A Hydrogen Bond between a Calixarene (as Host) and Its Guest: Crystal and Molecular Structure of the *p*-t-Butyldihomooxacalix[4]arene : Triethylamine (1 : 2) Complex/Clathrate

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Abstract. The structure of the *p*-t-butyldihomooxacalix[4]arene triethylamine (1 : 2) complex has been determined by X-ray crystallography. Crystals are monoclinic, space group *Cc*, $a = 22.821(3)$, $b = 15.257(3)$, $c = 16.365(2)$ Å, $\beta = 97.44(1)°$, $V = 5650(1)$ Å^3, $Z = 4$, $D_{calc} = 1.03$ g cm^{-3}. One triethylamine (Et$_3$N) molecule has one of its ethyl groups pointing inside the cavity of a calixarene molecule; its nitrogen atom is directed exo to this calixarene molecule and is involved in a hydrogen bond with one of the hydroxy groups of a neighbouring calixarene molecule. This scheme leads to columns of alternating host and guest molecules. The other Et$_3$N molecule is in the interhost space. This feature allows us to define the title compound as a complex/clathrate hybrid.

Key words. Inclusion compounds, calixarene, crystal structure, hydrogen bonding, amines.

1. Introduction

Homooxacalixarenes belong to the group of calixarenes, well known for their ability to form inclusion complexes. Up to now, only a few of their crystal structures have been determined [1, 2]. Recently we published results concerning the 1 : 1 complex of *p*-t-butyldihomooxacalix[4]arene with *m*-xylene [3]. Here we report a study concerning a complex between the same calixarene and triethylamine. In one of his papers [4] Gutsche presents a study of the interactions of calixarenes and amines in solution: he suggests a proton transfer from the calixarene to the amine to form an ammonium cation and a calixarene anion and then a complexation by association of the ions.

$$A_2OH + R_3N \rightleftharpoons ArO^- + R_3NH^+ \rightleftharpoons ArO^- \cdots {}^+HNR_3$$
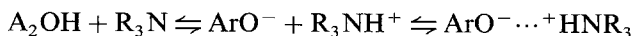
Here we present an example of the interaction of a calixarene with an amine in the solid state.

2. Experimental

2.1. CRYSTALLISATION

Transparent prismatic crystals were obtained by evaporation at room temperature of an Et_3N solution of the powdered calixarene.

2.2. X-RAY STRUCTURE ANALYSIS

A colourless crystal $(0.3 \times 0.1 \times 0.4\,\text{mm})$ was sealed in a glass capillary. The X-ray measurements were performed at room temperature on a Nonius CAD4 diffractometer using graphite monochromatized CuK_α radiation. Lattice parameters were refined by least-squares fit of 25 $(\theta, \varphi, \omega, \kappa)_{hkl}$ reflections in the range $17 \leqslant \theta \leqslant 27\,^\circ$. Intensities were collected in the range $1^\circ < \theta < 73^\circ$ using the $\omega - 2\theta$ scan mode. Three standard reflections were measured every hour to test intensity variations and a test was performed to check the orientation of the crystal every 100 measurements.

2.2.1. *Crystal Data*

$C_{45}O_5H_{58}$, $2\,C_6NH_{15}$, $M = 888.3$, Monoclinic, Space group Cc, $a = 22.821(3)$, $b = 15.257(3)$, $c = 16.365(2)$ Å, $\beta = 97.44(1)^\circ$, $V = 5650(1)$ Å^3, $Z = 4$, $D_{calc} = 1.03$ g cm^{-3}, $F(000) = 1936$, $\lambda = 1.5418$ Å, $\mu(CuK_\alpha) = 4.71$ cm^{-1}.

6016 reflections were collected. Their intensities were corrected for Lorentz, polarization and absorption effects. Of these, 5488 were unique (internal $R = 0.04$) and 2054 with $I_{hkl} > 3\sigma(I_{hkl})$ were considered as observed. The calculations were performed by programs of the SDP System [5].

The structure was solved by MULTAN [6] and refined using SHELX[7]. Successive Fourier E maps revealed progressively all the non-hydrogen atoms. Atoms of an Et_3N molecule situated in the interhost space were found with very high temperature factors but all attempts to solve disorder for this molecule failed; constraints on lengths had to be applied to this molecule during the refinement. Some hydrogens were found from difference Fourier maps, others were calculated at theoretical positions; rigid body techniques were used to refine them and they were constrained to have a fixed isotropic thermal parameter. Hydrogens of the four hydroxy groups of the calixarene and those belonging to the Et_3N molecules situated in the interhost space were not taken into account. Anisotropic temperature factors were assigned to all the non hydrogen atoms. The final R value was 0.069 with unit weights. The final difference electron density map showed the highest residual peak of 0.16 e Å^{-3} followed by other peaks less than 0.097 e Å^{-3}. Scattering factors for non-hydrogen atoms were taken from the International Tables for X-Ray Crystallography [8].

3. Results and Discussion

The atomic numbering scheme is shown in Figure 1. Final fractional coordinates and equivalent isotropic thermal parameters are reported in Table I. Bond distances and angles are listed in Tables II and III.

Table I. Final fractional coordinates and equivalent isotropic thermal parameters for non-H atoms

Atom	x	y	z	B_{eq}
O(1)	−0.0283(3)	0.4990(4)	0.0774(5)	5.6(2)
C(25)	−0.0679(4)	0.4275(8)	0.081(1)	7.4(4)
O(29)	0.0125	0.3439(5)	0.1980	6.5(2)
C(1)	−0.0370(5)	0.3457(7)	0.0609(8)	5.7(3)
C(2)	−0.0461(5)	0.3114(8)	−0.0152(8)	5.6(3)
C(3)	−0.0168(5)	0.2337(7)	−0.0369(7)	5.1(3)
C(30)	−0.0277(5)	0.1939(8)	−0.1212(8)	6.4(3)
C(31)	0.0258(7)	0.161(1)	−0.155(1)	13.7(7)
C(32)	−0.0707(8)	0.115(1)	−0.113(1)	12.4(6)
C(33)	−0.054(1)	0.253(1)	−0.191(1)	14.4(7)
C(4)	0.0226(4)	0.1962(7)	0.0240(7)	4.6(3)
C(5)	0.0342(4)	0.2327(7)	0.1031(6)	4.3(3)
O(28)	0.1319(3)	0.3258(4)	0.2733(4)	5.0(2)
C(7)	0.1418(4)	0.2271(6)	0.1616(6)	4.5(3)
C(8)	0.1747(6)	0.1974(7)	0.1027(7)	5.7(3)
C(9)	0.2308(5)	0.2288(8)	0.0945(7)	5.5(3)
C(90)	0.2626(6)	0.193(1)	0.0286(8)	7.5(4)
C(91)	0.2767(7)	0.0962(9)	0.040(1)	10.6(5)
C(92)	0.2298(6)	0.211(1)	−0.0559(8)	9.8(5)
C(93)	0.3260(6)	0.239(1)	0.0258(9)	9.1(5)
C(10)	0.2534(5)	0.2892(7)	0.1524(7)	4.9(3)
C(11)	0.2237(4)	0.3204(6)	0.2135(6)	4.0(2)
O(27)	0.1526(3)	0.4893(4)	0.2974(4)	4.3(2)
C(13)	0.2495(4)	0.4780(6)	0.2579(5)	4.2(2)
C(14)	0.2971(5)	0.5192(7)	0.2303(7)	5.0(3)
C(15)	0.2988(5)	0.6067(8)	0.2124(7)	5.6(3)
C(150)	0.3530(5)	0.6546(9)	0.1871(9)	7.7(4)
C(151)	0.3973(6)	0.589(1)	0.157(2)	13.3(8)
C(152)	0.3800(9)	0.707(2)	0.258(1)	19(1)
C(153)	0.3398(8)	0.703(2)	0.112(1)	21(1)
C(16)	0.2486(5)	0.6560(7)	0.2241(7)	5.2(3)
C(17)	0.1995(4)	0.6178(6)	0.2516(5)	4.1(2)
O(26)	0.0504(3)	0.5537(4)	0.2366(5)	5.6(2)
C(19)	0.0974(4)	0.6878(7)	0.1976(6)	4.3(2)
C(20)	0.0939(5)	0.7599(7)	0.1482(7)	5.3(3)
C(21)	0.0477(5)	0.7784(7)	0.0873(7)	5.5(3)
C(210)	0.0405(7)	0.8613(9)	0.0373(9)	8.1(4)
C(211)	0.002(1)	0.921(1)	0.074(2)	19(1)
C(212)	0.023(1)	0.848(1)	−0.048(1)	19(1)
C(213)	0.0973(8)	0.914(1)	0.048(1)	16.9(9)
C(22)	0.0022(5)	0.7158(7)	0.0793(7)	5.3(3)
C(23)	0.0032(4)	0.6421(7)	0.1266(7)	5.1(3)
C(26)	0.0515(4)	0.6228(7)	0.1866(7)	4.9(3)
C(27)	0.1990(4)	0.5276(6)	0.2688(6)	4.3(3)
C(28)	0.1644(4)	0.2903(6)	0.2173(6)	4.2(3)
C(29)	0.0038(4)	0.3078(8)	0.1204(7)	5.2(3)
C(18)	0.1474(5)	0.6770(6)	0.2692(7)	5.4(3)
C(12)	0.2524(4)	0.3827(6)	0.2810(6)	4.6(3)
C(6)	0.0796(5)	0.1892(7)	0.1688(8)	5.9(3)
C(24)	−0.0478(4)	0.5748(8)	0.1184(9)	6.8(4)

Table I.   *(Continued)*.

| Atom	x	y	z	B_{eq}
N(1)	0.1424(4)	0.5275(5)	−0.0438(5)	5.4(2)
C(50)	0.2009(6)	0.5598(8)	0.0006(8)	7.9(4)
C(51)	0.2495(5)	0.491(1)	−0.0089(9)	9.1(4)
C(52)	0.0976(6)	0.6018(8)	−0.0429(8)	7.6(4)
C(53)	0.0383(5)	0.5768(9)	−0.0883(8)	8.7(4)
C(54)	0.1225(5)	0.4422(9)	−0.0114(8)	7.4(4)
C(55)	0.1180(6)	0.447(1)	0.0731(9)	9.1(5)
N(2)	0.2699(9)	0.024(1)	0.324(1)	15.4(6)
C(56)	0.320(1)	−0.002(3)	0.278(2)	28(2)
C(57)	0.373(1)	−0.033(1)	0.337(2)	19(1)
C(58)	0.286(1)	0.118(2)	0.341(2)	26(2)
C(59)	0.256(1)	0.144(2)	0.414(2)	20(1)
C(60)	0.220(1)	0.007(3)	0.256(2)	37(2)
C(61)	0.167(1)	−0.012(2)	0.298(1)	23(1)
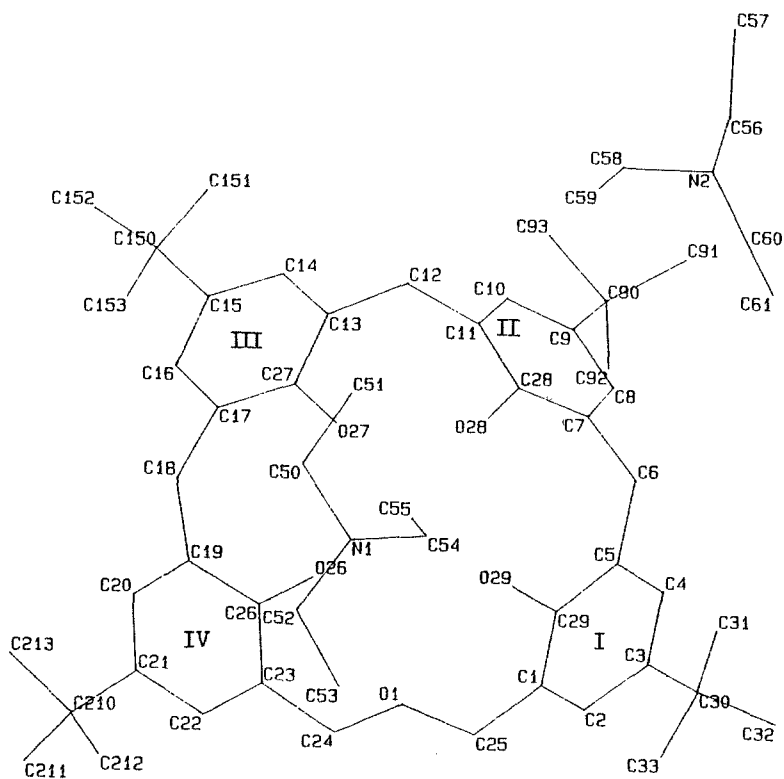
Fig. 1.   Atomic numbering scheme.

Table II. Bond distances (Å) for non-H atoms

Atoms	Distance	Atoms	Distance	Atoms	Distance
O(1)—C(25)	1.42(1)	C(8)—C(9)	1.39(2)	C(16)—C(17)	1.39(1)
O(1)—C(24)	1.44(1)	C(9)—C(90)	1.48(2)	C(17)—C(27)	1.40(1)
C(25)—C(1)	1.49(2)	C(9)—C(10)	1.37(2)	C(17)—C(18)	1.55(1)
O(29)—C(29)	1.37(1)	C(90)—C(91)	1.51(2)	O(26)—C(26)	1.34(1)
C(1)—C(2)	1.34(2)	C(90)—C(92)	1.51(2)	C(19)—C(20)	1.36(1)
C(1)—C(29)	1.38(2)	C(90)—C(93)	1.62(2)	C(19)—C(26)	1.44(1)
C(2)—C(3)	1.43(2)	C(10)—C(11)	1.37(2)	C(19)—C(18)	1.53(1)
C(3)—C(30)	1.50(2)	C(11)—C(28)	1.44(1)	C(20)—C(21)	1.38(1)
C(3)—C(4)	1.38(1)	C(11)—C(12)	1.54(1)	C(21)—C(210)	1.50(2)
C(30)—C(31)	1.49(2)	O(27)—C(27)	1.34(1)	C(21)—C(22)	1.40(2)
C(30)—C(32)	1.57(2)	C(13)—C(14)	1.38(1)	C(210)—C(211)	1.46(3)
C(30)—C(33)	1.52(2)	C(13)—C(27)	1.41(1)	C(210)—C(212)	1.42(2)
C(4)—C(5)	1.40(1)	C(13)—C(12)	1.50(1)	C(210)—C(213)	1.52(2)
C(5)—C(29)	1.39(2)	C(14)—C(15)	1.37(2)	C(22)—C(23)	1.36(2)
C(5)—C(6)	1.54(1)	C(15)—C(150)	1.54(2)	C(23)—C(26)	1.41(1)
O(28)—C(28)	1.36(1)	C(15)—C(16)	1.40(2)	C(23)—C(24)	1.54(1)
C(7)—C(8)	1.37(2)	C(150)—C(151)	1.55(2)	N(1)—C(50)	1.52(1)
C(7)—C(28)	1.38(1)	C(150)—C(152)	1.48(3)	N(1)—C(52)	1.53(1)
C(7)—C(6)	1.55(1)	C(150)—C(153)	1.43(3)	N(1)—C(54)	1.50(2)
C(50)—C(51)	1.55(2)	N(2)—C(56)	1.51(4)	C(56)—C(57)	1.50(4)
C(52)—C(53)	1.51(2)	N(2)—C(58)	1.50(3)	C(58)—C(59)	1.51(5)
C(54)—C(55)	1.40(2)	N(2)—C(60)	1.51(3)	C(60)—C(61)	1.51(4)

Whereas the calixarene molecule in the m-xylene complex (MXCA) has a symmetry plane through O(1) and C(12), the one in the title compound does not exhibit any internal element of symmetry. Nevertheless both conformations are rather similar.

C—OH distances vary from 1.34(1) to 1.37(1) Å (1.381(6) and 1.391(5) in MXCA); C—O distances in the dimethyleneoxo bridge are 1.42(1) and 1.44(1) Å (1.419(5) in MXCA). In the phenolic ring, lengths have expected values except for C(11)—C(28) = 1.44(1) and C(19)—C(26) = 1.44(1) Å.

The angles of the methylene groups around C(6), C(12) and C(18) vary from 108.9(9) to 115.7(9)° (112.7(3) and 113.1(4) in MXCA) and in the dimethyleneoxo bridge they have the following values: C(23)—C(24)—O(1) = 107.5(8)°, C(24)—O(1)—C(25) = 111.3(7)° and C(1)—C(25)—C(1) = 108.3(8)° (108.8(4), 111.6(4) and 108.8(4)° in MXCA).

As in MXCA, the plane C(6)—C(12)—C(18) is chosen as the reference plane (R); the phenolic rings containing C(29), C(28), C(27) and C(26) are called I, II, III and IV, respectively. The inclinations of the rings are 127.9(4)° (ring I), 124.6(3)° (ring II), 139.4(2)° (ring III) and 138.2(4)° (ring IV) (cf. with 136.5(1), 124.2(1) 124.2(1) and 136.5(1)° for the corresponding values in MXCA). This result emphasizes the main conformational difference between the calixarene molecule in the m-xylene and triethylamine complexes: a symmetrical orientation of I and IV and of II and III in MXCA, a stronger inclination for III and IV than for I and II in the title compound. The dissymmetrical localisation of the guest in the host and an assymetrical bonding scheme may be connected with this loss of symmetry.

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Table III. Bond angles (deg) for non-H atoms

Atoms	Angles	Atoms	Angles	Atoms	Angles
C(25)—O(1)—C(24)	111.3(7)	C(8)—C(7)—C(8)	120(1)	C(27)—C(13)—C(12)	119.9(9)
O(1)—C(25)—C(1)	108.3(8)	C(8)—C(7)—C(6)	121.3(9)	C(13)—C(14)—C(15)	124(1)
C(25)—C(1)—C(2)	121(1)	C(28)—C(7)—C(6)	118.5(9)	C(14)—C(15)—C(150)	125(1)
C(25)—C(1)—C(29)	119(1)	C(7)—C(8)—C(9)	123(1)	C(14)—C(15)—C(16)	117(1)
C(2)—C(1)—C(29)	120(1)	C(8)—C(9)—C(90)	119(1)	C(150)—C(15)—C(16)	119(1)
C(1)—C(2)—C(3)	122(1)	C(8)—C(9)—C(10)	116(1)	C(15)—C(150)—C(151)	111(1)
C(2)—C(3)—C(30)	123(1)	C(90)—C(9)—C(10)	125(1)	C(15)—C(150)—C(152)	108(1)
C(2)—C(3)—C(4)	117(1)	C(9)—C(90)—C(91)	113(1)	C(15)—C(150)—C(153)	113(1)
C(30)—C(3)—C(4)	121(1)	C(9)—C(90)—C(92)	111(1)	C(151)—C(150)—C(152)	112(1)
C(3)—C(30)—C(31)	116(1)	C(9)—C(90)—C(93)	112(1)	C(151)—C(150)—C(153)	98(2)
C(3)—C(30)—C(32)	105(1)	C(91)—C(90)—C(92)	111(1)	C(152)—C(150)—C(153)	114(2)
C(3)—C(30)—C(33)	117(1)	C(91)—C(90)—C(93)	105(1)	C(15)—C(16)—C(17)	121.7(9)
C(31)—C(30)—C(32)	109(1)	C(92)—C(90)—C(93)	103(1)	C(16)—C(17)—C(27)	120.3(9)
C(31)—C(30)—C(33)	100(1)	C(9)—C(10)—C(11)	124(1)	C(16)—C(17)—C(18)	119.1(9)
C(32)—C(30)—C(33)	109(1)	C(10)—C(11)—C(28)	118.6(8)	C(27)—C(17)—C(18)	120.5(9)
C(3)—C(4)—C(5)	122(1)	C(10)—C(11)—C(12)	122.4(9)	C(20)—C(19)—C(26)	119.8(9)
C(4)—C(5)—C(29)	118.5(9)	C(28)—C(11)—C(12)	118.9(9)	C(20)—C(19)—C(18)	121.4(9)
C(4)—C(5)—C(6)	120.1(9)	C(14)—C(13)—C(27)	119.2(9)	C(26)—C(19)—C(18)	118.7(9)
C(29)—C(5)—C(6)	121.4(9)	C(14)—C(13)—C(12)	120.8(9)	C(19)—C(20)—C(21)	125(1)
C(20)—C(21)—C(210)	126(1)	O(26)—C(26)—C(23)	121.2(9)	O(1)—C(24)—C(23)	107.5(8)
C(20)—C(21)—C(22)	114(1)	C(19)—C(26)—C(23)	116(1)	C(50)—N(1)—C(52)	107.7(8)
C(210)—C(21)—C(22)	120(1)	O(27)—C(27)—C(13)	120.3(9)	C(50)—N(1)—C(54)	113.6(8)
C(21)—C(210)—C(211)	109(1)	O(27)—C(27)—C(17)	121.5(8)	C(52)—N(1)—C(54)	114.0(9)
C(21)—C(210)—C(212)	114(1)	C(13)—C(27)—C(17)	118.2(9)	N(1)—C(50)—C(51)	109.4(9)
C(21)—C(210)—C(213)	111(1)	O(28)—C(28)—C(7)	122.2(8)	N(1)—C(52)—C(53)	111.5(9)
C(211)—C(210)—C(212)	113(2)	O(28)—C(28)—C(11)	119.8(8)	N(1)—C(54)—C(55)	112(1)
C(211)—C(210)—C(213)	100(1)	C(7)—C(28)—C(11)	117.9(9)	C(56)—N(2)—C(58)	99(2)
C(212)—C(210)—C(213)	108(2)	O(29)—C(29)—C(1)	119(1)	C(56)—N(2)—C(60)	98(2)
C(21)—C(22)—C(23)	123(1)	O(29)—C(29)—C(5)	120.2(9)	C(58)—N(2)—C(60)	117(2)
C(22)—C(23)—C(26)	122(1)	C(1)—C(29)—C(5)	121(1)	N(2)—C(56)—C(57)	111(2)
C(22)—C(23)—C(24)	123(1)	C(17)—C(18)—C(19)	115.7(9)	N(2)—C(58)—C(59)	106(2)
C(26)—C(23)—C(24)	115.7(9)	C(11)—C(12)—C(13)	114.7(8)	N(2)—C(60)—C(61)	106(2)
O(26)—C(26)—C(19)	122.5(8)	C(5)—C(6)—C(7)	108.9(9)		

The four oxygens of the phenolic groups are coplanar ($\chi^2 < 1$); the angle between their mean plane (P) and (R) is 7(1)°.

Oxygen O(1) is inside the cavity of the calixarene, situated at 1.628(7) Å from (P) (1.072(4) Å in MXCA), C(24), O(1) and C(25) lie respectively at 0.63(1), 1.269(7) and 0.75(1) Å from (R) (corresponding values are 1.091(5), 1.341(4) and 1.091(5) Å in MXCA).

The lengths of the O···O contacts in the calixarene molecule are 3.082(7), 2.606(9, 2.560(9)), 2.855(6) and 3.145(8) Å for O(1)···O(26), O(26)···O(27), O(27)···O(28), O(28)···O(29) and O(29)···O(1) (In MXCA those lengths have the following values: 2.779(5), 2.812(5), 2.754(6), 2.812(5) and 2.779(5) Å).

Torsional angles around atoms forming the macrocyclic ring are given in Table IV; in this complex, atoms of the dimethyleneoxo bridge C(23), C(24), O(1), C(25) and C(1) exhibit no coplanarity: their distances from their mean plane vary from 0.63(1) to 1.269(7) Å.

Figure 2 shows the cone conformation of the calixarene molecule: the distances C(30)—C(90), C(90)—C(150), C(150)—C(210) and C(210)—C(30) give information about the space available inside the macrocycle and have the following values: 6.76(2), 7.70(2), 7.89(2) and 10.57(2) Å. Similar values were obtained in MXCA. The distances of the plane (P) from C(30), C(90), C(150) and C(210), which are 4.39(1), 4.94(1), 3.87(1) and 3.31(1) Å respectively, characterize the depth of this cone.

As can be seen in Figure 2, the host–guest connection exhibits a double feature: encapsulation by the macrocycle of one of the triethylamine molecules and binding of the same host molecule with another Et_3N molecule related to the previous one by a $(x, \bar{y} + 1, z + \frac{1}{2})$ symmetry. These Et_3N molecules are situated in calixarene cavities with one of their ethyl groups pointing inside the intramolecular cavities; the distances of C(54) and C(55) from plane (P) are respectively 4.44(1) and 3.09(1) Å. Short distances of C(55) from planes of the four rings (3.52(1) Å for ring I, 3.43(1) Å for ring II, 3.62(1) Å for ring III and 3.55(1) for ring IV) and close contacts of the hydrogens of this —CH_3 group with atoms belonging to the phenolic rings (values from 2.58(2) to 3.04(2) Å) indicates CH_3–π interactions between this ethyl group and the macrocycle. The two other ethyl groups are more distant from (P) (values between 4.85(1) and 5.71(1) Å). The nitrogen atom is situated at 5.227 (8) Å from (P); it is directed *exo* to the calixarene molecule in

Table IV.   Torsional angles (deg)

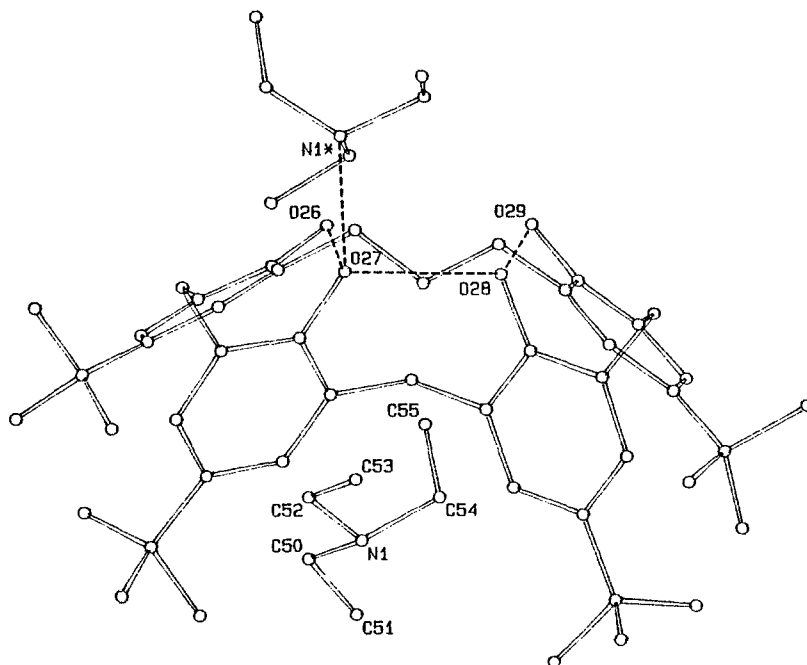| Atoms	Angles	Atoms	Angles
O(1)—C(25)—C(1)—C(29)	77(1)	C(12)—C(13)—C(27)—C(17)	176(1)
C(25)—C(1)—C(29)—C(5)	−178(1)	C(13)—C(27)—C(17)—C(18)	−175(1)
C(1)—C(29)—C(5)—C(6)	−180(1)	C(27)—C(17)—C(18)—C(19)	−91(1)
C(29)—C(5)—C(6)—C(7)	−92(1)	C(17)—C(18)—C(19)—C(26)	85(1)
C(5)—C(6)—C(7)—C(28)	101(1)	C(18)—C(19)—C(26)—C(23)	172(1)
C(6)—C(7)—C(28)—C(11)	176(1)	C(19)—C(26)—C(23)—C(24)	−177(1)
C(7)—C(28)—C(11)—C(12)	−173(1)	C(26)—C(23)—C(24)—O(1)	−74(1)
C(28)—C(11)—C(12)—C(13)	−98(1)	C(23)—C(24)—O(1)—C(25)	169(1)
C(11)—C(12)—C(13)—C(27)	85(1)	C(24)—O(1)—C(25)—C(1)	−163(1)

Fig. 2. Side view of the calixarene with the encapsulated triethylamine molecule and with a symmetry generated one to show plausible H-bonds contacts.

which the guest is encapsulated; it is connected by a hydrogen bond to the phenolic group $O(27)$—H belonging to a calixarene molecule related by symmetry to the previous one. The $O(27)\cdots N(1)$ distance is 2.65(1) Å. A hydrogen bond between a calixarene and a nitrogen of a guest situated *exo* to the calixarene has been found in the *p*-t-butylcalix[7]arene 1 : 3 pyridine complex [9] with a $O\cdots N$ distance of 2.632(8) Å; this complex also exhibits the encapsulation of the guest by the host. Another hydrogen bond between a calixarene, in a chairlike conformation, and a nitrogen of one of its guests has been found in the *p*-t-butylcalix[8]arene pyridine (1 : 8) clathrate [10] with $O\cdots N = 2.708(6)$ Å; in this complex, the conformation of the host does not allow any encapsulation of the guest.

The two Et_3N molecules do not exhibit the same conformation: in the molecule found in the interhost space, the three terminal carbons are all on the same side of the plane $C(56)$, $C(58)$ and $C(60)$; with values of 0.94(3), 0.86(3), and 0.90(3) Å, their distances from this plane are all approximately the same. In the encapsulated molecules, the carbon $C(55)$ pointing inside the cavity of the calixarene and the two other terminal carbons are on opposite sides of the plane $C(50)$, $C(52)$ and $C(54)$; the distance of $C(55)$ to this plane is 1.39(1) Å, the corresponding values for $C(51)$ and $C(53)$ are 0.59(1) and 0.44(1) Å; on the other hand atoms $C(50)$, $C(51)$ and $C(53)$, $C(52)$ are situated in pseudo symmetrical positions on each side of the plane $C(55)$, $C(54)$, $N(1)$.

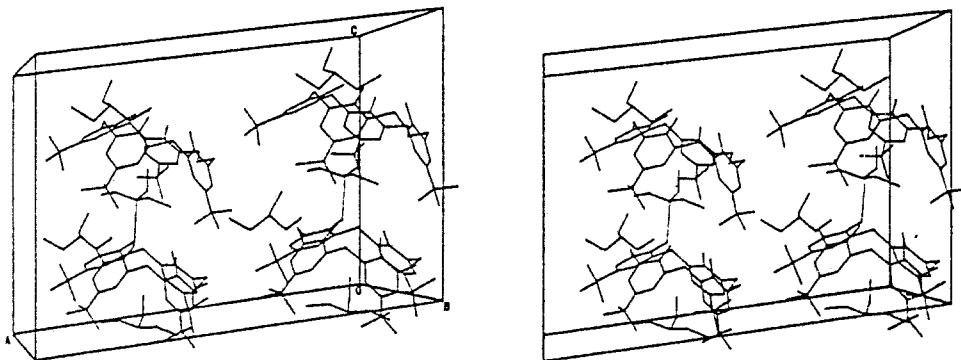Figure 2 shows the interactions between atoms $N(1)$, $O(26)$, $O(27)$, $O(28)$ and $O(29)$. The geometry around $N(1)$ $[C(50)—N(1)\cdots O(27) = 108.5(7)°,$

Fig. 3.   Stereo view of the crystal structure.

C(52)—N(1)···O(27) = 103.0(6°) and C(54)—N(1)···O(27) = 109.4(6)°] indicates that the dipole of the Et_3N molecule is oriented in such a way that its negative charge is facing the phenolic oxygen O(27); the O(27)···N(1) hydrogen bond is made via the lone pair of the nitrogen which is in the tetrahedral sp^3 orbital [11] and N(1) acts as an acceptor to a H bond from O(27); O(27) is a double acceptor from O(26) and O(28); O(28) is also an acceptor from O(29); this plausible logic is consistent with the presence of a single protonated ammine, while the other Et_3N molecule in the interhost space is neutral. On the other hand, the highest residual peak of the final difference electron density map is situated exactly halfway between O(27) and N(1) and it may correspond to the delocalised proton of the O(27)···N(1) bond. Nevertheless, due to the experimental uncertainty in the structure determination, it is not possible to confirm for the title compound, in the solid state, Gutsche's suggestion about proton transfer in solution.

Figure 3 is a stereo view showing the arrangement in the crystal: the stacking of encapsulated guests hydrogen bonded with neighbouring encapsulating hosts leads to columns parallel to the c axis of alternating host and guest molecules; the cavities of calixarenes in all columns have the same orientation. The other triethylamine molecules are in the interhost space between two neighbouring columns. Following the proposal for classification and nomenclature of host-guest type compounds given by Weber and Josel [12] this study allows us to define the title compound as a complex/clathrate hybrid.

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