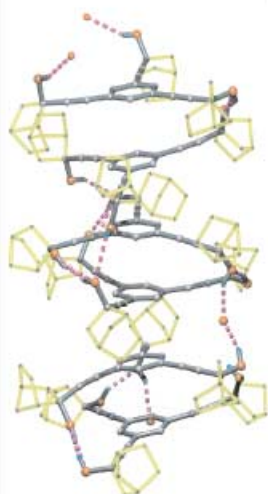
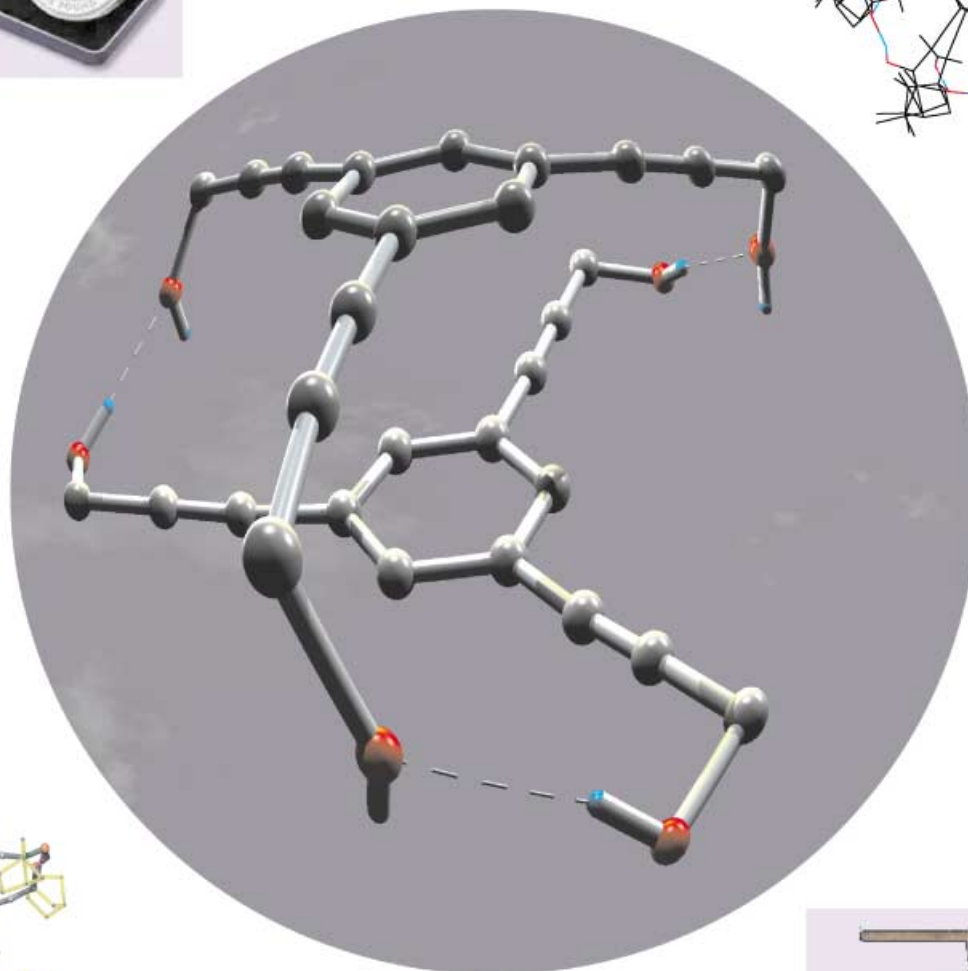
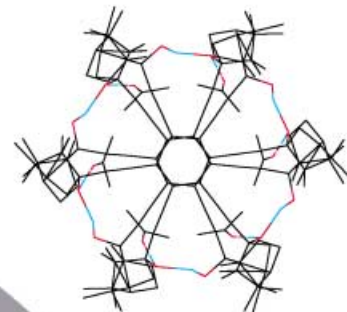
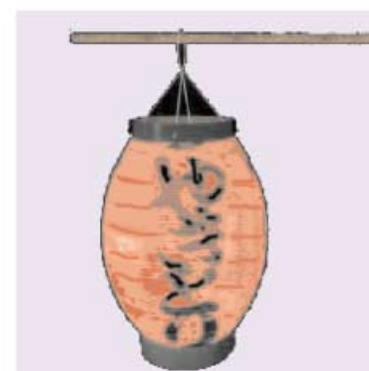


## Supramolecular [6]Chochin and “Big Mac” Structures



Pairs of Piedfort units (the Piedfort notation comes from special coins struck at double thickness for collectors) form a supramolecular [6]chochin analogue (similar in shape to Japanese lanterns) and “Big Mac”-like structures. For more details see the following pages.



# Supramolecular [6]Chochin and “Big Mac”<sup>[+]</sup> Made from Chiral Piedfort Assemblies

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Dedicated to Professor Jack D. Dunitz on his 80th birthday

**Abstract:** Facile chemical synthesis of the natural chiral-pool-derived host **1** and its subsequent crystallization (“supramolecular synthesis”) from different solvents yielded crystalline assemblies. Crystal structure determinations of five of the so formed solvent-inclusion compounds (**1a–1e**) reveal hexagonal symmetries in four cases. The structural characteristics of these chiral host–guest ensembles with varying stoichiometries can be best described as assem-

blies formed through intra-pair hydrogen bridges of host molecules into Piedfort pairs of differing complexity. Hitherto undescribed, these Piedfort pairs also form even larger regular assemblies that we designate “Big

**Keywords:** chiral Piedfort unit · crystal engineering · host-guest system · self-assembly · supramolecular chemistry

Mac”-like shapes. In the only nonhexagonal case, six independent host molecules form a huge supramolecular analogue of [6]benzocyclophane, also known as [6]chochin, extending this giant supermolecule through intermolecular hydrogen bonds into macroscopic (mm-size) dimensions. As all these crystals are inherently chiral, and new model systems for solid-state applications can be envisaged.

## Introduction

Investigation of *sym*-threefold-substituted aromatic molecules is the focus of research for many reasons, not in the least for their aesthetic appeal.<sup>[1]</sup> A certain amount of research has been devoted to the utilization of threefold symmetry for nonlinear optics (NLO) applications,<sup>[2]</sup> but other areas such as molecular paneling through coordination,<sup>[3]</sup> tailoring extra-large pores,<sup>[4]</sup> extending dimensions into the nanosize domain,<sup>[5]</sup> use in chemical reactions such as asymmetric catalysis,<sup>[6]</sup> providing self-assembling metallocycles,<sup>[7]</sup> and selective binding of ionic and neutral guest species<sup>[8]</sup> are also well represented.

The so-called Piedfort-type assemblies (named after the special coins struck at least with double thickness for collectors) constitute an interesting class of inclusion host compounds that are also based on *sym*-trisubstituted molecules.<sup>[9]</sup> Interest arose among others due to their promising NLO activity.<sup>[2]</sup> Supramolecular self-assembly of molecules yields the original triazine-ring-based Piedfort complexes. Evidence shows that such difficult Piedfort arrangements may be also constructed from a pure benzene core.<sup>[10]</sup> Benzene rings with proper 1,3,5-trisubstitution yield an unequal electron density distribution with threefold symmetry. Thus it is possible to self-complement themselves by using electrostatic interactions by Piedfort pairing.

In search of new types of Piedfort assemblies we recently studied a series of crystal structures involving compound **1**. These not only gave aesthetic crystal structures, but also revealed curious structural properties. The findings prompted us to report on five crystal structures of inclusion compounds formed with **1**; these are the first examples of chiral Piedfort associates.

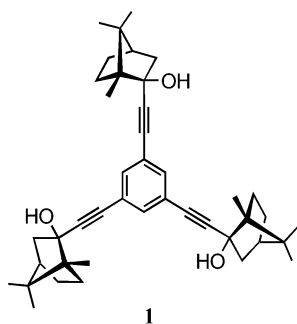
## Results and Discussion

**Molecular design and synthesis:** Actually, compound **1** was contrived along with similar compounds with chiral molecular recognition in mind by using the chiral pool and the rigid

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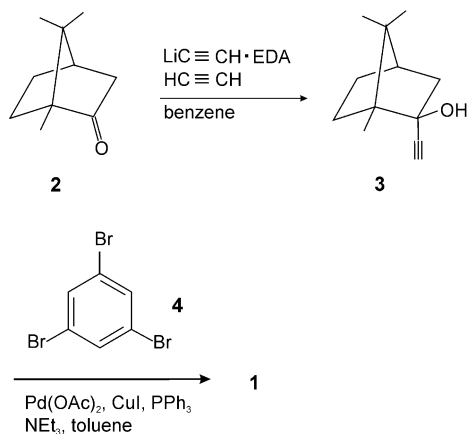
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[+] Use of this name does not imply either *gusto* preference or any relation to McDonald's Inc. of these authors.



1a: 1 · DMF (1:1)      1d: 1 · EtOH (2:5)  
 1b: 1 · Acetone (1:1)    1e: 1 · H<sub>2</sub>O (6:1)  
 1e: 1 · Acetic acid (1:1)

molecular frame concept.<sup>[11]</sup> Making use of borneol units as chiral building blocks and ethynyl spacers appended to a *sym*-trisubstituted benzene core provides alternating polarization on the one hand and properly shaped spacers and electrostatic shielding on the other. Following this molecular design, the synthesis of **1** (Scheme 1) started with (+)-camphor (**2**), which



Scheme 1. Synthesis of compound **1**.

**Abstract in Hungarian:** A természet királis készletéből egyszerű kémiai szintézissel előállítottuk **1** gazda-molekulát és különböző oldószerekből való kristályosításával ("szupramolekuláris szintézis") a kristályos asszociátumait. Az így képződött öt oldószer zárvány (**1a–1e**) kristályszerkezetének meghatározása négy esetben hexagonális szimmetriát tárt föl. E változó sztöchiométriájú, királis gazda-vendég együttesek szerkezeti rendszerét legjobban asszociátumaikon belül H-hidakkal összetartott, különféle bonyolultságú Piedfort-párokba rendezett gazda molekulák társulásaként jellemezhetjük. A Piedfort párok eddig le nem írt módon állnak össze még nagyobb szabályos asszociátumokká, amelyeket "Big Mac" alakzatoknak nevezünk. Az egyetlen nem-hexagonális esetben hat független gazda molekula alkot egy óriás, szupramolekuláris [6]benzociklofán ("[6]chochin") analógot, intermolekuláris H-hidak révén kiterjesztve ezt az óriás szupermolekulát a makroszkópikus (mm-es) méretekre. Mivel mindegyik kristály eredendően királis, szilárdfázisú alkalmazások új model rendszereit látjuk bennük.

was ethynylated with lithium acetylide/ethylenediamine and ethyne to give the ethynyl-substituted borneol **3**.<sup>[12]</sup> Compound **3** was then coupled with tribromide **4** according to the methods of Hagihara<sup>[13]</sup> and Austin<sup>[14]</sup> to yield **1**. Slow evaporation of saturated solutions of **1** from their respective guest solvents gave the corresponding inclusion crystals **1a–1d**; compound **1e** was obtained from toluene that apparently contained traces of water.

**Structural study:** The five crystal structures of inclusions of **1** (**1a–1e** and Table 1) prove that hydrogen-bonding-aided Piedfort formation occurs (Figure 1) with characteristic mean

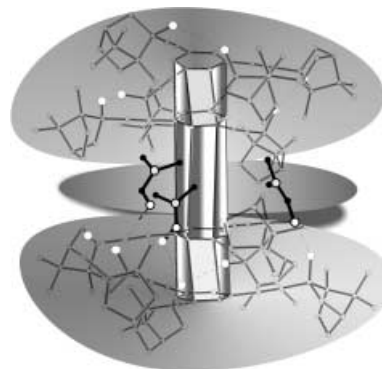


Figure 1. Binding of guest molecules in "Big Mac" fashion in **1a** (**1**·DMF 1:1) showing Piedfort units. Shaded polygons indicate spaces between rings, "buns" atop and below represent the shielding regions of the two Piedfort pairs.

plane distances of about 3.4 Å (Tables 2 and 3). Apparently host **1** not only complements itself via the Piedfort pairing, but also fixes this supramolecular structure through well-defined hydrogen bonds (Table 4) between the OH functions of neighboring side arms (Figure 1). This is a recurring and evidently powerful motif. The host behavior also corresponds to the expected "coordinationcathrate" feature:<sup>[15]</sup> the binding of all guest solvents occurs through hydrogen bonding to the host OH functions and encapsulation into the space between next Piedfort units; we call this the supramolecular "Big Mac" (Figure 1). This supramolecular arrangement of four hosts and the guests resembles the cuisine analogue in that respect, too, that guest molecules act like the filling between the two Piedfort pairs. The Piedfort stacks are placed nearly twice as far from each other as the rings within the stacks (Tables 2 and 3). This building method is employed in many Piedfort structures, though its presence was not recognized earlier.<sup>[2c, 3, 9, 10, 16]</sup>

Moreover, these crystalline architectures evolve to a pattern of increasing complexity as one proceeds from the highly symmetric smaller structures (**1a**, **1b**, and **1c**) to the more complex ones (**1d** and **1e**). One can thus divide the crystal structures into three classes based on the different Piedfort stacking of the host molecules, for example, on the organization of Piedfort stacks into "Big Mac"-like assemblies and their placement in their respective crystal lattices.

An example of the first type of packing arrangements is shown in Figure 2. In the isostructural<sup>[17]</sup> compounds **1a**, **1b**

Table 1. Crystal data and structure refinement details of compounds **1a–1e**.

|  | <b>1a</b>  | <b>1b</b>   | <b>1c</b>  | <b>1d</b>   | <b>1e</b>  |
|--|--|---|--|---|--|
| formula  | C <sub>42</sub> H <sub>54</sub> O <sub>3</sub> ·C <sub>3</sub> H <sub>7</sub> NO | C <sub>42</sub> H <sub>54</sub> O <sub>3</sub> ·C <sub>3</sub> H <sub>6</sub> O | C <sub>42</sub> H <sub>54</sub> O <sub>3</sub> ·C <sub>2</sub> H <sub>4</sub> O <sub>2</sub> | C <sub>42</sub> H <sub>54</sub> O <sub>3</sub> ·2.5 C <sub>2</sub> H <sub>6</sub> O | C <sub>42</sub> H <sub>54</sub> O <sub>3</sub> ·1/6 H <sub>2</sub> O |
| <i>T</i> [K]   | 293(2)   | 293(2)  | 293(2)   | 293(2)  | 293(2)   |
| crystal system   | hexagonal  | hexagonal   | hexagonal  | hexagonal   | triclinic  |
| space group  | <i>P</i> 6 <sub>3</sub> (No. 173)  | <i>P</i> 6 <sub>3</sub> (No. 173)   | <i>P</i> 6 <sub>3</sub> (No. 173)  | <i>R</i> 3 (No. 146)  | <i>P</i> 1 (No. 1)   |
| <i>a</i> [Å]   | 19.268(1)  | 19.349(3)   | 19.326(1)  | 19.348(3)   | 16.909(1)  |
| <i>b</i> [Å]   | 19.268(1)  | 19.349(3)   | 19.326(1)  | 19.348(3)   | 18.772(1)  |
| <i>c</i> [Å]   | 19.415(1)  | 18.628(6)   | 18.678(5)  | 42.266(8)   | 21.346(1)  |
| $\alpha$ [°]   | 90   | 90  | 90   | 90  | 111.46(1)  |
| $\beta$ [°]  | 90   | 90  | 90   | 90  | 103.38(1)  |
| $\gamma$ [°]   | 120  | 120   | 120  | 120   | 107.74(1)  |
| <i>V</i> [Å <sup>3</sup> ]   | 6242.2(6)  | 6040(2)   | 6042(2)  | 13702(4)  | 5538.4(5)  |
| <i>Z</i>   | 6  | 6   | 6  | 12  | 6  |
| $\rho_{\text{calcd}}$ [Mg m <sup>-3</sup> ]  | 1.085  | 1.097   | 1.100  | 1.050   | 1.097  |
| crystal size [mm]  | 0.30 × 0.25 × 0.18   | 0.50 × 0.45 × 0.40  | 0.40 × 0.20 × 0.14   | 0.50 × 0.50 × 0.45  | 0.50 × 0.30 × 0.25   |
| 2 $\theta$ completeness [%]  | 99.0   | 95.3  | 99.3   | 97.0  | 99.4   |
| reflections collected  | 11 421   | 12 758  | 21 069   | 8047  | 24 436   |
| independent reflections/ <i>R</i> <sub>int</sub>   | 4337/0.040   | 4979/0.063  | 8007/0.038   | 6101/0.026  | 23417/0.020  |
| data/restraints/parameters   | 4337/267/452   | 4979/571/447  | 8007/286/442   | 6101/1200/650   | 23417/3477/2503  |
| goodness-of-fit on <i>F</i> <sup>2</sup>   | 0.90   | 0.92  | 0.97   | 1.11  | 0.99   |
| final <i>R</i> <sub>1</sub> / <i>wR</i> <sup>2</sup> [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )] | 0.0446/0.1034  | 0.0950/0.2467   | 0.0377/0.0926  | 0.0969/0.2665   | 0.0663/0.1764  |
| <i>R</i> <sub>1</sub> / <i>wR</i> <sup>2</sup> (all data)                                  | 0.0860/0.1218  | 0.1597/0.2790   | 0.0779/0.1040  | 0.1229/0.2874   | 0.1002/0.1988  |
| largest difference peak/hole [e Å <sup>-3</sup> ]  | 0.18/−0.13   | 0.26/−0.28  | 0.15/−0.14   | 0.33/−0.32  | 0.41/−0.24   |

Table 2. Piedfort distances (*d*<sub>p</sub>), “Big Mac” distances (i.e., distances between two innermost ring centers of consecutive Piedfort pairs in a “Big Mac” sandwich, *d*<sub>B</sub>), and angles of Piedfort aromatic ring centers in **1a–1d** and with mean values with sample standard deviations of six values for **1e**.

|           | <i>d</i> <sub>p</sub> [Å] | <i>d</i> <sub>B</sub> [Å] | Angle [°] |
|-----------|---------------------------|---------------------------|-----------|
| <b>1a</b> | 3.346                     | 6.362                     | 180.0     |
| <b>1b</b> | 3.326                     | 5.988                     | 180.0     |
| <b>1c</b> | 3.346                     | 5.993                     | 180.0     |
| <b>1d</b> | 3.334                     | 6.773                     | 180.0     |
| <b>1e</b> | 3.57(12)                  | 7.15(13)                  | 172(6)    |

Table 3. Six independent residue center distances [Å] in Piedfort pairs and their respective angles of adjoining Piedfort aromatic ring centers in **1e** as compared for those in [4]chochin<sup>[19c]</sup> (tetramethyl quadruple-layered cyclophane, refcode MPCPHT10 in CSD<sup>[20]</sup>), the only structure of a close covalent analogue of [6]cyclophane known to date.<sup>[a]</sup>

| <b>1e</b>      | 1                | 2     | 3     | 4     | 5     | 6     | i <sup>ii</sup> | A <sub>1</sub> ...A <sub>2</sub> ...A <sub>3</sub> | Residues [°]                          |
|----------------|------------------|-------|-------|-------|-------|-------|-----------------|--|---------------------------------------|
| 6 <sup>i</sup> | 3.537            |       |       |       |       |       |                 | 175.7  | 5 <sup>i</sup> ...6 <sup>i</sup> ...1 |
| 1              |                  | 3.730 |       |       |       |       |                 | 176.0  | 6...1...2                             |
| 2              |                  |       | 3.577 |       |       |       |                 | 176.3  | 1...2...3                             |
| 3              |                  |       |       | 3.426 |       |       |                 | 172.2  | 2...3...4                             |
| 4              |                  |       |       |       | 3.743 |       |                 | 161.5  | 3...4...5                             |
| 5              |                  |       |       |       |       | 3.447 |                 | 164.8  | 4...5...6                             |
| 6              |                  |       |       |       |       |       | 3.537           | 175.7  | 5...6...1 <sup>ii</sup>               |
| [4]chochin 2   | 3 <sup>[b]</sup> |       |       |       |       |       |                 | A <sub>1</sub> ...A <sub>2</sub> ...A <sub>3</sub> | Residues [°]                          |
| 1              |                  | 3.021 |       |       |       |       |                 | 176.8  | 1...2...3                             |
| 2              |                  |       | 3.029 |       |       |       |                 |  |                                       |

[a] Symmetry operators: i: *x*, *y*, *z* + 1; ii: *x*, *y*, *z* − 1; **1a** = **1**·DMF 1:1, **1b** = **1**·acetic acid 1:1, **1c** = **1**·EtOH 2:5, **1d** = **1**·H<sub>2</sub>O 6:1. [b] Residue 3 is the symmetry equivalent of residue 1 in [4]chochin.<sup>[19c]</sup>

and **1c**, all host molecules have molecular threefold symmetry that arises from the corresponding threefold rotation axes they sit on (space group *P*6<sub>3</sub> for **1a**, **1b**, and **1c**,

Table 4. Hydrogen bridge geometries in **1a–1e**.

|                          | D–H...A <sup>[a]</sup>                   | <i>d</i> <sub>(D–H)</sub> [Å] | <i>d</i> <sub>(H...A)</sub> [Å] | <i>d</i> <sub>(D...A)</sub> [Å] | D–H...A [°] |
|--------------------------|--|-------------------------------|---------------------------------|---------------------------------|-------------|
| <b>1a</b> <sup>[b]</sup> | O11C–H11...O13 <sup>i</sup>              | 0.85                          | 2.09                            | 2.894(4)                        | 156.6       |
|                          | O13–H13...O12                            | 0.85                          | 2.01                            | 2.832(3)                        | 162.3       |
|                          | O12–H12...O1d <sup>ii</sup>              | 0.69                          | 2.13                            | 2.760(4)                        | 152.3       |
| <b>1b</b> <sup>[b]</sup> | O11–H11...O13 <sup>iii</sup>             | 0.82                          | 2.06                            | 2.831(7)                        | 156.0       |
|                          | O12–H12...O11 <sup>iv</sup>              | 0.82                          | 2.17                            | 2.948(8)                        | 157.7       |
|                          | O13–H13...O14 <sup>v</sup>               | 0.85                          | 2.01                            | 2.86(1)                         | 179.8       |
| <b>1c</b> <sup>[b]</sup> | O11–H11...O12 <sup>vi</sup>              | 0.82                          | 1.99                            | 2.778(2)                        | 161.5       |
|                          | O12–H12...O14                            | 0.82                          | 2.09                            | 2.870(2)                        | 159.0       |
|                          | O13–H13...O11 <sup>vii</sup>             | 0.82                          | 2.03                            | 2.806(2)                        | 158.5       |
| <b>1d</b> <sup>[b]</sup> | O404–H404...O13 <sup>viii</sup>          | 1.07                          | 1.72                            | 2.750(2)                        | 159.1       |
|                          | O11–H11...O26                            | 0.85                          | 1.88                            | 2.732(7)                        | 179.9       |
|                          | O12–H12...O13                            | 0.85                          | 1.97                            | 2.821(6)                        | 179.7       |
|                          | O13–H13...O25 <sup>ix</sup>              | 0.82                          | 2.12                            | 2.877(8)                        | 153.5       |
|                          | O14–H14...O26 <sup>x</sup>               | 0.82                          | 2.19                            | 2.87(1)                         | 140.4       |
|                          | O25–H15...O26                            | 0.83                          | 2.15                            | 2.94(1)                         | 156.1       |
|                          | O27–H17...O28                            | 0.85                          | 1.55                            | 2.19(7)                         | 128.6       |
| <b>1e</b> <sup>[c]</sup> | O1(1)–H1(1)...O1''(2)                    | 0.82                          | 2.24                            | 2.930(5)                        | 142.3       |
|                          | O1(2)–H1(2)...O1(4)                      | 0.82                          | 2.5                             | 2.926(3)                        | 113.5       |
|                          | O1'(2)–H1'(2)...O1''(3)                  | 0.82                          | 2.16                            | 2.905(5)                        | 151.0       |
|                          | O1''(2)–H1''(2)...O1(1)                  | 0.82                          | 2.37                            | 2.930(5)                        | 126.7       |
|                          | O1(3)–H1(3)...O1x                        | 0.82                          | 2.14                            | 2.84(1)                         | 143.0       |
|                          | O1'(3)–H1'(3)...O1(4)                    | 0.82                          | 2.1                             | 2.832(3)                        | 147.7       |
|                          | O1''(3)–H1''(3)...O1'(4)                 | 0.82                          | 2.1                             | 2.846(4)                        | 150.9       |
|                          | O1(4)–H1(4)...O1'(3)                     | 0.82                          | 2.15                            | 2.832(3)                        | 140.9       |
|                          | O1'(4)–H1'(4)...O1''(3)                  | 0.82                          | 2.43                            | 2.846(4)                        | 112.8       |
|                          | O1''(4)–H1''(4)...O1(3)                  | 0.82                          | 2.06                            | 2.841(3)                        | 158.7       |
|                          | O1(5)–H(5)...O1x                         | 0.82                          | 2.13                            | 2.890(8)                        | 154.3       |
|                          | O1(5)–H(5)...O1y                         | 0.82                          | 2.35                            | 2.99(2)                         | 135.5       |
|                          | O1'(5)–H'(5)...O1''(6)                   | 0.84                          | 2.05                            | 2.894(5)                        | 179.8       |
|                          | O1''(1)–H''(1)...O1'(6 <sup>xi</sup> )   | 0.82                          | 2.12                            | 2.881(4)                        | 155.3       |
|                          | O1''(1)–H''(1)...O1''(6 <sup>xii</sup> ) | 0.82                          | 2.46                            | 3.156(4)                        | 143.4       |

[a] Crystallographic symmetry codes to generate atoms: i = *y*, −*x* + *y*, −1/2 + *z*; ii = −*y*, *x* − *y*, *z*; iii = 2 − *x*, 2 − *y*, 1/2 + *z*; iv = *x*, *y*, 1 + *z*; v = 2 − *y*, 1 + *x* − *y*, −1 + *z*; vi = −*x*, 2 − *y*, −1/2 + *z*; vii = 1 + *x*, *y*, 1 + *z*; viii = 1 − *x*, 2 − *y*, −1/2 + *z*; ix = −1/3 + *x*, −2/3 + *y*, 1/3 + *z*; x = 2/3 − *x* + *y*, 7/3 − *x*, 1/3 + *z*; xi = *x*, *y*, *z* + 1. [b] Only asymmetric unit contacts are shown for **1a–1d**. Thus the total number hydrogen bonds is actually three times higher due to the threefold symmetry. [c] Both the disordered water sites have hydrogen bridges to O1(5), hence, this is counted as one hydrogen bond.

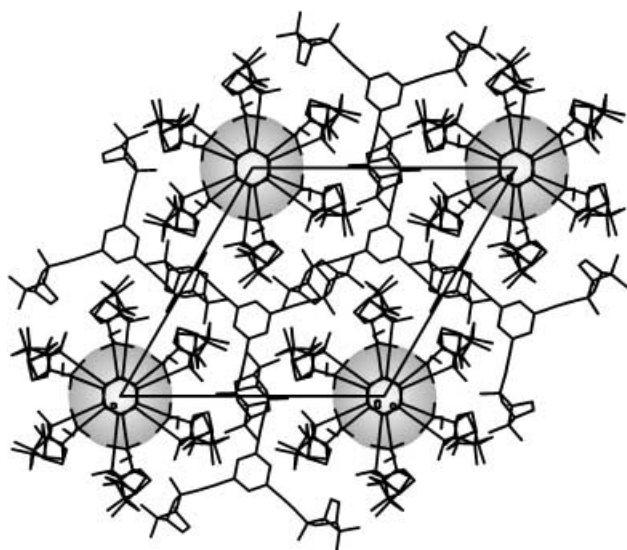


Figure 2. Packing diagram of **1a** with the "Big Mac" constructs sitting at cell corners, while other threefold axes are occupied by lone host molecules. This framework applies for both **1b** and **1c**.

Table 1).<sup>[18]</sup> In these inclusion crystals only two of the three independent molecules, both at  $\{0,0,z\}$ , form Piedfort assemblies that act as hosts. The third, passive molecule resides on a threefold axis at  $\{1/3,2/3,z\}$ . This class of molecules of **1** can be seen as "self-enclathrated" in the "Big Mac" framework at the cell corners (Figure 2).

The structure of **1d** with its large  $R3$  unit cell (Table 1) reveals the second kind of molecular self-assembly and association, governed by the interplay with the ethanol guests. Compound **1d** now has all threefold axis sites, both at  $\{0,0,z\}$  and at  $\{1/3,2/3,z\}$ , occupied by Piedfort stacks, unlike in **1a–1c**, and is now built on a modified Big Mac; the guests are bound between intra-pair hydrogen-bonded (Table 4) Piedfort units and single hosts flanking both sides of the Piedfort units (Figure 3). Stacked hosts on independent axes are half-way raised to each other resulting in the approximate doubling of the  $c$  axis to  $\sim 42$  Å as compared with  $\sim 19$  Å for the  $c$  axis in **1a**, **1b**, and **1c**, or  $\sim 21$  Å for the  $c$  axis in **1e**.

The *third* structure type is found in **1e** (Figure 4, Tables 2 and 3) with the odd stoichiometry of *six* host molecules **1** and *one* water molecule. The first difference is the triclinic  $P1$  space group (Table 1). Six independent host molecules, propagated by translations along the  $c$  axis, clasp themselves into an infinite stack of Piedfort pairs, to give complete, infinite, and macroscopic Piedfort embrace of almost mm-size. Further peculiarity arises from a topological analysis of the placements of the aromatic rings together with the large number of independent hydrogen bonds (Table 4). Fourteen hydrogen bridges link all these molecules in the cell together. The analysis reveals an amazing similarity of these links with the covalent bond arrangement observed in the covalent [6]chochin molecule<sup>[19]</sup> (Figure 4). If we consider the topological role of hydrogen bonds to be like that of covalent bonds, then the similarity of the planar molecular graph (Figure 5) in the **1e** crystal and of the covalent [6]chochin is evident. Consequently a whole series of cyclophanes and their fascinating supramolecular analogues can be constructed.

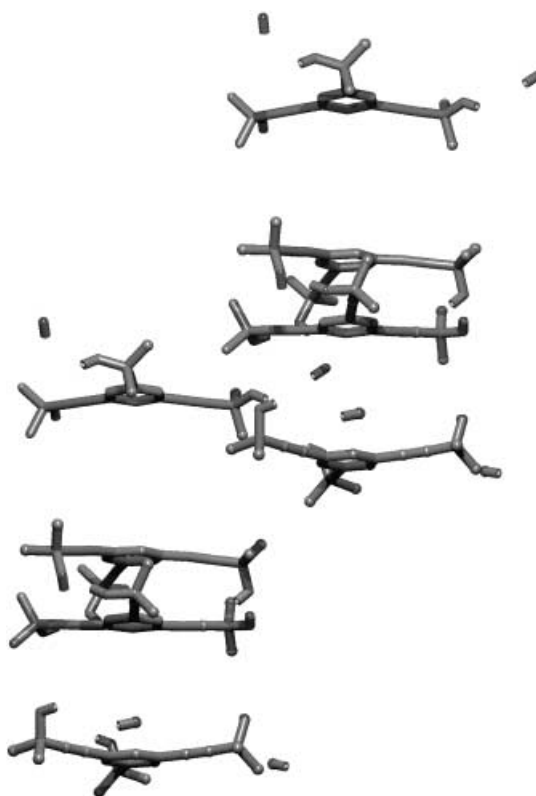


Figure 3. Packing excerpt from the crystal of **1d** showing two asymmetric units of truncated hosts and guests. All but the OH hydrogen atoms and most of the borneol skeleton as well as methyl termini for guests are omitted for clarity.

Comparison of the covalent constructs against the supramolecular ones is illuminating. Firstly, the softer supramolecular links do not force the aromatic rings to bend, while interplanar distances indicate the presence of strong base-stacking. Secondly, the ring centres are aligned quite well (Table 1).

## Conclusion

The  $C_3$ -symmetrical compound **1**, which was synthesized by Pd-catalyzed coupling (Scheme 1), has proven to be the first example of a chiral Piedfort assembly. The respective structures unravel a startling regularity that partly pertains to their host behavior. Their structural characteristics suggests that the new threefold-symmetrical chiral selector extends the crystal engineering possibilities through solvent tuning.<sup>[20]</sup> The odd structure of **1d** is also a prototype of an infinite polymeric stack of host **1**. The multiple hierarchy of the self-assembly of **1** holds promising application possibilities of supramolecular synthesis,<sup>[21]</sup> including new NLO model systems.<sup>[22]</sup>

## Experimental Section

**General methods:** The NMR spectra were recorded on a Bruker MSL 300 spectrometer at 25 °C. Chemical shifts are reported in ppm with TMS as an internal standard ( $\delta = 0$  ppm). IR spectra were obtained using a Perkin-Elmer 1600 FT-IR instrument. The FAB mass spectrum was determined on

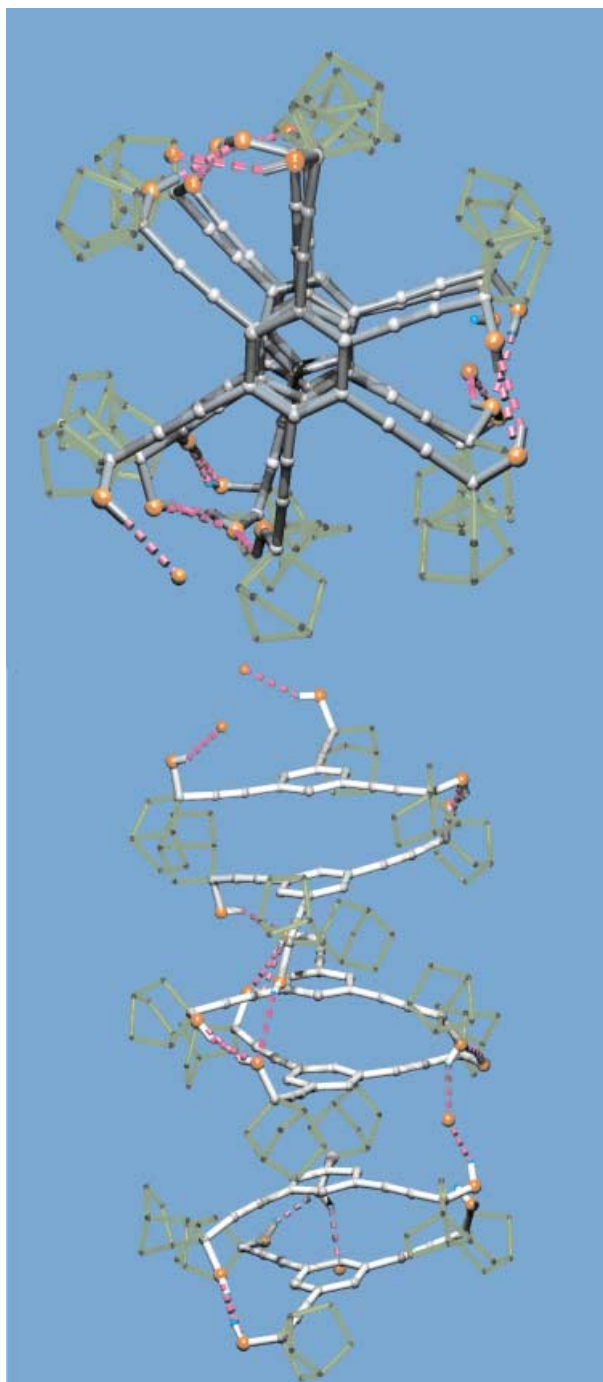


Figure 4. Top and side views of the asymmetric unit and crystal structure of **1e** with relevant features emphasized, such as hydrogen bonds and ring stacks; irrelevant H atoms are omitted, borneol C atoms are depicted with glassy bonds to ensure clarity.

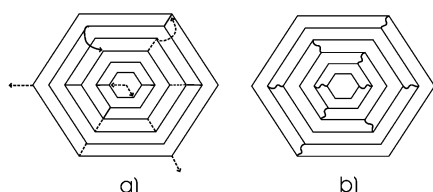


Figure 5. Planar molecular graph representations of a) **1d**, with forward hydrogen bond contacts shown in full lines and backward ones with broken lines; arrows indicate hydrogen bond connections between next unit cells; b) [6]Chochin, reprinted with permission from reference [19b].

a Kratos Concept 1H instrument. The elemental analysis was performed with a Heraeus CHN rapid analyzer.

**Starting materials:** (+)-2- $\alpha$ -Ethynyl-1,7,7-trimethylbicyclo[2.2.1]heptane-2 $\beta$ -ol (**3**) was synthesized in 90% yield by ethynylation of (D)-(+)-camphor (**2**) with lithium acetylide/ethylenediamine and ethyne in benzene according to the literature.<sup>[11, 12]</sup> 1,3,5-Tribromobenzene (**4**) was purchased from Aldrich.

**(+)-2- $\alpha$ ' $\alpha$ '-[Benzene-1,3,5-triyltri(ethyne,2,1-diyl)]tris(1,7,7-trimethylbicyclo[2.2.1]heptan-2 $\beta$ -ol) (**1**):** A solution of tribromide (**4**) (3.20 g, 10 mmol) and ethynyl compound **3** (5.70 g, 32 mmol) in triethylamine/toluene (2:1, 120 mL) was degassed with argon and treated with the catalyst composed of palladium(II) acetate (25 mg), triphenylphosphane (75 mg), and copper(I) iodide (25 mg), under gentle reflux to yield a red solution and a grey solid. After 5 h at reflux, the mixture was cooled to room temperature, the solid (triethylamine hydrobromide) was filtered off, and the solvent removed. The remaining solid was taken up with diethyl ether (250 mL), washed with 10% aqueous hydrochloric acid, water, saturated aqueous sodium bicarbonate, then water, in this sequence. Evaporation of the diethyl ether and recrystallization from ethanol/diethyl ether (2:1) yielded a clathrate (**1**·2EtOH), which decomposed on heating in vacuum (0.01 Torr) for 12 h at 120 °C to give pure **1** as colorless solid (5.21 g, 86%). M.p. > 310 °C;  $[\alpha]_D^{20} = +25.1$  ( $c = 2.1$  in diethyl ether); <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta = 0.91$  (s, 9H; CH<sub>3</sub>), 1.01 (s, 9H; CH<sub>3</sub>), 1.12 (s, 9H; CH<sub>3</sub>), 1.17–1.24 (m, 3H; bornyl), 1.47–1.58 (m, 3H; bornyl), 1.69–1.82 (m, 6H; CH<sub>2</sub>), 1.89–1.95 (m, 6H; CH<sub>2</sub>), 2.02 (s, 3H; OH), 2.28–2.32 (m, 3H; CH-bornyl), 7.38 ppm (s, 3H; ArH); <sup>13</sup>C NMR (100.6 MHz, CDCl<sub>3</sub>):  $\delta = 10.4$  (CH<sub>3</sub>), 21.0 (CH<sub>3</sub>), 21.4 (CH<sub>3</sub>), 27.0 (CH<sub>2</sub>), 32.6 (CH<sub>2</sub>), 45.5 (CH), 48.0 (CH<sub>2</sub>), 48.3 (qC), 53.9 (qC), 78.4 (C–OH), 82.1 ppm (C $\equiv$ C–Ar), 94.7 (C $\equiv$ C–Ar), 123.7 (Ar–C $\equiv$ C), 134.0 (Ar–H); IR (KBr):  $\tilde{\nu} = 3465$  (OH), 3001 (ArH), 2952, 2875 (CH, bornyl), 2235 (C $\equiv$ C), 1581 (C $\equiv$ C, Ar), 1060 (C–O), 878 cm<sup>-1</sup> (ArH); FAB-MS (mNBA + NaOAc):  $m/z$ : 629.4 [ $M^+$ +Na]; elemental analysis calcd (%) for C<sub>42</sub>H<sub>54</sub>O<sub>3</sub>: C 83.12, H 8.97; found C 82.96, H 9.13.

**X-ray structure determination:** Crystal data and other pertinent details of the structure determinations are summed up in Table 1. Suitable single crystals for the diffraction experiments were grown by slow evaporation of their respective guest solvents in parafilm semisealed ampoules. Compound **1e** was an exception in that respect; these crystals were formed from toluene that apparently either contained traces of water or absorbed moisture from the air. X-ray data sets were collected on automated four-circle instruments with Cu<sub>K $\alpha$</sub>  radiation in all but one case (**1b**, Mo<sub>K $\alpha$</sub> ). Initial structure models were obtained by SHELXS-97;<sup>[23]</sup> in the case of **1d** and **1e** (**1e** by CRUNCH<sup>[24]</sup>) only after considerable difficulties. Full-matrix least-squares refinement<sup>[25]</sup> on  $F^2$  proceeded smoothly for **1a**, **1b**, **1c**, and **1e**, less trivially for **1d** in which extensive disorder in the guest sites occurred. CCDC-166400, CCDC-166401, CCDC-166402, CCDC-166403, and CCDC-166404 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via [www.ccdc.cam.ac.uk/conts/retrieving.html](http://www.ccdc.cam.ac.uk/conts/retrieving.html) (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK, (fax: (+44)1223-336-033; or deposit@ccdc.cam.ac.uk).

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