



## C–H··· $\pi$ Interaction and N···H–O Hydrogen Bonding in the Chair-like *p*-*tert*-Butylcalix[8]arene Complex Including Four Pyridine Molecules\*

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### Abstract

Crystal structure analysis shows that the *p*-*tert*-butylcalix[8]arene host and its four pyridine guests sit around an inversion center in the  $P2_1/c$  crystal lattice. The monoclinic cell parameters and its volume are:  $a = 19.617(4)$ ,  $b = 9.912(2)$ ,  $c = 25.178(5)$  Å,  $\beta = 101.03(3)^\circ$ ,  $V = 4805.27(17)$  Å<sup>3</sup>. For  $Z = 2$  and  $M_w = 1614.18$ , the calculated density  $D_{\text{calc}} = 1.116$  g/cm<sup>3</sup>. A host calixarene molecule includes four pyridine guests in two different ways: by hydrogen bonding and by possible C–H··· $\pi$  interaction between the molecules. The hydrogen bonding drives the host macrocycle into a chair-like conformation.

### Introduction

Calixarenes are known for their ability to include various organic molecules, generally resulting in the distortion of their conformations [1–9]. By introducing different additive species into the solution, a calixarene host can include guest species with different numbers of molecules. For instance, the first single crystal of *p*-*tert*-butylcalix[8]arene with the “cone” conformation was developed in a solution of pyridine [10]. By adding Cu<sup>+</sup> ions into the pyridine solution of *p*-*tert*-butylcalix[8]arene, a 1:8 clathrate was obtained in a “chair-like” conformation [11]. The calixarenes, including other numbers of pyridine molecules, such as 1:2 and 1:3 complexes have also been reported with different host–guest interactions [12, 13]. In this paper, we report an inclusion species of *p*-*tert*-butylcalix[8]arene with four pyridine molecules in which two kinds of interaction, N···H–O hydrogen bonding and C–H··· $\pi$  interaction, are involved. The hydrogen bonding drives the host molecule into the “chair-like” shape, while the C–H··· $\pi$  interaction shrinks the cavity in the host molecule.

### Experimental

#### Synthesis

The title inclusion compound was obtained by selectively including perchlorinated carbon clusters synthesized by

discharge reactions [14]. A mixture of the cluster compounds was added to a saturated pyridine solution of *p*-*tert*-butylcalix[8]arene. The solution was refluxed for 1 h and then cooled to room temperature. After three months, suitable crystals were obtained for X-ray diffraction.

#### Crystal structure analysis

##### Crystal data

*p*-*tert*-Butylcalix[8]arene:4pyridine C<sub>108</sub>H<sub>132</sub>N<sub>4</sub>O<sub>8</sub>,  $M_w = 1614.18$ , monoclinic, space group  $P2_1/c$ ,  $a = 19.617(4)$ ,  $b = 9.912(2)$ ,  $c = 25.178(5)$  Å,  $\beta = 101.03(3)^\circ$ ,  $V = 4805.27(17)$  Å<sup>3</sup>,  $Z = 2$ ,  $D_{\text{calc}} = 1.116$  g/cm<sup>3</sup>,  $F(000) = 1744.0$ .

##### Data collection

A slightly brown crystal of the title species with approximate dimensions of  $0.60 \times 0.60 \times 0.40$  mm was used for diffraction analysis. Preliminary examination and data collection were performed with Mo–K $\alpha$  radiation on the CAD-4 diffractometer equipped with a graphite crystal incident beam monochromator. Cell parameters of the crystal are determined from the least-squares refinement of the setting angles of 25 reflections ( $15 < \theta < 16^\circ$ ). The data were collected with  $2 < 2\theta < 52^\circ$  ( $0 < h < 31$ ,  $0 < k < 12$ ,  $-24 < l < 23$ ) in  $\omega/2\theta$  scan mode at 293 K. The data were corrected for absorption by Psi scan.

##### Structure analysis

The structure of the title inclusion compound was solved by direct methods and refined by full-matrix least-squares on  $F^2$ . 3425 observations with  $I > 2\sigma(I)$ , out of 9409 unique reflections measured ( $R_{\text{int}} = 0.0520$ ) were used in the analysis. 542 parameters have been refined. All non-hydrogen atoms were treated anisotropically. The methyl carbon atoms

\* **Supplementary data:** crystallographic data (atomic coordinates, anisotropic displacement parameters, selected bond distances and angles) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre with CCDC 147778 as supplementary publication.

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Table 1. Atomic coordinates ( $\times 10^4$ ) and equivalent isotropic displacement parameters  $U(\text{eq})$  ( $\text{\AA}^2 \times 10^3$ )

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> (eq)		<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> (eq)
O(1)	1214(2)	5074(3)	4084(2)	55(1)	C(27)	-2315(3)	2316(5)	5663(2)	44(1)
O(2)	-12(2)	3909(4)	4192(2)	57(1)	C(28)	-2121(3)	3771(5)	6508(2)	47(1)
O(3)	-1395(2)	2391(4)	4561(2)	59(1)	C(29)	2965(4)	1540(7)	3172(3)	80(2)
O(4)	-1615(2)	2311(4)	5649(2)	59(1)	C(30)	2861(7)	122(9)	3261(6)	207(7)
C(1)	1636(2)	4176(5)	3874(2)	45(1)	C(31)	2890(9)	1792(12)	2591(5)	253(10)
C(2)	2089(2)	4726(5)	3574(2)	44(1)	C(32)	3710(5)	1820(17)	3428(8)	281(11)
C(3)	2519(3)	3855(5)	3357(2)	52(1)	C(33)	-295(3)	-837(6)	2879(2)	62(2)
C(4)	2509(3)	2469(6)	3427(2)	56(2)	C(34)	231(7)	-1847(10)	3084(5)	236(9)
C(5)	2061(3)	1975(5)	3746(2)	51(1)	C(35)	-214(8)	-439(10)	2337(4)	198(7)
C(6)	1617(2)	2805(5)	3969(2)	45(1)	C(36)	-993(6)	-1529(11)	2803(5)	184(6)
C(7)	1117(2)	2185(5)	4284(2)	49(1)	C(37)	-3857(3)	1522(8)	3004(3)	71(2)
C(8)	428(2)	1862(5)	3930(2)	43(1)	C(38)	-4330(7)	560(20)	3156(6)	313(13)
C(9)	355(3)	716(5)	3613(2)	47(1)	C(39)	-3738(6)	1120(30)	2488(5)	335(16)
C(10)	-250(3)	400(5)	3256(2)	49(1)	C(40)	-4199(8)	2752(14)	2896(10)	384(19)
C(11)	-807(3)	1268(5)	3242(2)	53(1)	C(41)	-4539(3)	2522(6)	5553(3)	64(2)
C(12)	-765(2)	2444(5)	3561(2)	44(1)	C(42)	-4747(4)	3736(10)	5848(4)	138(4)
C(13)	-141(2)	2734(5)	3889(2)	39(1)	C(43)	-4809(4)	1257(10)	5773(5)	160(5)
C(14)	-1405(3)	3322(5)	3519(2)	53(1)	C(44)	-4868(4)	2723(11)	4960(3)	126(3)
C(15)	-2018(2)	2586(5)	3665(2)	45(1)	C(45)	1346(3)	3182(7)	5805(3)	81(2)
C(16)	-2623(3)	2377(6)	3294(2)	52(1)	C(46)	1422(4)	1801(8)	5785(3)	81(2)
C(17)	-3187(3)	1677(6)	3414(2)	52(1)	C(47)	857(4)	1035(7)	5601(3)	72(2)
C(18)	-3111(3)	1137(5)	3928(2)	51(1)	C(48)	233(3)	1654(6)	5426(3)	71(2)
C(19)	-2519(3)	1333(5)	4321(2)	46(1)	C(49)	197(3)	3034(7)	5449(3)	68(2)
C(20)	-1985(2)	2105(5)	4189(2)	48(1)	C(50)	3281(5)	4378(14)	6063(6)	127(4)
C(21)	-2467(3)	680(5)	4870(2)	52(1)	C(51)	3175(6)	5105(11)	5651(8)	141(5)
C(22)	-2757(3)	1553(5)	5276(2)	46(1)	C(52)	3084(5)	4578(19)	5158(6)	142(6)
C(23)	-3460(3)	1615(5)	5256(2)	53(1)	C(53)	3149(5)	3119(18)	5146(5)	128(4)
C(24)	-3757(3)	2416(5)	5610(2)	51(1)	C(54)	3254(4)	2420(7)	5562(5)	86(2)
C(25)	-3300(3)	3073(5)	6007(2)	50(1)	N(1)	740(3)	3805(5)	5648(2)	69(1)
C(26)	-2582(3)	3031(5)	6051(2)	43(1)	N(2)	3317(4)	3003(13)	6014(5)	148(3)

of *tert*-butyl group are disordered. All hydrogen atoms were positioned at their calculated positions and were assigned common isotropic temperature factors. The final residuals were  $R_1 = 0.0917$  and  $wR_2 = 0.3125$  for 3425 reflections with  $I > 2\sigma(I)$ , goodness of fit  $S = 0.993$ , and the maximum residual density  $0.65 \text{ e}\text{\AA}^{-3}$ . All calculations have been performed on a personal computer with the SHELX program package [15]. The structure of the title inclusion compound is displayed in Figures 1 and 2, the selected geometric parameters are given in Table 2, and the hydrogen bonding data in Table 3.

## Results and discussion

As shown in Figure 1, the host molecule, *p*-*tert*-butylcalix[8]arene, can be described as two partial "cones" like a half-basket made up of three phenyl rings linked by the methylene group, which are combined by two other phenyl groups. Thus, the molecule has an inversion symmetry and an open conformation like a "chair". The conformation was postulated to exist in solution and has not been found in the solid state as a pure *p*-*tert*-butylcalix[8]arene host [10].

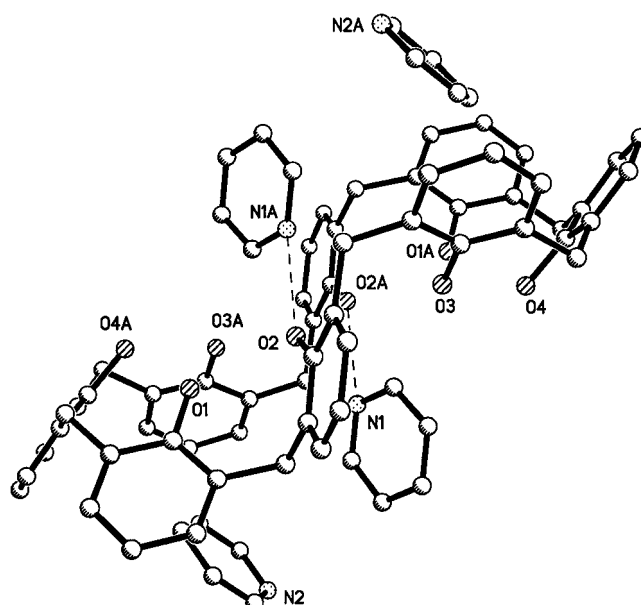


Figure 1. The side-view of the chair-like conformation of the inclusion compound. The hydrogen bonds between the nitrogen atom of the pyridine molecule and phenolic oxygen atom of the host molecule are shown by dash lines. All hydrogen atoms and *tert*-butyl groups are omitted for clarity.

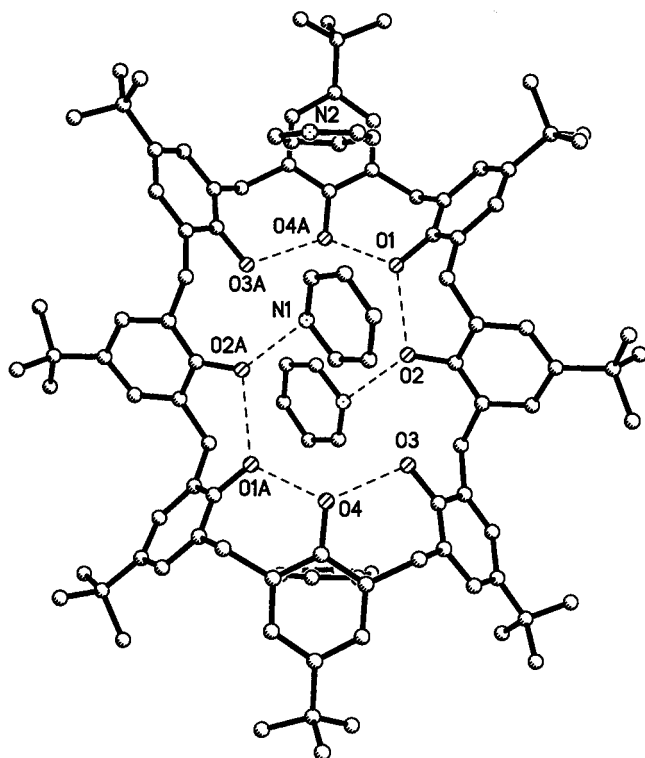


Figure 2. Perspective view of the inclusion compound. The hydrogen bonds between pyridine and phenolic oxygen and the intramolecular hydrogen bonds of interphenolic hydroxyl groups are shown by dash lines.

In the inclusion compound, four pyridine molecules are included in two different ways: two are bonded by hydrogen bonding between the nitrogen atom of a pyridine molecule and a phenolic oxygen atom of the host molecule ( $O \cdots N$  distance  $2.7477(60)\text{\AA}$ , see Figure 2). The other two pyridine molecules sit flatly inside the half-basket. These two pyridine molecules are oriented in such a way that the nitrogen atom is well away from the surrounding phenyl arms. The centroids of the three phenyl rings are apart from the hydrogen atoms of pyridine (H51A, H52A and H53A) with distances of 2.77, 2.80, and  $3.54\text{\AA}$ , respectively. Hence, the pyridine molecules are most probably included by the  $C-H \cdots \pi$  interaction between the pyridine edge and arene face.

The calixarenes, especially calix[8]arenes, are known to have rather flexible structures and their "calix" conformation is maintained by the ring of  $O \cdots O$  hydrogen bonds between the adjacent phenolic  $-OH$  groups. In the title inclusion compound, the cyclic hydrogen-bonding array in the "calix" conformation is disrupted by one hydrogen bond from the included pyridine molecule in the asymmetric unit (cf. Table 3). The interaction drives the conformation from a regular "calix" to a "chair-like" one. In fact, a similar conformation was also observed in the *p*-tert-butylcalix[8]arene: pyridine (1 : 8) inclusion species [11]. It is shown in the structure of the inclusion species that two of the pyridine molecules are also linked to the host through hydrogen bonds [11].

In the 1 : 8 species, however, the other two pyridine molecules simply fill the interstitial voids of the lattice maintained by the calix[8]arene host matrix, while in the 1 : 4

Table 2. Selected bond lengths [ $\text{\AA}$ ] and angles [deg.]

O(1)–C(1)	1.387(6)	C(21)–C(22)	1.528(7)
O(2)–C(13)	1.389(6)	C(22)–C(23)	1.373(7)
O(3)–C(20)	1.373(6)	C(22)–C(27)	1.396(7)
O(4)–C(27)	1.382(6)	C(23)–C(24)	1.400(7)
C(1)–C(6)	1.381(7)	C(24)–C(25)	1.373(7)
C(1)–C(2)	1.384(7)	C(24)–C(41)	1.517(7)
C(2)–C(3)	1.389(7)	C(25)–C(26)	1.391(7)
C(2)–C(28)#1	1.507(7)	C(26)–C(27)	1.388(7)
C(3)–C(4)	1.386(7)	C(26)–C(28)	1.512(7)
C(4)–C(5)	1.387(7)	C(45)–N(1)	1.332(8)
C(4)–C(29)	1.510(8)	C(45)–C(46)	1.378(9)
C(5)–C(6)	1.391(7)	C(46)–C(47)	1.351(9)
C(6)–C(7)	1.507(7)	C(47)–C(48)	1.364(8)
C(7)–C(8)	1.503(7)	C(48)–C(49)	1.372(8)
C(8)–C(9)	1.381(7)	C(49)–N(1)	1.329(7)
C(8)–C(13)	1.400(6)	C(50)–C(51)	1.247(15)
C(9)–C(10)	1.381(7)	C(50)–N(2)	1.372(14)
C(10)–C(11)	1.386(7)	C(51)–C(52)	1.326(16)
C(10)–C(33)	1.543(7)	C(52)–C(53)	1.453(16)
C(11)–C(12)	1.408(7)	C(53)–C(54)	1.240(14)
C(12)–C(13)	1.371(7)	C(54)–N(2)	1.262(12)
C(12)–C(14)	1.514(7)	C(6)–C(1)–C(2)	121.5(5)
C(14)–C(15)	1.511(7)	C(6)–C(1)–O(1)	121.9(5)
C(15)–C(16)	1.378(7)	C(2)–C(1)–O(1)	116.6(5)
C(15)–C(20)	1.394(7)	C(8)–C(7)–C(6)	112.1(4)
C(16)–C(17)	1.388(7)	C(15)–C(14)–C(12)	113.2(4)
C(17)–C(18)	1.382(7)	C(19)–C(21)–C(22)	113.6(4)
C(17)–C(37)	1.516(8)	C(2)#1–C(28)–C(26)	114.1(4)
C(18)–C(19)	1.387(7)	C(49)–N(1)–C(45)	116.8(6)
C(19)–C(20)	1.388(7)	C(54)–N(2)–C(50)	122.5(11)
C(19)–C(21)	1.512(7)		

Table 3. Hydrogen bonds [ $\text{\AA}$  and deg.]

D–H $\cdots$ A	d(D–H)	d(H $\cdots$ A)	d(D $\cdots$ A)	<(DHA)
O1–H1A $\cdots$ O2	0.82	1.91	2.7293(49)	176.9
O2–H2A $\cdots$ N1A	0.82	2.05	2.7477(60)	141.8
O4A–H4AA $\cdots$ O1	0.82	1.94	2.7542(51)	172.9
O3–H3B $\cdots$ O4	0.82	2.03	2.8554(53)	175.4

species, the other two guest pyridine molecules are included by the phenyl arms of the host. As the result of the interactions, comparing with the structure of the 1 : 8 species, the void in the partial cone substructure in the 1 : 4 species is slightly shrunk. Another indication of the interactions is the unusual stability of the crystals: in the 1 : 4 species, the included pyridine did not evaporate at room temperature, but the crystals of the 1 : 8 species quickly decomposed into a white powder [11]. The difference is also shown in the different densities of their crystals, where the density of the title 1 : 4 species is higher than that of the 1 : 8 species ( $1.04\text{ g/cm}^3$ ) [11].

The structure of the title inclusion compound demonstrates the variety of possible interactions between pyridine and calixarenes, both of which are polar molecules, able to form either acceptor or donor hydrogen bonds and possessing  $\pi$ -electron systems. Different from the other calixarene/pyridine associates, such as the 1:8 inclusion compound [11], all pyridine molecules in the title species are included in two different ways. Production of the unusual structure must relate to the involvement of the perchlorinated carbon clusters, though they were not included into the complex, because evaporation of a pyridine solution of *p-tert*-butylcalix[8]arene produced the crystal of the pure calixarene compound [10]. As a matter of fact, the 1:8 complex crystal was developed from a solution of *p-tert*-butylcalix[8]arene and  $\text{CuClC}_5\text{H}_5\text{N}$ . Further studies are required to understand the formation of the supermolecular complex.

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