

A Rod-Shaped Guest Leads to Architectural Isomerism in a Multicomponent Crystalline Framework Based on a Resorcin[4]arene

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Received May 7, 2001; Revised Manuscript Received July 6, 2001

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ABSTRACT: Cocrystallization of *C*-methylcalix[4]resorcinarene **1** with 4,4'-bipyridine **2** in the presence of 4-bromobiphenyl (4-brbp) yields a molecular solid, of composition **3d**·(4-brbp), [where **3d** = **1**·2(**2**)], in which **1** assembles with **2** to form a one-dimensional hydrogen-bonded polymer **3d** that includes two copies of the biphenyl, within elliptical cavities of dimensions $\sim 11 \times 7 \times 6$ Å, as guests. The framework **3d** represents a third architectural isomer of three previously reported supramolecular isomers of the parent material **3**.

Architectural isomerism,^{1,2} a term that relates structures of two or more crystalline frameworks of identical composition and supramolecular connectivity yet of different topology, is emerging as a tool for the crystal engineering of host–guest solid-state architecture. Indeed, the variety of structures stemming from the ability of a set of molecular components to organize into isomeric forms^{1–3} has permitted such solids to be regarded as “soft-materials”,¹ compounds with building blocks that adapt to the size, shape, and functionality of targeted guest molecules. Guest template effects, similar to those encountered in zeolites,⁴ are largely responsible for directing assembly processes that lead to architectural isomerism and, correspondingly, continue to inspire the identification of guests, of increasing diversity, anticipated to induce formation of additional, unknown isomers of a given host system.

Our interests lie in the ability of the multicomponent host framework **1**·2(**2**)·guest **3** (where **1** = *C*-methylcalix[4]resorcinarene, **2** = 4,4'-bipyridine) to function as a soft-material.⁵ Previous work by ourselves,⁵ and others,⁶ has revealed the ability of the components of **3** to organize, upon crystallization with a suitable guest, into one of three supramolecular isomers that may be grouped according to the conformation of **1** (Scheme 1). For **3a**^{5b,d} and **3b**,^{5c} **1** adopts a bowl-shaped conformation in which single (e.g., *p*-cyclophane) or multiple (e.g., MeCN·THF) guests occupy the interior of the bowl. The upper rim of **1** in each of these frameworks is extended by four molecules of **2** that interact with **1** by way of four O–H···N hydrogen bonds. **3a** and **3b**, which define a 1D wavelike structure^{5b,d} and a 0D carcerand-like capsule,^{5c} respectively, are architectural isomers. For **3c**,^{5a,6} **1** adopts a “T-shaped” conformation in which multiple guests [e.g., decamethylruthenocene·2(EtOH)·2(H₂O), 4(*m*-xylene)] occupy large, box-shaped cavities of nanoscale dimensions. Four molecules of **2** cross-link,

by way of four O–H···N forces, upper rims of **1**, while adjacent molecules of **1** assemble, as 1D strands, by way of O–H···O forces. Owing to a different pattern of supramolecular connectivity,¹ **3c**, which defines a 2D symmetrical brick framework, is a supramolecular isomer,³ rather than an architectural isomer, of **3a** and **3b**.

In an effort to utilize **3b** as a host for rod-shaped guests (i.e., biphenyls), we have discovered the ability of the components of **3** to assemble in the solid state to form a 1D extended structure **3d**⁷ that is an architectural isomer of **3a** and **3b**. This fourth isomer, in **3d**·(4-brbp) (where 4-brbp = 4-bromobiphenyl), forms owing to the flexibility of the hydrogen bonds that hold the components of the framework together in which **2**, in the presence of rod-shaped guests, interacts with **1** in a splayed orientation. The discovery of **3d** demonstrates structural versatility that has been realized in a limited number of solid-state frameworks^{1–3} and provides insight into structural factors that lead to architectural isomerism in molecular crystalline solids, a topic of much current interest.

Addition of **1** (0.021 g) to a boiling aliquot of EtOH (1.0 mL) in the presence of **2** (0.012 g) and 4-brbp (0.063 g), according to (1), yielded, upon slow cooling, yellow crystals of **3d**·(4-brbp) suitable for X-ray analysis (yield: 71%). The formulation of **3d**·(4-brbp) was confirmed by single-crystal and X-ray powder diffraction,⁸ as well as ¹H NMR spectroscopy.



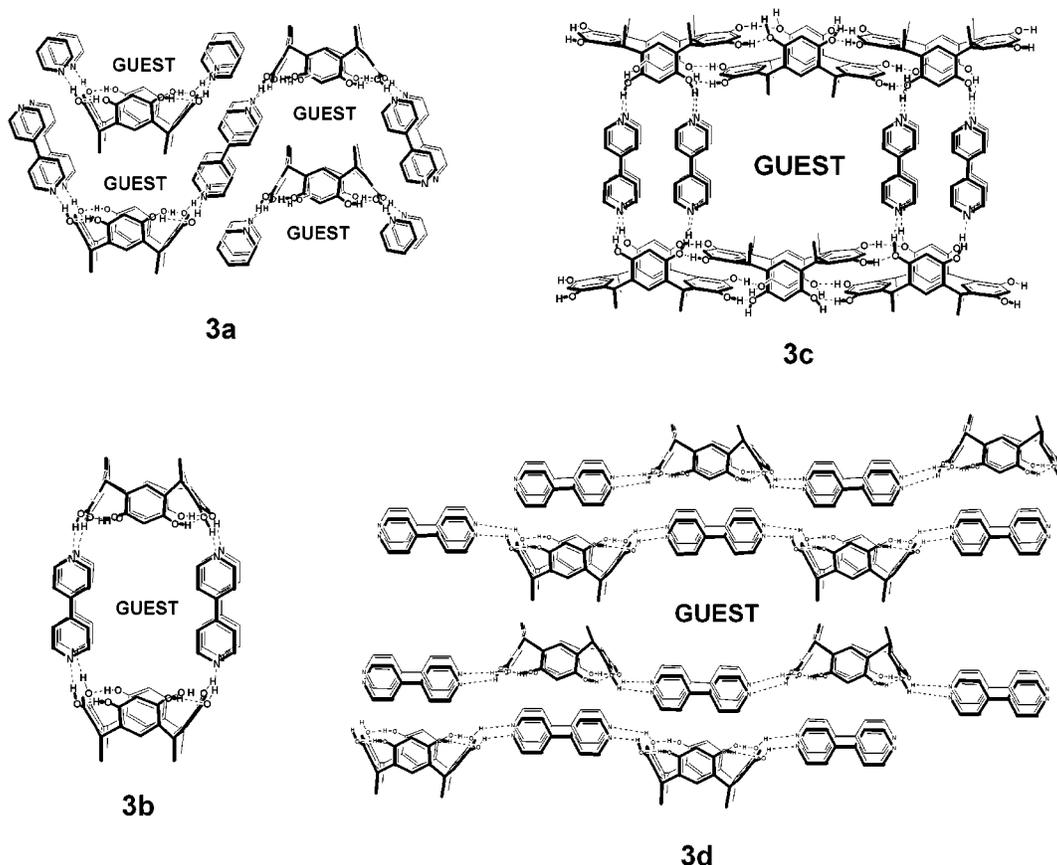
An ORTEP perspective, as well as a space-filling view of the X-ray crystal structure of **3d**·(4-brbp), is shown in Figure 1. As in the case of the wavelike framework **3a**,^{5b,d} the carcerand-like capsule **3b**,^{5c} and the brick framework **3c**,^{5a,6} four molecules of **2**, each of which serves as a bifunctional hydrogen bond acceptor, have assembled with **1**, participating in four intermolecular O–H···N hydrogen bonds with two opposite resorcinol units of the macrocycle [O···N separations (Å): O1···N1 2.786(7), O2···N3 2.647(7)]. Unlike **3c**,^{5a,6} how-

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Scheme 1



ever, yet in a similar way to **3a**^{5b,d} and **3b**,^{5c} four hydroxyl groups form four intramolecular O–H···O hydrogen bonds [O···O separations (Å): O3···O1 2.791(5), O4···O5 2.769(7), O7···O6 2.802(6), O8···O2 2.705(6)] along the upper rim of **1** such that **1** adopts a bowl-like conformation. In contrast to **3a** and **3b**, however, the bipyridines interact with **1** such that each molecule is subtended at an angle of approximately 90° with respect to the principal rotation axis of **1**, the bipyridines, in effect, adopting a splayed orientation along the upper rim of the bowl. As a consequence of these forces, the components of **3d** assemble, in a similar way to **3a**,^{5b,d} to form a 1D hydrogen-bonded polymer held together by a combination of O–H···N and O–H···O forces.

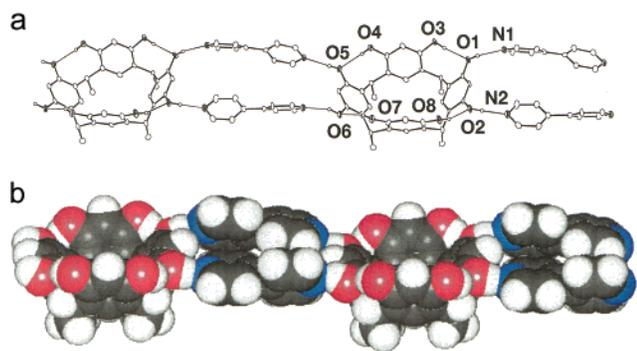


Figure 1. Views of the X-ray crystal structure of **3d** showing the hydrogen bonding along the upper rim of **1**: (a) ORTEP perspective and (b) space-filling model. Color scheme: gray = carbon, white = hydrogen, red = oxygen, blue = nitrogen.

Ⓜ A 3D rotatable image of (b) in xyz format is available.

Space-filling views depicting the extended structure of **3d** (4-brbp) are shown in Figure 2. The components of each polymer are organized in the solid-state such that the bowls of **1**, which are separated by a distance of 21.5 Å, are oriented, in contrast to **3a**, in the same direction along the polymer chain.⁷ Adjacent chains self-include such that two C–H groups of a single pyridyl unit of a bipyridine are directed into the cavity of **1**, interacting with **1** by way of C–H··· π forces. In this arrangement, the chains pack such that nearest-neighbor molecules of **1** are oriented in a tail-to-tail fashion which, in turn, gives rise to large, closed elliptical cavities (cavity dimensions $\sim 11 \times 7 \times 6$ Å) (Figure 2a) occupied by two identical biphenyl guests, each of which is disordered end-to-end across two sites (occupancies: 95:5). The guests, which possess aromatic rings twisted by 160.0°, assemble within each cavity such that the two molecules participate in face-to-face π – π interactions (π ··· π separation: 3.85 Å),⁹ being aligned head-to-tail (Figure 2b). Thus, in a similar way to **3a**–**c**,^{5,6} the structure behavior of **3d** may be attributed to guest template effects in which the size, shape, and functionality of the guest, presumably, does not favor an assembly process that leads to **3a**–**c**.^{5,6} Here, the flexibility of the hydrogen bonds, along with the shape of **1**, has provided access to a cavity that permits isolation of multiple guests,¹⁰ which self-organize in a stacked fashion.

In this report, we have demonstrated the ability of the components of **3** to display an additional form of architectural isomerism that permits alignment of multiple, rod-shaped guests in the solid state. With

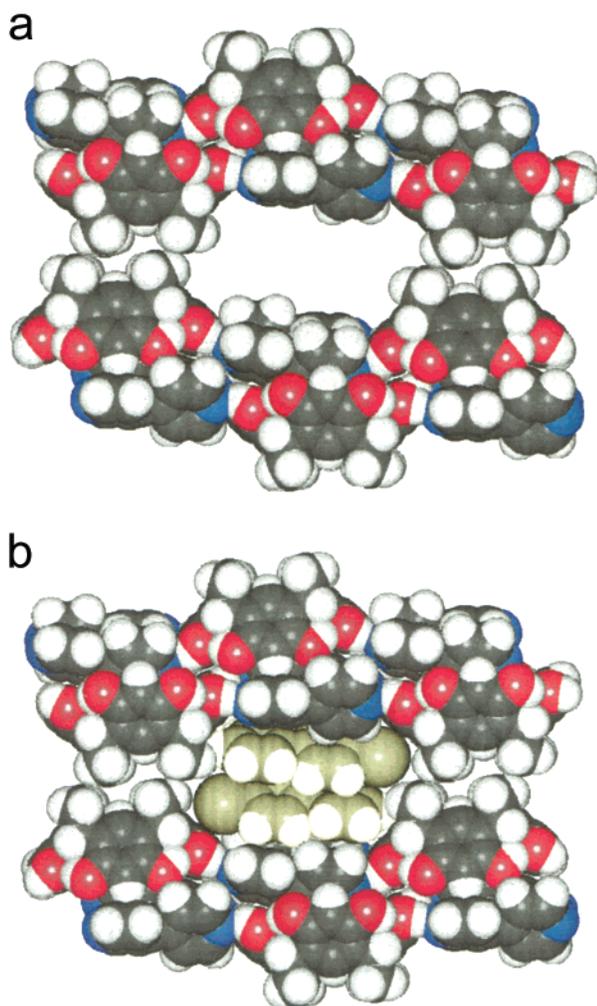


Figure 2. Space-filling view of the extended structure of **3d**: (a) the elliptical cavities created by the packing of the self-included chains and (b) the included guests (a single orientation of each guest is shown for clarity). Color scheme: gray yellow = included guests.

Ⓜ 3D rotatable images of Ⓜ (a) and Ⓜ (b) in xyz format are available.

these observations realized, we are currently developing guests that may be deliberately placed within **3d** to undergo reaction.^{11,12} Moreover, such observations attest to the utility of utilizing a multicomponent, supramolecular approach for the design of solid-state host-guest architecture,¹⁻⁶ in which case the flexibility of the components realized here permits realization of unexpected¹ host-guest behavior.

Note Added After ASAP Posting

A version of this article appeared ASAP on the web on 8/2/01 that did not include enhanced object informa-

tion. This updated version posted 9/5/01 includes this information.

Acknowledgment. We are grateful for funding from the University of Iowa and the Natural Sciences and Engineering Research Council of Canada (doctoral scholarship, J.L.R.).

Supporting Information Available: Crystallographic reports and tables of positional and thermal parameters, bond lengths and angles, X-ray powder patterns and ¹H NMR for **3d**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- (8) Crystal data for **3d**·(4-brbp): crystal size 0.10 × 0.15 × 0.20 mm, triclinic, space group P $\bar{1}$, $a = 11.806(1)$, $b = 14.243(2)$, $c = 17.011(2)$, $\alpha = 66.269(2)^\circ$, $\beta = 86.182(2)^\circ$, $\gamma = 89.557(2)^\circ$, $U = 2612.3(5) \text{ \AA}^3$, $2\theta = 45^\circ$, Mo K α radiation ($\lambda = 0.71070 \text{ \AA}$) for $Z = 2$ and $R = 0.073$.
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CG0155245