Pergamon

Tetrahedron Letters 40 (1999) 8883–8886

TETRAHEDRON
LETTERS

Self-assembly of cavitand tetracarboxylic acid: highly porous packing structure of one-dimensional hydrogen-bonded network

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Received 16 August 1999; revised 29 September 1999; accepted 1 October 1999

Abstract

When recrystallized from DMF and *p*-xylene, cavitand tetracarboxylic acid **1** self-assembles into a wave-ladder type of one-dimensional hydrogen-bonded network. The three-dimensional packing structure consists of huge chambers, each of which is filled with one molecule of *p*-xylene and five molecules of DMF. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: calixarenes; carboxylic acid derivatives; hydrogen bonding; X-ray crystal structure.

Calix[4]resorcinarenes and their cavitands are bowl-shaped macrocycles and have attracted considerable attention in host–guest and supramolecular chemistries as artificial receptors and building blocks for molecular containers.[1–3] Supramolecular approaches to self-assembly of molecular solids have proved to be reliable tools to realize a variety of hydrogen-bonded networks having large cavities and clathrates.[4–6] Macrocycles bearing multiple hydrogen bonding sites have been reported as potential candidates in order to prevent interpenetrations of porous networks.[7] However, the utility of cavitand family directed towards hydrogen-bonded polymeric networks has so far not been intensively studied.[8,9] Herein we report the one-dimensional hydrogen-bonded network in the solid state of calix[4]resorcinarene cavitand **1** having four carboxy groups at the upper rim, the packing structure of which affords huge chambers.

Cavitand tetracarboxylic acid **1**[10] has very low solubility in $CHCl_3$ due to self-aggregation. Slow diffusion of *p*-xylene into a solution of **1** in DMF gave single crystals composed of **1**:*p*-xylene:DMF=1:1:5 which were suitable for X-ray diffraction analysis.[11,12] The molecular structure of the adduct is shown in Fig. 1. Cavitand **1** has C_{2v} symmetry, and the dihedral angles between the carboxy groups and the aromatic rings are 67.8 and 77.7° probably due to the electronic repulsion between the oxygen atoms of carboxy and ether moieties. *p*-Xylene is accommodated in the macrocyclic cavity of **1** via CH···O and CH–π interactions,[4,13] where the distances between the aromatic carbon of *p*-xylene and the acid

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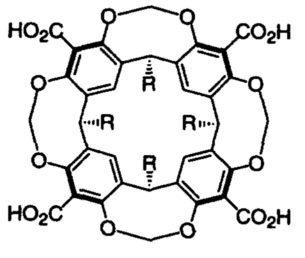
PII: S0040-4039(99)01903-6



1 R = (CH2)2Ph

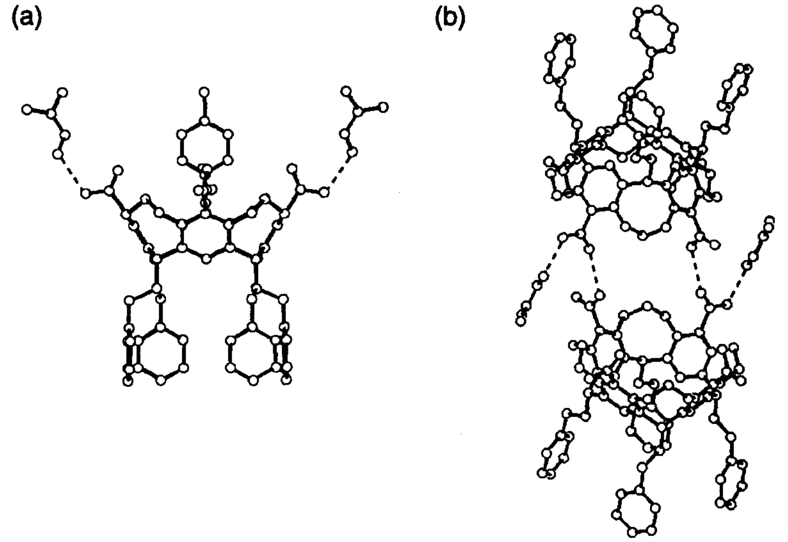


Figure 1. (a) X-Ray molecular structure of **1** with *p*-xylene and hydrogen-bonded DMF, and (b) hydrogen bonding motif of two molecules of **1** and DMF. Hydrogen-bonded interactions are shown as broken lines. Non-hydrogen-bonded DMF and all hydrogen atoms are omitted for clarity

carbonyl oxygen of **1** and between the methyl carbon of *p*-xylene and the center of resorcinol moiety of **1** are 3.36 and 3.65 Å, respectively. Two of five included DMF molecules hydrogen bond to alternate carboxy groups of **1**, where the O··· O distance is 2.53 Å. The other three DMF are highly disordered and are included in the void space of the crystal lattice (vide infra). The carboxy groups of **1** intermolecularly hydrogen bond to each other by a single hydrogen bonding motif as shown in Fig. 1b, where the O···O distance is 2.72 Å. Thus, neighboring molecules of **1** associate with each other via a two-point hydrogen bonding contact in a head-to-head staggered fashion.

As shown in Fig. 2, this hydrogen bonding pattern affords a wave-ladder type of one-dimensional hydrogen-bonded network of the cavitands (tape structure) parallel to the *c* axis so as to give deep grooves parallel to the *b* axis. Fig. 3 shows the three-dimensional packing arrangements of three molecular tape types 1, 2 and 3, i.e. (-a1-b1-a1-), (-a2-b2-a2-) and (-a3-b3-a3-), respectively. These tapes are parallel

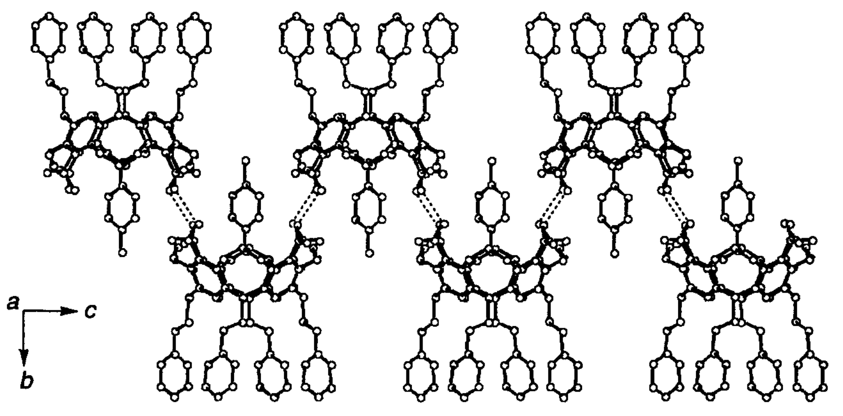


Figure 2. View of a one-dimensional hydrogen-bonded network (an individual tape) of **1** parallel to the *a* axis. Hydrogen-bonded interactions are shown as broken lines. DMF molecules are omitted for clarity

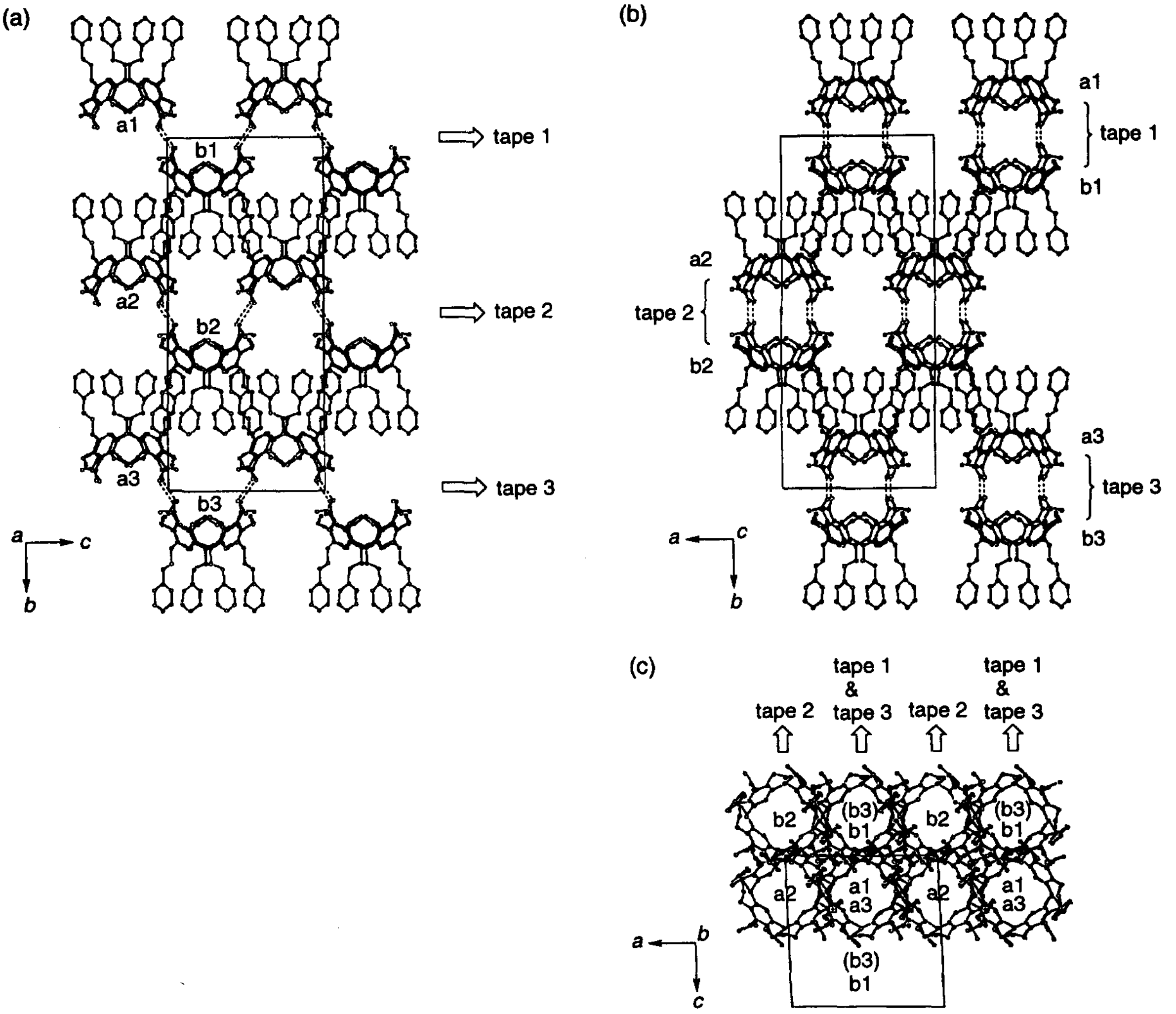


Figure 3. Packing diagrams of tapes of **1**: (a) front view parallel to the *a* axis, (b) side view parallel to the *c* axis, and (c) top view parallel to the *b* axis. Hydrogen-bonded interactions are shown as broken lines. All guests are omitted for clarity

to the *c* axis without any molecular translation (Fig. 3a). This generates channels of ca. 6.2×8.1 Å in cross-section running parallel to the *a* axis. A view down the *c* axis of the above arrangement shows the relative openness of the lattice (Fig. 3b). The tapes line up parallel to the *a* axis with a (tape center)-to-(tape center) distance of 15.50 Å. The tapes (-a1-b1-a1-) and (-a3-b3-a3-) line up parallel to the *bc* plane separated by a center-to-center distance of 35.99 Å. In contrast, with respect to tapes 1 and 3, the tapes 2 are translated by 7.75 and 18.00 Å along the *a* and *b* axes, respectively. This packing of the tape motifs generates channels of ca. 5.4×11.4 Å in cross-section running parallel to the *c* axis (Fig. 3b).

Hence, in three-dimension, the individual chambers present in the lattice are ca. 5.4×36.0×6.2 Å in size. A chamber has a box-like cavity formed by four $PhCH_2CH_2$- groups of a cavitand as its base (e.g. a3) and the macrocyclic cavity of another cavitand as its ceiling (e.g. a1), and has the side of a cavitand in the middle of two of its sides (e.g. a2 on the side parallel to the *bc* plane) and a b1 type molecule on each of the other two sides (e.g. parallel to the *ab* plane). Furthermore, these chambers are linked by a channel parallel to the *b* axis (Fig. 3c); and, the (a1-a3) and (b1-b3) type chambers, which are related by inversion, are linked by a wave-like passage parallel to the *c* axis. Each chamber is filled with one *p*-xylene, two hydrogen-bonded DMF, and three disordered non-hydrogen-bonded DMF. The packing coefficient and the pore size of cavitand **1** in the crystals are only 43% of the total volume of the unit cell and 0.66 mL g^{-1} with respect to the volume of empty space per gram of **1**, respectively.[5a]

In summary, we have demonstrated the utility of cavitand tetracarboxylic acid **1** for the formation of a wave-ladder type of one-dimensional hydrogen-bonded network, whose packing arrangement affords a very porous structure. Applications of **1** as building blocks to a coordination network and a multicomponent hydrogen-bonded molecular capsule are currently underway in our laboratory.

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