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The Structure of the Pyridine Complex of *p*-tetrakis(phenylazo)-tetra-hydroxythiacalix[4]arene *

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Abstract

p-Tetrakis(phenylazo)-tetra-hydroxythiacalix[4]arene shows complexing properties with neutral molecules. A complex with pyridine was crystallized and the crystal structure determined. The crystals are monoclinic, space group C2/c, $a = 49.953(10)$, $b = 21.566(4)$, $c = 23.448(5)$ Å, $\beta = 105.12(3)°$, V = 24386(8) Å^3, Z = 16. Two macrocycles are positioned in such a way that they form a cavity where two pyridine molecules are encapsulated giving a 2:2 endocomplex. 5.5 other pyridine molecules are trapped between the macrocycles, two of them giving H-bonds with the calixarenes.

Introduction

The synthesis of *p*-tetrakis(phenylazo)-tetra-hydroxythiacalix[4]arene and *p*-tetrakis(4-nitrophenylazo)-tetra-hydroxythiacalix[4]arene were realised in order to prepare species for non-linear optical applications [1]. This family of molecules has recently shown some interest for applications in optical power limiting devices [1] which are used for protection of electro-optical sensors to prevent damage due to laser radiation [2–4]. Although single crystals were easily obtained for *p*-tetrakis(4-nitrophenylazo)-tetra-hydroxythiacalix[4]arene and thus structural investigations performed, crystals of *p*-tetrakis(phenylazo)-tetra-hydroxythiacalix[4]arene were difficult to grow. In fact they were obtained by very slow evaporation of the solvent (pyridine) over several weeks. The solid-state structure of this species is depicted in this article. It has shown very interesting features from a crystallographic point of view.

Experimental

Data collection and structure refinement

The synthesis of *p*-tetrakis(phenylazo)-tetra-hydroxythiacalix[4]arene was performed following the procedure previously mentioned [1]. It was recrystallized from a pyridine/methanol solution.

A single crystal, in a plate form, protected by a thin film of oil was mounted on a glass fiber and cooled at 123 K in a stream of nitrogen. The data collection was performed on a Nonius Kappa CCD diffractometer. The detector was positioned 50 mm from the crystal; 153 frames were obtained by φ scans with 1° steps during 150 s. 19678 reflections were collected and 10369 used after merging.

The structure was solved by direct methods using the SHELXS97 [5] program. The refinement was performed using full-matrix least squares by SHELXL97 [6]. The structure consists of two macrocycles and 7.5 solvent molecules. All non-H atoms were refined anisotropically. For all H atoms, a riding model was used with B fixed at 1.2 Ueq of the bonded non H atom. One phenylazo group is disordered with occupancies of 0.56 and 0.44. The final R value was 0.074. The cell constants and details about data collection and refinement are given in Table 1.

Results and discussion

The numbering scheme of the calixarene is given in Figure 1; the solvent molecules are numbered NX00 → C X05 (X = 1 → 8). The structure consists of two macrocycles (one is noted A and N110 ...N160 ..., the other B and N210 ...N260 ...). Coordinates as well as bond lengths and angles are given as Supplementary data. The two calixarenes are positioned in such a way that they form a cage to encapsulate solvent molecules. The conformation of the calixarenes is "cone"; as usual we give the angles between the aryl groups and the mean plane of the sul-

* Supplementary Data relating to this article are deposited at the Cambridge Crystallographic Data Center, CCDC no. 179403.

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Table 1. Crystal data and structure refinement for the title compound

Empirical formula:	$C_{48}H_{32}N_8O_4S_4 - 3.75\ C_5H_5N$
Formula weight:	1209.68
Temperature:	173 K
Wavelength:	0.71073 Å
Crystal system, space group:	Monoclinic, C2/c
Unit cell dimensions:	$a = 49.953(10)$ Å
	$b = 21.566(4)$ Å
	$c = 23.448(5)$ Å
	$\beta = 105.12(3)°$
Volume:	24386(8) Å^3
Z, Calculated density:	16, 1.318 Mg/m3
Absorption coefficient:	0.216 mm^{-1}
F(000):	10072
Crystal size:	1.5 × 0.25 × 0.05 mm
Theta range for data collection:	1.03 to 19.40 deg
Limiting indices:	$-46 \le h \le 46, -19 \le k \le 20, -21 \le l \le 21$
Reflections collected / unique:	19667/10369 [R(int) = 0.0861]
Completeness to theta = 19.40:	99.5%
Absorption correction:	None
Max and min transmission:	0.9893 and 0.7379
Refinement method:	Full-matrix least-squares on F^2
Data/restraints/parameters:	10369/256/1538
Goodness of fit on F^2:	1.063
Final R indices [I > 2 sigma (I)]:	R1 = 0.0740, wR2 = 0.1939
R indices (all data):	R1 = 0.1495, wR2 = 0.2317
Largest diff. peak and hole:	1.093 and −0.538 e. Å^{-3}

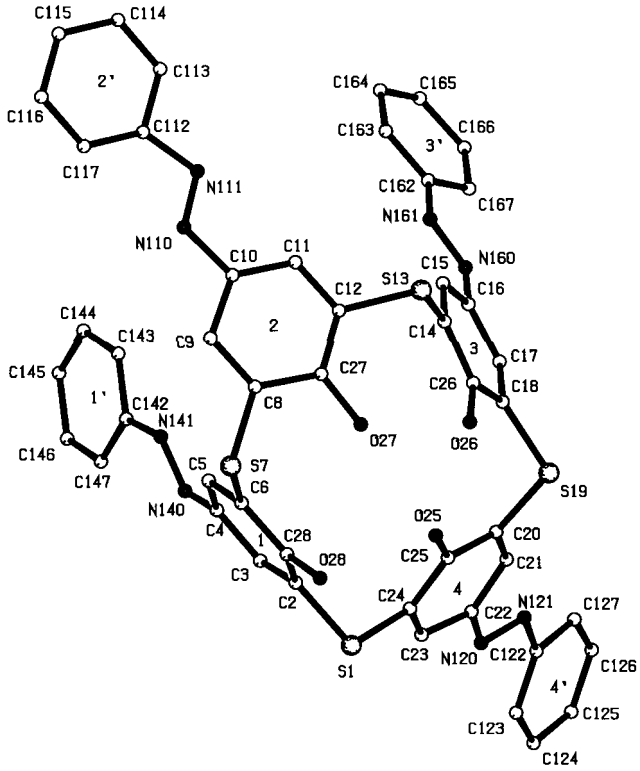

Figure 1. The numbering scheme of the calixarene macrocycle.

fur bridges: 91.2(3), 148.6(2), 120.5(4) and 149.1(2)° for molecule A, 90.8(2), 143.5(2), 120.5(2) and 150.4(3)° for molecule B. The mean value for the regular cone of *p*-tert-butylcalix[4]arene [7] is 123°. So it is seen that for each calixarene A and B two aryl groups are pushed out of the cavity (angles > 140°) while one another is tilted inside the cavity (angle near 90°).

In each calixarene the dihedral angles between the phenolic ring and the plane of the phenyl groups have been calculated. The values for the four moieties of A are 12.3(5) and 14.6(7) (disordered rings), 17.7(6), 19.0(5) and 40.9(3)°. For B the values are 4.3(6), 26.7 (4), 18.9(5) and 41.8(3)°. The moieties are near coplanarity except one in each calixarene 1A, 1A′ et 1B, 1B′ with angles near 40°; these moieties are the two tilted inside the cavity. The values for 3A, 3A′ and 3B, 3B′ (17.7 and 26.7°) lead to a difference between the conformation of the two macrocycles A et B. The two macrocycles are in such a way that two aryl groups of one of them are inside the cavity of the second giving a cage. The four azophenyl groups: 1A′, 3A′, 1B′ and 3B′ limit the volume of the cavity. The centroids of these four rings are the corners of a quadrilateral of which the lengths of the sides have values between 5.6 and 7.8 Å. However, two pyridines are encapsulated inside the cavity. The pyridine N100 → C105 has the shortest interactions with 1B, 3B and 1B′: distances between the centroids are 4.52, 3.83 and 4.93 Å. The second guest N200 → C205 has interactions of 4.57, 3.81 and 5.01 Å with 1A, 3A and 1A′. Figure 2 shows the 2:2 endocomplex between the two calixarenes and the two solvent molecules [8]. The N100–N200 distance between the two pyridine is particularly short: 2.623 Å. This fact has no explanation at present time; in the future, perhaps some other examples could permit an explanation.

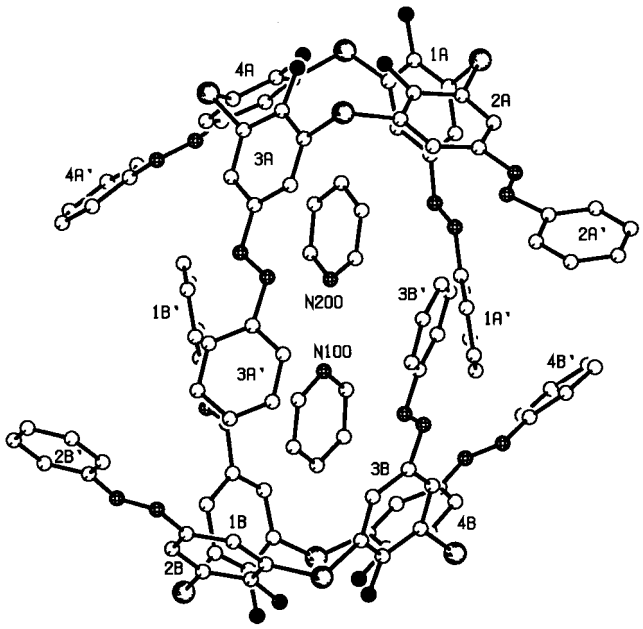

Figure 2. The 2:2 calixarene – pyridine endo-complex.

Table 2. Hydrogen bonds (Å)

	D–H	H . . . A	D . . . A	D–H . . . A
O25A–H25A . . . O26A	0.84	1.87 (9)	2.611(8)	146
O27A–H27A . . . O26A	0.84	1.74 (9)	2.492(9)	147
O25B–H25B . . . O26B	0.84	1.81 (9)	2.575(8)	150
O26B–H26B . . . O27B	0.84	1.99 (9)	2.553(9)	122
O28A–H28A . . . N400*	0.84	2.01 (9)	2.717(7)	142
O28B–H28B . . . N300**	0.84	2.03 (9)	2.746(6)	143

*X, 1 − Y, Z + 0.5; **X, 1 − Y, Z − 0.5.

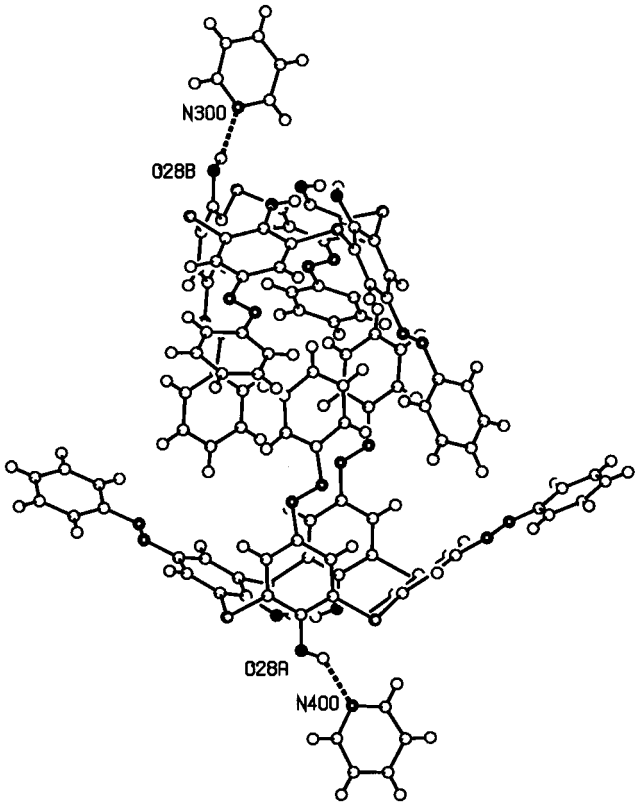

Figure 3. The two hydrogen – bonded pyridine N300 → C305 and N400 → C405.

Several other solvent molecules are trapped between the cages. Two of them are well refined with reasonable values of B factors: N300 → C305 and N400 → C405. In fact these two pyridines are bonded to the macrocycles by H-bonds: O28A . . . N400: 2.717 Å and O28B . . . N300: 2.746 Å as shown in Figure 3. These two H-bonds interrupt the cyclic array of H-bonds usually found in calixarenes in the cone conformation. However, we note strong H-bonds in the macrocycles listed in Table 2. Two other pyridine molecules, N600 → C605 and N700 → C705, are relatively well defined. They show interactions with the oxygen and sulfur atoms of both calixarenes A and B. O26B interacts

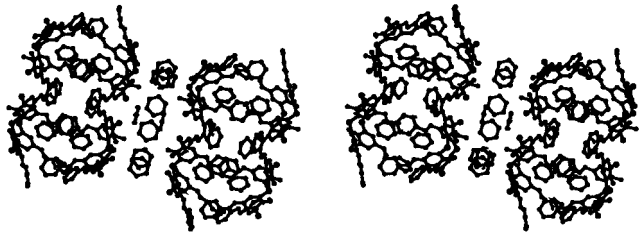

Figure 4. A part of the packing of the title compound: four 2:2 endo complexes and the different exo pyridine molecules.

with some carbon atoms of N600 → C605 and O26A with the same solvent molecule translated by $\vec{c}$ (distances are near 3.1 Å). Concerning the pyridine N700 → C705, it interacts with S1A and O28A and with S1B and O28B translated by $\vec{c}$ (distances are near 3.3 Å). At least two other solvent molecules (N500 → C505 and N800 → C805) lie in the network without strong interactions; the latter with an occupation factor of 0.5 lies very near a center of symmetry and was refined isotropically.

The packing is a little complicated due to the space groupe C2/c. However, it is seen that four cages are positioned around parallel solvent molecules as seen in Figure 3.

In conclusion this *p*-tetrakis(phenylazo)-tetra-hydroxy-thiacalix[4]arene complex can be defined as an intercalato-clathrate hybrid complex [8].

References

1. C. Desroches, S. Parola, F. Vocanson, N. Ehlinger, P. Miele, R. Lamartine, J. Bouix, A. Eriksson, M. Lindgren, and C. Lopes: *J. Mater. Chem.* **11**, 3014 (2001).
2. C.W. Spangler: *J. Mater. Chem.* **9**, 2013 (1999).
3. A.A. Said, C. Warmsley, D.J. Hagan, E.W. Van Stryland, B.A. Reinhardt, P. Roderer, and A.G. Dillard: *Chem. Phys. Lett.* **228**, 646 (1994).
4. J.D. Bhawalkar, G.S. He, and P.N. Prasad: *Rep. Prog. Phys.* **59**, 1041 (1996).
5. G.M. Sheldrick: SHELX97, *Program for Crystal Structure Solution*, University of Göttingen, Germany (1997).
6. G.M. Sheldrick: SHELX97, *Program for Crystal Structure Refinement*, University of Göttingen, Germany (1997).
7. C.D. Andreetti, R. Ungaro, and A. Pochini: *J. Chem. Soc., Chem. Commun.*, 1005, (1979).
8. E. Weber and H.P. Josel: *J. Incl. Phenom.* **1**, 79 (1983).