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Crystal Structure of C-(*n*-propyl)calix[4]resorcinarene and its Complex with Caffeine

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The crystal structures of the all-*cis* epimer of *C*-(*n*-propyl)calix[4]resorcinarene (1) and its caffeine complex are reported. 1 • CH_3CN • H_2O (2) crystallizes in the tetragonal space group $P\bar{4}$, $a = 14.3645(9)$, $c = 9.3344(8)$ Å, $V = 1926(2)$ Å^3. Refinement led to a final conventional R_1 value of 0.047 for 3406 reflections and 236 parameters. The caffeine complex 1 • $C_8H_{10}N_4O_2$ • CH_3OH • H_2O (3) crystallizes in the triclinic space group $P\bar{1}$, $a = 11.2892(4)$, $b = 13.0367(8)$, $c = 16.9700(11)$ Å, $\alpha = 82.902(2)$, $\beta = 79.713(3)$, $\gamma = 88.053(2)°$, $V = 2438(2)$ Å^3. Refinement led to a final conventional R_1 value of 0.067 for 6393 reflections and 641 parameters. The resorcinarene displays the usual bowl shape in both compounds. The caffeine molecule in 3 is hydrogen bonded to two resorcinarene and one water molecules and one of its methyl groups is included in the cavity of a third macrocycle, suggesting $CH_3 \cdots \pi$ interactions. Extended hydrogen bonding patterns involving phenolic protons and solvent molecules are also present in both compounds.

Keywords: Calix[4]resorcinarene; Caffeine; Hydrogen bonds; Supramolecular assembly

INTRODUCTION

Due to the presence of eight hydroxyl groups on their upper rim, *C*-alkylcalix[4]resorcinarenes, also termed octahydroxy[1^4]metacyclophanes (Scheme 1) are molecules with a high potential as multiple hydrogen bond donors. In the general case, four hydroxyl protons form intramolecular hydrogen bonds while the four remaining ones are involved in intermolecular bonding. This property has recently been used in the building by self-assembling processes of multi-component host frameworks with interesting recognition properties. For example, multi-component calixarenes result from the enlargement of the cavity by hydrogen-bonded pyridine derivatives [1,2]. *C*-methylcalix[4]resorcinarene has also been shown to crystallize with water as a hexamer defining a large spherical inner cavity [3] and with propan-2-ol,

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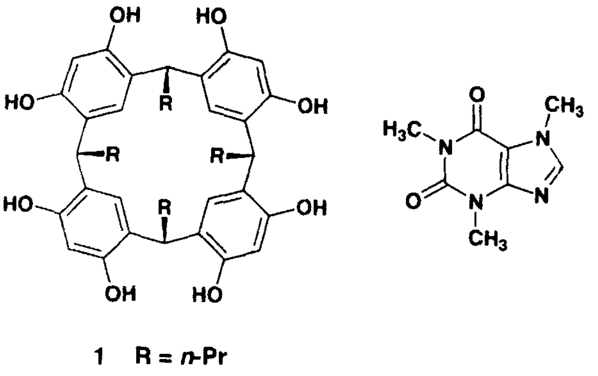

SCHEME 1 C-alkylcalix[4]resorcinarene and caffeine molecules.

as a dimeric carcerand-like dimer [4]. Hydrogen bonding with anions such as sulfate [5] or nitrate [6], leading to the formation of dimers or infinite chains, has also been reported. Apart from their use in the building of such assemblies, the hydrogen bond donor abilities of these compounds, together with the presence of four aromatic rings, can be used for complexing organic molecules. A particularly interesting case is that of cation complexation by multiple cation-π interactions such as those put in evidence in the case of various ammonium derivatives [7] or of the neurotransmitter acetylcholine trimethylammonium ion [8]. The caffeine molecule (3,7-dihydro-1,3,7-trimethyl-1H-purine-2,6-dione or 1,3,7-trimethylxanthine, represented on Scheme 1), which was used as a guest in the present work, is an alkaloid known to form complexes with a range of phenols and natural polyphenols [9]. Some of us reported earlier that it also forms host-guest complexes with resorcinarenes possessing alkyl chains of variable lengths on the methylene bridges, in aqueous methanol [10]. An infra-red spectroscopy investigation suggested that the complexation occurs *via* hydrogen bonding interactions with one of the carbonyl oxygen atoms of caffeine, while ^{1}H NMR indicated that the five-membered ring of the guest is included in the resorcinarene cavity. Some indications relative to the importance of water molecules in complexation were also derived from the data. We report herein the crystal structures of both C-(*n*-propyl)calix[4]resorcinarene as a solvate (**2**) and its 1 : 1 caffeine complex (**3**).

RESULTS AND DISCUSSION

The crystal structure of C-(*n*-propyl)calix[4]resorcinarene **1** in its solvated form **1** · CH_3CN · H_2O (**2**) presents the usual bowl shape with the four propyl groups assuming a nearly axial position, similar to that previously observed in the cases of the C-methyl and C-(*n*-butyl) derivatives [11]. The asymmetric unit in **2** comprises half a resorcinarene molecule, an acetonitrile molecule located along the binary axis which lies at the centre of the resorcinarene and two water molecules located on the $\bar{4}$ axis. Whereas the bowl shape in the C-methyl derivative is somewhat distorted, as in its nitrate complex [6], it appears more regular in **2** and in the C-(*n*-butyl) derivative. Four intramolecular hydrogen bonds are connecting the four units (Tab. I), which leads to a pseudo-*C2v* symmetry. The torsion angles ϕ and χ (as defined by Ugozzoli and Andreetti [12]), which characterize the conformation, are nearly equal for the two sets of rings (Tab. I). The dihedral angles between the two aromatic rings and the plane defined by the four methylene linkages are also equal, with values of 53.5 and 53.1° (to be compared to a mean value of 53.4° in the C-(*n*-butyl) derivative). If the hydrogen atoms are disregarded, the macrocycle adopts a pseudo-*C4v* symmetry.

In the crystal packing, the resorcinarene molecules are stacked in columns directed along the **c** axis, in a head-to-tail fashion. The molecules of acetonitrile are located between the resorcinarene molecules, on the column axis, with the nitrogen atom directed towards the lower rim of a resorcinarene [distances with the terminal carbon atoms of the *n*-propyl chains: 3.989(7) and 3.970(8) Å]. This arrangement is analogous to that observed in the 4,4′-bipyridine adduct of C-methylcalix[4]resorcinarene [1], but

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TABLE I Selected distances (Å) and torsion angles (°). Symmetry codes identical to those in the figures

Hydrogen bonds					
2					
O1···O4A	2.707(6)	H···O4A	1.643	O1—H···O4A	165.1
O2···O3	2.699(5)	H···O3	1.899	O2—H···O3	147.4
O3···O6	2.795(4)	H···O6	1.688	O3—H···O6	155.2
O4···O2C	2.712(2)	H···O2	1.731	O4—H···O2B	163.9
O5···O1*	2.772(4)				
3					
O1···O11	2.660(4)	H···O11	1.820	O1—H···O11	176.2
O2···O3	2.753(4)	H···O3	1.920	O2—H···O3	157.4
O3···O10	2.688(3)	H···O10	1.749	O3—H···O10	173.2
O4···O5	2.720(5)	H···O5	1.895	O4—H···O5	151.8
O5···O8A	2.944(4)	H···O8A	2.047	O5—H···O8A	167.5
O6···O7	2.793(4)	H···O7	1.938	O6—H···O7	157.8
O7···O11B	2.732(4)	H···O11B	1.704	O7—H···O11B	150.4
O8···N3C	2.771(4)	H···N3C	1.807	O8—H···N3C	170.5
O11···O13*	2.774(7)				
O12···O4*	2.712(8)				
O13···O9D*	2.847(6)				

	Torsion angles			
	2		**3**	
Rings	ϕ	χ	ϕ	χ
1–2	89.6(7)	−91.3(7)	−74.8(4)	101.9(4)
2–3	88.6(7)	−91.9(7)	−100.4(4)	79.5(4)
3–4			−75.6(4)	107.5(4)
4–1			−110.9(3)	72.9(4)

*H atoms of solvent oxygen atoms not localized.

the acetonitrile as a whole is nearest to the lower rim in **2** whereas it was nearest to the upper rim in the former compound: the interactions between the nitrogen atom and the alkyl chains in **2** seem to overcome the $CH_3\cdots\pi$ interactions. It may seem surprising that the nitrogen atom, and not the methyl end of acetonitrile, is nearest to the alkyl chains; however, a comparable situation has been reported in the case of the acetylcholine complex of the C-ethyl derivative [8], in which the carboxylic oxygen atom of the guest is closer to the chains than its methyl group [O···C distances in the range 3.68(3) to 3.83(3) Å]. In the C-(*n*-butyl) derivative also, the terminal carbon atoms of the chains are closer to the oxygen atom of an acetone molecule than to its methyl groups [O···C distances in the range 3.56 to 3.80 Å] [11]. Intermolecular hydrogen bonds between hydroxyl groups and the two water molecules located on special positions (each of them bonded to four equivalent hydroxyl groups) and between hydroxyl groups pertaining to neighbouring resorcinarene molecules are connecting the columns of resorcinarene molecules, giving rise to an infinite tridimensional network. Due to the symmetry requirements, the water hydrogen atoms involved in these bonds must be disordered.

The asymmetric unit in the structure of the caffeine complex **3** comprises one resorcinarene, one caffeine, one disordered and badly resolved methanol and one water molecules. The resorcinarene molecule assumes the same bowl shape as in **2**; however, one of the four intramolecular

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hydrogen bonds [between O(1) and O(8)] is missing (Fig. 2). The four resorcinol units are nevertheless interconnected, which imparts its rigidity to the macrocycle. The four aromatic rings are not equally tilted with respect to the pseudo-*C*2 axis of **1**, as indicated by the dihedral angles they make with the mean plane defined by the four methylenic carbon atoms, which are 70.9, 43.2, 66.2 and 35.8°. The two most 'vertical' and opposite aromatic rings correspond to two hydroxyl protons directed towards the nearest oxygen atom on the neighbouring aromatic ring, whereas the two other rings, closer to the mean plane, possess only one such proton, the three other ones being directed outwards to make intermolecular hydrogen bonds. The overall shape is close to that observed in the triethylammonium nitrate complex of C-methylcalix[4]-resorcinarene [6], in spite of the differences in the hydrogen bonds pattern.

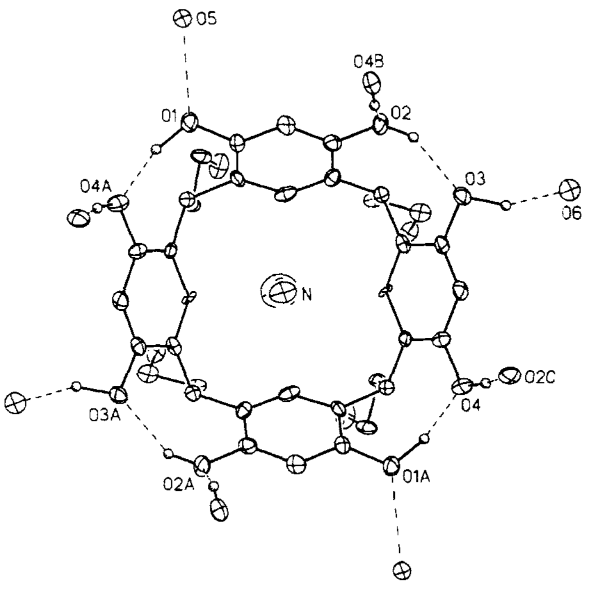

FIGURE 1 View of the molecular unit in **2**. Phenolic protons represented as small spheres of arbitrary radii, other hydrogen atoms omitted for clarity. Hydrogen bonds in dashed lines. Symmetry codes: A = 1 − *x*, −*y*, *z*; B = 1 − *y*, *x*, −*z*; C = *y*, 1 − *x*, −*z*. Ellipsoids drawn at the 50% probability level.

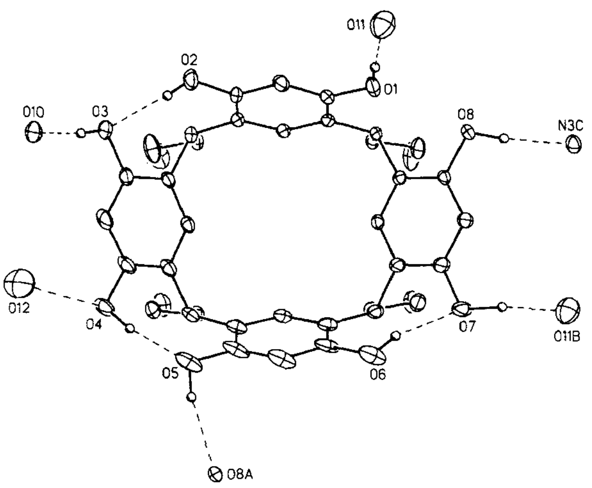

FIGURE 2 View of the resorcinarene unit in **3**. Phenolic protons represented as small spheres of arbitrary radii, other hydrogen atoms omitted for clarity. Hydrogen bonds in dashed lines. Symmetry codes: A = *x* − 1, *y*, *z*; B = 1 − *x*, 2 − *y*, 1 − *z*; C = 1 + *x*, *y* − 1, *z*; D = 1 − *x*, 3 − *y*, 1 − *z*. Ellipsoids drawn at the 50% probability level.

The caffeine molecule is hydrogen bonded to a hydroxyl group of **1** [O(3)] by one of its carbonyl oxygen atoms [O(10)] (Tab. I). The occurrence of such a hydrogen bond was previously suggested by infra-red spectroscopy results [10]. However, those results indicated a bond involving the other carbonyl group [O(9) in the present study], which appears instead to be hydrogen bonded to a water molecule [O(13)]. Another hydrogen bond links the nitrogen atom N(3) and the oxygen atom O(8) from another molecule of **1**. As evidenced on Figure 3, the caffeine molecules, with their mean planes nearly parallel to each other, are located between two head-to-head resorcinarene planes. The methyl group of the five-membered ring of each caffeine molecule is included in the cavity of a resorcinarene pertaining to a different plane than the hydrogen bonded one. This is likely a result of interactions with the aromatic systems, as often observed. It ensues that the complexation of the caffeine molecule is the result of both multiple hydrogen bonding and $CH_3 \cdots \pi$ interactions involving three different resorcinarene molecules. Other hydrogen bonds contribute to this arrangement. The water molecule [O(13)] which

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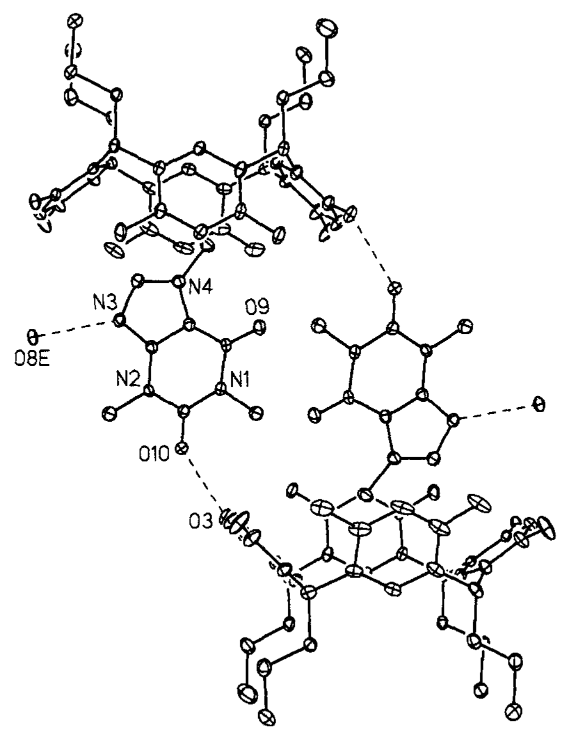

FIGURE 3 View showing the arrangement of **1** and caffeine molecules in **3**. Hydrogen atoms and solvent molecules omitted for clarity. Hydrogen bonds in dashed lines. Intramolecular hydrogen bonds are omitted. Symmetry code: E = 1 − *x*, −*y*, 1 − *z*. Ellipsoids drawn at the 30% probability level.

is bonded to a carbonyl group of the caffeine molecule is also bonded to one of the positions of the oxygen atom of the methanol molecule [O(11)]. As indicated previously, the oxygen atom of this methanol molecule is disordered over four positions, some of which [O(11), O(12)] are likely involved in hydrogen-bonds with the resorcinarene oxygen atoms O(1), O(4) and O(7). The crystal packing consists of bilayers of resorcinarene molecules facing each other by their alkyl chains separated by layers of caffeine and solvent molecules, all of them parallel to the **ab** plane. The cohesion inside the bilayers arises mainly from Van der Waals forces while the two different kinds of layers are linked by hydrogen bonds and $CH_3 \cdots \pi$ interactions. It may be noticed that the *n*-propyl substituents are not directly involved in caffeine bonding (complexation has also been demonstrated in solution for ethyl and *n*-nonyl derivatives [10]).

The structure of **3** confirms the results of the previous solution experiments. Apart from the role of both hydrogen bonding and $CH_3 \cdots \pi$ interactions in complexation, it also evidences the importance of water molecules which had been inferred from considerations about resorcinarene solubility (low in pure methanol or water, high in wet methanol) and likely formation of hydrates of both host and guest [10].

EXPERIMENTAL

Synthesis

C-(*n*-propyl)calix[4]resorcinarene (**1**) was prepared as described in the literature [11]. Recrystallization from acetonitrile gave colourless single-crystals of the solvate **2** suitable for X-ray crystallography.

Preparation of the inclusion complex **3**. Resorcinarene **1** (131 mg, 0.2 mmol) and caffeine (39 mg, 0.2 mmol) were dissolved in hot methanol (5 ml). The solution was allowed to stand at room temperature for two days. The crystalline material (128 mg) was collected by suction and yielded colourless single-crystals suitable for X-ray crystallography. The ^{1}H NMR analysis of the sample showed the ratio of **1** : caffeine : methanol to be 1 : 1 : 1. ^{1}H NMR (acetone-d_6, 30°C) δ 0.934 (t, 12H, CH_3), 1.303 (sex, 8H, CH_2), 2.268 (q, 8H, CH_2), 3.111 (q, 1H, CH_3*OH*, *J* 4.9 Hz), 3.271 (s, 3H, N(1)—CH_3), 3.301 (d, 3H, *C*H_3OH), *J* 4.9 Hz), 3.463 (s, 3H, N(2)—CH_3), 3.962 (s, 3H, N(4)—CH_3), 4.316 (t, 4H, bridge CH), 6.223 (s, 4H, intraannular ArH), 7.546 (s, 4H, extraannular ArH), 7.790 (s, 1H, C(8)—H), 8.455 (s, 8H, OH). The sample dried at 80°C for 8 hours under 1.3 × 10^2 Pa was subjected to elemental analysis. Calc. for $C_{40}H_{48}O_8 \cdot C_8H_{10}O_2N_4 \cdot 1/2H_2O$: C, 67.04; H, 6.92; N, 6.52%. Found: C, 67.10; H, 6.85; N, 6.73%.

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^{1}H NMR spectra at 270 MHz were recorded on a JEOL JNM GX-270 spectrometer. Elemental analyses were performed at the Microanalysis Center of Kyoto University.

Crystal Data

1 · $CH_3CN \cdot H_2O$ (**2**), $C_{42}H_{53}O_9N_1$, $M = 715.85$; tetragonal, space group $P\bar{4}$, $a = 14.3645(9)$, $c = 9.3344(8)$ Å; $V = 1926(2)$ Å^3; $Z = 2$; $D_x = 1.234$ g cm^{-3}; $\mu = 0.086$ mm^{-1}; F(000) = 768; crystal size 0.50 × 0.40 × 0.35 mm; $T = 100(2)$ K.

1 · $C_8H_{10}N_4O_2 \cdot CH_3OH \cdot H_2O$ (**3**), $C_{49}H_{64}O_{12}N_4$, $M = 901.04$; triclinic, space group $P\bar{1}$, $a = 11.2892(4)$, $b = 13.0367(8)$, $c = 16.9700(11)$ Å, $\alpha = 82.902(2)$, $\beta = 79.713(3)$, $\gamma = 88.053(2)°$, $V = 2438(2)$ Å^3 $Z = 2$; $D_x = 1.227$ g cm^{-3}; $\mu = 0.088$ mm^{-1}; $F(000) = 964$; crystal size 0.25 × 0.25 × 0.25 mm; $T = 150(2)$ K.

Data Collection, Structure Determination and Refinement

The diffraction experiments were performed with a Nonius Kappa-CCD area detector diffractometer using graphite monochromated MoK_α radiation (0.71073 Å). The crystals were introduced in Lindemann glass capillaries. The lattice parameters were determined from ten images recorded with 1° ϕ-scans and later refined on all data. A 180° ϕ -range was scanned with 2° steps during data recording. The crystal-to-detector distance was fixed at 33 and 28 mm for **2** and **3**, respectively. The data were processed with the HKL package [13]. No absorption correction was done. The structures were solved by direct methods with SHELXS-86 [14] and subsequent Fourier-difference synthesis and refined by full-matrix least-squares on F^2 with SHELXL-93 [15]. All non-hydrogen atoms were refined anisotropically. One terminal carbon atom of a propyl chain in **3** was found disordered over two positions, with occupation factors refined to 0.69 and 0.31. Based on ^{1}H NMR results, the amount of methanol in **3** was assumed to be of one molecule *per* macrocycle. This methanol molecule was found disordered over two positions, each of these positions having in its turn two alternative positions for the oxygen atom. Due to the bad resolution of these positions, the occupation factors have not been refined. The phenolic protons were found on the difference-Fourier maps and introduced as riding atoms with a displacement parameter equal to 1.2 times that of the parent oxygen atom. All other hydrogen atoms, unless those of water and methanol molecules, were introduced at calculated positions as riding atoms with a displacement parameter equal to 1.2 (CH, CH_2) or 1.5 (CH_3) times that of the attached carbon atom. Analytical scattering factors for neutral atoms were corrected for the anomalous dispersion terms $\Delta f'$ and $\Delta f''$. The numbers of total, unique and 'observed' [$I > 2\sigma(I)$] reflections and the number of refined parameters were 11620, 3406, 2309, 236 for **2** and 18597, 6393, 4885, 641 for **3**. The R_{int} factors were 0.032 and 0.046 for **2** and **3**, respectively. The final R and S values were $R_1 = 0.047$, $wR_2 = 0.120$, $S = 1.049$ for **2** and $R_1 = 0.067$, $wR_2 = 0.164$, $S = 1.064$ for **3** ($R_1 = \Sigma||F_o| - |F_c|| / \Sigma|F_o|$, calculated on 'observed' reflections, $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/[\Sigma w F_o^4]\}^{1/2}$ with $w = [\sigma^2(F_o^2) + (xP)^2 + yP]^{-1}$ where $P = (F_o^2 + 2F_c^2)/3$ and x and y are refined values and $S = \{\Sigma[w(F_o^2 - F_c^2)^2]/(n - p)\}^{1/2}$ where n and p are the number of reflections and the number of parameters refined respectively). The maximum residual densities were 0.36 and 0.48 eÅ^{-3} for **2** and **3**, respectively. The drawings were done with SHELXTL [16]. All calculations were performed on a Silicon Graphics R5000 workstation.

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