A Bidirectional Tunnel-like Structure with a Rigid, Thick, and Chiral Aromatic Macrocycle Prepared by Self-complementary 6,6′-Substituted Binaphthyl Monomer

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A rigid, thick, and optically active aromatic macrocycle having 6,6′-binaphthylylene moieties was successfully obtained in a moderate yield by synthesis and $\mathrm{S_NAr}$ of 6-(4-fluorobenzoyl)-6′-hydroxy-2,2′-dimethoxy-1,1′-binaphthyl. The X-ray crystal structural analysis of the obtained macrocycle reveals rigid concavo–concave shape of the molecule and the bidirectional tunnel-like structure assembly consisting of two types of channels along *a* axis and *c* axis originated by intra- and intermolecular cavities, respectively.

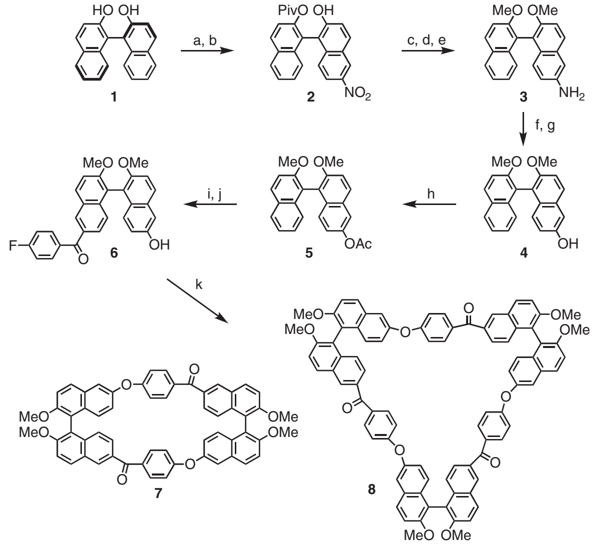
Rigid macrocycle is one of the most fascinating subjects in recent organic chemistry. For effective synthesis of such rigid cyclic skeleton, the thermodynamically advantageous macrocyclic structure and the choice of the synthetic route employing the best-fitted precursor for cyclization are essential. Thus, the design of the ring-closing precursor of depressed perturbation of conformation is naturally required with fine combination of several synthetic strategies to prevent uncontrolled oligomerization during macrocycle synthesis.[1a] The utilization of the coplanarly stretched subunit such as cyclic phenyleneethynylenes has been reported, which enables to fix the bond-forming functional groups at the preferable positions for selective ring closing.[1]

On the other hand, some of the designed rigid planar macrocycles have revealed to form unidirectional channels in the assembled solid state.[1d] In a natural course of this, nonplanar rigid macrocycles are expected to achieve higher ordered intermolecular stacking. One of the most appropriate candidates for the starting molecule of this transformation is 1,1′-binaphthalene-2,2′-diol (BINOL). BINOL has optically active rigid molecular skeleton and relatively large cavity. There have been reported many synthetic studies of BINOL-based macrocyclic compounds with flexible linkers at 2,2′-positions.[2] However, there have been reported only a few homologous compounds having rigid linkers. This is presumed to be due to difficulty of controlled introduction of rigid and bulky linker units to sterically hindered 2,2′-positions. Furthermore, there have been also only a few reports on the synthesis of the macromolecules by enchainment at the 6,6′-positions though the 6,6′-positions are situated at the open edge of the wide cavities in BINOL unit.[3]

The authors' group has reported the selective 6,6′-aroylation reaction of 2,2′-dimethoxy-1,1′-binaphthyl and the application to aromatic polyketone synthesis.[4] The results prompted the authors to construct macrocyclic compounds by bond formation at the 6,6′-positions leaving the 2,2′-oxy group free to be applicable against another chemical modification. In this paper, the authors discuss the synthesis of rigid and thick macrocycles utilizing the unsymmetrical 6,6′-functionalization of 2,2′-dimethoxy-1,1′-binaphthyl followed by cyclization at the 6,6′-positions and the X-ray crystal structure of the resulting macrocyclic dimer.

To perform this macrocycle synthesis, hydroxy and 4-fluorobenzoyl groups are the choice of substituents for unsymmetrically 6,6′-functionalized binaphthyl **6**. Precursor **6** was obtained by 10 steps in a 30% yield (Scheme 1).[5] For details, see ESI.[6] The condensation reaction of precursor **6** yielded binaphthyl dimer **7** as the main product and trimer **8** as a subproduct.[7,8] The successful intermolecular cyclodimerization is probably attributed to the suitable geometry of 4-fluorobenzoyl and hydroxy groups against intramolecular bond formation in the open dimeric intermediate formed after the first nucleophilic aromatic substitution. However, this open dimer probably has still sufficient width of the groove of the binaphthylylene moiety to react intermolecularly yielding the trimer as subproducts and also oligomers as minor ones.

Single crystal of cyclic dimer **7** containing three EtOAc and one MeOH molecules per each macrocycle was obtained as yellow cube of the chiral space group $C222_1$.[9] The macrocycle is roughly donut-like shaped with an internal cavity of 4.0 Å



Scheme 1. Synthesis of binaphthyl dimer **7** and trimer **8**: (a) PivCl, Et_3N, CH_3CN; (b) HNO_3 H_2SO_4, Et_2O, 82% (two steps); (c) KOH, H_2O, THF; (d) MeI, K_2CO_3, acetone; (e) $SnCl_2 \cdot 2H_2O$, EtOH, 72% (three steps); (f) H_2SO_4, $NaNO_2$, AcOH, H_2O; (g) H_2SO_4, reflux, 70% (two steps); (h) AcCl, Et_3N, CH_2Cl_2, quant.; (i) 4-fluorobenzoyl chloride, $AlCl_3$, CH_2Cl_2; (j) KOH, H_2O, THF, 74% (three steps); (k) K_2CO_3, DMF, reflux, dimer **7**, 40%; trimer **8**, 6%.

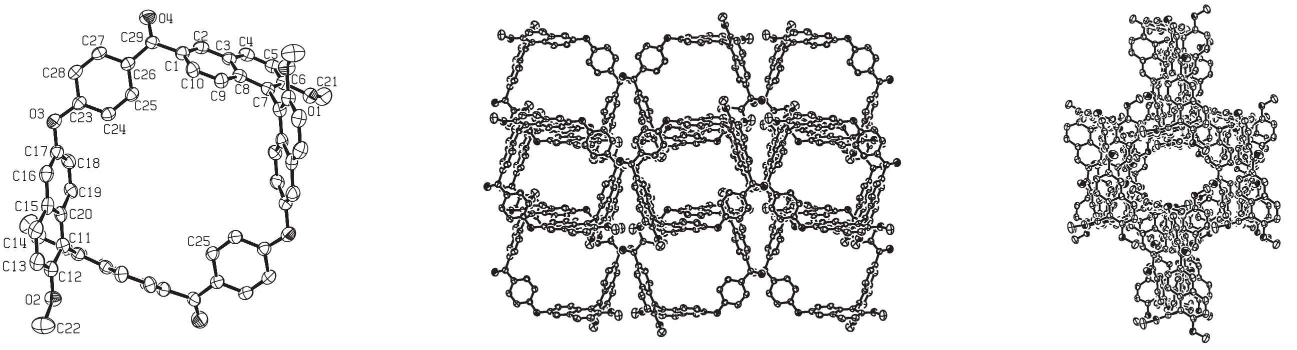


Figure 1. (Left) ORTEP drawing of cyclic dimer **7** with thermal ellipsoids at the 50% probability level. (Center) View down the *a* axis of crystal packing. (Right) View down the *c* axis. (H atoms and solvent molecules are omitted for clarity.) For details, see ESI.[6]

[H(24)···H(25a)] by 8.1 Å [C(7)···C(7a)]. The dihedral angle between the phenylene ring and the ether-linked naphthalene ring is 64.4(1)°, that between the phenylene ring and carbonyl-linked naphthalene ring is 86.6(1)°, and that between the naphthalene rings is 71.6(1)° (Figure 1; Left). The phenylene rings are parallel to each other and almost coplanar with the best plane of the macrocycle, while the two types of naphthalene rings are nearly perpendicular. The assembled solid structure of macrocycle **7** possesses two different types of channels along the *a* axis (Figure 1; Center) and the *c* axis (Figure 1; Right).

Macrocycle **7** has dual peak-to-trough periphery giving concavo–concave molecular surface. One face of the molecule has two salient naphthalene rings linked to carbonyl groups and the other has the in-plane naphthalene rings linked to ethereal oxygen. The characteristically shaped molecules should be locked with the adjacent molecules by two noncovalent interactions of the phenylene rings and the salient naphthalene groups with deviation of half a period. Thus, macrocycle **7** is aligned at a tilt in the *ab* plane with the common direction, making a thick and monomolecular-layer sheet.

In this sheet, rhombus-arranged unit of unidirectional macrocycles forms a cavity making the sheet porous. The sheets having the counter direction of the macrocycle are accumulated along *c* axis alternately with superposition of the pores through the accumulated sheets. Moreover, the sheets have another type of parallel channels formed by the superposition of the cavity along the columns of the macrocycles penetrating the monomolecular layer of the sheets parallel to each other and perpendicular to the first channels. Then, a bidirectional tunnel-like structured organic solid is formed.

Similar bidirectional porosity has been reported by Tykwinski et al. in the study on the solid structure of the metal complex of arylene–ethynylene macrocycle (AEM).[10] The formation of additional channel was explained as a result of the conformational change of the AEM to boat-like brought about by the metal-assisted face-to-face dimerization.

The characteristic solid structure of macrocycle **7** bearing two types of channels without the aid of metal additives is presumably attributed to the rigid, thick, and optically active concavo–concave molecular structure.

The bidirectional tunnel-like structure assembly thus obtained displays the novel area for finely designed higher ordered organic solid, especially that composed of only C, H, and O elements. In a natural course, the findings mentioned above imply the significance of further investigation of the isomeric macrocycles and the homologous ones in the selective synthesis and the expression of structure aiming organic materials having unique cavity.

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6 Supporting Information is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.

7 Typical procedure for the nucleophilic aromatic substitution cyclization is described in the followings: A solution of 6-(4-fluorobenzoyl)-6′-hydroxy-2,2′-dimethoxy-1,1′-binaphthyl (**6**, 0.2 mmol) in 20 mL of DMF was added K_2CO_3 (0.3 mmol) and stirred in refluxing for 24 h. The mixture was poured into water (40 mL) and extracted with EtOAc. The organic layer was washed with brine and dried over $MgSO_4$. After removal of the solvent in vacuo, the reaction mixture was separated by PTLC ($CHCl_3$) to afford dimer **7** (40%) and timer **8** (6%).

8 Dimer **7**: ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.76 (3H, s), 3.85 (3H, s), 6.91 (1H, d, $J = 9$ Hz), 6.96 (1H, d, $J = 9$ Hz), 6.99–7.07 (2H, m), 7.42 (1H, dd, $J = 9$, 2 Hz), 7.47 (1H, d, $J = 9$ Hz), 7.53 (1H, d, $J = 9$ Hz), 7.60 (1H, d, $J = 2$ Hz), 7.85 (2H, d, $J = 9$ Hz), 7.92 (1H, d, $J = 9$ Hz), 8.14 (1H, d, $J = 9$ Hz), 8.56 (1H, d, $J = 2$ Hz); ^{13}C NMR (75 MHz, $CDCl_3$): δ 56.6, 56.9, 114.5, 115.0, 115.1, 117.5, 118.1, 118.2, 121.9, 123.5, 125.9, 126.4, 127.3, 128.7, 129.0, 130.1, 130.5, 131.1, 131.4, 132.4, 132.9, 133.0, 135.6, 143.4, 149.8, 154.8, 193.8; IR (KBr): 1653, 1612, 1592, 1501, 1477, 1246 cm^{-1}; HRMS $[M + H]^+$ m/z 865.2772 (calcd for $C_{58}H_{41}O_8$, 865.2801).

9 Crystal data for cyclic dimer **7**: $C_{58}H_{41}O_8{\cdot}3C_4H_8O_2{\cdot}CH_4O$ $M_r = 1160.25$, Orthorhombic, space group $C222_1$, $a = 13.1320(2)$, $b = 17.5489(3)$, $c = 26.8074(5)$ Å, $V = 6177.82$ Å^3, $Z = 4$, $D_{calcd} = 1.2475(1)$ g cm^{-3}, $T = -155$ °C, $R_1 = 0.09$ (all data), $wR_2 = 0.26$ (all data), GOF = 1.074 for 5646 reflections and 375 parameters.

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