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Organic crystals bearing both channels and cavities formed from tripodal adamantane molecules

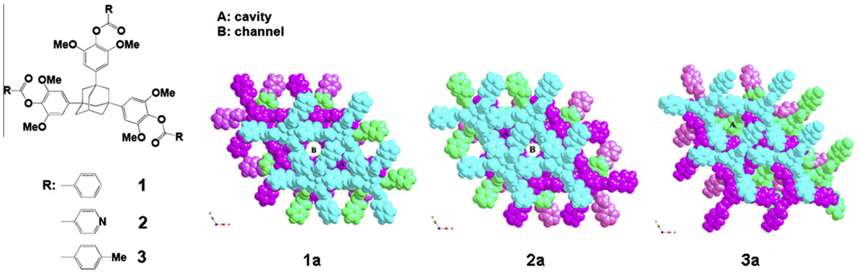
Masahide Tominaga *, Akitaka Iekushi, Kosuke Katagiri, Kazuaki Ohara, Kentaro Yamaguchi, Isao Azumaya *

Faculty of Pharmaceutical Sciences at Kagawa Campus, Tokushima Bunri University, 1314-1 Shido, Sanuki, Kagawa 769-2193, Japan

HIGHLIGHTS

- Three adamantane-cored tripodal molecules were synthesized.
- X-ray crystallographic analyses were performed on single-crystals of tripodal molecules.
- Three tripodal molecules afforded molecular organic networks bearing internal spaces.
- Two crystals exhibited the formation of both 1D channels and cavities.
- One crystal showed the generation of only cavities in the crystalline lattices.

GRAPHICAL ABSTRACT



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ABSTRACT

Three adamantane-based tripodal molecules bearing either a benzene, pyridine, or toluene unit (**1**–**3**) form molecular organic networks (**1a**–**3a**) with internal spaces, via intermolecular non-covalent interactions such as CH/π, CH/N, and CH/O interactions in the solid state. Crystals of **1a** and **2a** formed both one-dimensional channels and cavities, where guest molecules were encapsulated. The channels were derived from the alignment of the hexagonal cavities formed from six component molecules, while cavities formed between the 2D layers. In contrast, **3a** contained only cavities built from the six component molecules, which correspond to the spaces which connected to form channels in **1a** and **2a**.

1. Introduction

The construction of channels and cavities in molecular organic networks are important subjects in the fields of crystal engineering and materials science [1–4]. Organic materials which have inner spaces are of considerable interest due to their ability to recognize molecules selectively, stabilize unstable guest species, and perform chemical transformations [5–15]. Especially, C_3-symmetric organic molecules with rigid frameworks are useful building blocks for the production of organic crystals with channels or cavities [16–19]. For example, tris(o-phenylenedioxy)cyclotriphosphazene forms a porous crystal with a permanent one-dimensional channel, where gases, linear π–conjugated molecules, and polymers can be encapsulated [20–22]. Substituted 1,3,5-triazine molecules provide channel-type structures, and can accommodate large molecules such as fullerenes in addition to small aromatic molecules [23,24]. However, examples of molecular organic networks containing both channels and cavities are quite limited. The generation of these higher orders of network structures containing inner spaces is an intrinsically important task for the development

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* Corresponding authors. Tel.: +81 87 894 5111; fax: +81 87 894 0181.
E-mail addresses: tominagam@kph.bunri-u.ac.jp (M. Tominaga), azumayai@kph.bunri-u.ac.jp (I. Azumaya).

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of host-guest systems for the molecular recognition of gasses, organic molecules, and others [25–36]. Thus, we envisioned molecules with non-planar C_{3v}, to bent planar C_3 symmetric compounds would be appropriate for the preparation of crystalline materials which have both channels and cavities. This is because these molecules may form a cavity separate from the channels due to their three-dimensional shape, whilst maintaining the channel structures. Tri-substituted adamantane is a suitable skeleton for the design of C_{3v}-symmetric molecules. Recently, we presented hydrogen-bonded organic networks with channels that were built from adamantane-based tripodal molecules containing dimethoxyphenol moieties [37]. Herein we report three different adamantane-centered tripodal molecules bearing either a benzene, pyridine, or toluene moiety and the molecular organic networks they form through intermolecular non-covalent interactions such as CH/π, CH/N, and CH/O interactions.

2. Experimental

2.1. General

All the reagents and solvents used were commercially available and employed as received without further purification. The ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker AV-400M spectrometer at 27 °C using $CDCl_3$ as the solvent and TMS as an internal reference. Melting points were determined on an ASONE ATM-01 melting point apparatus and were uncorrected. FAB mass was performed on a JEOL JMS-700 using an *m*-nitrobenzylalcohol (NBA) matrix. Elemental analyses were performed with a Perkin-Elmer 2400 elemental analyzer. IR spectra were recorded with a Jasco FT/IR-6300 instrument. X-ray data for the crystals **1a**–**3a** were collected on a CCD diffractometer with graphite monochromated Mo Kα (λ = 0.71073 Å) radiation. Data collection was carried out at 100 K using a Japan Thermal Eng. Col., Ltd. Cryostat system equipped with a liquid nitrogen generator. The crystal structures were solved by direct methods (SHELXS 97, Sheldrick, 1997) [38]. Refinements were carried out by full-matrix least squares on F^2, with anisotropic temperature factors for non-H atoms. In all structures, H atoms were included as their calculated positions. SHELXTL was used for refinement of the structure and structure analysis. Column chromatography was performed using a Wakogel C200, and thin-layer chromatography was carried out on 0.25 mm Merck precoated silica gel glass plates. Gel permeation Chromatography (GPC) was performed using a recycling preparative HPLC system (LC-9204, Japan Analytical Industry Co., Ltd.) fitted with a JAIGEL H series column (Japan Analytical Industry Co., Ltd.).

2.2. Synthesis

2.2.1. 1,3,5-Tris(4-benzoyloxy-3,5-dimethoxyphenyl)adamantane (1)

To a solution of 1,3,5-tris(4-hydroxy-3,5-dimethoxyphenyl)adamantane (0.59 g, 1.00 mmol) in dry THF (20 mL), benzoyl chloride (0.46 g, 3.30 mmol) was added under an argon atmosphere at 0 °C. After 10 min, triethylamine (1.5 mL) was added into the solution, and stirred for 2 d at room temperature. After evaporation to dryness, the residue was dissolved in $CHCl_3$, and washed with a saturated aqueous $NaHCO_3$ solution, then H_2O, and finally brine. The organic layer was dried over anhydrous Na_2SO_4 and filtered. Evaporation of the solvent followed by silica gel column chromatography (eluent: $CHCl_3$) and gel permeation chromatography (JAIGEL 1H+2H, $CHCl_3$) afforded **1** as a white solid (0.74 g, 0.82 mmol) in 82% yield. m.p. 170–172 °C. FT-IR (ATR, cm^{-1}): 2932, 2850, 1739, 1599, 1514, 1450, 1412, 1327, 1262, 1212, 1125, 1059, 704. ^{1}H NMR (400 MHz, $CDCl_3$, 27 °C) δ 8.24 (d, 6H, J = 7.6 Hz), 7.60 (t, 3H, J = 7.2 Hz), 7.48 (t, 6H, J = 8.0 Hz), 6.75 (s, 6H), 3.84 (s, 18H), 2.59 (s, 1H), 2.20–2.06 (m, 12H). ^{13}C NMR (100 MHz, $CDCl_3$, 27 °C) δ 164.60, 152.01, 148.25, 133.24, 130.29, 129.33, 128.33, 127.18, 102.24, 56.25, 48.27, 41.42, 38.83, 30.06. MS (FAB, *m/z*) calcd for $C_{55}H_{53}O_{12}$ (M+H$^+$) 905.35, found 905.1. Anal. Calcd for $C_{55}H_{52}O_{12}\cdot 0.1H_2O$: C, 72.85; H, 5.80. Found: C, 72.56; H, 5.78.

2.2.2. 1,3,5-Tris(4-isonicotinoyloxy-3,5-dimethoxyphenyl) adamantane (2)

To a solution of 1,3,5-tris(4-hydroxy-3,5-dimethoxyphenyl)adamantane (0.59 g, 1.00 mmol) in dry THF (20 mL), isonicotinoyl chloride hydrochloride (0.59 g, 3.30 mmol) was added under an argon atmosphere at 0 °C. After 10 min, triethylamine (2.5 mL) was added into the solution, and stirred for 3 d at room temperature. After evaporation to dryness, the residue was dissolved in $CHCl_3$, and washed with a saturated aqueous $NaHCO_3$ solution, then H_2O, and finally brine. The organic layer was dried over anhydrous Na_2SO_4 and filtered. Evaporation of the solvent followed by silica gel column chromatography (eluent: $CHCl_3$:MeOH = 50:1) and gel permeation chromatography (JAIGEL 1H+2H, $CHCl_3$) afforded **2** as a white solid (0.58 g, 0.64 mmol) in 64% yield. m.p. 232–233 °C. FT-IR (ATR, cm^{-1}): 2931, 2847, 1748, 1587, 1508, 1451, 1413, 1324, 1248, 1212, 1124, 847, 687. ^{1}H NMR (400 MHz, $CDCl_3$, 27 °C) δ 8.85 (s, 6H), 8.05 (d, 6H, J = 5.6 Hz), 6.75 (s, 6H), 3.86 (s, 18H), 2.62 (s, 1H), 2.22–2.08 (m, 12H). ^{13}C NMR (100 MHz, $CDCl_3$, 27 °C) δ 163.22, 151.75, 150.55, 148.63, 136.54, 126.61, 123.40, 102.02, 56.16, 48.20, 41.33, 38.87, 29.98. MS (FAB, *m/z*) calcd for $C_{52}H_{50}N_3O_{12}$ (M+H$^+$) 908.33, found 908.9. Anal. Calcd for $C_{52}H_{49}N_3O_{12}\cdot 1H_2O$: C, 67.45; H, 5.55; N, 4.54. Found: C, 67.14; H, 5.41; N, 4.53.

2.2.3. 1,3,5-Tris(4-(4-methylbenzoyloxy)-3,5-dimethoxyphenyl) adamantane (3)

To a solution of 1,3,5-tris(4-hydroxy-3,5-dimethoxyphenyl)adamantane (0.59 g, 1.00 mmol) in dry THF (20 mL), *p*-toluoyl chloride (0.51 g, 3.30 mmol) was added under an argon atmosphere at 0 °C. After 10 min, triethylamine (1.5 mL) was added into the solution, and stirred for 2 d at room temperature. After evaporation to dryness, the residue was dissolved in $CHCl_3$, and washed with a saturated aqueous $NaHCO_3$ solution, then H_2O, and finally brine. The organic layer was dried over anhydrous Na_2SO_4 and filtered. Evaporation of the solvent followed by silica gel column chromatography (eluent: $CHCl_3$) and gel permeation chromatography (JAIGEL 1H+2H, $CHCl_3$) afforded **3** as a white solid (0.67 g, 0.71 mmol) in 71% yield. m.p. 163–165 °C. FT-IR (ATR, cm^{-1}): 2933, 2849, 1733, 1598, 1515, 1452, 1411, 1325, 1263, 1211, 1128, 1061, 816, 746. ^{1}H NMR (400 MHz, $CDCl_3$, 27 °C) δ 8.13 (d, 6H, J = 8.0 Hz), 7.29 (d, 6H, J = 8.4 Hz), 6.73 (s, 6H), 3.83 (s, 18H), 2.59 (s, 1H), 2.43 (s, 9H), 2.18–2.05 (m, 12H). ^{13}C NMR (100 MHz, $CDCl_3$, 27 °C) δ 164.69, 152.09, 148.20, 144.02, 130.40, 129.07, 127.30, 126.63, 102.32, 56.31, 48.31, 41.48, 38.86, 30.11, 21.65. MS (FAB, *m/z*) calcd for $C_{58}H_{59}O_{12}$ (M+H$^+$) 947.39, found 946.8. Anal. Calcd for $C_{58}H_{58}O_{12}\cdot 0.1H_2O$: C, 73.42; H, 6.18. Found: C, 73.08; H, 6.10.

2.3. Crystallization

The appropriate tripodal molecule (0.02 mmol) was stirred in tetrahydrofuran (10.0 mL) for **1** or acetonitrile (10.0 mL) for **2** and **3** at room temperature for 1 h. Colorless single crystals of **1a**–**3a** were obtained by slow evaporation of the solvent after a few days.