# ONE-DIMENSIONAL HYDROGEN BONDED POLYMERS BASED ON *C*-METHYL-CALIX[4]RESORCINARENE AND A CRYSTAL ENGINEERING DESIGN STRATEGY

**L.R. MacGillivray, K.T. Holman, and J.L. Atwood\***

Department of Chemistry, University of Missouri-Columbia, Columbia, MO 65211, USA

**ABSTRACT**

The X-ray crystal structures of co-crystals involving *C*-methylcalix[4]resorcinarene **1** and *exo*-bidentate pyridines **2** are reported. The components assemble such that the calixarenes adopt a $C_{2v}$ conformation and the pyridines serve as bifunctional hydrogen bond acceptors. In the case of linear bridging units, 4,4′-bipyridine **2a** and 4,4′-dipyridyl butanedioate **2b**, the assembly process yields 1D wave-like hydrogen bonded polymers **4a** and **4b**, respectively, which include guest solvent molecules within **1**. In the case of an angular bridging unit, pyrimidine **2c**, the assembly process yields a 1D chain **5** which exhibits self-inclusion. Thermal analysis of **4a** demonstrates that the thermal behavior of these compounds is independent of the nature of the included guest, the solvent-included lattices being stable up to 190°C.  © *1998 Elsevier Science Ltd*

KEYWORDS: A. organic compounds, C. thermogravimetric analysis (TGA), C. X-ray diffraction, D. crystal structure

## INTRODUCTION

We recently exploited the ability of the $C_{2v}$ conformer of *C*-methylcalix[4]resorcinarene **1** to function as a quadruple hydrogen bond donor by forming co-crystals with pyridines **2** (Fig. 1a) [1]. Four pyridine units were observed to extend the cavity of **1**, *via* the formation of four

---

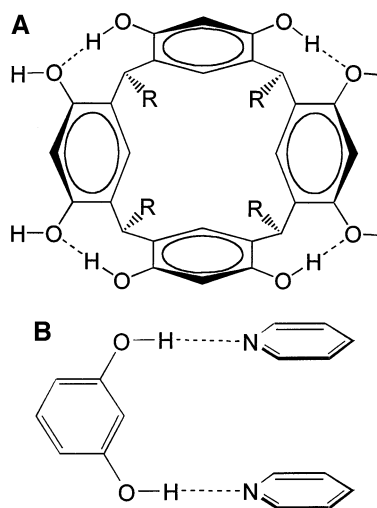*To whom correspondence should be addressed.

FIG. 1

(*A*) $C_{2v}$ conformation of **1**, (*B*) supramolecular synthon **3**.

O-H···N hydrogen bonds, which in turn gave rise to *multi*component hosts that form host-guest complexes with guests previously unobserved for **1**. Notably, the design strategy for the construction of these assemblies relied on the exploitation of a supramolecular synthon **3** recently employed for the crystal engineering of one- (1D) and two- (2D) dimensional resorcinol-based lattices (Fig. 1b) [2].

TABLE 1

Crystallographic Data

| | **4a·MeCN**[a] | **4a·MeNO$_2$** | **4b·MeCN** |
|---|---|---|---|
| CCDC deposit no. | - | CCDC-1290/28 | CCDC-1290/29 |
| Formula | $O_8N_5C_{54}H_{51}$ | $O_{10}N_5C_{53}H_{51}$ | $O_{16}N_5C_{62}H_{59}$ |
| Formula weight | 898.03 | 918.01 | 1130.17 |
| Cryst. system | monoclinic | monoclinic | monoclinic |
| Space group | P 2$_1$/m | P 2$_1$/m | C 2/c |
| T, °C | 20 | −100 | −100 |
| $a$, Å | 7.893(1) | 7.7904(6) | 33.555(2) |
| $b$, Å | 29.243(3) | 29.307(2) | 7.3619(4) |
| $c$, Å | 10.054(1) | 9.9817(7) | 22.832(1) |
| β, deg | 99.67(1) | 100.551(1) | 101.914(1) |
| $V$, Å$^3$ | 2287.8(5) | 2240.5(3) | 5518.6(5) |
| Z | 2 | 2 | 4 |
| $\rho_{calc}$, g cm$^{-3}$ | 1.30 | 1.36 | 1.36 |
| μ, mm$^{-1}$ | 0.685 | 0.091 | 0.074 |
| $R$[b] | 0.0362 | 0.0509 | 0.0372 |
| $wR_2$[b] | 0.0963 | 0.1175 | 0.0930 |

[a]Ref. 1.

[b]$I_{net} > 2.0$ ($I_{net}$)

Specifically, **3** is a consequence of the ability of resorcinol to function as a double hydrogen bond donor. As demonstrated by Aoyama [2], the meta relationship displayed by its two hydroxyl groups allows two aromatic-based hydrogen bond acceptors (e.g., quinones) to participate in two O-H⋯X (X = O, N) hydrogen bonds to the resorcinol moiety such that they form face-to-face stacked dimers and lie approximately orthogonal to its aromatic ring. In essence, the three components that make up **3** function as a single unit by collectively directing the assembly process.

An attractive feature of our design strategy for the construction of extended cavity structures based on **1** lies in its modularity. Considering the myriad of commercially available substituted pyridines, it is possible to readily generate deep cavity frameworks, usually in a single step, which, traditionally, have been designed *via* the elaborate formation and breakage of covalent bonds. Moreover, it is our hope that these new classes of compounds will: a) provide insight into molecular recognition processes involving noncovalent forces, and b) serve as models for the construction of covalently modified calixarenes.

In this paper we report further progress in the area of rationally designed *multi*component calixarenes. In particular, focus is placed on linear and angular *exo*-bidentate pyridines and their ability to generate 1D polymeric host lattices by serving as bifunctional hydrogen bond acceptors in the solid state. Such observations bear relevance in the area of supramolecular polymer design where understanding the influence of noncovalent forces on extended self-assembled frameworks, and their resulting host-guest behavior, is of much current interest [2–4].

## EXPERIMENTAL

**General Methods.** All reagents, unless otherwise stated, were purchased from Aldrich Chemical Co. and were used without further purification. The formulations of **4a**·MeNO$_2$,

## TABLE 1
### (Continued)

| **4b**·MeNO$_2$ | **4b**·(Me)$_2$CO | **5**·2(*p*-xylene) |
|---|---|---|
| CCDC-1290/30 | CCDC-1290/31 | CCDC-1290/32 |
| O$_{18}$N$_5$C$_{61}$H$_{59}$ | O$_{17}$N$_4$C$_{63}$H$_{62}$ | O$_8$N$_4$C$_{56}$H$_{60}$ |
| 1150.16 | 1147.20 | 917.11 |
| monoclinic | monoclinic | monoclinic |
| C 2/c | C 2/c | P 2$_1$/m |
| −100 | −100 | −100 |
| 33.607(2) | 33.354(3) | 12.676(1) |
| 7.2914(5) | 7.4623(6) | 15.927(1) |
| 22.825(1) | 22.721(2) | 12.951(1) |
| 102.140(1) | 101.567(2) | 112.849(1) |
| 5468.1(6) | 5540.3(8) | 2409.6(2) |
| 4 | 4 | 2 |
| 1.40 | 1.38 | 1.26 |
| 0.092 | 0.090 | 0.087 |
| 0.0443 | 0.0736 | 0.0394 |
| 0.1150 | 0.1627 | 0.091 |

**4b·MeCN**, **4b·MeNO$_2$**, **4b·(Me)$_2$CO**, and **5** were confirmed by single-crystal X-ray diffraction. The formulation of **4a·(Me)$_2$CO** was confirmed by $^1$H NMR spectroscopy.

**Synthesis of *Multi*component Calixarenes. 4a·MeNO$_2$ [4a = 1·2(4,4′-bipyridine)], 4a·(Me)$_2$CO, 4b·MeCN [4b = 1·2(4,4′-dipyridyl butanedioate)], 4b·MeNO$_2$, 4b·(Me)$_2$CO:** In a typical synthesis involving a bipyridine (**2a** or **2b**), **1** (0.01 g) was added to a hot solution of the solvent guest (3 mL) containing 2 equiv of the bipyridine which, upon cooling, yielded a yellow precipitate. Compounds involving **2b** were notably much more soluble than those containing **2a**. Crystals of **4a·MeNO$_2$**, **4b·MeCN**, **4b·MeNO$_2$**, and **4b·(Me)$_2$CO** suitable for X-ray analysis were obtained by dissolving a portion of the precipitate in a hot aliquot of the solvent (2 mL) and allowing the solution to slowly cool and stand over a period of approximately 1 day. Repeated attempts at growing single crystals of **4a·(Me)$_2$CO** for X-ray diffraction failed. We infer its structure to be similar to that of **4a·MeCN** and **4a·MeNO$_2$** from $^1$H NMR spectroscopy, thermal analysis, and a related structure, **4b·(Me)$_2$CO**. **5·2(*p*-xylene)** [**5 = 1·2(pyrimidine)**]: Addition of **2c** (0.10 g) to a hot solution of *p*-xylene (5 mL) containing **1** (0.01g) yielded crystals of **5** upon cooling.

**Synthesis of 4,4′-dipyridyl butanedioate (2b).** To a stirring solution of ethylene glycol (0.14 g) and isonicotinoyl chloride hydrochloride (0.80 g) in CH$_2$Cl$_2$ (50 mL) at room temperature was added 4 equiv of triethylamine (0.91 g). After approximately 1.5 h, a white precipitate formed. Following the addition of a saturated aqueous solution of sodium bicarbonate (20 mL) to the reaction mixture, the organic phase was separated, dried over anhydrous potassium carbonate, and filtered. The CH$_2$Cl$_2$ was then removed using a rotary evaporator yielding a white powder. The powder was then re-crystallized from ethylacetate giving pure **2b**.

**X-ray Crystallography.** Single crystals of **4a·MeNO$_2$**, **4b·MeCN**, **4b·MeNO$_2$**, **4b·(Me)$_2$CO**, and **5** were individually mounted on the end of a glass fiber and optically centered in the X-ray beam of the Siemens SMART system for data collection. Initial sets of cell constants were calculated from reflections harvested from three sets of 25 frames. Final cell constants were calculated from reflections obtained from the data collection. All structures were solved using direct methods. After anisotropic refinement of all non-hydrogen atoms, methine, methylene, methyl, aromatic, and hydroxyl hydrogen atoms were placed by modeling the moieties as rigid groups with idealized geometry, maximizing the sum of the electron density at the calculated hydrogen positions. A summary of data collection parameters is given in Table 1. Structure solutions were accomplished with the aid of SHELXS-86 [5], and refinement was conducted using SHELX93 [6] locally implemented on a pentium-based IBM compatible computer. All crystallographic manipulations were performed with the aid of RES2INS [7].

**Thermal Analysis.** Thermal gravimetric analysis was performed under N$_2$ at a scan rate of 10°C/min. using a CAHN TG-121 system. Each sample had an initial mass of approximately 8 mg. Results are reported as a percent weight loss.

## RESULTS AND DISCUSSION

**Parent 1-D Assembly.** In our initial report, we demonstrated that co-crystallization of **1** with **2a** from MeCN yields a 1D wave-like hydrogen bonded polymer **4a**, owing to the ability of
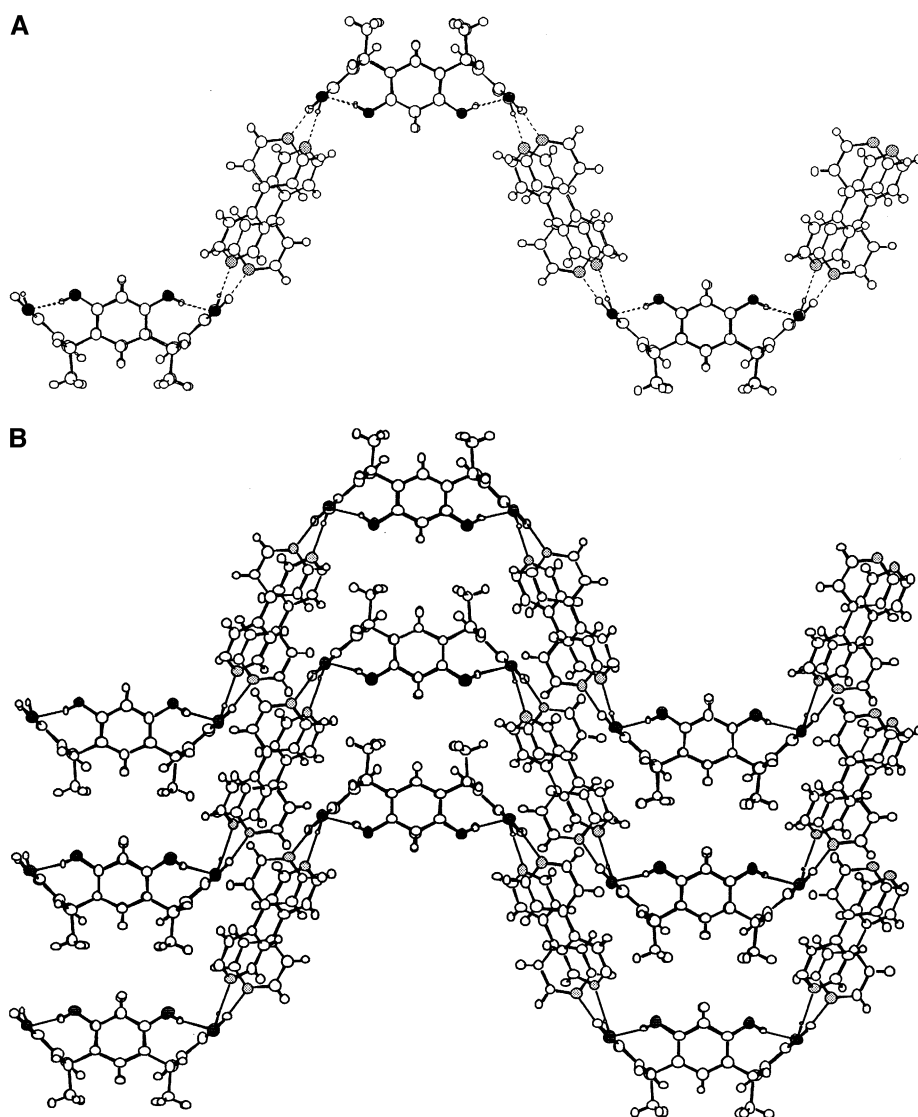
FIG. 2

Crystal structure of **4a**: (*A*) 1D hydrogen-bonded strand, (*B*) 2D layered architecture.

**2a** to function as a linear bifunctional hydrogen bond acceptor [1]. The polymer, which is held together by a repeating unit of four hydrogen bonds, was observed to self-include, giving rise to a 2D layered architecture (Fig. 2), with a molecule of MeCN located within the cavity of **1**, interacting with **1** *via* C-H···π-arene interactions.

**Linear Spacer Units—4,4′-bipyridine (2a).** To determine whether **4a** is capable of hosting a different guest, **1** was co-crystallized with **2a** from $MeNO_2$. The assembly process yields a virtually identical 1D wave-like framework in which a disordered molecule of $MeNO_2$ is
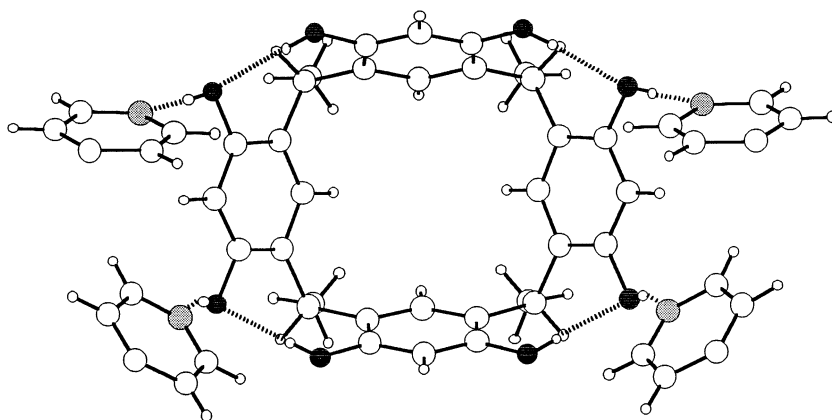
FIG. 3

The tilting displayed by the pyridine units of **4a** (only half of **2a** is shown for clarity).

located within the cavity of **1** and interacts with **1** *via* C-H⋯π-arene interactions. As in **4a·**MeCN, the calixarene is bisected by a crystallographic mirror plane, such that both pyridine units are tilted away from one of the resorcinol moieties (Fig. 3), and the network is propagated along the *b*-axis, by a crystallographic center of inversion, as a $2_1$ screw aggregate [8]. Notably, the "wavelengths" of the strands of **4a·**MeCN and **4a·**MeNO$_2$ and the distance between adjacent calixarenes along each strand are 29 Å and 15 Å, respectively [9]. In fact, compounds **4a·**MeCN and **4a·**MeNO$_2$ are isostructural (Table 1).

**4,4′-dipyridyl butanedioate (2b).** To determine whether the topologies of the 1D frameworks of **4a** may be produced using a different linear bridging ligand, **1** was co-crystallized with **2b** from MeCN, MeNO$_2$, and (Me)$_2$CO. As shown in Figure 4A for **4b·**(Me)$_2$CO, the assembly process yields networks which are topologically equivalent to **4a**. As expected, owing to the length of **2b**, the wavelength of each polymer and the distance between adjacent calixarenes along each strand in **4b·**MeCN (44.31 Å, 21.51 Å), **4b·**MeNO$_2$ (44.42 Å, 20.56 Å), and **4b·**(Me)$_2$CO (43.96 Å, 21.49 Å) are longer than the corresponding distances in **4a**. Surprising, however, is the observation that, although compounds involving **4a** crystallize in the same space group, **4a·**guest and **4b·**guest are not isostructural (Table 1). Moreover, in contrast to **4a·**guest, each calixarene in **4b·**guest sits on a crystallographic 2-fold rotation axis such that the pyridine units are tilted in opposite directions along the wider rim of **1** (Fig. 4B) [10]. As in **4a·**guest, however, the polymers of **4b·**guest are propagated by a crystallographic center of inversion which, in turn, gives rise to the wave-like structure.

As shown in Figure 4C, the included molecule of (Me)$_2$CO in **4b·**(Me)$_2$CO interacts with **1**, *via* C-H⋯π-arene interactions, by pointing both methyl groups within the cavity of **1**. The observation that (Me)$_2$CO, a good hydrogen bond acceptor, may be isolated within **4b** suggests that the hydrogen bonds that hold **4** together are somewhat insensitive to the nature of the included guest [11].

**Angular Spacer Unit—Pyrimidine (2c).** We have discovered that a 1D topology based on **1** and **3** may be produced using an angular *exo*-bidentate bridging ligand. As shown in Figure 5A, co-crystallization of **1** with **2c** from *p*-xylene yields a 1D hydrogen bonded array **5** in
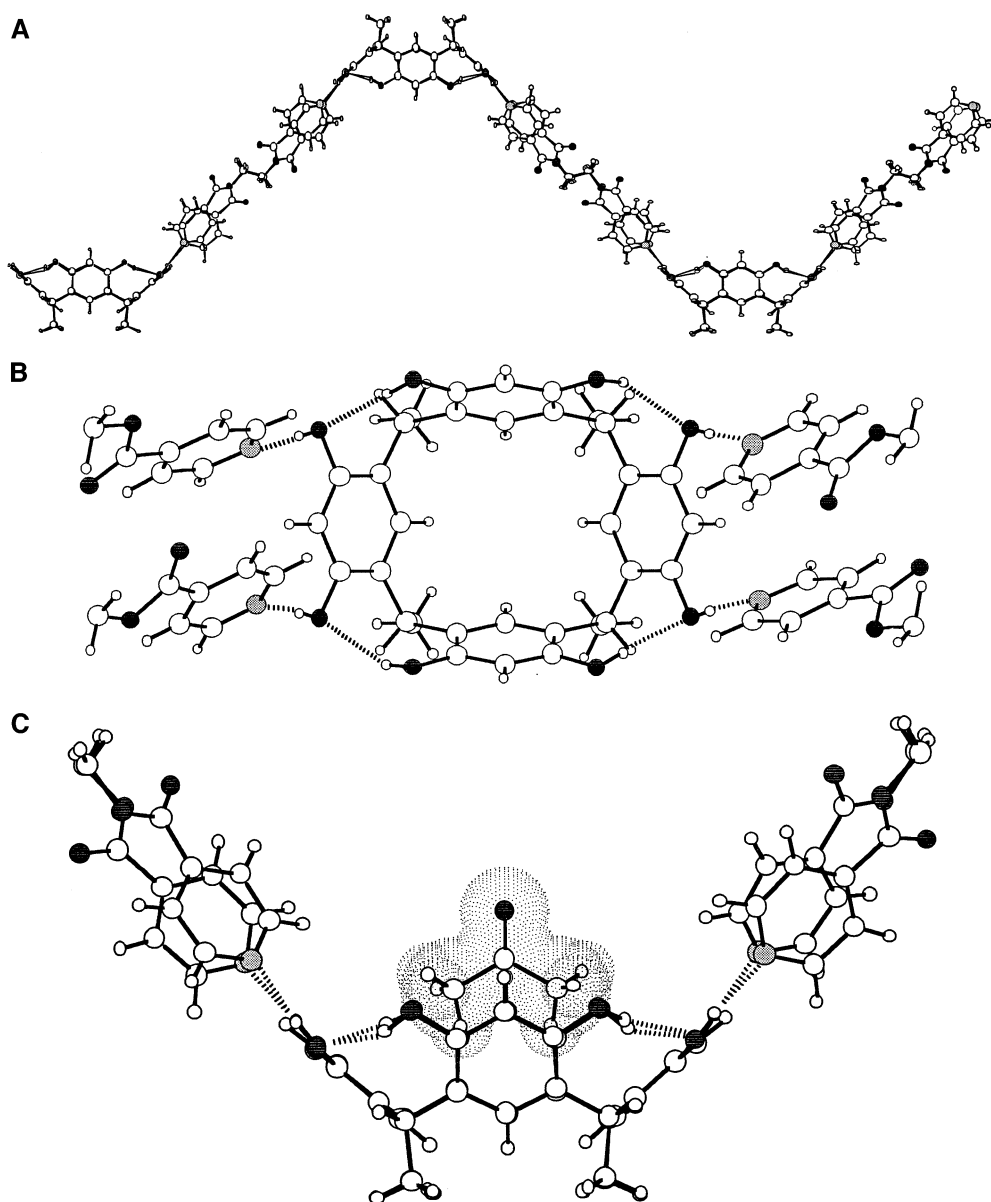
**A**

**B**

**C**

FIG. 4

Wave-like polymers based on **2b**: (*A*) 1D hydrogen-bonded strand, (*B*) the tilting displayed by the pyridine units of **4b** (only half of **2b** is shown for clarity), (*C*) inclusion of (Me)$_2$CO.

which two molecules of **2c**, in a way similar to **4**, link together molecules of **1**. Unlike **4**, however, the calixarenes of **5** are aligned, along the crystallographic *b*-axis, such that the bowls of **1** point in the same direction along the chain. Notably, each molecule of **1** and **2c** of **5** is bisected by a crystallographic mirror plane and the calixarenes are separated by a distance of 15.93 Å. Interestingly, owing to their complementarity, the strands are observed
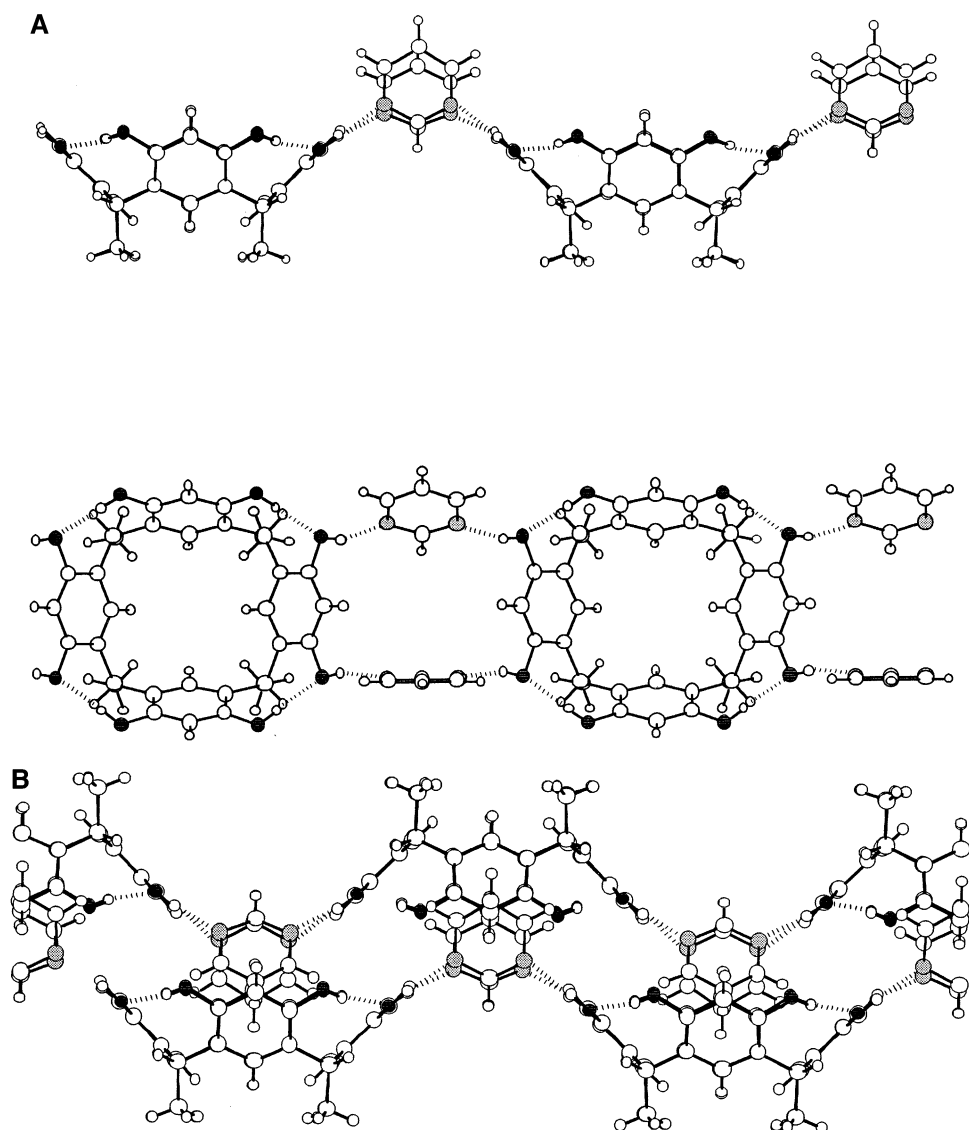
FIG. 5

Crystal structure of **5**: (*A*) the 1D hydrogen-bonded chain, (*B*) self-inclusion of complementary chains.

to self-associate in pairs, as $2_1$-screw aggregates [8], such that one of the two bridging **2c** molecules of neighboring strands is included within the calixarene (Fig. 5B). To facilitate this mode of self-inclusion, the bridging units of **2c** pinch a resorcinol unit of **1**. The included *p*-xylene molecules are located between adjacent double-stranded arrays.

**Exploiting 3 for Rational Solid State Design.** The goal of crystal engineering is to recognize, understand, and exploit supramolecular synthons for the rational design of solid

TABLE 2
Thermal Analysis of **4a**·guest

| Guest | Temp. Range, °C | Observed Loss, % | Material Lost | Calculated Loss, % |
|-------|-----------------|------------------|---------------|--------------------|
| MeCN | 196–252 | 5.0 | MeCN | 4.6 |
| | 252–348 | 34.5 | 4,4′-bipyridine | 34.8 |
| MeNO$_2$ | 200–245 | 7.5 | MeNO$_2$ | 6.6 |
| | 245–327 | 34.2 | 4,4′-bipyridine | 34.0 |
| (Me)$_2$CO | 194–235 | 6.7 | (Me)$_2$CO | 6.3 |
| | 235–332 | 34.2 | 4,4′-bipyridine | 34.1 |

state architecture [12]. To be considered a supramolecular synthon, a structural unit must be robust enough such that it can be exchanged from one structure to another. In such a context, it is clear that **3**, owing to its repeatability in the presence of different bridging ligands and different guest species, may be regarded a supramolecular synthon exploitable for the design of 1D polymeric networks based on **1**.

**Structural Flexibility of 3.** In addition to repeatability, we note that **3** exhibits structural flexibility, a feature commonly encountered in solid state supramolecular arrays [13]. As observed in **4a** and **4b**, the bridging pyridines adopt different orientations along the rim of **1** while retaining their functional integrity. This quality is also displayed by **5** where the bridging molecules of **2c** pinch a resorcinol unit of **1** to permit self-inclusion of the chains.

**Thermal Behavior of 4a-c.** Thermal analysis of **4a** reveals that the included guest in each compound begins to dissociate from the solid at approximately 190°C (Table 2). Immediately following loss of the solvent, an abrupt weight loss from approximately 240°C to 340°C, which corresponds to **2a**, is observed, leaving behind **1**. From these observations we conclude that the thermal behavior of **4a** is independent of the nature of the included guest.

## CONCLUSION

The results reported herein illustrate that **1** and **3** may be exploited for the design of 1D hydrogen bonded polymeric arrays by utilizing either linear or angular *exo*-bidentate pyridine-based bridging units. Thermal studies of **4a** reveal that the thermal behavior of **4a** is independent of the nature of the included guest, the inclusion networks being stable up to approximately 190°C. We anticipate further studies involving **1** and **3** to focus on the design of similar 1D networks involving related bridging units and other guest species. Such studies should provide further insight into the structural flexibility of **3**, and hence the structural parameters concerning the wave-like framework of **4** (e.g., wavelength vs. amplitude), which we believe will play an important role in determining further host-guest properties of these systems.

## ACKNOWLEDGMENT

## REFERENCES

1.  L.R. MacGillivray and J.L. Atwood, *J. Am. Chem. Soc.* **119**, 6931 (1997).

2.  Y. Aoyama, K. Endo, T. Anzai, Y. Yamaguchi, T. Sawaki, K. Kobayashi, N. Kanehisa, H. Hashimoto, Y. Kai, and H. Masuda, *J. Am. Chem. Soc.* **118**, 5562 (1996).

3.  J.-M. Lehn. *Supramolecular Chemistry*, VCH, Weinheim, 1995.

4.  a) S. Krishnamohan and M.J. Zaworotko, *Chem. Commun.* 2655 (1996); b) O.M. Yaghi, L. Hailian, and T.L. Groy, *J. Am. Chem. Soc.* **118**, 9096 (1996).

5.  G.M. Sheldrick, *Acta. Crystallogr. A* **46**, 467 (1990).

6.  G.M. Sheldrick, *SHELXL93*, University of Göttingen, Germany, 1993.

7.  L.J. Barbour, *RES2INS*, University of Missouri-Columbia, Missouri, USA, 1997.

8.  J. Perlstein, *J. Am. Chem. Soc.* **116**, 455 (1994).

9.  Since the structures of **4a**·MeCN and **4a**·MeNO$_2$ were collected at different temperatures, we cannot make a detailed comparison of the wavelengths of the polymers.

10. It is presently unclear why the bridging ligands of **4a** and **4b** tilt in their respective directions, which ultimately gives rise to the different space groups.

11. P. Brunet, M. Simard, and J.D. Wuest, *J. Am. Chem. Soc.* **119**, 2737 (1997).

12. G.R. Desiraju, *Angew. Chem., Int. Ed. Engl.* **34**, 2311 (1995).

13. V.A. Russell and M.D. Ward, *Chem. Mater.* **8**, 1654 (1996).