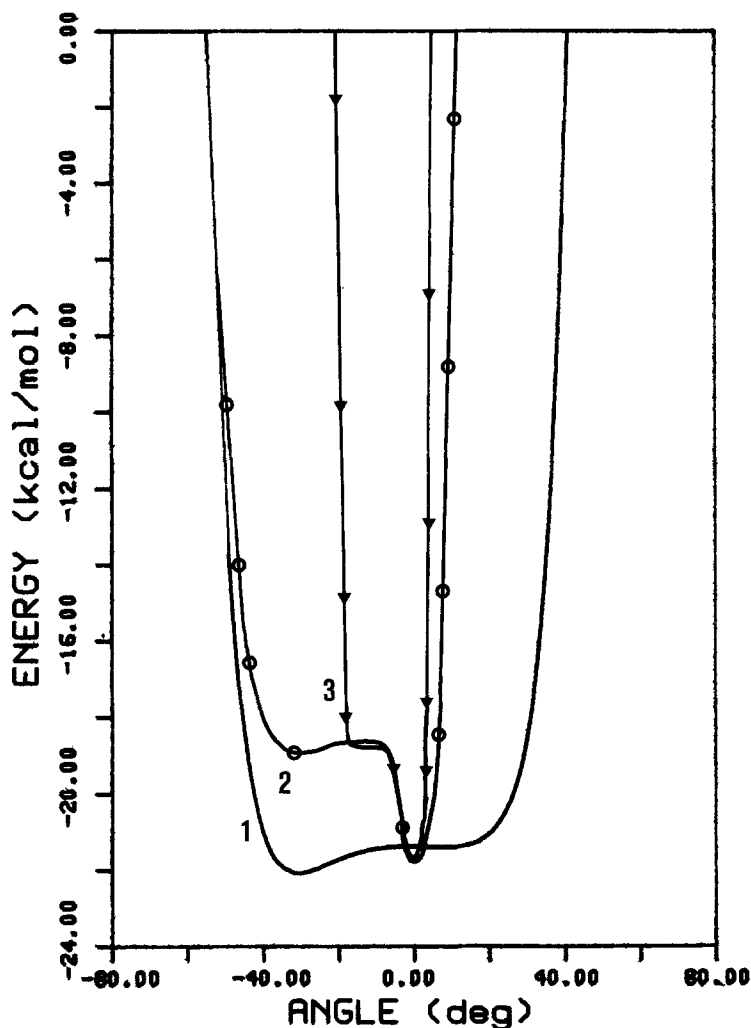
Fig. 3. Potential energy of the system. (1) Van der Waals + Coulomb contributions calculated as a function of rotation around C(1G)—C(4G), C(2G)—C(5G) and C(3G)—N(6G). (2) Van der Waals + Coulomb + H bonds ($D_N = 1$ kcal/mol) contributions calculated as a function of rotation around C(1G)—C(4G) and C(2G)—C(5G). (3) Van der Waals + Coulomb + H bonds + $CH_3 \cdots \pi$ contributions calculated as a function of rotation around C(1G)—C(4G) and C(2G)—C(5G).

The presence of the N atom in the guest induced us to take into account the possibility of an intermolecular H bond interaction between the methyl groups of the host and the N atom of the pyridine [14].

The shortest possible host-guest contacts are C(8G)—H(4C)$\cdots$N(6G) with H(4C) $\cdots$ N(6G) of 2.58 Å. So a H bond type interaction was introduced in the calculation of the potential energy of the system. It was described by an effective potential U_{eff} derived from that proposed by Morse [15] which was rewritten as follows:

$$U_{eff} = \begin{cases} D[1 - \exp(\ln 2(r - r_0)/(r_1 - r_0))]^2 - D & \text{for } r < R \\ \text{vdw} + \text{electrostatic contribution} & \text{for } r > R \end{cases} \tag{3}$$

where the center of force are the donor and acceptor atoms separated by a distance r. r_0 represents the distance at which the minimum $U_{eff} = -D$ occurs. For $r < r_1$ the interaction becomes repulsive. The value of R is determined by imposing the continuity condition. Although various models to describe a bonded system based on 'effective potential' exist (see for example ref. [16]) the revised Morse potential offers a greater number of parameters.

Two calculations of the total potential energy of the system were performed as a function of rotations around the two axes of the pyridine which do not pass through the N atoms: namely $C(2G)$—$G(5G)$ and $C(1G)$—$C(4G)$. The calculations were performed using, for the H bond contribution, $r_0 = 2.58$, $r_1 = 2.5$, $R = 3.5°$, and the value of the constant $D_{C-H \cdots N} = 1 \sim 2$ kcal/mole was derived from Kollman [17] who has showed that the energy involved in a contact $HC \equiv CH \cdots NH_3$ is 2.5 kcal/mole. Taking into account that the values of the electronegativity of the $C(sp^3)$ and $C(sp)$ are 2.48 and 3.29 [18] respectively, we have estimated $D_{C-H \cdots N}$ as follows

$$D_{C-H \cdots N} = 2.5 \frac{2.48}{3.29} = 2.0 \text{ kcal/mole}$$

Both calculations gave the same pattern which is reported in Figure 3(2). The potential energy shows a well pronounced minimum at $\varphi = 0$ in good agreement with the observed crystal structure; so it seems that the interaction between the N atom of the guest and the H atoms of the Bu' of the host is enough to stabilize the complex. Table III reports the atomic fractional coordinates of the H atoms of the Bu' groups which give the minimum of the potential energy of the system.

In attempting to calculate the potential energy of the system with the contributions (1) + (2) + (3) as a function of the rotation φ around the axis which passes through the N atom ($C(3G)$—$N(6G)$) we obtained the pattern of Figure 4(1), which still contradicts the observed crystal structure. Therefore it seems that an attractive CH_3-π interaction between the methyl groups of the host and the aromatic nucleus of the guest has to be invoked to stabilize the energy of the system for rotation around $C(3G)$–$N(6G)$.

Table III.   Atomic fractional coordinates of the H atoms involved in C—$H \cdots N(6G)$ and C—$H \cdots \pi$ interactions which gives the minimum of potential energy.

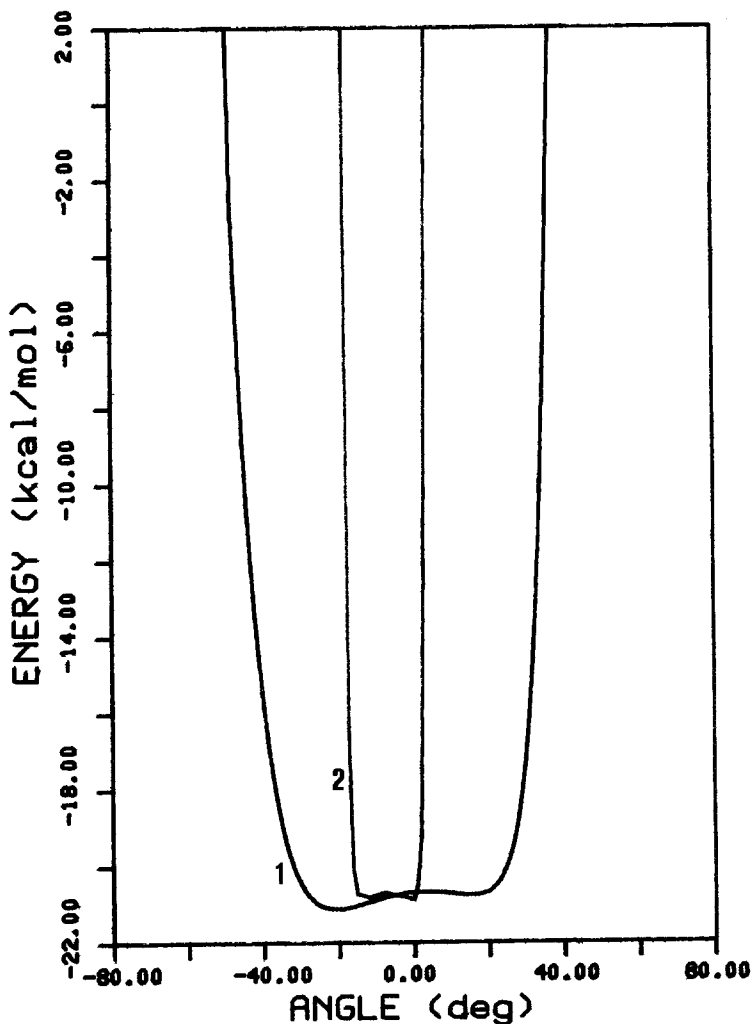|			
H(3C)	0.0910	−0.0772	0.2750
H(4C)	0.1611	0.0232	0.2842
H(5C)	0.2300	−0.0652	0.3573
H(9C)	0.1063	0.0085	0.1146
H(10C)	0.0418	−0.0923	0.1151
H(11C)	0.1420	−0.0876	0.0738
H(6A)	0.0409	0.4827	0.1390
H(7A)	0.1100	0.3846	0.1373
H(8A)	0.1205	0.4783	0.0782
H(9A)	0.2348	−0.5281	0.3546
H(10A)	0.2269	0.4129	0.3395
H(11A)	0.1066	0.4780	0.2858

Fig. 4. Potential energy of the system calculated as a function of rotation around C(3G)—N(6G). (1) Van der Waals + Coulomb + H bonds ($D_N = 1$ kcal/mol) contributions. (2) Van der Waals + Coulomb + H bonds + $CH_3 \cdots \pi$ contributions.

This hypothesis is based on the experimental evidence that the calix[4]arenes form intramolecular complexes with aromatic molecules when Bu^t groups are present at the phenyl nuclei [19, 20, 21]. When the Bu^t groups were removed from the calix[4]arene intramolecular complexes were never obtained, but clathrates [22].

This new interaction has been introduced in the calculation of the potential energy of the system by putting the center of forces on the H atoms of the Bu^t groups attached to the phenolic units A and C (whose mean plane are almost parallel to the plane through pyridine) and on the six non H atoms of the guest. It must be emphasised that the coordinates of the H atoms were unchanged (Table III). Then the CH_3-π contribution to the potential energy is calculated from equation (3) using a very low coupling constant $D = 0.1$ kcal/mole; while $r_0 = 2.71$, $r_1 = 2.68$ and $R = 3.5$ Å were assumed. The value of $D = 0.1$ kcal/mole has been estimated from ref. [20] which gives an energy contribution of 0.9 kcal/mole for an H—F$\cdots\pi$ interaction. Then we have adjusted this value according to

the ratios between the dipole moments μ_{C-H} and μ_{F-H} as follows:

$$D_{C-H\cdots\pi} = D_{F-H\cdots\pi}\frac{\mu_{C-H}}{\mu_{F-H}}$$

The plot of the total potential energy of the system as a function of the rotation around the C(3G)—N(6G) axis is shown in Figure 4(2) which results in good agreement with the crystallographic data.

Finally in Figure 3(3) is reported the plot of the potential energy of the system obtained from (1) + (2) + (3) + CH$_3$-π contribution as a function of the rotations around the two axes of the pyridine which do not pass through the N atoms. This result, if compared with the curve of Figure 3(2) results in better agreement with the crystallographic data. These results seem to confirm the important role played by the CH$_3$-π attractive interaction in blocking the pyridine molecule into the intramolecular cavity. All the calculations of the potential energy were performed using the program LEGO [23]. Geometrical calculations were performed using PARST [24].

4. Conclusions

The crystal and molecular structure of the crowned *p-t*-butyl-calix[4]arene (1 : 1) pyridine complex was obtained from single crystal X-ray diffraction analysis.

The molecular conformation of the complex compared with the empty form, shows that two opposite phenyl rings are rotated around their CH$_2$ bridges to form an elliptical aperture of greater area (the axis of the aperture being 11.71(4) and 8.62(2) Å) which accommodates a molecule of pyridine.

Also the crown conformation is influenced: passing from the empty form to the complex, the crown is bent towards the mean molecular plane to form a dihedral angle of 27.0(3)° with it.

With the aim of clarifying the factors which govern the host-guest interactions, some calculations of the potential energy of the system as a function of the rotational degrees of freedom of the pyridine were undertaken.

A first calculation of the potential energy of the system performed taking into account only the Van der Waals and Coulomb interactions gave a result which is not in agreement with the X-ray crystal structure.

An important contribution to the stabilization of the guest seems to be the H bond between atoms of the Bu^t groups of the host and the N atom of the guest. However there still remains a rotational degree of freedom of the pyridine around the axis of the molecule which passes through the N atom. The potential energy of the system reaches a minimum only if the contribution of an attractive CH$_3$-π interaction between the methyl groups of the host and the aromatic moiety of the pyridine is introduced in the calculations.

Acknowledgement

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