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A novel scoop-shaped conformation of *C*-methylcalix[4]resorcinarene in a bilayer structure†

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A new scoop-shaped conformation of *C*-methylcalix[4]resorcinarene has been identified; it is a hybrid of the previously observed crown- and flattened cone conformations.

Supramolecular host–guest chemistry based on calixarene and calixresorcinarene building blocks is continuing to develop rapidly.[1] Due to its numerous hydroxy groups and its unusual flexibility, the *C*-methylcalix[4]resorcinarene (CMCR) molecule serves as the primary building block in a wide variety of solids. In combination with bifunctional pillar molecules, such as 4,4′-bipyridine, *trans*-bis(4-pyridyl)ethylene and substituted terpyridine, a variety of supramolecular frameworks have been synthesized.[2–4]

Frequently water molecules are incorporated into the framework through hydrogen bonding with the CMCR molecules. In the 3D stepped network [CMCR·3bipy],[3b] for example, water molecules are interspersed between adjacent CMCR molecules, thus extending the size of cavity, and allowing inclusion of bulkier guest molecules. Similarly, MacGillivray and Atwood have reported a self-assembled CMCR hexamer, forming a snub cube, held together by eight water molecules.[5] In such cases water molecules play a significant role in the self-assembly process.

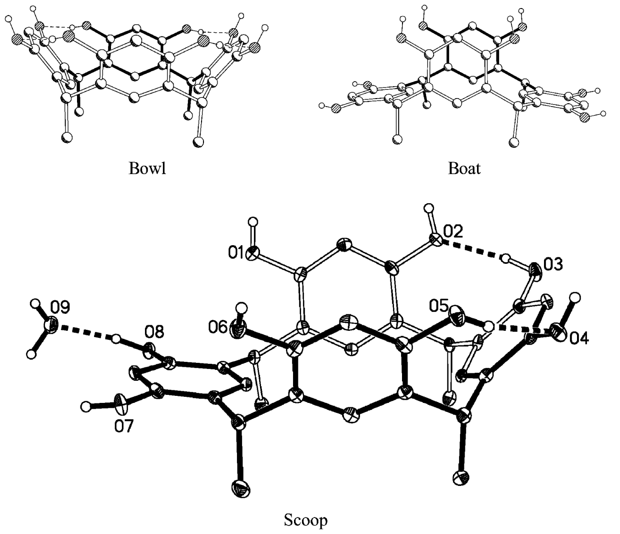
To further examine the role of water in framework formation, we have applied the hydrothermal method, used previously in our work on CMCR based supramolecular complexes,[3] to the CMCR–H_2O system, without the addition of potential guest molecules. A new phase, CMCR·H_2O **1**, in which the CMCR adopts a novel scoop-shaped conformation, is described here.

Compound **1** was obtained by recrystallizing CMCR from water in a sealed tube at 150 °C, followed by slow cooling over a three-day period.[6] Low temperature X-ray diffraction analysis shows the crystals contain one CMCR and one water molecule in an asymmetric unit of space group $P\bar{1}$.[7] Three of the CMCR aryl rings face upwards and are interlinked by intramolecular hydrogen bonds [O3···O2 = 2.732(2) Å, O3–H3···O2 = 159(3)°; O5···O4 = 2.742(2) Å, O5–H5···O4 = 168(3)°], whereas the flattened fourth ring is only linked through H-bonding to neighboring molecules. Unlike the crown-like conformation (C_{4v}) and the recently observed boat-like 'flattened cone' conformation (C_{2v}) in which the four intramolecular hydrogen bonds along the upper rim of CMCR are broken, the scoop-shaped conformation is a hybrid of the two, with a lower C_s symmetry (Fig. 1), which can be considered an intermediate in the interconversion of crown- and boat-shaped conformations.

Four types of conformations: crown, boat, chair and saddle, have been identified by solution NMR methods.[8] The crown- and boat-like conformations have been observed quite frequently in crystalline solids,[3d] while the chair conformation of CMCR was first obtained by hydrothermal synthesis.[3b] So far, the saddle conformation has not been observed by diffraction methods. To our knowledge, the scoop conformation has not been observed in any other member of the resorcin[*n*]arene family.

It may be noted that the architecture of CMCR-based solids strongly depends on the CMCR conformation. The crown-like conformation tends to form a wave-like polymer or a carcerand capsule;[2d,3c] the flattened cone conformation gives rise to the brick wall like framework;[3a,3d] while the chair conformation is found in a stepped network.[3c] The possibility of incorporating the scoop-like conformation into a novel framework including pillar molecules such as bipyridyl remains to be explored.

Two of the four intramolecular hydrogen bonds of the crown-like conformation are broken in the new conformation. One of the hydroxy groups of the flattened phenyl ring forms a donor hydrogen bond with the water molecule [O8···O9 = 2.638(2) Å, O8–H8···O9 = 172(3)°], while the water molecule is linked to the crown part by donation of an H-atom into another hydrogen bond [O9···O7a = 2.834(2) Å, O9–H10···O7a = 160(3)°; a = −x + 2, −y + 1, −z + 2]. Each CMCR molecule is linked to adjacent CMCRs by phenoxy O–H···O hydrogen bonds from the crown-like segment [O4···O8b = 2.737(2) Å, O4–H4···O8b = 163(3)°; b = x, y, z − 1] and from the flattened phenyl ring [O7···O3c = 2.676(2) Å, O7–H7···O3c = 170(3)°; c = x + 1, y, z + 1]. These hydrogen bonds run parallel to the crystallographic [001] and [101] directions respectively, thus connecting the molecules into a two-dimensional sheet (Fig. 2). The adjacent sheets are interlocked by aromatic π–π interactions between crown phenyl rings of adjacent molecules [center-to-center and interplanar distances being 4.234 and 3.334 Å, respectively], one phenyl ring fitting into the cavity of the molecule in the adjacent sheet (as illustrated in Figure S1 in supporting material†), and further linked through hydrogen bonds involving the water molecules [O9···O5d = 2.876(2) Å, O9–H9···O5d = 149(3)°; d = x, y, z + 1], producing a bilayer structure (Fig. 3). The hydrophilic 'inner' plane of the bilayer is comprised of the phenolic groups and water molecules, while



Bowl

Boat

Scoop

Fig. 1 The CMCR scoop conformation as observed in **1**.

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† Electronic supplementary information (ESI) available: Figure showing interlocked CMCR molecules between adjacent sheets. See http://www.rsc.org/suppdata/cc/b1/b110193p/

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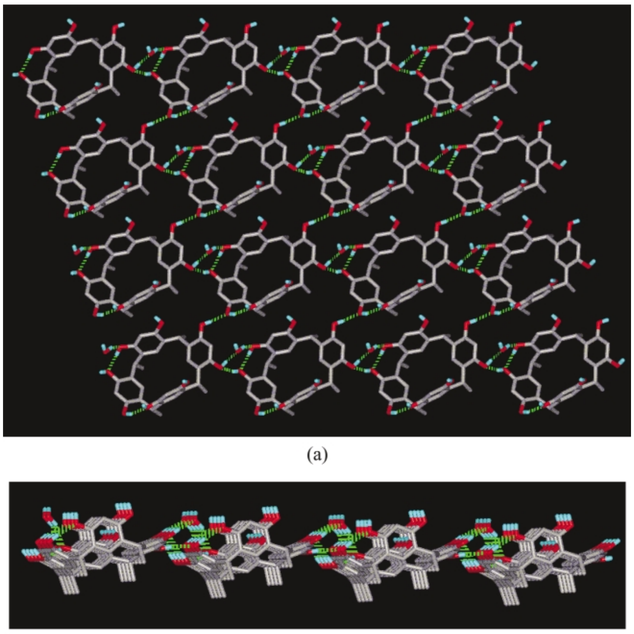
(a)

(b)

Fig. 2 Two-dimensional sheet formed by CMCR and water molecule in **1**; a) the top view, b) the side view.

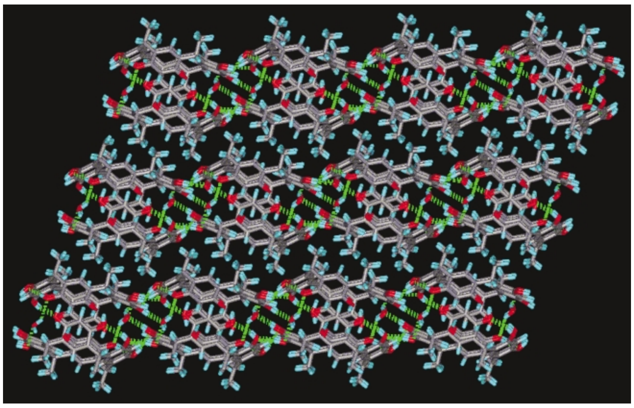

Fig. 3 Bilayer structure of **1**.

the external hydrophobic surface consists of the methyl groups on the bridging carbon atoms of CMCR.

The structure of **1** may be compared with those of CMCR·2H_2O (with CMCR in the chair conformation) and CMCR·3H_2O (boat conformation),[9] which form stepped sheet and brick-wall like frameworks, respectively. However, these two phases were obtained as byproducts in the synthesis of guest-containing solids. Although the starting CMCR–water ratios were the same as for **1**, towards the end of the hydrothermal synthesis process the CMCR–water ratio may have become quite low, as CMCR containing host–guest phases may have been formed earlier, leading to a depletion of the CMCR content of the reaction mixture.

In summary, a novel scoop-shaped conformation of CMCR has been synthesized by hydrothermal methods and identified by low-temperature X-ray crystallography. The result again demonstrates the remarkable versatility of the CMCR moiety and suggests that many CMCR-based solids remain to be discovered.

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6 Compound **1** was prepared as follows. An aqueous solution (4 ml) of *C*-methylcalix[4]resorcinarene (0.025 mmol) was sealed in a heavy walled Pyrex glass tube (*ca.* 6 ml). The mixture was maintained 150 °C for 1day in an oven, and subsequently cooled to rt at a rate of 20° day^{-1}. Colorless block crystals were collected. No other phases were found in the reaction mixture.

7 *Crystal data* for compound **1**: $C_{32}H_{34}O_9$: $Mr = 562.59$, triclinic, space group $P\bar{1}$, $a = 9.9289(4)$, $b = 12.4936(6)$, $c = 12.6547(7)$ Å, $\alpha = 104.290(2)$, $\beta = 106.652(2)$, $\gamma = 108.593(2)°$, $U = 1322.91(11)$ Å^3, $Z = 2$, $Dc = 1.412$ Mg m^{-3}, crystal size 0.18 × 0.10 × 0.08 mm^3, μ (Mo-Kα) = 0.103 mm^{-1}, $F(000) = 595$, $GoF = 0.903$. Among 21607 reflections, 7549 reflections are unique ($R_{\text{int}} = 0.1171$). The final $R1$ and $wR2$ are 0.0583 and 0.1050, respectively, for 506 parameters and 3856 reflections [$I > 2\sigma(I)$]. The data were collected on a Bruker SMART1000 CCD with Mo-Kα radiation ($\lambda = 0.71073$ Å) at 90(1) K. Reflections were reduced by the SAINT program. The structures were solved by direct methods and refined by a full matrix least squares technique based on F^2 using SHELXL 97 program. CCDC 173809. See http://www.rsc.org/suppdata/cc/b1/b110193p/ for crystallographic data in .cif or other format.

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