

Novel Hydrophilic Cages Based on Acetone Complex with Calix[4]arene Dimethoxycarboxylic Acid

Zhao-Yang Xie, Nai-Tao Hou, Yi-Zhou Zhu, Hai-Bin Song, and Jian-Yu Zheng*

State Key Laboratory and Institute of Elemento-Organic Chemistry, Nankai University, Tianjin 300071, P. R. China

(Received January 21, 2008; CL-080063; E-mail: jyzheng@nankai.edu.cn)

Novel cages based on acetone complex with dimeric units of calix[4]arene dimethoxycarboxylic acid extend along different directions to form polymeric cages, and the polymers interlock to form layer arrays, that in turn antiparallel pack in a bilayer architecture.

Calixarenes are widely used as blocks in crystal engineering for building up complex assemblies in the solid state¹ owing to their single bowl-shaped conformation. Various modifications at the rims have been attempted to design fragments for self-assembled dimeric capsules,² nanotubes,³ catenanes,⁴ and so on.⁵ *p*-Sulfonatocalix[*n*]arenes (*n* = 4, 5, 6, and 8), functionalized at the upper rim, have attracted more attention since they can construct not only conventional bilayer arrays⁶ but also several supramolecular architectures including molecule capsules,⁷ water channels,⁸ spheres,⁹ and tubular arrays.¹⁰ Other calixarene derivatives with different acidic arms at the lower rim give rise to architectures such as inclusion polymers¹¹ or nanotubes.¹² For example, calix[4]arene dihydroxyphosphonic acids can also generate different solid-state modes such as aqua-channels¹² or cages¹³ in the presence of different guests. Recently, O,O'-dicarboxymethylcalix[4]arene have been studied¹⁴ due to multi-carboxylic functions, providing the possibility to form hydrogen-bonding dimers.¹⁵ Here, we demonstrate the crystal structure of O,O'-dicarboxymethylcalix[4]arene **1** complex with acetones. Molecule **1** formed hydrophilic cages with a cyclic hydrogen-bonding system assisted by acetones.

Calix[4]arene **1** (Figure 1) was synthesized according to a reported method.¹⁶ Crystals of $\mathbf{1}_2 \cdot (\text{CH}_3\text{COCH}_3)_2$ were grown from acetone by slow evaporation at room temperature.

Calix[4]arenes **1** maintain the asymmetric cone conformation through intramolecular hydrogen bonds (the bond lengths are 1.959 and 1.906 Å), which exist between the unsubstituted phenolic hydroxy groups and the oxygen atoms coupled to two carboxylic acid arms. The cone angles formed by opposite aromatic cycles of the calixarene are 77.2 and 34.1°, respectively.

As show in Figure 2, a cage is formed by complex **1** with acetones. Unlike the classical dimeric motif that favors interdigitation of aromatic crowns,^{12,13} two units of **1** take a tail-to-tail self-assembled dimeric structure through the intermolecular

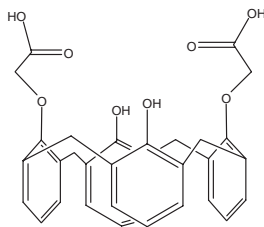


Figure 1. Schematic structure of **1**.

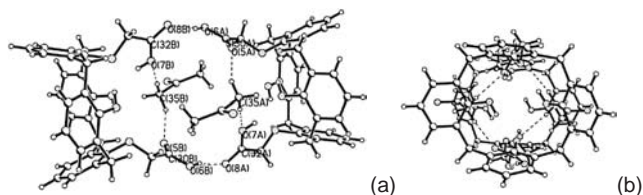


Figure 2. View of the cage $\mathbf{1}_2 \cdot (\text{CH}_3\text{COCH}_3)_2$ (a) along the *a* axis; (b) along the *c* axis (the cyclic array of hydrogen bonds was clearly found). Atoms of disordered acetones have been omitted for clarity.

hydrogen bonds of the two pendant OCH_2COOH groups (the distance and angle are $\text{O8A} \cdots \text{H6B} - \text{O6B} = \text{O8B} \cdots \text{H6A} - \text{O6A} = 1.884 \text{ \AA}$, 163.8°).

A more intriguing feature has been found that acetones fix two arms to form a cage with the intermolecular hydrogen bonds (Figure 2). The distance and angle between CH atoms of acetone and O atoms of carboxyl acid groups are $\text{O7A} \cdots \text{H35C} - \text{C35A} = \text{O7B} \cdots \text{H35F} - \text{C35B} = 2.459 \text{ \AA}$, 173.0° and $\text{O5A} \cdots \text{H35B} - \text{C35A} = \text{O5B} \cdots \text{H35E} - \text{C35B} = 2.162 \text{ \AA}$, 151.9° (Figure 2a). And along the *c* axis, we can clearly find a cyclic array assisted by hydrogen bonds of the two arms of **1** and acetone molecules (Figure 2b), which further form a hydrophilic cavity.

Interestingly, these cages extend along different directions to form different one-dimensional polymeric cages. They assemble infinitely along the crystallographic *b* axis to form equatorial polymeric cages through the aromatic ring T-shaped edge-to-face interactions of neighboring cages (Figure 3a). The centroid separation and dihedral angle of aromatic rings are 4.827 Å and 112.9° , the distance and dihedral angle of C–H \cdots centroid of aromatic ring are 2.994 Å and 80.1° . While along the *c* direction the aromatic ring heads of **1** are ready for the head-to-head parallel-displaced π interactions. The distance between two phenyl rings is 3.430 Å and the dihedral angle is 0.0° (Figure 4). Therefore, the spectacular structure of so-called axial polymeric cages is presented (Figure 3b).

As can be readily recognized from Figure 5, adjacent polymers weave a higher-order 2-D supramolecular layer spreading on the *bc* plane which is perpendicular to the plane of the page (see Supporting Information Figure S1).¹⁸ This suggests the hydrophobic midsections of adjacent molecules mutually engage in intermolecular π - π stacking interactions and T-shaped edge-to-face interactions.

Figure 5 shows the calixarenes in neighboring layers assemble antiparallel (see Supporting Information Figure S2). Thus, the layers extending perpendicular form the bilayer structures through van der Waals interactions. These bilayers are reminiscent of clays with clear hydrophilic and hydrophobic regions.

This overall packing mode is similar to the reported *para*-sulfonatocalix[4]arene systems, and the up-down arrangement

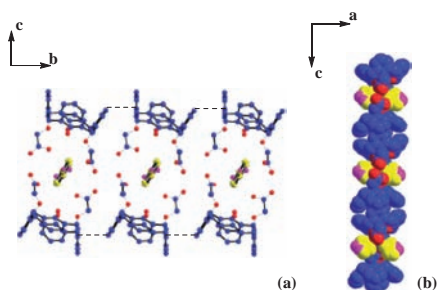


Figure 3. (a) View of the equatorial polymeric cages (the artificial dashed lines represent the mutually T-shaped edge-to-face interactions, C–H...centroid of aromatic ring are 2.994 Å and 80.1°); (b) Space-filling illustration of assembled axial polymer of $1_2 \cdot (\text{CH}_3\text{COCH}_3)_2$. All hydrogen atoms have been omitted for clarity. The carbons and oxygens of acetones colored in yellow and purple respectively.

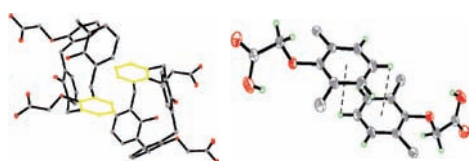


Figure 4. View of the mutually penetrating structure of **1**, the two artificial dashed lines represent the parallel-displaced π - π interactions of two aromatic rings colored in yellow (the distance between two phenyl rings is 3.430 Å and the dihedral angle is 0.0°, C–H...centroid of aromatic ring: 3.456 Å, 89.7°).

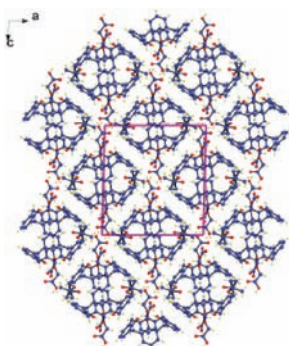


Figure 5. Overall packing diagram showing the multipolymer antiparallel aggregate of complex $1_2 \cdot (\text{CH}_3\text{COCH}_3)_2$, in which each layer extending perpendicular to the plane of the page, the cell edges colored in purple.

forms classical clay-like bilayer systems which show remarkable inclusion properties encompassing ionic guests and molecules.^{6,17} As an extension of the bilayer architecture, the up-up arrangement would lead to curved structures such as spheres⁹ and tubules¹⁰ under appropriate conditions. Our research provides that calixarene derivatives with carboxylic groups also can overcome their bilayer arrays through controlling conditions, resulting in the formation of spheroidal or tubular arrays. And recently, Coleman et al. reported that in water-methanol solution, three molecules of **1** formed an equilateral-trigonal geometry with hydrogen bonds and hydrophobic interactions, in turn, assembled into helical aquatubes, while not the bilayer structure.^{14a}

In summary, the solid-state structure of **1** with acetones shows intriguing features. A hydrophilic cavity is generated by hydroxy groups of calix[4]arenes and a cyclic hydrogen-bonding system assisted by carboxymethyl arms and acetones. These cages extend infinitely along the crystallographic *b* or *c* axis to form one-dimensional equatorial or axial polymeric cages, which weave a higher-order 2-D supramolecular layer in the *bc* plane, that in turn pack an antiparallel bilayer 3-D architecture. Endeavors to study the complex of **1** with another guest and the parallel (up-up) arrangement supramolecular architectures of this kind of compound under different conditions are currently in progress.

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- 18 Supporting Information is available electronically on the CSJ-Journal Web site, <http://www.csj.jp/journals/chem-lett/>: Synthesis of modified calixarene **1**, crystal details and CIF file for complex $1_2 \cdot (\text{CH}_3\text{COCH}_3)_2$.