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Structure of *p*-Tetrakis-(4-nitrophenylazo)calix[4]-arene-4-Picoline (1 : 4) Complex

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Abstract. The structure of the *p*-tetrakis-(4-nitrophenylazo)calix[4]arene-4-picoline (1 : 4) complex has been determined by X-ray crystallography. Crystals are monoclinic, space group $C2/c$, a = 24.9097) Å, b = 8.425(6) Å, c = 33.81(1) Å, β = 101.13(2)°, D_c = 1.330 g/cm^3, Z = 4, final R value = 0.067. The cone conformation adopted by this azocalixarene is disturbed by the positions of the picoline molecules. Two of them are inside the macorocycle cavity and the two others are outside.

Key words: Calixarene-dye, crystal structure, inclusion compound.

Supplementary Data relating to this article are deposited with the British Library as Supplementary Publication No. Sup. 82190 (32 pages).

1. Introduction

We recently published the first crystal structure of an azocalixarene: the *p*-tetrakis-(phenylazo)calix[4] arene-N,N-dimethylformamide 1 : 1 complex [1], crystals of which had a specific mass of 1.290 g/cm^3. We explained this high density by the interpenetration of the macrocycles. The DMF molecules and the host are linked both by hydrogen bonds and $CH_3 \cdots \Pi$ interactions. The theoretical planarity of two phenyl/azophenyl groups was disturbed by these interactions.

To extend our understanding of azocalixarenes in the solid state, we describe here the structure of *p*-tetrakis-(4-nitrophenylazo)calix[4]arene with picoline as guest. The aim is to study the influence of a hydrophobic substituent upon the planarity of the moieties and upon the interpenetration of the macrocycles.

2. Experimental

2.1. SYNTHESIS

p-Tetrakis-(4-nitrophenylazo)calix[4]arene was prepared by the method used by Shinkai *et al.* [2]: 0.5 g of calix[4]arene (1.18 mmol) and 1.42 g of *p*-nitrobenzene-diazonium tetrafluoroborate (6 mmol) were dissolved in 20 mL of tetrahydrofuran at a temperature of about 0 °C. A diazo coupling reaction was initiated by the addition of 1 mL of pyridine to give an orange precipitate with a red mother liquor.

TABLE I. Crystal data.

Molecular formula:	$C_{52}H_{36}N_{12}O_{12}$; $C_{24}H_{28}N_4$		
Molecular weight	1020.932; 372.516		
Crystal system:	monoclinic		
Space group	Cc or $C2/c$ (the last confirmed by the analysis)		
$a = 24.909(7)$ Å	$b = 8.425(6)$ Å	$c = 33.81(1)$ Å	$\beta = 101.13(2)°$
Volume:	6961(5) Å^3		
$Z = 4$			
$D = 1.330$ g/cm^3			
$F(000) = 2912$			
CuK_α radiation:	$\lambda = 1.54056$ Å, $\mu = 7.25$ cm^{-1}		

The solution was filtered and the precipitate was washed successively with tetrahydrofuran and methanol to give p-tetrakis-(4-nitrophenylazo)calix[4]arene with a yield of 62%. This product was identified by IR, NMR and mass spectroscopy.

2.2. CRYSTALLIZATION

The final product is insoluble in most common organic solvents with the exception of pyridine, N,N-dimethylformamide and dimethylsulfoxide. Crystallization of the azocalix[4]arene from these solvents by slow evaporation of saturated solutions gave crystals which were too small for X-ray work. Suitable red needles were obtained by using a methylpyridine, 4-picoline, as solvent.

2.3. X-RAY STRUCTURE ANALYSIS

2.3.1. *Crystal Data*

A crystal of dimensions 0.12 × 0.12 × 0.40 mm was sealed with mother liquor in a glass Lindemann capillary. Cell parameters were determined by least-squares from 25 reflections ($11 < \theta < 44°$) measured on an Enraf-Nonius CAD-4 diffractometer. The crystal data are given in Table I. Intensity data were measured using the (ω-2θ) scan technique with monochromated CuK_α radiation. Three standard reflections were measured every hour to control intensity variation. A total of 8966 reflections were measured. All the unique data measured (5373) were used in the refinement.

The intensities were corrected for Lorentz and polarization effects and for absorption with the programs PSI and EAC of SDP[3] ($T_{\min} = 0.856$, $T_{\max} = 0.999$). Due to the number of symmetry positions in the cell of the monoclinic $C2/c$ space group, the asymmetric unit is represented by only a half molecule.

TABLE II. Positional parameters and their estimated standard deviations.

Atom	x	y	z	B (Å^2)
C(1)	0.1323(2)	0.2653(7)	0.7232(1)	4.6(1)
C(2)	0.0908(2)	0.3187(5)	0.6871(1)	4.2(1)
C(3)	0.1071(2)	0.4144(6)	0.6573(1)	4.8(1)
C(4)	0.0678(2)	0.4603(6)	0.6235(2)	5.0(1)
C(5)	0.0133(2)	0.4180(6)	0.6197(1)	4.7(1)
C(6)	−0.0032(2)	0.3249(6)	0.6493(1)	4.2(1)
C(7)	0.0354(2)	0.2733(5)	0.6825(1)	4.0(1)
O(7)	0.0212(1)	0.1776(3)	0.70989(8)	4.65(9)
N(40)	0.0940(2)	0.5529(5)	0.5948(1)	6.2(1)
N(41)	0.0618(2)	0.5781(5)	0.5645(1)	6.6(1)
C(40)	0.0891(3)	0.6711(7)	0.5363(2)	5.8(2)
C(41)	0.1426(3)	0.7147(8)	0.5464(2)	6.7(2)
C(42)	0.1671(3)	0.8024(8)	0.5178(2)	6.7(2)
C(43)	0.1330(3)	0.8372(6)	0.4823(2)	5.5(2)
C(44)	0.0786(3)	0.7930(6)	0.4726(2)	6.3(2)
C(45)	0.0570(3)	0.7073(7)	0.5004(2)	7.0(2)
M(43)	0.1557(3)	0.9246(6)	0.4516(1)	6.6(2)
O(43)	0.1245(2)	0.9756(5)	0.4224(1)	8.8(2)
O(44)	0.2054(2)	0.9385(6)	0.4559(1)	10.3(2)
C(8)	−0.0621(2)	0.2796(7)	0.6451(2)	4.8(1)
C(9)	−0.0924(2)	0.3514(6)	0.6752(1)	4.3(1)
C(10)	−0.1150(2)	0.5018(6)	0.6665(1)	4.5(1)
C(11)	−0.1428(2)	0.5775(6)	0.6935(1)	4.4(1)
C(12)	−0.1474(2)	0.5009(6)	0.7294(1)	4.3(1)
C(13)	−0.1262(2)	0.3497(6)	0.7382(1)	4.2(1)
C(14)	−0.0991(2)	0.2772(6)	0.7104(1)	4.4(1)
O(14)	−0.0789(2)	0.1302(4)	0.71847(9)	6.9(1)
N(110)	−0.1640(2)	0.7305(5)	0.6805(1)	4.8(1)
N(111)	−0.1887(2)	0.7999(5)	0.7042(1)	4.9(1)
C(110)	−0.2089(2)	0.9541(6)	0.6886(1)	4.5(1)
C(111)	−0.2041(3)	1.0089(7)	0.6509(2)	6.1(2)
C(112)	−0.2236(3)	1.1591(8)	0.6391(2)	6.4(2)
C(113)	−0.2474(2)	1.2467(6)	0.6646(1)	4.6(1)
C(114)	−0.2535(2)	1.1946(6)	0.7019(2)	4.9(1)
C(115)	−0.2335(2)	1.0447(6)	0.7139(1)	4.8(1)
N(113)	−0.2671(2)	1.4105(6)	0.6521(2)	6.2(2)
O(113)	−0.2842(2)	1.4912(4)	0.6769(1)	7.7(1)
O(114)	−0.2644(2)	1.4504(5)	0.6182(1)	9.3(2)
N(200)	0.1080(3)	0.3744(7)	0.4364(2)	8.9(2)
C(201)	0.1603(4)	0.4073(9)	0.4491(3)	9.5(3)
C(202)	0.1847(4)	0.371(1)	0.4481(3)	8.9(3)
C(203)	0.1581(3)	0.3028(7)	0.5156(2)	7.0(2)

TABLE II. Continued.

Atom	x	y	z	B (Å^2)
C(204)	0.1857(4)	0.271(1)	0.5579(2)	10.2(3)
C(205)	0.1048(3)	0.2678(8)	0.5018(2)	8.3(2)
C(206)	0.0812(4)	0.3062(9)	0.4631(2)	8.7(3)
N(300)	0.0176(5)	0.783(1)	0.7089(4)	14.0(4)
C(301)	0.0684(6)	0.804(1)	0.7102(4)	13.8(5)
C(302)	0.0856(4)	0.864(1)	0.6781(5)	10.1(4)
C(303)	0.0485(6)	0.9025(9)	0.6409(4)	10.1(4)
C(304)	0.0638(5)	0.979(1)	0.6038(3)	14.3(5)
C(305)	−0.0043(5)	0.868(1)	0.6422(5)	11.5(5)
C(306)	−0.178(7)	0.804(2)	0.6748(7)	16.4(9)

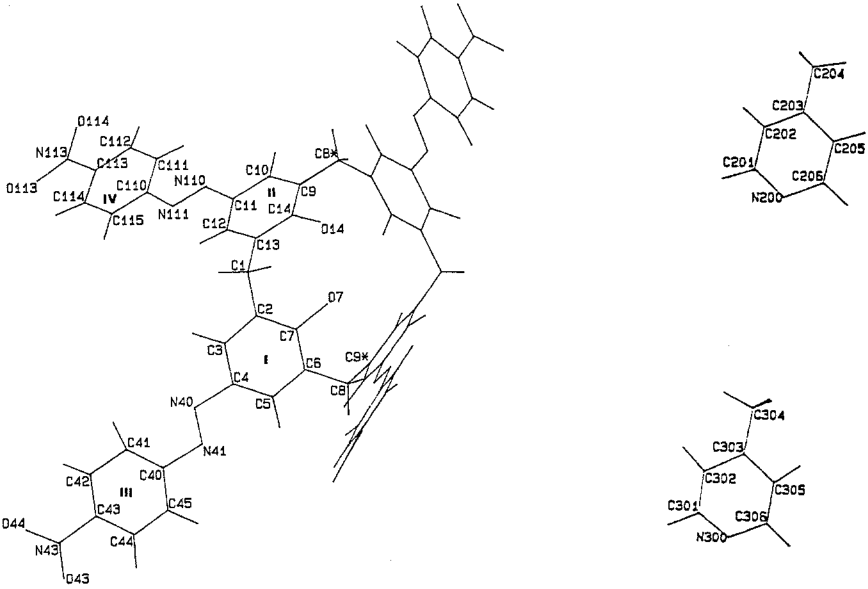

Fig. 1. Numbering scheme.

2.3.2. *Structure Analysis and Refinement*

The structure was solved by direct methods using MULTAN [4] and refined on F by SHELX-76 [5]. A Fourier map computed from several cycles of full-matrix least squares calculations with isotropic B factors revealed all the non-hydrogen atoms of the azocalixarene asymmetrical unit with two molecules of picoline. The hydrogen atoms were located at theoretical positions and refined isotropically. The non-H atoms were then refined anisotropically. The final R value was 0.067 and the highest residual peak has a value of ca. 0.64 e Å^{-3}.

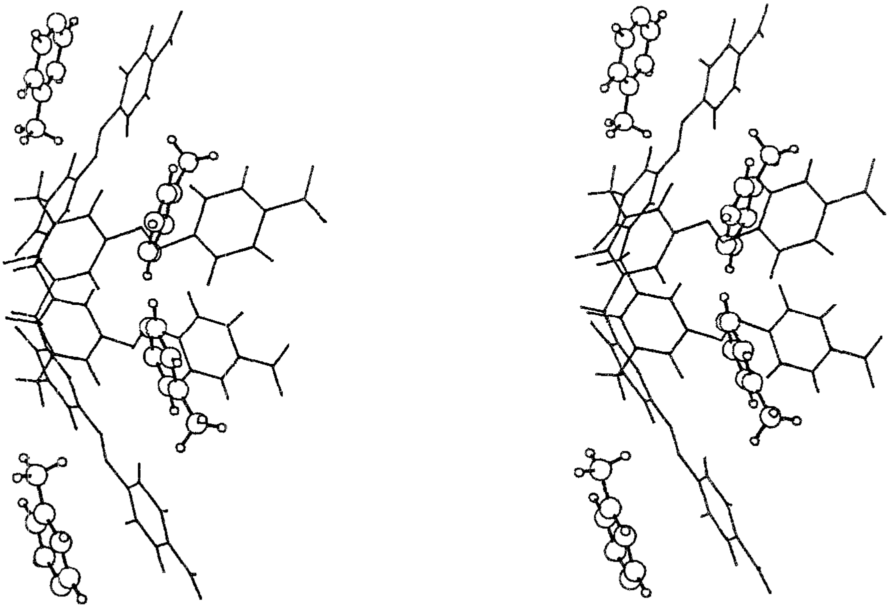

Fig. 2. Conformation of the azocalix[4]arene and guest positions.

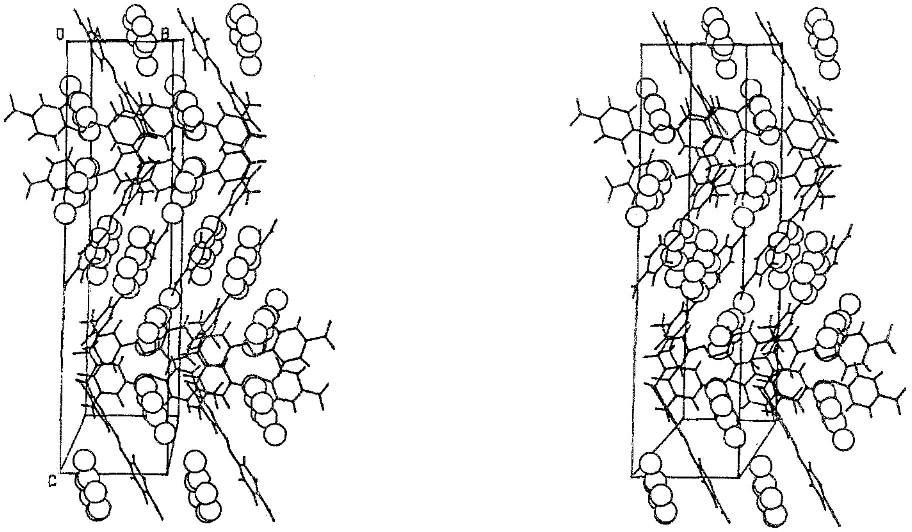

Fig. 3. Packing of the azocalixarene along [100].

Final atomic coordinates and equivalent thermal parameters are listed in Table II (for the non-H-atoms) using the numbering scheme given in Figure 1. The bond lengths and angles calculated from PARST [6] are shown in Tables III and IV.

TABLE III. Bond distances (Å).

Atom 1	Atom 2	Distance	Atom 1	Atom 2	Distance	Atom 1	Atom 2	Distance
C(1)	C(2)	1.508(6)	C(45)	C(40)	1.355(8)	C(114)	C(115)	1.389(7)
C(1)	C(13)	1.519(7)	N(43)	O(43)	1.212(6)	C(115)	C(110)	1.375(7)
C(3)	C(4)	1.407(7)	N(43)	O(44)	1.223(8)	N(113)	O(113)	1.218(7)
C(3)	C(2)	1.409(7)	C(10)	C(11)	1.401(7)	N(113)	O(114)	1.209(7)
C(4)	C(5)	1.385(8)	C(10)	C(9)	1.394(7)	C(201)	C(202)	1.37(1)
C(4)	N(40)	1.491(7)	C(11)	C(12)	1.399(7)	C(201)	N(200)	1.32(1)
C(5)	C(6)	1.396(7)	C(11)	N(110)	1.429(6)	C(202)	C(203)	1.37(1)
C(6)	C(7)	1.398(6)	C(12)	C(13)	1.389(7)	C(203)	C(205)	1.35(1)
C(6)	C(8)	1.497(8)	C(13)	C(14)	1.399(7)	C(203)	C(204)	1.489(9)
C(7)	C(2)	1.412(7)	C(14)	C(9)	1.383(7)	C(205)	C(206)	1.37(1)
C(7)	O(7)	1.327(6)	C(14)	C(14)	1.344(6)	C(206)	N(200)	1.35(1)
N(40)	N(41)	1.192(6)	C(9)	C(8)	1.506(8)	C(301)	C(302)	1.34(2)
N(41)	C(40)	1.493(8)	N(110)	N(111)	1.246(6)	C(301)	N(300)	1.27(2)
C(41)	C(42)	1.44(1)	N(111)	C(110)	1.456(6)	C(302)	C(303)	1.45(2)
C(41)	C(40)	1.36(1)	C(111)	C(112)	1.386(9)	C(303)	C(305)	1.36(2)
C(42)	C(43)	1.361(8)	C(111)	C(110)	1.383(8)	C(303)	C(304)	1.52(2)
C(43)	C(44)	1.383(9)	C(112)	C(113)	1.357(8)	C(305)	C(306)	1.33(3)
C(43)	N(43)	1.473(8)	C(113)	C(114)	1.369(7)	C(306)	N(300)	1.32(2)
C(44)	C(45)	1.375(9)	C(113)	N(113)	1.499(7)			

3. Discussion

The p-tetrakis-(4-nitrophenylazo)calix[4]arene has a cone conformation, as has already been found for p-tetrakis(phenylazo)calix[4]arene. The phenolic units I and II make angles of 144.0(2)° and 116.9(2)°, respectively, with the least-squares plane defined by the atoms: C(2), C(6), C(9), C(13) (Figure 2). The two azobenzene skeletons of the asymmetrical unit are approximately planar. Indeed, the dihedral angles between planes of the phenyl rings on both sides of the —N=N— bonds are:

planes I and III 7.4(2)°
planes II and IV 4.7(2)°

The intramolecular (O–O distances are: O(7)···O(14) 2.574(5) Å and O(7)···O(14^i) 2.606(4) Å ($i = -x, y, -z+1.5$). The values are in good agreement with those usually found in calix[4]arenes.

This azocalix[4]arene crystallizes with four picoline molecules. Two of the solvent molecules (N(300) → C(306)) lie inside the cavity (Figure 2) of the macrocycle and are approximatively parallel to the planes I and III (respectively 12.4(2)°, 10.9(3)°).

The picoline molecule N(300) → C(306) with the symmetry (x, y, z) is near the phenyl ring I of the macrocycle with the symmetry ($x, y + 1, z$). Particularly the

Table IV. Bond angles (deg.).

Atom 1	Atom 2	Atom 3	Angle	Atom 1	Atom 2	Atom 3	Angle	Atom 1	Atom 2	Atom 3	Angle
C(2)	C(1)	C(13)	113.0(4)	C(43)	C(44)	C(45)	118.2(5)	C(11)	N(110)	N(111)	115.1(4)
C(4)	C(3)	C(2)	119.1(5)	C(44)	C(45)	C(40)	119.4(7)	N(110)	N(111)	C(110)	111.3(4)
C(3)	C(4)	C(5)	121.5(5)	N(41)	C(40)	C(41)	121.8(5)	C(112)	C(111)	C(110)	118.8(6)
C(3)	C(4)	N(40)	110.4(5)	N(41)	C(40)	C(45)	115.3(6)	C(111)	C(112)	C(113)	119.0(5)
C(5)	C(4)	N(40)	128.1(4)	C(41)	C(40)	C(45)	122.9(6)	C(112)	C(113)	C(114)	123.4(5)
C(4)	C(5)	C(6)	119.7(4)	C(43)	N(43)	O(43)	118.6(6)	C(112)	C(113)	N(113)	118.7(5)
C(5)	C(6)	C(7)	119.9(5)	C(43)	N(43)	O(44)	118.6(5)	C(114)	C(113)	N(113)	117.9(5)
C(5)	C(6)	C(8)	119.6(4)	O(43)	N(43)	O(44)	122.7(6)	C(113)	C(114)	C(115)	117.5(5)
C(7)	C(6)	C(8)	120.5(4)	C(11)	C(10)	C(9)	120.5(4)	C(114)	C(115)	C(110)	120.1(5)
C(6)	C(7)	C(2)	120.7(4)	C(10)	C(11)	C(12)	119.2(4)	C(111)	C(110)	C(111)	123.2(5)
C(6)	C(7)	O(7)	121.0(4)	C(10)	C(11)	N(110)	114.2(4)	C(111)	C(110)	C(115)	115.7(4)
C(2)	C(7)	C(7)	118.4(4)	C(12)	C(11)	N(110)	126.6(5)	C(111)	C(110)	C(115)	121.1(5)
C(1)	C(2)	C(3)	120.2(5)	C(1)	C(12)	C(13)	121.1(5)	C(113)	N(113)	O(113)	117.3(5)
C(1)	C(2)	C(7)	120.6(4)	C(1)	C(13)	C(12)	121.0(4)	C(113)	N(113)	O(114)	116.7(5)
C(3)	C(2)	C(7)	119.1(4)	C(1)	C(13)	C(14)	120.9(4)	O(113)	N(113)	O(114)	126.0(5)
C(4)	N(40)	N(41)	110.3(5)	C(12)	C(13)	C(14)	118.1(4)	C(6)	C(8)	C(9)	116.3(4)
N(40)	N(41)	C(40)	109.2(5)	C(13)	C(14)	C(9)	122.3(4)	C(202)	C(201)	N(200)	119.5(8)
C(42)	C(41)	C(40)	119.4(6)	C(13)	C(14)	O(14)	118.4(4)	C(201)	C(202)	C(203)	124.1(8)
C(41)	C(42)	C(43)	115.5(6)	C(9)	C(14)	O(14)	119.3(4)	C(202)	C(203)	C(205)	115.5(7)
C(42)	C(43)	C(44)	124.6(6)	C(10)	C(9)	C(14)	118.8(5)	C(202)	C(203)	C(204)	122.4(7)
C(42)	C(43)	N(43)	118.2(6)	C(10)	C(9)	C(8)	117.3(4)	C(205)	C(203)	C(204)	122.0(7)
C(44)	C(43)	N(43)	117.2(5)	C(14)	C(9)	C(8)	124.0(4)	C(203)	C(205)	C(206)	119.2(8)
C(205)	C(206)	N(200)	124.4(8)	C(302)	C(303)	C(305)	113.0(1)	C(305)	C(306)	N(300)	123.0(1)
C(201)	N(200)	C(206)	117.2(6)	C(302)	C(303)	C(304)	126.0(1)	C(301)	N(300)	C(306)	120.0(2)
C(302)	C(301)	N(300)	120.0(1)	C(305)	C(303)	C(304)	121.0(1)				
C(301)	C(302)	N(303)	123.0(1)	C(303)	C(305)	C(306)	121.0(1)				

Numbers in parentheses are estimated standard deviations in the least significant digits.

bond distances between C(304) (x, y, z) and C(2) → C(7^{ii}) $(ii = x, y+1, z)$ with values of 3.83(1) → 4.11(1) Å show $CH_3 \cdots \Pi$ interactions.

In addition, we note the following distances:

N(300) $\cdots$ O(7^{ii}) 3.34(1) Å
N(300) $\cdots$ O(14^{ii}) 3.83(1) Å
C(304) $\cdots$ N(40) 3.71(1) Å
C(304) $\cdots$ N(41) 3.65(1) Å

The two other picoline molecules (N(200) → C(206)) are outside the cavity and make angles of 12.3(2)° and 6.15(2)° with the planes I and III (Figure 3). There is also a weak interaction between the methyl group C(204) and N(40)—(41):

C(204) $\cdots$ N(40) 3.68(1) Å
C(204) $\cdots$ N(41) 4.07(1) Å

Generally, when calix[4]arenes crystallize with aromatic compounds, one guest molecule lies inside the macrocycle cavity, the mean plane of the aromatic ring being perpendicular to the mean plane of the four methylene bridges. This is the case, for example for a crown-bridged *p*-*t*-butylcalix[4]arene (1 : 1) pyridine complex [7] and for the *p*-*t*-butylcalix[4]arene (1 : 1) toluene complex [8] where the guest molecule lies on a four fold axis passing through the C—CH_3 bond.

For the title compound, the guest positions are unusual because two picoline molecules lie in the macrocycle cavity and are almost parallel to two moieties. An illustration of the packing is given in Figure 3. In the *b* direction, the azocalixarenes line up with the aperture of the cones, half in one direction, half in the opposite direction. In the *a* direction all columns have the aperture in the same direction. In the *c* direction, the columns interact with each other, with picoline molecules (N(200) → C(206)) occupying the free space between the columns. This packing results in a high value for the specific mass (1.330 g cm^{-3}).

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