Two Novel Self-Assemblies of the Calix[4]arene Derivatives and Their Structures

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Abstract

Two newly identified supramolecule structures arise from self-assembly of the Calix[4]arenes derivatives **1** and **2**: one ethyl ester of **1** (or **2**) enters into the cavity of another **1** (or **2**) forming a 1D long chain structure. The interaction force of the molecules and the crystallization energy might be an important driving force for forming the self-assembled calix[4]arene.

Supplementary Data relating to this article (atomic coordinates, hydrogen coordinates, isotropic displacement parameters, anisotropic displacement parameters, selected geometrical parameters and observed and calculated structure factors) are deposited in the British Library.

Introduction

There is currently a great deal of interest in utilizing non-covalent forces for the construction of self-assembly [1]. Assemblies of small molecules provide a means for exploring the intermolecule forces involved in molecular recognition and provide the information expressed when the suprastructure emerges. Calix[4]arenes have been proved to be a powerful building-platform for the construction of highly sophisticated host molecules, sensors, and larger molecular assemblies with a well-predefined structure [2]. The driving force of host–guest complexation involving electrostatic interactions, hydrogen bonding and the van der Waals interactions including CH-π interaction has received much attention [3]. Recently the behavior of hydrogen-bonded aggregates [4] and self-assembly of calix[4]arene [5] by coordination have been studied by many groups, but studies of calix[4]arene assembly *via* van der Waals interaction are few [6].

In the present contribution we report the structure characterization of two calix[4]arene derivatives showing a one-dimensional self-assembly chain.

Results and discussion

The ORTEP drawings of calix[4]arene derivatives **1** and **2** are shown in Figure 1. The calix[4]arene derivative **1** crystallizes in the triclinic system with space group P-1, while the derivative **2** is monoclinic with space group P2$_1$/n. The crystal structures of calix[4]arene derivatives **1** and **2** reveal

a pinched cone conformation. There are hydrogen bonds between hydroxy group and ethoxycarbonyl at the lower rim, which dominates the conformation of these molecules: in the derivative **1**: O(2)—H(2a)$\cdots$O(4), 2.010 Å; O(2)—H(2a)$\cdots$O(6), 2.794 Å; O(1)—H(1a)$\cdots$O(3), 2.027 Å; O(1)—H(1a)$\cdots$O(5), 2.754 Å; in the derivative **2**, O(2)—H$\cdots$O(1), 2.040 Å; O(2)—H$\cdots$O(5), 2.605 Å; O(4)—H$\cdots$O(3), 1.875 Å; O(4)—H$\cdots$O(6), 2.936 Å.

The angles between the plane of phenyl ring (A, B, C and D) and the least-squares plane (mean deviation from the best plane 0.1135) of four CH$_2$ moieties which links the phenyl ring are 135.5°, 108.5°, 135.6°, and 107.8° in the derivative **1**, 128.5°, 110.1°, 134.1° and 115.7° in the derivative **2**. The angles between two opposite phenyl rings A and C inclined toward the outside of the cavity are 91.1° in compound **1** and 97° in the derivative **2**, while the angles between phenyl rings B and D titled away from the calix[4]arene cavity are 36.3° and 45.8° in the derivatives **1** and **2**, respectively. Both angles are bigger in the derivative **2** than that in the derivative **1**. The reason is that two —NO$_2$ groups at the upper rim of the derivative **2** make the conformation of the derivative **2** different from the derivative **1**. The pinched cone conformation of the derivatives **1** and **2** leads to the distance (3.321 Å) between O(1) and O(2) shorter than that (4.634 Å) between O(3) and O(4) in the derivative **1** and the distance (3.489 Å) between O(2) and O(4) is shorter than that (4.432 Å) between O(1) and O(3) in the derivative **2** either. The C—C separations of C(17) and C(5); C(11) and C(23) are 9.162 Å and 7.104 Å respectively in the derivative **1** and 8.827 Å and 7.564 Å in the derivative **2**. The conformation adopted by the derivative **1** creates a little bit of larger cavity, which is able to accommodate a bigger mo-

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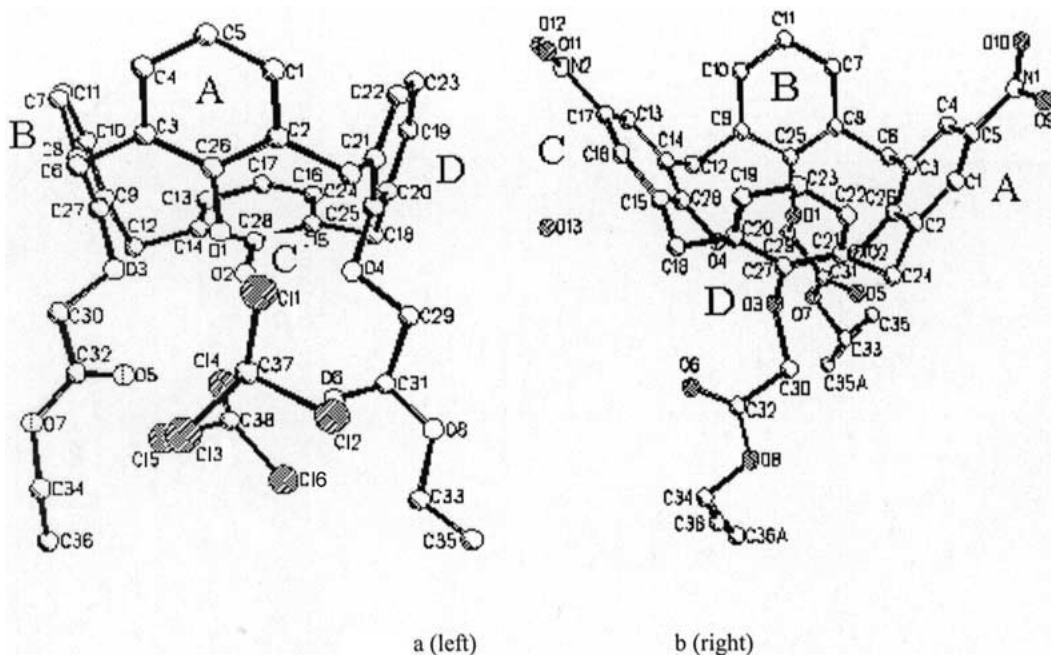* Author for correspondence. E-mail: Zhengxu@netra.nju.edu.cn

Figure 1. (a) Left: Crystal structure of calix[4]arene **1**. (b) Right: Crystal structure of calix[4]arene **2**.

lecule. One ethyl ester of the derivative **1** enters into the cavity of another derivative **1** to form a long chain supramolecule (Figure 2a). The distances between C(36) and the center of the phenyl rings (A, C, B and D) in the host derivative **1** are 3.54, 3.704, 3.895 and 4.324 Å, respectively. It means that the alkyl chain almost locates at the center of the calix[4]arene cavity. Considering the range of the molecules interaction (0.3–0.5 nm) [7] and the distances between the alkyl chain and the phenyl rings, we might deduce that the interaction force of molecules and the crystallization energy play an important role in the formation of the complex.

In the derivative **2**, the terminal carbon atoms (C(36) and C(35)) of ethoxyl groups at lower rim are disordered over two positions with occupancy factor 0.5. Figure 1b shows that the solvent water molecule is not included into the cavity, but locates at the place between derivative **2**. One ethyl ester of derivative **2** enters into the cavity of another derivative **2** to form a long chain supramolecule either, but it is quite different from derivative **1** that one of two ethyl esters of derivative **2** alternatively enters into the cavity of another derivative **2**. The distances of C(36) (C(36a)) to the center of the phenyl ring (A, C, B and D) in the host derivative **2** are 3.771, 3.575, 4.213 and 4.156 Å, respectively. Obviously, the alkyl chain almost locates at the center of the calix[4]arene cavity as well.

In conclusion, we report two crystal structures of the self-assembled calix[4]arene derivatives. The interaction force of molecules and the crystallization energy might be an important driving force for forming the self-assembled calix[4]arene derivatives.

Experimental

Synthesis

The derivatives **1** and **2** were prepared according to the literature procedures [8]. Colorless transparent single crystal of derivative **1** and pale yellow crystalline of derivative **2** suitable for X-ray diffraction studies were obtained by slow evaporation of the solution in $CHCl_3$/EtOH.

X-ray crystallography

Data were collected on a Siemens smart diffractometer equipped with CCD area detector. The structure was solved by direct methods and refined on F^2 by full-matrix least-squares methods using SHELXTL version 5.03 [9]. The positions of all remaining non-H atoms were obtained from successive Fourier syntheses. The positions of hydrogen atoms were calculated using idealized geometry except the hydrogen atoms of water, which were obtained from successive Fourier syntheses.

Crystal data for calix[4]arene derivative **1** (25,27-Bis[(ethoxycarbonyl)methoxy]-26,28-dihydroxycalix[4]-arene) (colorless, 293(2) K). $C_{36}H_{34}O_8 \cdot 2CHCl_3$, $M = 833.56$, triclinic, space group P-1, $a = 10.295(2)$ Å, $b = 10.334(2)$ Å, $c = 19.063(4)$ Å, $\alpha = 96.355(4)°$, $\beta = 101.511(4)°$, $\gamma = 97.069(4)°$, $V = 1953.0(8)$ Å^3, $D_c = 1.293$ mg cm^{-3}, $Z = 2$, μ(Mo-Kα) = 0.145 mm^{-1}, 8156 reflections were collected, of which 818 reflections with $I > 2\sigma(I)$, $R_1 = 0.1085$, $wR_2 = 0.3063$ and GOF = 1.049.

Crystal data for calix[4]arene derivative **2** (25,27-Bis[(ethoxycarbonyl)methoxy]-26,28-dihydroxy-5,17-dinitrocalix[4]arene) (pale yellow, 293(2) K). $C_{36}H_{36}N_2O_{12} \cdot H_2O$, $M = 706.34$, monoclinic, space group P2$_1$/n, $a = 10.4373(2)$ Å, $b = 15.748(2)$ Å,
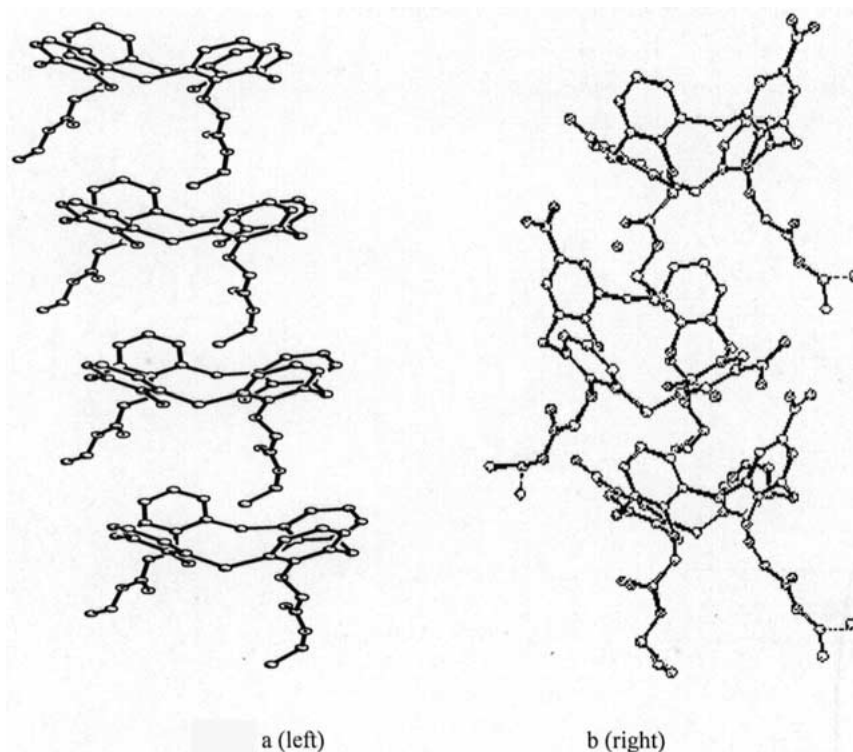
Figure 2. (a) Left: Columnar packing structure of crystal derivative **1**. (b) Right: Columnar packing structure of crystal derivative **2**.

$c = 21.064(2)$ Å, $\beta = 98.240(3)°$, $V = 3426.4(6)$ Å^3, $D_c = 1.335$ mg cm^{-1}, $Z = 6$, μ(Mo-Kα) $= 0.101$ mm^{-3}, 20987 reflections were collected, of which 1448 reflections with $I > 2\sigma(I)$, $R_1 = 0.0651$, $wR_2 = 0.1579$ and GOF = 0.830.

Acknowledgement

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