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Novel Host Compounds, 1,1′-Binaphthyl-2,2′-Dihydroxy-5,5′- and 6,6′-Dicarboxylic Acid, Which Trap Guest Molecules Tightly in Their Inclusion Crystals

KOICHI TANAKA[1,*], HIDEYUKI TAKANO[1] and ZOFIA URBANCZYK-LIPKOWSKA[2]
[1]*Department of Applied Chemistry, Faculty of Engineering & High Technology Research Center, Kansai University, 564-8680, Suita, Osaka, Japan;* [2]*Institute of Organic Chemistry, Polish Academy of Sciences, Kasprzaka 44/52, 01-224, Warszawa, Poland*

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Abstract

The host compounds 1,1’-binaphthyl-2,2′-dihydroxy-5,5′-dicarboxylic acid (**1**) and 1,1′-binaphthyl-2,2′-dihydroxy-6,6′-dicarboxylic acid (**2**) have been synthesized, and their inclusion properties have been studied. Inclusion complexes formed by **1** and **2** with volatile guests such as acetone and methanol release the guests only at much higher temperatures than their boiling points. The crystal structures of the inclusion complexes have been determined from single crystal X-ray diffraction data and show different host lattices.

Introduction

In recent years, there has been increasing interest in host-guest inclusion systems because of their potential applications in analytical, synthetic, and material sciences [1]. Previously, we reported that 2,2′-dihydroxy-1,1′-binaphthyl (**3**) is very useful as a host for the optical resolution of racemic guests [2] and as a chiral NMR shift reagent for the determination of chiral compounds [3]. It has also been reported that 1,1′-binaphthyl-2,2′-dicarboxylic acid (**4**) is a versatile host compound giving crystalline inclusion complexes with a wide range of organic guest molecules [4]. We have now designed and synthesized the title novel host compounds (**1** and **2**) having both COOH and OH groups in the molecules. The carboxyl groups of **1** and **2** may be linked by hydrogen bonding to form rigid frameworks and the OH groups can be used to trap guest molecules through hydrogen bonding, as illustrated in Scheme 1.

Experimental

Synthesis

General

^{1}H-NMR spectra were recorded in $CDCl_3$ on a JEOL Lambda 300 FT-NMR spectrometer. IR spectra were recorded with a JASCO FT-IR 4100 spectrometer. Thermogravimetric analyses (TG) were performed on a Rigaku TG-8120 instrument. The inclusion crystals were obtained by recrystallization of the host compound from the respective guest solvent.

*Synthesis of Host Compounds **1** and **2** (Scheme 2)*

1,1′-binaphthyl-2,2′-dihydroxy-5,5′-dicarboxylic acid (**1**). A solution of 6-hydroxy-1-naphthoic acid methyl ester (25 g, 0.124 mol) and $FeCl_3 \cdot 6H_2O$ (67 g, 0.248 mol) in H_2O (250 mL), heated at 70 °C under stirring for 20 h, precipitated crystals that were filtered by suction and dried in air. Recrystallization of the crude product from MeOH gave 1,1′-binaphthyl-2,2′-dihydroxy-5,5′-dicarboxylic acid methyl ester (12.5 g, 50%) as colorless needles. Mp 238–240 °C. IR (Nujol) 3298–3453, 1700 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ 4.04 (s, 6H), 5.02 (s, 2H), 9.06–7.35 (m, 10H). A solution of 1,1′-binaphthyl-2,2′-dihydroxy-5,5′-dicarboxylic acid methyl ester (12 g, 0.03 mol) in 10% aq. NaOH was heated under reflux for 1 h. The solution was acidified by adding conc. H_2SO_4 (10 mL) to afford crude crystals, which upon recrystallization from MeOH gave 1,1′-binaphthyl-2,2′-dihydroxy-5,5′-dicarboxylic acid (**1**) as colorless needles (11.1 g, 99%). Mp >300 °C. IR (Nujol) 3144–3497, 1708 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ 5.02 (s, 2H), 7.11–8.79 (m, 10H), 9.47 (s, 2H). Analysis: calc. for $C_{22}H_{14}O_6$: C 70.59, H 3.77; found C 70.31, H 3.56.

1,1′-binaphthyl-2,2′-dihydroxy-6,6′-dicarboxylic acid (**2**). A solution of 6-hydroxy-2-naphthoic acid methyl ester

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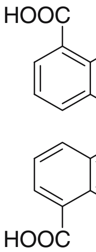
* Author for correspondence. E-mail: ktanaka@ipcku.kansai-u.ac.jp



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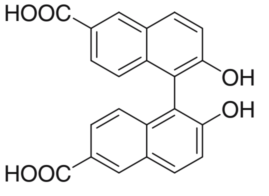

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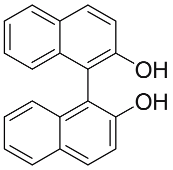

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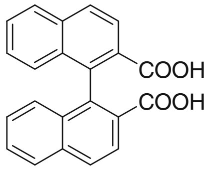

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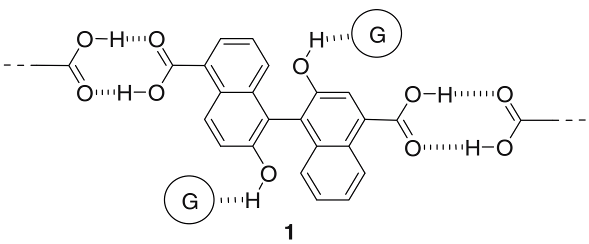
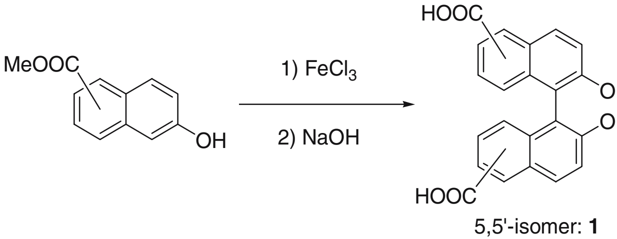


Scheme 1.



Scheme 2.

(25 g, 0.124 mol) and $FeCl_3{\cdot}6H_2O$ (67 g, 0.248 mol) in H_2O (250 mL), heated at 70 °C under stirring for 20 h, precipitated crystals that were filtered by suction and dried in air. Recrystallization of the crude product from MeOH gave 1,1′-binaphthyl-2,2′-dihydroxy-6,6′-dicarboxylic acid methyl ester (13 g, 52%) as colorless needles. Mp >300 °C. IR (Nujol) 3161–3418, 1700 cm^{-1}. ^1H-NMR ($CDCl_3$) δ 3.90 (s, 6H), 5.02 (s, 2H), 7.44–8.60 (m, 10H). A solution of 1,1′-binaphthyl-2,2′-dihydroxy-6,6′-dicarboxylic acid methyl ester (12 g, 0.03 mol) in 10% aq. NaOH was heated under reflux for 1 h. The solution was acidified by adding conc. H_2SO_4 (10 mL) to afford crude crystals, which upon recrystallization from MeOH gave 1,1′-binaphthyl-2,2′-dihydroxy-6,6′-dicarboxylic acid (**1**) as colorless needles (11 g, 98%). Mp >300 °C. IR (Nujol) 3135–3452, 1693 cm^{-1}. ^1H-NMR (DMSO-d_6) δ 5.02 (s, 2H), 6.96–8.54 (m, 10H), 9.75 (s, 2H). Analysis: calc. for $C_{22}H_{14}O_6$: C 70.59, H 3.77; found C 70.62, H 3.57.

Crystallography

X-ray Data Collection, Structure Solution, and Refinement

Suitable crystals of **1** · 3THF and **2** · 2MeOH were mounted on glass fibers and covered by epoxy glue. Data collections were performed at 200 and 295 K on a Nonius BV MACH diffractometer with graphite monochromated CuKα radiation ($\lambda = 1.54178$ Å), for 1 · 3THF and 2 · 2MeOH, respectively. Both structures were solved with direct methods using the SHELXS97 [5] program and refined with SHELXL97 [6] software included in the WINGX suite of programs [7]. Refinements were performed anisotropically for all non-hydrogen atoms of the two hosts and the majority of the guest molecules using the full-matrix least-squares method. In general, hydrogen atoms were placed in idealized positions and were allowed to ride with thermal parameters fixed at $1.2U_{eq}$ of the parent atom. In the case of complex **1** · 3THF, two guest molecules could be located and refined; the third THF molecule is highly disordered and identified atoms were refined isotropically. Details of data collection and structure refinement are shown in Table 1.

Result and discussion

*Inclusion capabilities of **1** and **2***

The host compound **1** incorporates a wide variety of guest compounds into stable inclusion complexes in the ratios indicated in Table 1. The host:guest stoichiometric ratios of 1:3 (THF and dioxane) and 1:4 (DMSO) are exceptionally large, which indicates the high efficiency of guest accommodation of the host 1. (Figure 1)

Host compound **2** also included various kinds of guest molecules as shown in Table 2. DSC measurements demonstrated the remarkable stability of these complexes. For example, the 1:1 inclusion complex of 1 with acetone decomposed at 180 °C. (Figure 2) The decomposition temperature of the complex exceeds the boiling point of the guest acetone (56 °C) by 124 °C. Similarly, the temperature differences in the cases of MeOH and THF are 100 and 51 °C, respectively.

X-ray structures

The isomeric host molecules **1** and **2** adopt conformations with two-fold symmetry and nearly perpendicular orientations of the two naphthyl units. Although temperature was lowered to 200 K during exposure to X-rays, exact positions for carbon atoms and protons for one out of three THF molecules in the complex with 1 could not be found. Crystal packing in the 1:3 complex of host 1 and THF could easily be deduced from the short O ··· O contacts. As shown in Figure 3, the expected H-bonded dimeric motif typical for carboxylic

Table 1. Crystal data and structure refinement for original **1**:3THF and **2**:2MeOH

Inclusion complex	**1**:THF	**2**:2MeOH
Empirical formula	$C_{22}H_{14}O_6 \cdot 3(C_4H_8O)$	$C_{22}H_{14}O_6 \cdot 2(CH_3OH)$
Formula weight	590.66	438.42
Crystal system, space group	Monoclinic, C2/c	Monoclinic, C2/c
Unit cell dimensions: (Å, °)		
a:	27.010(5)	20.4960(16)
b:	11.130(2)	9.0950(14)
c:	20.274(4)	13.4820(10)
β:	107.15(3)	120.830(6)
Volume (Å^3)	5824(2)	2158.1(4)
Z, Calculated density (Mg m^{-3})	8, 1.347	4, 1.349
Absorption coefficient (mm^{-1})	0.799	0.853
F(000)	2512	920
Crystal size (mm)	0.48 × 0.35 × 0.35	0.55 × 0.42 × 0.28
θ-range for data collection (°)	3.42–74.77	5.03–74.25
Reflections collected / unique	5814/5648	2245/2150
Completeness to $\theta = \theta_{max}$	94.5%	97.8%
Absorption correction	None	Psi-scan
Max. and min. transmission		0.9960 and 0.9088
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5648/0/353	2150/0/190
Goodness of fit on F^2	1.036	1.029
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.1124$, w$R_2 = 0.2949$	$R_1 = 0.0504$, w$R_2 = 0.1240$
R indices (all data)	$R_1 = 0.3091$, w$R_2 = 0.3949$	$R_1 = 0.1267$, w$R_2 = 0.1541$
Extinction coefficient	0.0005(2)	0.0018(2)

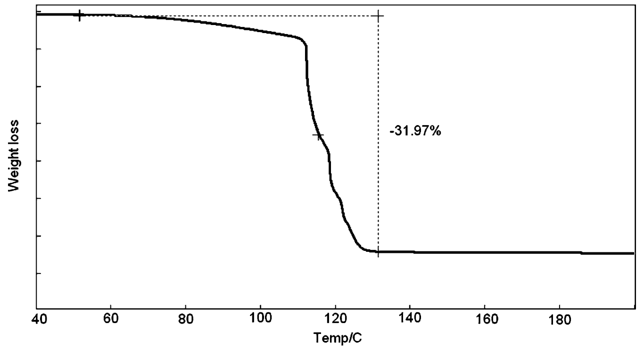


Figure 1. DSC trace of 1:3 THF complex of **1**.

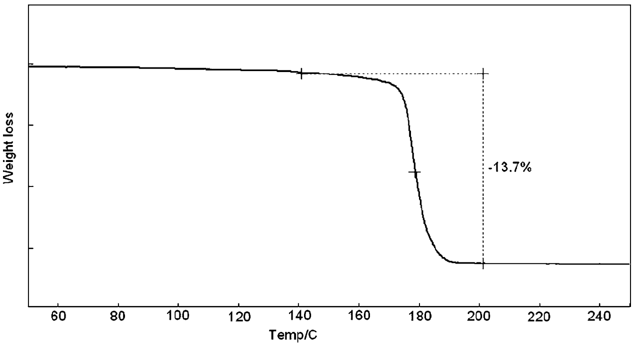


Figure 2. DSC trace of 1:1 acetone complex of **2**.

Table 2. Host-guest ratio of inclusion complex of **1**

Guest	H:G[a]	T$_{dec}$(°C)[b]	Crystal Form
MeOH	1:2	40	needles
EtOH	1:2	100	prisms
Acetone	2:1	100	prisms
cyclopentanone	1:2	120	prisms
γ-butyrolactone	1:2	110	prisms
EtOAc	1:1	63	needles
THF	1:3	109	prisms
dioxane	1:3	95	prisms
DMF	1:2	135	prisms
DMSO	1:4	140	prisms
MeCN	2:1	83	needles
H_2O	1:1	103	needles

[a]Host-guest ratios were determined by TG and NMR.
[b]Decomposition temperature.

Table 3. Host-guest ratio of inclusion complex of **2**

Guest	H:G[a]	T$_{dec}$(°C)[b]	Crystal Form
MeOH	1:2	164	prisms
EtOH	1:3	63	needles
Acetone	1:1	180	prisms
cyclopentanone	–[c]	–	–
γ-butyrolactone	–	–	–
EtOAc	1:1	87	needles
THF	1:2	116	prisms
dioxane	–	–	–
DMF	1:2	167	prisms
DMSO	1:1	180	prisms
MeCN	1:2	89	prisms
H_2O	1:3	46	needles

[a] Host-guest ratios were determined by TG and NMR.
[b] Decomposition temperature.
[c] No inclusion complexation occurred.

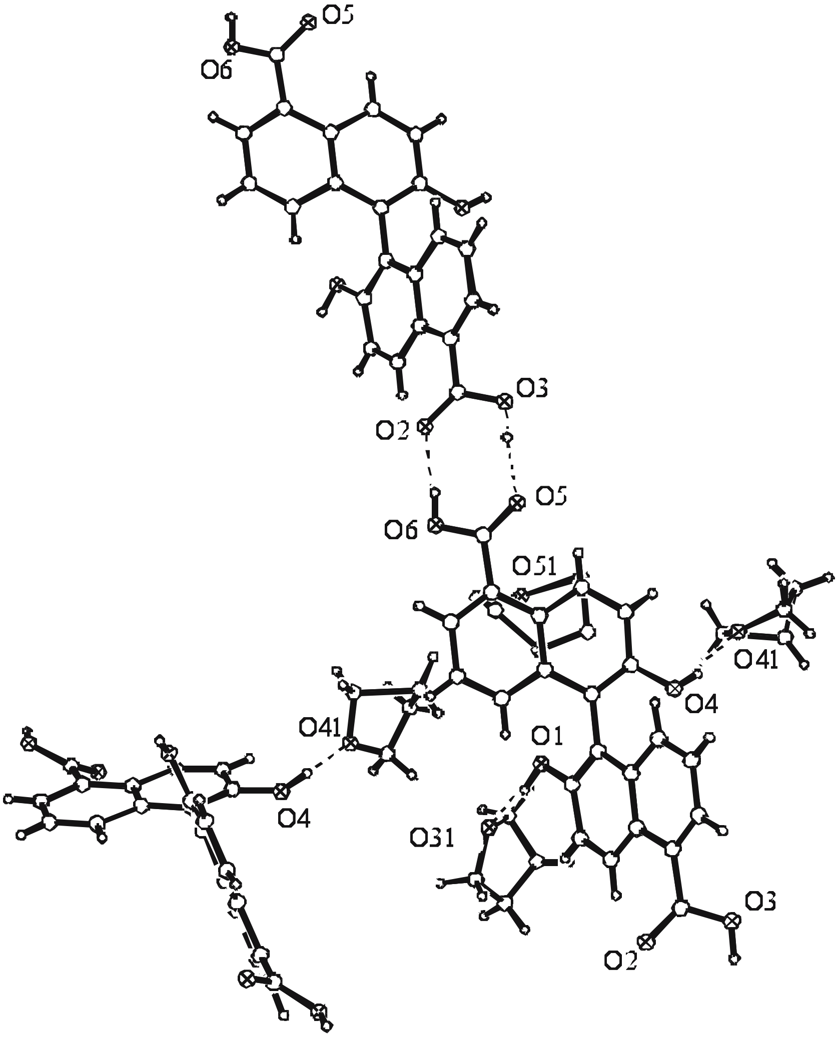


Figure 3. Basic motifs of crystal packing in the 1:3 complex of **1** and THF are: ribbons of hydrogen bonded host molecules [geometry: O2···O6 = 2.637(8), O2···H = 1.78(9), Å O6-H...O2 = 172(9)°; O3···O5 = 2.677(8), O5···H = 1.73(8) Å, O3-H···O5 = 174(7)°]; and THF – host interactions (geometry: O1···O31 = 2.796(8), O31···H = 1.90(9) Å, O1-H1...O31 = 163(8)°; O4···O41 = 2.734(9), O41···H = 1.83(11) Å, O4-H···O41 = 165(10)°].

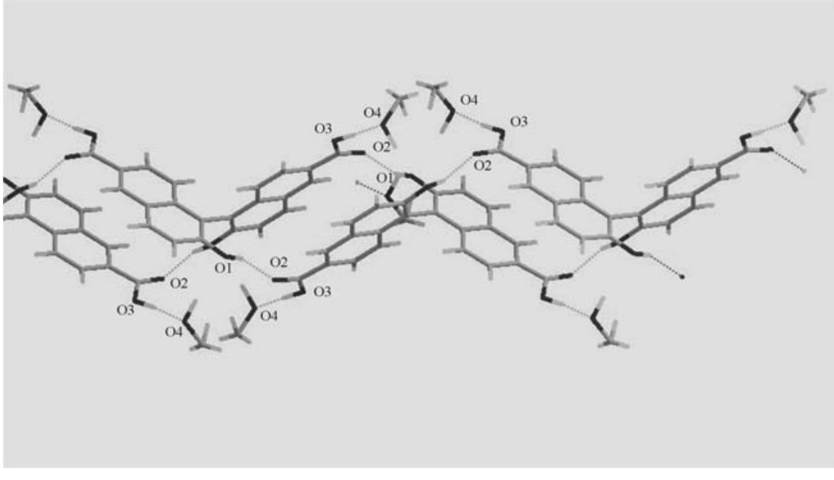


Figure 4. Basic packing motifs found in the 1:2 complex between host **2** and MeOH are: tapes of hydrogen bonded hosts [geometry: O1···O2 = 2.679(3), H1···O2 = 1.86(4) Å, angle 152(3)°]; and host ··· MeOH interactions [geometry: O31···O4 = 2.608(3), H31···O4 = 1.71(4) Å, angle 161(4)°].

acids is an essential force in crystal formation. Three THF molecules are inserted between two hydrogen-bonded host ribbons: two of them form relatively strong hydrogen bonds with hydroxyl groups of the host (for geometry see Figure 3 captions). The third disordered THF molecule, shown in back side of the host 1 is included in void space with no short non-bonding distances with any of the proton donors observed.

The crystal structure of the 1:2 complex of **2** and MeOH is shown in Figure 4. The asymmetric unit contains a half of the host molecule located on two fold axis. These molecules are linked into a three-dimensional framework structure by a set of OH...O hydrogen bonds between host and methanol molecules. The expected dimeric arrangement of the carboxylic hosts is absent in this case. Similarly as in the case of the previous complex, the two hydroxyl groups of the host **2** donate their H-atoms to form hydrogen bonds with the carboxyl O-atoms of the neighboring host molecules (for geometry see Figure 4). These H-bonds hold together an extended-tape motif. Additionally, hydroxyl group O-atoms act as acceptors for the protons of MeOH molecules [geometry: O4···O1 = 2.958(4), H4···O1 = 2.2(1) Å, O4-H4···O1 angle 124(10)°], binding two perpendicular systems of tapes.

In summary, the isomeric hosts **1** and **2** form different host lattices. Host **1** form ribbons sandwiching layers of THF molecules. Host **2** forms perpendicular tapes with hydrogen-bonded molecules located between the tapes.

Supplementary Data relating to this article have been deposited in the Cambridge Crystallographic Data Base: CCDC–291175 (**1** · 3THF) and CCDC-291176 (**2** · 2MeOH) contain the supplementary crystallographic data for this paper, which can be obtained free of charge at "http://www.ccdc.cam.ac.uk/conts/retrieving.html" [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; E-mail: deposit@ccdc.cam.sc.uk].

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