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The 'boat' Conformation of a Resorcin[4]arene Self-assembles as a 'T-shaped' Building Block in the Solid State to Form a Linear 1D Hydrogen-bonded Array

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Co-crystallization of *C*-methylcalix[4]resorcinarene 1 with 4-benzylpyridine (4-bzylpy) results in the formation of a linear 1D hydrogen-bonded array, 1·4(4-bzylpy) 2, in which the boat conformation of 1, in the form of an eightfold hydrogen bond donor, serves as a 'T-shaped' building block in the solid state. Crystal data for 2: triclinic, space group $P\bar{1}$, a=14.992(1), b=16.256(1), c=16.365(1)Å, α=108.065(1), β=96.140(1), γ=116.260(1)°, U=3258.1(3)Å^3, D_c= 1.25 g cm^{-3}, Mo-Kα radiation (λ=0.71070 Å) for Z=2. Least-squares refinement based on 6045 reflections with $I_{net} > 2.0\sigma(I_{net})$ (out of 8151 unique reflections) led to a final value of R = 0.048.

Keywords: Calixarene; Resorcinarene; Crystal engineering

Resorcin[4]arenes [1] (*e.g.*, *C*-methylcalix[4]resorcinarene **1**) are a class of π-rich cyclic tetramers which, owing to their ability to adopt a bowl-shaped conformation, have been exploited as building blocks for the design of host molecules that serve as molecular receptors in solution [2] and the solid state [3]. Upper [2–5] and lower [6] rim derivatization of resorcin[4]arenes, through the making and breaking of covalent bonds, can be readily achieved and often leads to receptors with cavities deeper than the parent host molecule.

In such a context, we have recently shown that it is possible to deepen the bowl-shaped conformation of **1** supramolecularly by utilizing pyridine [7], and its derivatives [8], as hydrogen bond extender units in the solid state (Scheme 1). Specifically, this approach exploits a resorcinol-based supramolecular synthon [9] for host design in which four pyridine units assemble along the upper rim of **1**, as two face-to-face stacked dimers, to form four O—H···N hydrogen bonds which, in turn, gives rise to a discrete, six-component, host-guest complex, **1**·4 (pyridine)·guest (pyridine = pyridine, 4-picoline, 4,10-phenanthroline; guest = pyridine, MeNO$_2$, MeCN) [7,8].

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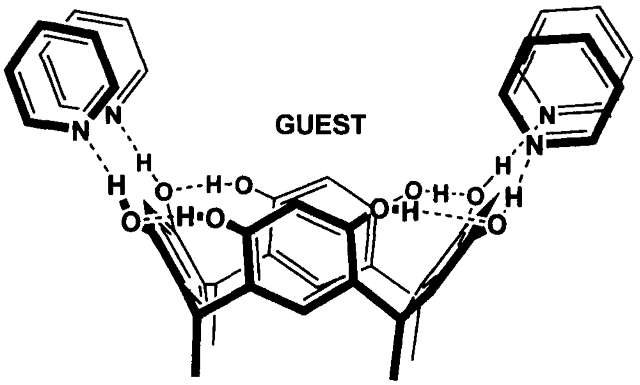


1·4(pyridine)·guest

SCHEME 1

With the realization that these *multi*-component host-guest systems may be designed using rigid extenders achieved, we now focus our attention on the use of flexible pyridines for their design. Along these lines, during studies aimed at determining the ability of 4-benzylpyridine (4-bzylpyr) to elaborate the cavity of **1**, we have discovered the ability of the 'boat' conformation of **1** [4], in **1** · 4(4-bzylpy) **2**, to self-assemble in the solid state to form a hitherto unseen linear one-dimensional (1D) hydrogen bonded array (Scheme 2). Whereas such 'T-shaped' building blocks, as either single or multiple components, have been recently exploited for the construction of 2D transition-metal-based coordination polymers [10–14] and guanidium-based host lattices [15], respectively, the ability of a supramolecular host such as **1** to serve a similar structural role is, to our knowledge, unprecedented. We now report the synthesis and structure behavior of **2**.

Addition of **1** (0.020 g) to a boiling aliquot of 4-bzylpy (2 mL) according to (1) yielded yellow crystals of **2** suitable for X-ray analysis by allowing the solution to cool and stand for a period of approximately three days. The formulation of **2** was confirmed by single-crystal X-ray diffraction and ^{1}H NMR spectroscopy [16].

$$\mathbf{1} + 4\text{-bzylpy (excess)} \rightarrow \mathbf{1} \cdot 4(4\text{-bzylpy})\ \mathbf{2} \tag{1}$$

A view of the X-ray crystal structure of **2** is shown in Figure 1. As in **1**·4(4-pyridine)·pyridine **3a** [7] and **1**·4(4-picoline)·$MeNO_2$**3b** [8], four pyridine units have assembled along the upper rim of **1** and participate in four O—H···N hydrogen bonds

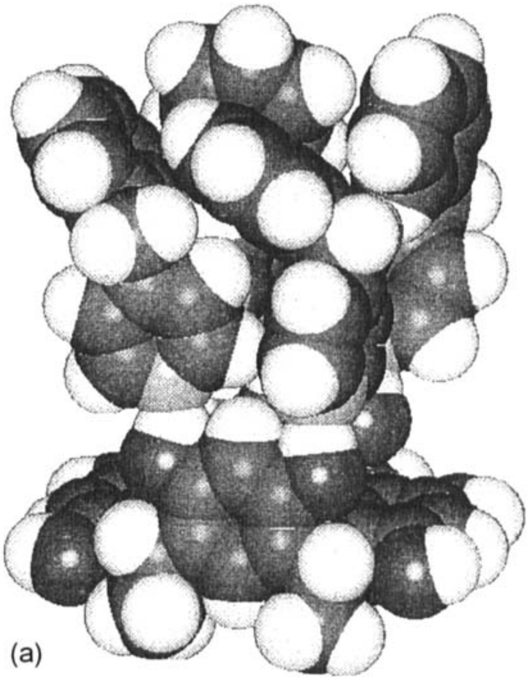
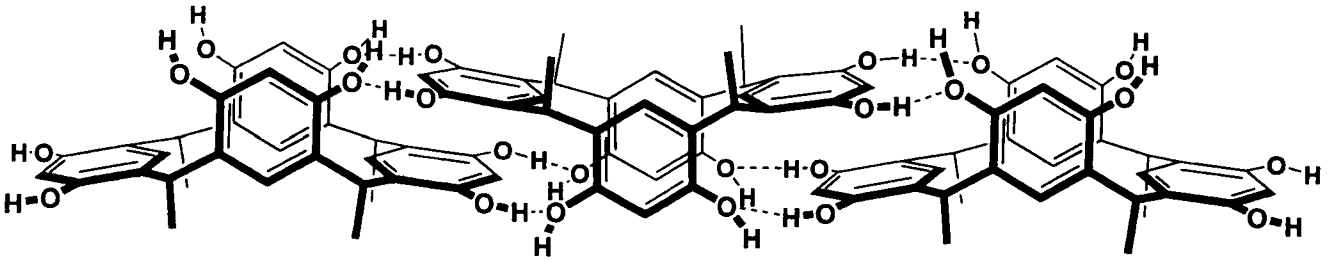


FIGURE 1 X-ray crystal structure of **2**: (a) space-filling view of the five-component complex and (b) the 1D hydrogen bonded array.



SCHEME 2

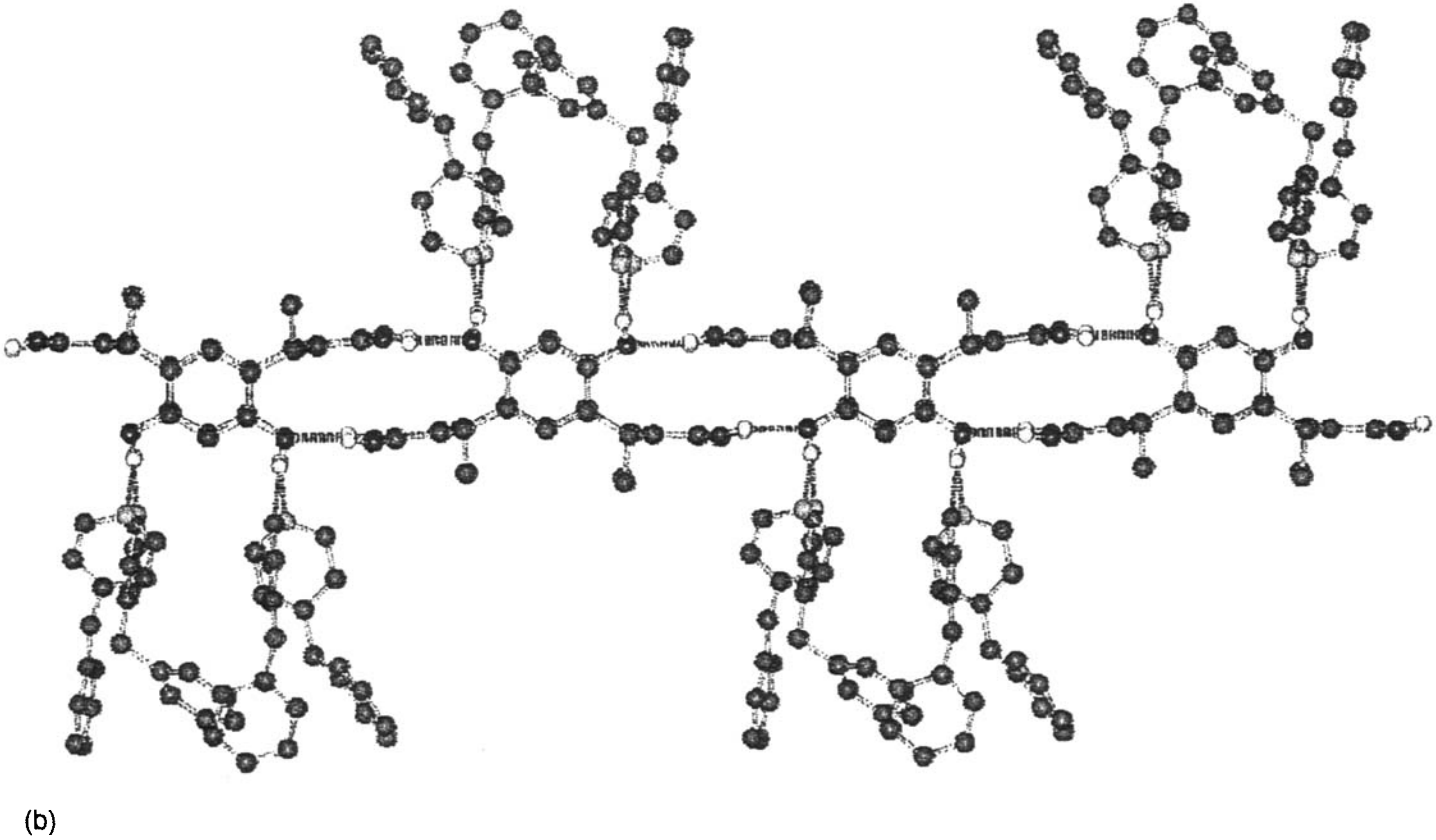


FIGURE 1 (Continued).

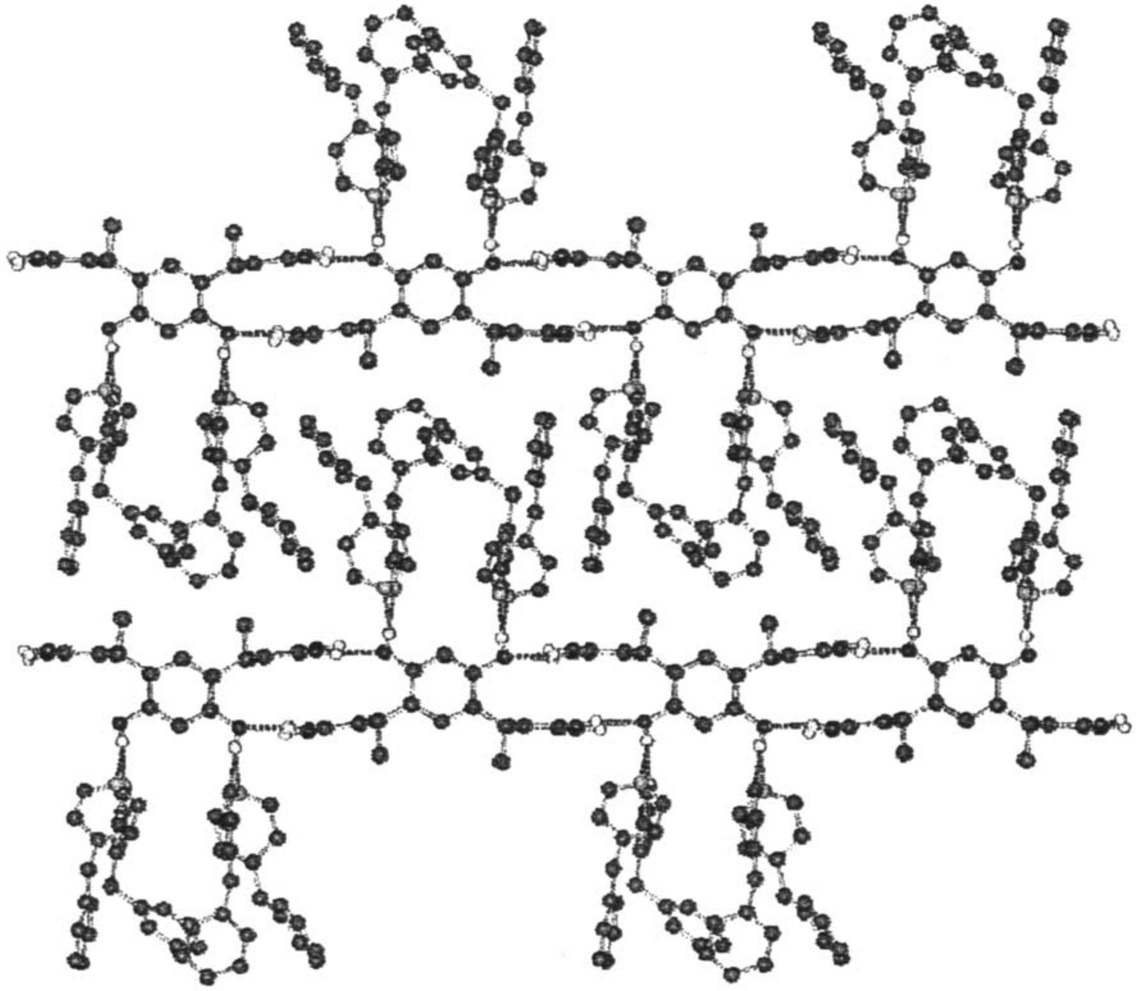


FIGURE 2 View of the X-ray crystal structure of **2** along the crystallographic *a*-axis displaying the self-inclusion of the 1D strands.

with two opposite resorcinol units of the macrocycle [O···N separations (Å): O(1)···N(1) 2.729(3), O(2)···N(2) 2.749(3), O(3)···N(3) 2.695(3), O(4)···N(4) 2.736(3)]. Unlike **3a** and **3b**, however, the pyridine units of **2** interact with **1** such that they form edge-to-face, rather than face-to-face, $\pi-\pi$ interactions [17] in which the benzyl groups of the ligand are effectively 'wrapped' around each other. As a consequence of these forces, the resorcinol units of **1** which interact with the pyridines have been 'pulled' together which, in turn, has induced the cavity of **1** to close. The remaining resorcinol moieties, which are co-planar and lie approximately perpendicular to the resorcinol units that participate in the O—H···N forces, are then observed to form four intermolecular O—H···O hydrogen bonds with two neighboring molecules of **1**, making **1** an overall eightfold hydrogen bond donor [O···O separations (Å): O(5)···O(3) 2.775(3), O(6)···O(1) 2.740(3), O(7)···O(2) 2.783(3), O(8)···O(4) 2.760(3)]. As a result, a 1D hydrogen bonded polymer, in which the 4-bzylpy moieties alternate along each side of the framework, has formed. To our knowledge, **2** represents the first case in which the boat conformation of **1** has been observed in the solid state [18].

A view along the crystallographic *a*-axis depicting the extended structure of **2** is shown in Figure 2. The 1D chains have assembled such that they self-include to form a 2D layered architecture. In this arrangement, adjacent polymers lie offset such that the 4-bzylpy units of one chain lie between the 4-bzylpy units of another in which the complementary shape of the strands has permitted interdigitation of neighboring networks [8].

The ability of **1**, in the form of a five-component complex, to self-assemble in the solid state as a 'T-shaped' building block is reminiscent of the ability of metal centers in a number of Cd [10], Ag [11, 12] and Co [13, 14] coordination polymers, as well as ions of guanidinium-based lattices [15], to serve a similar structural role in 1D ladder and 2D brick host frameworks. In such examples, the 'T-shaped' units represent nodes of a lattice and, correspondingly, corners of a host cavity. Indeed, although the components of **2** do not assemble to form any one of the four possible structure types based upon a 'T-shaped' moiety [11], such structures could, in principle, be generated from an assembly process involving **1** and a linear bipyridine (stoichiometry 1:2) [19]. Notably, such frameworks would constitute supramolecular isomers [14] of a recently reported wave-like structure involving **1** [7] owing, in part, to the ability of the host to adopt either the boat or bowl-shaped conformation.

In conclusion, we have revealed the ability of a resorcin[4]arene to self-assemble as a 'T-shaped' building block in the solid state. In addition to providing the first solid state characterization of the boat conformation of **1**, we recognize the rather unexpected ability of **1** to serve as a bridging 'T-shaped' unit in which case this modular approach to molecular self-assembly has provided structural information typically not accessible by conventional methods to elaborating the cavities of such receptor molecules (*i.e.*, covalent derivatization) [2–6].

Acknowledgements

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Supplementary Material Available

Crystallographic report, tables of positional and thermal parameters, bond lengths and angles (12 pages). Ordering information is given on any current masthead page.

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[16] Crystal data for **2**($O_8N_4C_{80}H_{76}$, f.w. = 1221.50 g mol^{-1}): triclinic, space group $P\bar{1}$, $a = 14.992(1)$, $b = 16.256(1)$, $c = 16.365(1)$, $\alpha = 108.065(1)$, $\beta = 96.140(1)$, $\gamma = 116.260(1)$, $U = 3258.1(3)$ Å^3, $D_c = 1.25$ g cm^{-3}, Mo-Kα radiation ($\lambda = 0.71070$ Å) for $Z = 2$. Least-squares refinement based on 6045 reflections with $I_{net} > 2.0\ \sigma\ (I_{net})$ (out of 8151 unique reflections) led to a final value of $R = 0.048$. Aromatic and hydroxy hydrogen atoms were placed by modelling the moieties as rigid groups with idealized geometry, maximizing the sum of the electron density at the calculated positions. Structure solution was accomplished using SHELXS-86 (Sheldrick, G. M., *Acta. Crystallogr., Sect. A*, (1990), **46**, 467) and refinement was conducted using SHELXL93 (Sheldrick, G. M., SHELXL93, University of Göttingen, Germany, 1993) locally implemented on a pentium-based IBM compatible computer. Structure refinements and production of figures were accomplished with the aide of RES2INS (Barbour, L. J. RES2INS, University of Missouri-Columbia, Missouri, USA, 1997).

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[18] Upper rim derivatized analogues of **1** in the boat conformation have been isolated in the solid state. Such molecules do not possess the ability to self-assemble *via* hydrogen bonds [4].

[19] A skewed brick framework has been isolated based upon **1**·(4,4′-bipyridine) (stoichiometry 1:1) (MacGillivray, L. R., Holman, K. T. and Atwood, J. L., submitted).