ORIGINAL ARTICLE

X-ray crystal structure of a *p*-hydroxycalix[6]arene derivative

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Abstract The first molecular structure of a *p*-hydroxycalix[6]arene **6** has been determined by a single crystal X-ray diffraction study. The calix[6]arene molecule assumes a 1,2,3-alternate conformation with all OH groups at the upper rim engaged in H-bonds with pyridine molecules. The stacking of molecules of *p*-hydroxycalix[6]arene **6** along the *a* and *c* axes gives rise to a solvent pseudo-cylindrical cavity at the centre of the cell.

Keywords Calixarenes · Calixhydroquinones · X-ray crystal structure · 1,2,3-alternate conformation · Solvent channel

Introduction

Calixarenes [1] are a class of hosts particularly studied in supramolecular chemistry thanks to their conformational versatility and to their easy chemical modification. Among the different groups that it is possible to introduce at the *upper* or *wider rim* (the *para* position), considerable attention has been devoted to the hydroxyl function, amenable of further functionalization [2]. In addition, the capability of this group to engage intermolecular H-bonds makes *p*-hydroxycalixarenes particularly attractive as building blocks for crystal engineering [3, 4]. In fact, in the last decade very interesting solid-state architectures based on calixarene derivatives bearing hydroquinone moieties have been reported [4]. Thus, organic nanotubes have been obtained by Kim et al. [5] by solid state self-assembling of a calix[4]tetrahydroquinone derivative. Neri et al. [6] have shown that a *p-tert*-butylcalix[4]dihydroquinone forms a nanoporous architecture characterized by the simultaneous existence of hydrophilic channels and very large unoccupied hydrophobic cavities. In both instances, the three-dimensional architecture is hold by a network of intermolecular H-bonds among the OH groups at the upper rim.

Several solid state structures have been reported for *p*-hydroxycalix[4]arenes derivatives, [5, 6], whereas the larger calix[*n*]arenes (*n* = 5, 6, 7 and 8) remain largely less investigated. At this regard, the only X-ray crystal structure has been reported by Leverd et al. for a octa(*p*-hydroxy)octakis(propyloxy)calix[8]arene derivative [7]. In particular, it was found that the calix[8]arene macrocycle adopts, in the solid state, a chair-like conformation [8] with all *para*-OH groups forming hydrogen bonds with pyridine and water molecules [7].

Regarding the *p*-hydroxycalix[6]arenes derivatives, to the best of our knowledge, no crystal structures have been reported and, consequently, no information is currently available concerning the solid state behavior of this kind of derivatives. Here we whish to report the synthesis and X-ray crystal structure of 5,11,17,23,29,35-hexahydroxy-37,38,39,40,41,42-hexapentoxycalix[6]arene **6**.

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Experimental

Materials and Methods

ESI(+) MS measurements were performed on a BIO-Q triple quadrupole mass spectrometer (MICROMASS) equipped an electrospray ion source, using a mixture of H_2O/CH_3CN (1:1) and 5% HCOOH as solvent. Flash chromatography was performed on Merck silica gel (60, particle size: 0.040–0.063 mm). All chemicals were reagent grade and were used without further purification. p-tert-Butylcalix[6]arene **1** was prepared according to procedures reported by Gutsche, [9] and debutylated by treatment with $AlCl_3$ in toluene to give **2** [10]. All NMR spectra were recorded at 400 (^1H) and 100 (^{13}C) MHz on a Bruker Avance-400 spectrometer. Chemical schifts are reported relative to the residual solvent peak ($CHCl_3$: $\delta = 7.26$, $CHCl_2CHCl_2$: $\delta = 6.00$, $CDCl_3$: $\delta = 77.2$, $CDCl_2CDCl_2$: $\delta = 73.8$). Reaction temperatures were measured externally. Reactions were monitored by TLC on Merck silica gel plate (0.25 mm) and visualized by UV light and spraying with H_2SO_4–$Ce(SO_4)_2$.

37,38,39,40,41,42-Hexapentoxycalix[6]arene 3

NaH (1.5 g, 62.5 mmol) was added, under stirring, to a solution of **2** (1.6 g, 2.5 mmol) in a mixture of dry THF/DMF (10/1, v/v, 55 mL). The mixture was kept at reflux, under stirring and after 30 min, 1-bromopentane (19.3 g, 16 mL, 128 mmol) was added. The reaction was stirred at reflux for 48 h, then quenched with H_2O (50 mL), and extracted with CH_2Cl_2 (3 × 30 mL). The combined organic layer was washed with 1N HCl (50 mL) and brine (50 mL) and dried over Na_2SO_4. The crude product was subjected to flash chromatography on silica gel, using dichloromethane/petroleum ether (30/70, v/v), (56%, 1.5 g): ESI(+) MS m/z 1057 (MH+); ^1H NMR (400 MHz, $CDCl_3$, 298 K) δ 0.92 (t, CH_3, $J = 7.2$ Hz, 18H), 1.26–1.60 (overlapped, 36H), 3.22 (br s, OCH_2, 12H), 3.92 (br s, $ArCH_2Ar$, 12H), 6.80 (br s, ArH, 6H), 7.01 (br s, ArH, 12H); ^{13}C NMR (100 MHz, $CDCl_3$, 298 K) δ 14.4 [CH_3, q], 22.9 [CH_2, t], 28.6 [CH_2, t], 29.7 [CH_2, t], 30.5 [CH_2, t], 71.2 [OCH_2, t], 123.5 (d, $C_{Ar}H$), 129.2 (d, $C_{Ar}H$), 134.8 (s, $C_{Ar}CH_2$), 155.2 (s, $C_{Ar}O$); Anal. calcd. for $C_{72}H_{96}O_6$: C, 81.77%; H, 9.15%. Found: C, 81.67%; H, 9.23%.

5,11,17,23,29,35-Hexaacetyl-37,38,39,40,41,42-hexapentoxycalix[6]arene 4

A mixture of aluminium chloride (4.5 g, 34.0 mmol) and acetyl chloride (10 mL, 140 mmol) in dry CH_2Cl_2 (15 mL)

was added dropwise over 1 h to a solution of **3** (1.5 g, 1.4 mmol) in dry CH_2Cl_2 (40 mL) at –6 °C under nitrogen. The reaction mixture was stirred for 7 h, and then quenched with water (100 mL). The layers were separated and the aqueous layer was extracted with CH_2Cl_2 (3 × 50 mL). The combined organic layer was dried over Na_2SO_4 and the solvent evaporated. The residue was dissolved in hot CH_2Cl_2 and precipitated by addition of methanol. The product was collected on filter glass, dried and purified by flash chromatography on silica gel, using dichloromethane/diethyl ether (85/15, v/v), (49%, 0.9 g): m.p. 247–249 °C; ESI(+) MS m/z 1309 (MH+); ^1H NMR (TCDE, 378 K, 400 MHz) δ 0.68 (t, CH_3, $J = 7.4$ Hz, 18H), 1.05–1.42 (overlapped, 36H) 2.21 (s, $COCH_3$, 18H), 3.50 (t, OCH_2, $J = 6.6$ Hz, 12H), 3.86 (br s, $ArCH_2Ar$, 12H), 7.43 (s, ArH, 12H); ^{13}C NMR (TCDE, 378 K, 100 MHz) δ 11.6 (q, CH_3), 20.7 (t, CH_2), 26.6 (q, $COCH_3$), 27.8 (t, CH_2), 28.1 (t, CH_2), 28.4 (t, CH_2), 68.9 (t, OCH_2), 121.4 (d, $C_{Ar}H$), 127.2 (s, $C_{Ar}CH_2$), 132.6 (s, $C_{Ar}CO$), 156.7 (s, $C_{Ar}O$), 196.7 (s, C=O). Anal. calcd. for $C_{84}H_{108}O_{12}$: C, 77.03%; H, 8.31%. Found: C, 77.12%; H, 8.23%.

5,11,17,23,29,35-Hexaacetoxy-37,38,39,40,41,42-hexapentoxycalix[6]arene 5

Compound **4** (0.9 g, 0.7 mmol) and m-chloroperbenzoic acid (6.9 g, 40 mmol) was dissolved in $CHCl_3$ (130 mL) and kept at 4 °C for 10 days. Chloroform was added (100 mL), and the mixture was washed with a solution 2 M of sodium sulfite (50 mL) and successively with 0.2 M pH = 7.2 phosphate buffer (50 mL). The organic layer was dried with Na_2SO_4, filtered and evaporated. The crude product was subjected to flash chromatography on silica gel, using ethyl acetate/hexane (2/1, v/v), (91%, 0.9 g): m.p. 148–150 °C; ESI(+) MS m/z 1405 (MH+); ^1H NMR (TCDE, 378 K, 400 MHz) δ 0.83 (t, CH_3, $J = 6.2$ Hz, 18H), 1.27–1.33 (overlapped, 36H) 2.0 (s, $COCH_3$, 18H), 3.35 (br t, OCH_2, 12H), 3.79 (br s, $ArCH_2Ar$, 12H), 6.59 (s, ArH, 12H); ^{13}C NMR (TCDE, 388 K, 100 MHz) δ 10.8 (q, CH_3), 20.7 (t, CH_2), 23.3 (t, CH_2), 28.4 (t, CH_2), 29.3 (q, $COCH_3$), 31.4 (t, CH_2), 73.8 (t, OCH_2), 121.6 (d, $C_{Ar}H$), 134.5 (s, $C_{Ar}CH_2$), 146.4 (s, $C_{Ar}O$), 152.8 (s, $C_{Ar}O$), 169.0 (s, C=O). Anal. calcd. for $C_{84}H_{108}O_{18}$: C, 71.77%; H, 7.74%. Found: C, 71.69%; H, 7.83%.

5,11,17,23,29,35-Hexahydroxy-37,38,39,40,41,42-hexapentoxycalix[6]arene 6

5 (0.9 g, 0.6 mmol) was dissolved in a methanolic solution 0.7 M in NaOH (100 mL). The solution was stirred

for 4 h at room temperature and successively acidified with HCl conc. The methanol was evaporated under reduced pressure, and water was added (30 mL). The precipitate was filtered and dried. The crude product was subjected to flash chromatography on silica gel, using chloroform/methanol (70/30, v/v), (53%, 0.37 g); m.p. > 270 °C dec; ESI(+) MS m/z 1153 (MH$^+$); ^{1}H NMR (DMSO, 378 K, 400 MHz) δ 0.87 (t, CH$_3$, $J = 7.0$ Hz, 18H), 1.18–1.53 (overlapped, 36 H), 3.37 (t, OCH$_2$, $J = 5.0$ Hz, 12 H), 3.71 (br s, ArCH$_2$Ar, 12H), 6.38 (s, ArH, 12H) 8.01 (br s, ArOH, 6H); ^{13}C NMR (DMSO, 378 K, 100 MHz) δ 13.3 (q, CH$_3$), 21.4 (t, CH$_2$), 27.4 (t, CH$_2$), 28.8 (t, CH$_2$), 29.5 (t, CH$_2$) 72.5 (t, OCH$_2$), 115.0 (d, C$_{Ar}$H), 133.6 (s, C$_{Ar}$CH$_2$), 147.3 (s, C$_{Ar}$O), 151.7 (s, C$_{Ar}$O). Anal. calcd. for C$_{72}$H$_{96}$O$_{12}$: C, 74.97%; H, 8.39%. Found: C, 74.87%; H, 8.46%.

X-ray crystallography

Crystal data for 5,11,17,23,29,35-Hexahydroxy-37,38,39, 40,41,42-hexapentoxycalix[6]arene **6**: C$_{72}$H$_{96}$O$_{12}$·6C$_5$H$_5$N· 2C$_6$H$_6$, $M = 1784.30$, triclinic, space group P-1 (no. 2), $a = 14.522(5)$, $b = 15.645(9)$, $c = 13.578(4)$ Å, $\alpha = 100.11$ (3), $\beta = 104.49(3)$, $\gamma = 114.20(3)°$, $V = 2586(2)$ Å^3, $Z = 1$, $D_c = 1.15$ g cm^{-3}, μ(Cu-Kα) = 0.58 cm^{-1}, $F(000) = 960$. Single crystals of **6**, suitable for X-ray analysis, were obtained by slow evaporation from a benzene/pyridine solution. A crystal (0.35 × 0.22 × 0.12 mm) was sealed with its mother liquid in a Lindemann capillary and used for data collection at room temperature on a Rigaku AFC5R diffractometer with graphite-monochromated Cu$_{k\alpha}$ radiation and a 12 kW rotating anode generator. Out of 8539 reflections collected till $2\theta_{max} = 124°$, 8170 were considered unique and corrected for LP and absorption ($R_{int} = 0.018$). Not decay was observed. The structure was solved and refined with the SIR97 program [11]. Non-hydrogen atoms were refined anisotropically and all hydrogen atoms (except the observed OH hydrogens) were positioned geometrically (riding model). Final anisotropic refinements were carried out according to the full-matrix least-squares method, based on 6014 reflections with $F_o > 5.0\sigma(F_o)$ and 595 variable parameters (ratio 10.1): $R = 0.080$, $R_w = 0.083$, $w = \sin\theta/\lambda$, S = 6.95. Maximum and minimum peaks of the final difference Fourier map: $\rho_{max} = 0.40$ and $\rho_{min} = -0.27$ e Å^{-3}.

Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-631187. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: int. code +(44) 1223-336033; e-mail: deposit@ccdc.cam.ac.uk).
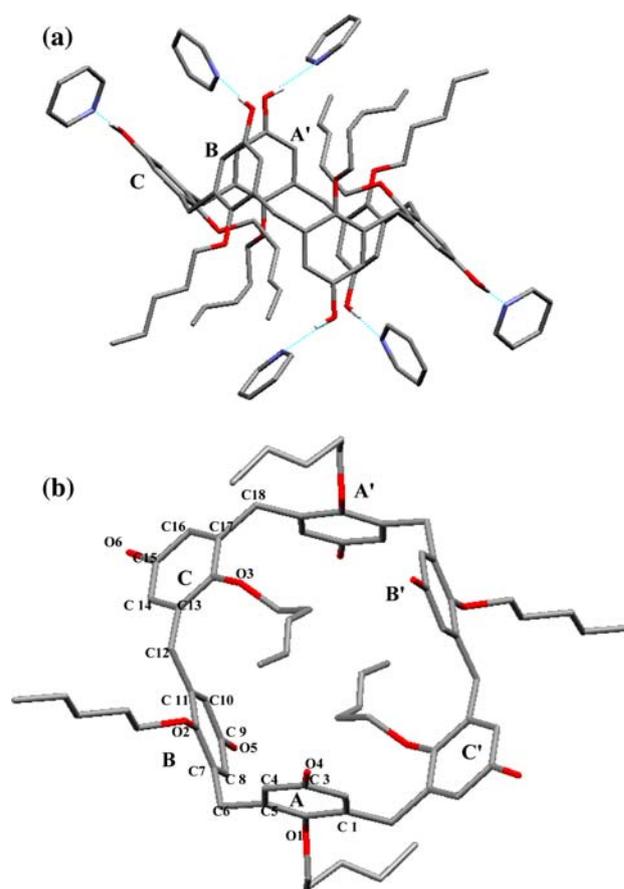
Fig. 1 X-ray molecular structure of hexahydroxy-hexapentoxyca-lix[6]arene **6**. (**a**) Side-view showing the 1,2,3-alternate conformation. (**b**) Top-view with the numbering scheme

Results and discussion

The introduction of OH groups at the upper rim of the calix[6]arene skeleton was obtained by exploiting a Bae-yer-Villiger oxidation of a suitable *p*-acetyl precursor, as previously reported by Mascal et al. for analogous deriv-atives [12]. Thus, hexapentoxycalix[6]arene **3** was obtained in 55% yield by alkylation of *p*-H-calix[6]arene **2** [10] with 1-bromopentane in the presence of NaH as base (Scheme 1). Compound **3** was treated with a mixture of aluminium chloride and acetyl chloride in dry dichlorom-ethane at –6 °C, to give 5,11,17,23,29,35-hexaacetyl-37,38,39,40,41,42-hexapentoxycalix[6]arene **4** in 49% yield (Scheme 1). Baeyer-Villiger oxidation of compound **4** at 4 °C for 10 days, resulted in the formation of 5,11,17,23,29,35-hexaacetoxy-37,38,39,40,41,42-hexa-pentoxycalix[6]arene **5** in 91% yield. Finally, compound **5** was hydrolyzed, in the presence of 0.7 M methanolic solution of NaOH, to give 5,11,17,23,29,35-hexahydroxy-37,38,39,40,41,42-hexapentoxycalix[6]arene **6** in 53% yield.

Scheme 1
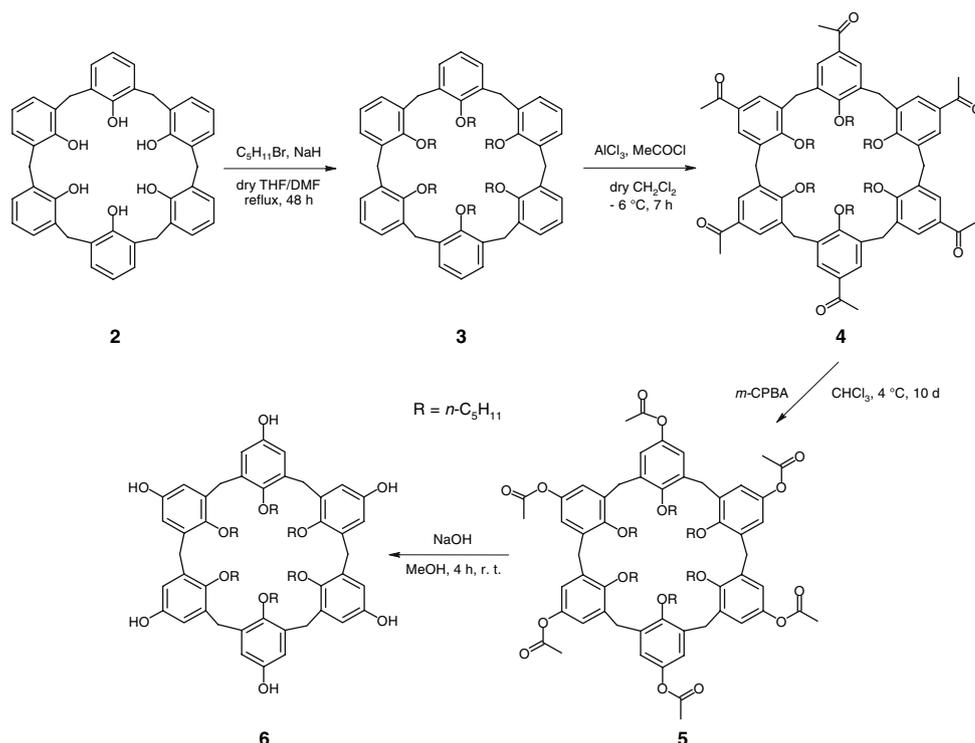
Compounds **3**–**6** were mainly characterized by spectral analysis. Their molecular formulas were confirmed by the presence of the pseudo-molecular ion peak in the ESI(+) mass spectrum. The presence of broad signals in their room-temperature ^{1}H NMR spectra indicated a low conformational mobility of the macrocycle. Sharp signals were normally observed at higher temperatures becuase of the increased conformational mobility. Thus, for example, the ^{1}H NMR spectrum (DMSO, 378 K, 400 MHz) of hexahydroxy-hexapentoxycalix[6]arene **6** showed a broad singlet at 8.01 ppm relative to the OH protons at the upper rim of the macrocycle, a singlet at 6.38 ppm relative to the aromatic protons, an ArCH$_2$Ar broad singlet at 3.71 ppm, and a triplet at 3.37 ppm relative to OCH$_2$ protons.

Single crystals of 5,11,17,23,29,35-hexahydroxy-37,38,39,40,41,42-hexapentoxycalix[6]arene **6**, suitable for X-ray analysis, were obtained by slow evaporation from a benzene/pyridine solution. The asymmetric unit is formed by half molecule of **6**, three pyridine and one benzene molecules. The crystal structure, as seen in Fig. 1a, shows the whole **6** compound, with its centre of symmetry present in the centre of the molecule. The calix[6]arene macrocycle adopts a 1,2,3-alternate conformation (Fig. 1a) composed by two *anti* oriented 3/4-cone subunits. This is in accordance with the results reported by Bott [13], that indicated that the calix[6]arene macrocycle adopts a 1,2,3-alternate conformation when the cyclic array of hydrogen bonding at the *lower* or *smaller rim* is interrupted or absent. All hydroxyl groups present at the upper rim of the macrocycle of **6** are engaged in strong H-bonds with pyridine molecules (the distances O(4)···N(1), O(5)···N(2), and O(6)···N(3) of the asymmetric unit are 2.741, 2.801, and 2.768 Å, respectively) with a mean O···N distance equal to 2.770 Å. In accord with the results of Leverd et al. [7], this value is slightly longer than the O···N distances found for the H-bonds that phenolic OH groups of native calixarene engage with pyridine molecules [8a, 14, 15]. The angles between O(4)–H···N(1), O(5)–H···N(2) and O(6)–H···N(3) are respectively 156.1°, 175.4° and 176.2°. The examination of the torsion angle φ and χ around the methylene bridges [16] (Table 1), reveals that the 1,2,3-alternate conformation of hexahydroxy-hexapentoxycalix[6]arene **6**

Table 1 Torsion angles (°) around the ArCH$_2$Ar bonds found in the X-ray structure of **6**

	φ		χ
C(4)–C(5)–C(6)–C(7)	102.3	C(5)–C(6)–C(7)–C(8)	96.0
C(10)–C(11)–C(12)–C(13)	−18.9	C(11)–C(12)–C(13)–C(14)	84.2
C(16)-C(17)-C(18)-C(1)	−92.2	C(17)–C(18)–C(1)–C(2)	40.7
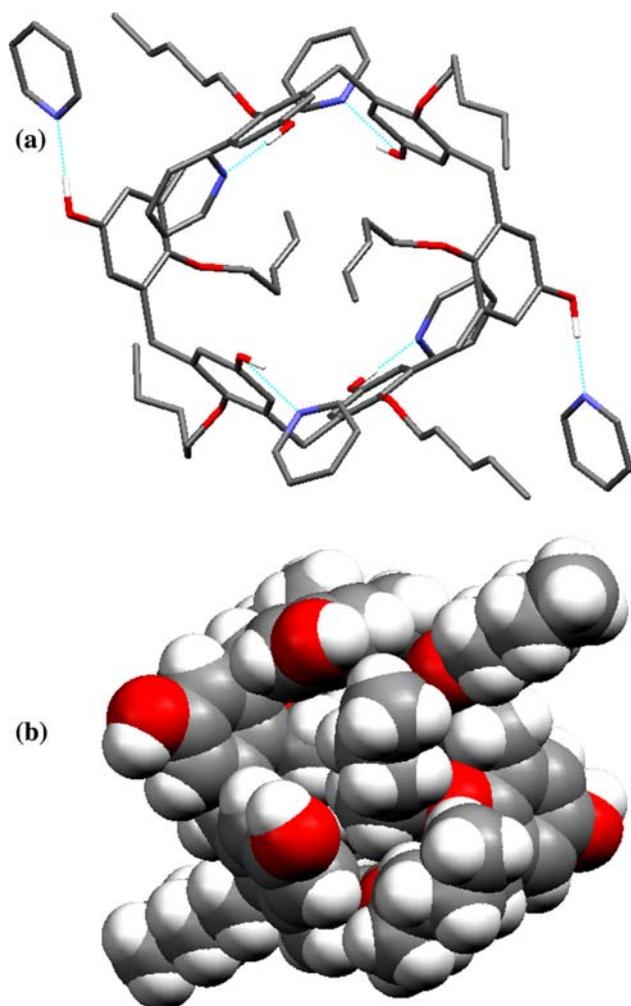
Fig. 2 Top-view of the X-ray molecular structure of hexahydroxy-hexapentoxycalix[6]arene **6**. (**a**) Polytube model with hydrogen atoms omitted for clarity. (**b**) CPK-model showing the self-filling of the calix[6]arene cavity

is characterized by the following signs: + +, − +, − +, − −, + −, + −. Because of this conformation, the three contiguous *p*-OH groups of each 3/4-cone subunit are oriented on the opposite side of the mean molecular plane. In each 3/4-cone the aromatic rings A′ e B are almost perpendicular to the mean plane of the ArCH₂Ar groups with canting angles of 84.4° and 105.3°, respectively. Their phenolic group point towards the pyridine solvent molecules, while their two *n*-pentyl chains point towards the same direction. The pentyl group of ring A′ is bent over ring C almost covering it, whereas that of ring B is projected toward the external of the molecule. The central ring C presents a canting angle of 45.8°, and points its pentoxy group toward the inside of the cavity partially filling it. From the top, the intrannular space could be roughly approximate to a parallelogram with the two diagonals of 10.6 Å each (Fig. 2a). The self-inclusion of the two symmetry-related pentoxy groups and the inward inclination of rings A′ and B, leave no space for solvent molecules (Fig. 2b). This topology is in accordance with analogous crystal structures of *O*-alkylated calix[6]-arene [17] and calix[8]arene [7, 8b] derivatives, in which the H-bonds at the lower rim are absent.

Two views of the ORTEP plot of hexahydroxy-hexa-pentoxycalix[6]arene **6** are reported in Fig. 3, while its packing diagram is shown in Fig. 4. The calix[6]arene molecules are stacked respectively along the *a* and *c* axes, leaving a channel at the centre of the cell, containing pyridine and benzene molecules, as shown in Figs. 4 and 5. In fact, two molecules of pyridine and two molecules of benzene are stacked along a direction almost parallel to *b* and *c* axes and almost perpendicular to *a* (Fig. 4). The stacking of these solvent molecules is interrupted along the direction of the *b* and *c* axes by the presence of calix[6]arene molecules as shown in Fig. 6. Therefore, the channel should be more appropriately seen as a definite

Fig. 3 Top-view (**a**) and side-view (**b**) of the ORTEP plot of **6** (H atoms omitted). Ellipsoids are drawn at 20% probability level
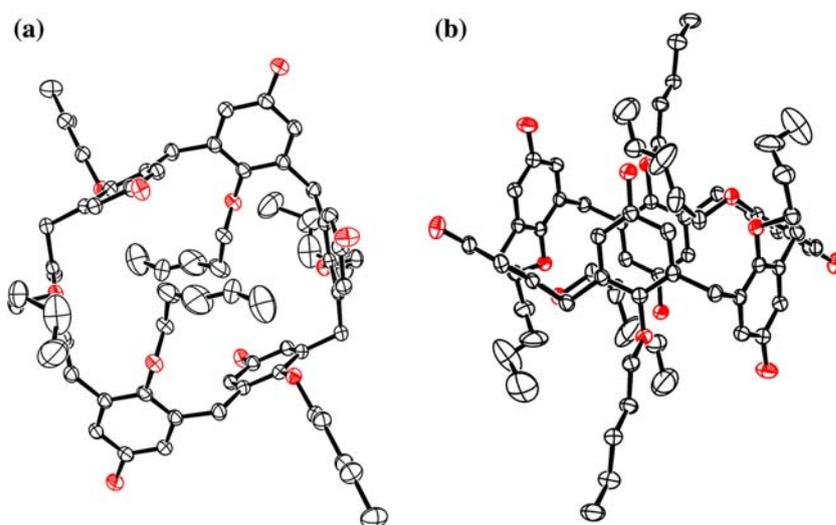
Fig. 4 Crystal packing of **6** seen along the *a* (**a**), *b* (**b**), and *c* (**c**) axis, respectively
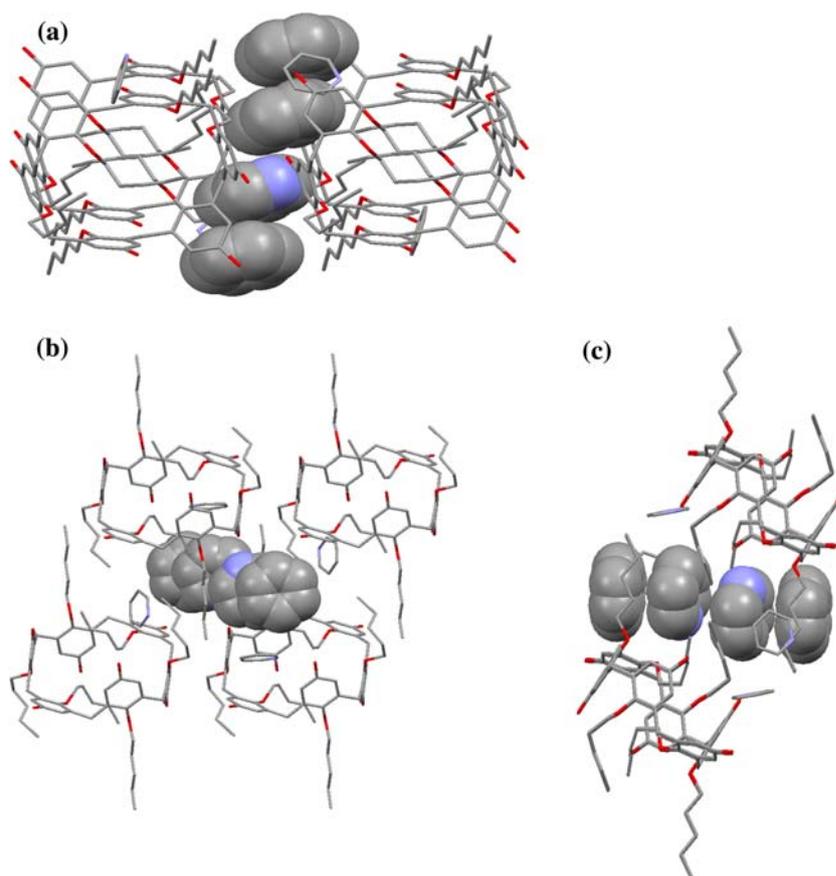
cavity. Adjacent molecules of benzene and pyridine, presents in this cavity, have their least-squares mean planes almost parallel (11.9°) and the average distance between correspondent atoms of the rings is 4.05 Å. The packing of the solvent is therefore mainly governed by H-bond and π–π interactions, while the packing of the asymmetric moiety is mainly governed by π–π and van der Waals interactions.

Conclusions

The results reported in this paper represent an interesting contribution to the limited information currently available for the conformational features of the larger calix[*n*]arene macrocycles. In particular, it is here demonstrated that hexahydroxy-hexapentoxycalix[6]arene **6** adopts, in the solid state, a 1,2,3-alternate conformation, with all the OH

Fig. 5 Space-filling model of the unit cell of **6** showing the central pseudo-cylindrical cavity. Solvent molecules are in the ball-and-stick model (**a**) or are omitted (**b**)
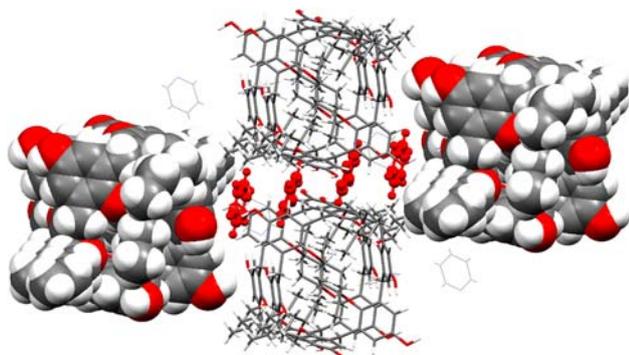
Fig. 6 Combined model of the crystal packing of **6** showing the ending of the central pseudo-cylindrical cavity as seen along the *a* (**a**) and *b* (**b**) axis, respectively

groups at the upper rim engaged in strong H-bonds with pyridine molecules. Also in this instance, it is evident the propensity of the calix[6]arene macrocycle to assume a 1,2,3-alternate conformation when the intramolecular hydrogen bonding at the lower rim is absent. As in other circumstances, a deviation from the ideal geometry is observed because the self-inclusion tendency leads to less usual inclinations of the aromatic rings. The packing of hexahydroxy-hexapentoxycalix[6]arene **6** generates a pseudo-cylindrical cavity at the centre of the cell, filled with solvent molecules. In principle, this cavity could be able to host also different kind of guests leading to interesting potential applications. Therefore, the replacement and/or the removal of these solvent molecules are currently under study in our laboratory.

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