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Two-dimensional hexagonal hydrogen-bonded network with triangle-like large cavities: hexakis(4-carboxyphenyl)benzene

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Abstract

Hexakis(4-carboxyphenyl)benzene (**1**) as a radially functionalized hexagonal host was synthesized by the Co-catalyzed cyclotrimerization of diarylacetylene. When recrystallized from MeOH, host **1** self-assembles into a two-dimensional hexagonal hydrogen-bonded network having triangle-like large cavities (one side of ca. 15.2 Å), each of which is filled with guest molecules without interpenetration of the crystal lattice.

Keywords: carboxylic acids; carboxylic acid derivatives; hydrogen bonding; supramolecular chemistry; X-ray crystallography.

Particular attention has recently been focused on the rational design of microporous solids from the viewpoint of specific properties such as selective adsorption[1] and catalytic activity.[2] The formation of hydrogen-bonded networks having large cavities, however, often tends to self-interpenetrate, filling the voids left in the initial host structure.[3] The uses of hexagonal rigid macrocycles having multiple hydrogen bonding sites[4] and of the orthogonal aromatic triad strategy for the preorganization of host molecules[5] have so far been reported in order to prevent interpenetrations of porous networks. We have recently described the self-assembly of hexakis(4-hydroxyphenyl)benzene which is radially capable of bearing divergent and multi-point hydrogen bonding sites and deploying an orthogonal factor between the interactive and core moieties.[6] Herein we report a two-dimensional hexagonal hydrogen-bonded network of hexakis(4-carboxyphenyl)benzene (**1**) having triangle-like large cavities.[7,8]

The cobalt(0)-catalyzed cyclotrimerization of bis(4-ethoxycarbonylphenyl)acetylene (90% yield) followed by the hydrolysis of the resulting hexaarylbenzene (>98% yield) afforded host **1** as shown in Scheme 1.[9] Slow evaporation of a solution of **1** in MeOH with and without 2 equivalents of 2,7-dimethoxynaphthalene (**2**) gave inclusion co-crystals composed of **1**·2(**2**) and **1**·4(MeOH), respectively. This suggests that guest **2**, even without hydrogen bonding sites, is more favorably included in the crystal

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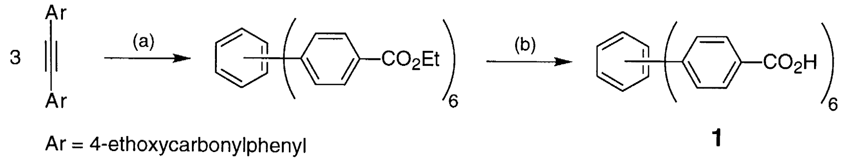
lattice of **1** as compared with MeOH. The single crystal X-ray crystallographic analysis of **1**·2(**2**) revealed the following aspects.[10,11]



Scheme 1. (a) $Co_2(CO)_8$ (5 mol%), dioxane, 100°C, 90%; (b) (i) KOH, MeOH–THF, 60°C; (ii) conc. HCl, >98%

The molecular structure of **1** possesses a center of symmetry (Fig. 1). The side aromatic rings which have carboxylic acid groups are nearly orthogonal with respect to the core aromatic ring, but not identical. Namely, the respective dihedral angles are 83.5(3), 85.6(3), and 91.7(4)°. Each **1** has six nearest neighbors. As a result of the formation of hydrogen-bonded carboxylic acid dimers, host **1** forms a two-dimensional hexagonal hydrogen-bonded network as shown in Fig. 2. The hydrogen bonding distances of O(1)H$\cdots$O(4), O(3)H$\cdots$O(2), and O(5)H$\cdots$O(6) for carboxylic acid dimers are 2.559(4), 2.662(4), and 2.666(3) Å, respectively. The hydrogen bonding pattern of O(5)H$\cdots$O(6) is aligned along the *b* axis. Thus, the hexagonal hydrogen-bonded network of **1** leads to a flat molecular sheet having triangle-like large cavities surrounded by three walls of the aromatic carboxylic acid dimer. The lengths of three sides of the triangular cavity are ca. 15.2, 15.2, and 15.4 Å. This network motif may be regarded as a hydrogen-bonded analog of the hypothetical graphdiyne network.[12]

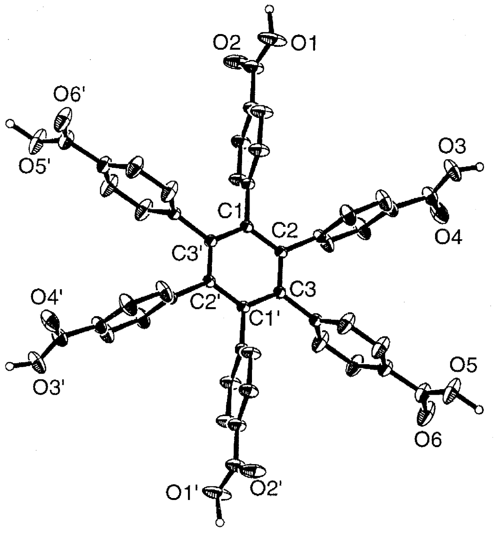


Fig. 1. ORTEP view of **1** (30% probability thermal ellipsoids)

As shown in Fig. 3, the adjacent sheets of **1** are separated by ca. 5.6 Å and layered in an ··ABAB·· sequence without interpenetration, which are translated by 6.34, 9.11, and 13.41 Å along the *a*, *b*, and *c* axes, respectively. This stacking motif of the sheets still leaves significant void space and generates three types of channels of ca. 7.9×5.8 Å (parallelogram), ca. 7.9×7.9×7.8 Å (triangle), and ca. 5.8×5.8×7.8 Å (triangle) in cross-section running parallel to the *a* axis. The packing coefficient and the pore size of host **1** in the crystals are 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,[5b] which are comparable to the crystals of hexakis(4-hydroxyphenyl)benzene.[6]

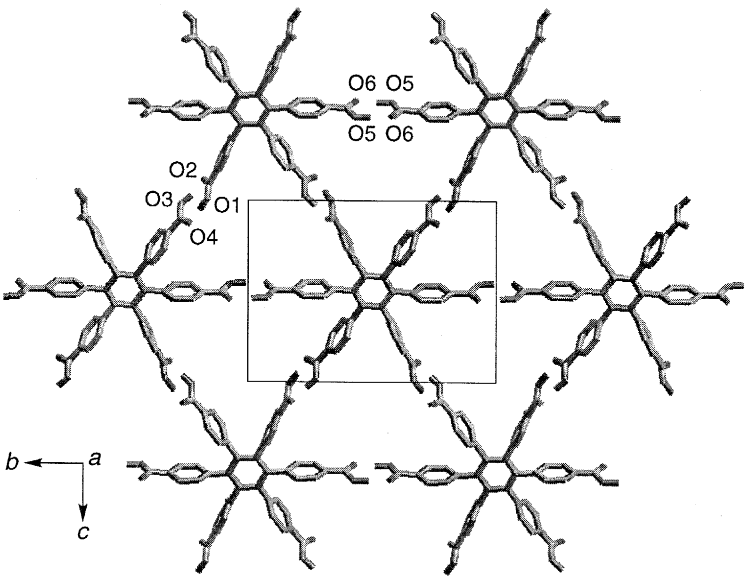


Fig. 2. Two-dimensional hexagonal hydrogen-bonded network of **1** (one sheet) parallel to the *a* axis. Guest molecules are omitted for clarity

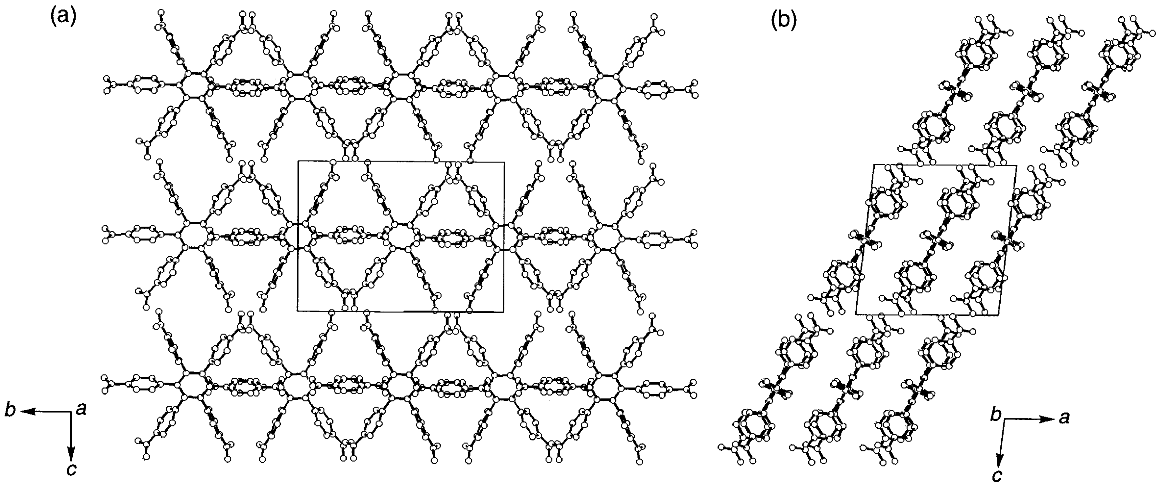


Fig. 3. Packing diagrams (with one unit cell outline) of three neighboring sheets of **1** parallel to (a) the *a* axis; and (b) the *b* axis. Guest molecules are omitted for clarity

Each of these triangular cavities in a sheet as shown in Fig. 2 are filled with a half of guest **2** in the same sheet and the methoxy group of **2** from an adjacent sheet. Guest **2** accommodated in a cavity is oriented so as to maximize CH–π interaction between one methoxy group of **2** and the side aromatic ring of **1**, and face-to-face (between a half of naphthalene ring and carboxylic acid dimer) and edge-to-face π–π interactions (Fig. 4a and Fig. 4b), with the closest C···C contact distances of 3.39, 3.53, and 3.39 Å, respectively. Another methoxy group of **2** in a sheet interacts with a half of a naphthalene ring of **2** from an adjacent sheet via CH–π interaction (the closest C···C contact distance, 3.72 Å) as shown in Fig. 4c. This guest stacking motif could serve as a pillar to connect the adjacent sheets to each other.[1a,f]

In summary, we have demonstrated that hexakis(4-carboxyphenyl)benzene (**1**) as a radially functio-

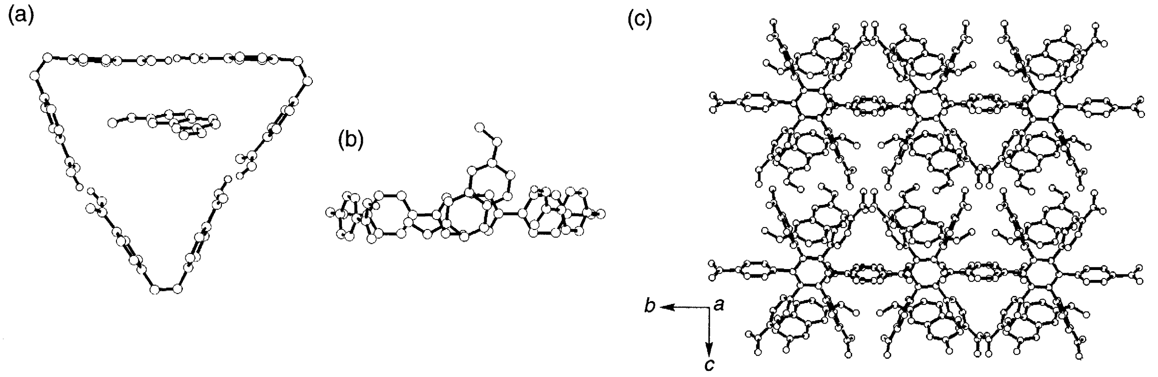


Fig. 4. (a) Top view of one cavity of **1** with guest **2**; (b) side view of one cavity of **1** with **2**; and (c) packing diagram of four neighboring sheets of **1** with **2** parallel to the *a* axis

nalized hexagonal host assembles into a two-dimensional hexagonal hydrogen-bonded network having triangle-like large cavities without interpenetration. Studies are in progress for the extension of the cavity size of **1** by changing the aromatic spacer of the interactive moiety and for a metal-coordination network using **1** based on the present strategy.

Acknowledgements

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9. Selected data for compound **1**: mp >400°C; ^{1}H NMR (DMSO-d_6, 25°C) δ 7.04 (d, J=8.1 Hz, 2H), 7.45 (d, J=8.1 Hz, 2H); ^{13}C NMR (DMSO-d_6, 80°C) δ 127.3, 128.1, 130.7, 138.9, 143.3, 166.3; ESI-MS (MeOH) m/z 821 (M^++Na). Anal. calcd for $C_{48}H_{30}O_{12}\cdot H_2O$: C, 70.59; H, 3.95. Found: C, 70.84; H, 4.05.
10. Crystal data for 0.5(**1**)·**2**: $C_{36}H_{27}O_8$, M=587.60, 0.13×0.35×0.40 mm, monoclinic, space group $P2_1/a$ (#14), a=12.680(2), b=18.229(3), c=13.408(2) Å, β=96.94(1)°, V=3076.6(7) Å^3, Z=4, D_c=1.269 g cm^{-3}, μ(Mo-Kα)=1.79 cm^{-1}, T=296 K, $2\theta_{max}$=61.0°, 9947 reflections measured, 9576 unique (R_{int}=0.031). The refinement (411 variables) based on F converged with R=0.051, R_w=0.043, and GOF=1.26 using 3492 unique reflections ($I>3.0\sigma(I)$).
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