

Supramolecular Networks in Crystalline Inclusion Complexes Formed from a New Host: 2,2-Bis(4-hydroxy-3-phenylphenyl)-1*H*indene-1,3(2*H*)-dione

Kenta Kasugai,[†] Suzumi Hashimoto,[†] Kazunori Imai,[†] Aya Sakon,[‡] Kotaro Fujii,[‡] Hidehiro Uekusa,[‡] Naoto Hayashi,[§] and Keiji Kobayashi^{*,†}

⁺Department of Chemistry, Graduate School of Material Science, Josai University, Sakado, Saitama 350-0295, Japan ⁺Department of Chemistry and Material Science, Tokyo Institute of Technology, Ookayama, Meguro-ku, Tokyo 152-8551, Japan [§]Graduate School of Science and Engineering, University of Toyama, Gofuku, Toyama, 930-8555, Japan

Supporting Information

ABSTRACT: A scissors-shaped compound, 2,2-bis(4-hydroxy-3-phenylphenyl)-1*H*-indene-1,3(2*H*)-dione (1), has been prepared as a new host species for crystalline host-guest complexes. Compound 1 afforded complexes of 1:1 host-to-guest ratio with acetone, EtOH, and CH_2Cl_2 , and a 2:3 complex with benzene. The crystal structures of these complexes were elucidated. In all four crystals, a side-by-side dimer linked by head-to-tail >C=O···HO- hydrogen bonds is formed and



functions as the building unit of supramolecular networks. Except for $(1)_2$ (benzene)₃, the complexes featured intermolecular carbonyl–carbonyl interactions resulting in all-planar antiparallel alignment with markedly short C···O distances (< 3.15 Å). In (1)(EtOH), the four-centered interaction including two hydroxyl and two carbonyl groups was observed and designated as a quasi-bifurcated hydrogen bonding motif. Such a four-centered interaction has been observed to occur widely in crystal structures as proved by database searches from the Cambridge Structural Database (CSD). In all the crystals, the host molecules formed a channel-type void occupied by guest molecules. The crystal structure of the desolvated crystals of 1 has been elucidated for its polycrystalline solids by ab initio structure determination from powder X-ray diffraction data followed by the Rietveld refinement.

INTRODUCTION

The design of crystalline inclusion complexes is a challenging subject because there are no general methods for the prediction of organic crystal structures by computational methods despite recent developments.¹ Strategies for host—guest assembly rely on programmed recognition between topologically and chemically complementary functional groups through noncovalent interactions, referred to as supramolecular synthons.² Hydrogen bonds are commonly employed as a reliable adhesive to produce specific and robust patterns.³ The presence of rigid and bulky moieties within the host structure has also been identified as a positive attribute to provide suitable cavities to accommodate a guest molecule.⁴ From the geometric point of view, scissors-shaped,⁵ roof-shaped,⁶ and wheel-and-axle-shaped hosts⁷ have been shown to form crystalline supramolecular assemblies with suitable guests.

We have now tested a host design involving a scissors-shaped basic skeleton, 2,2-bis(4-hydroxy-3-phenylphenyl)-1*H*-indene-1,3(2*H*)-dione (1).⁸ Almost all scissors-shaped host compounds reported to date incorporate one type of functional group, principally, the hydroxyl function, to engage in $OH \cdots (H)O$ hydrogen bonding. In contrast, compound 1 consists of two functional groups, hydroxyl and carbonyl groups, that can interact not only between the host molecules complementarily but also between the host and guest components. If a possible conformation of Cs symmetry is retained, host 1 is expected to form a three-dimensional hydrogen bonding network by using all functional groups as cross-linked $>C=O\cdots HO-hydro$ gen bonding sites. Although this intention was not realized, host compound 1 has been found to form inclusion complexes with solvent molecules as guest species, and their crystal structures showed peculiar supramolecular networks consisting of inter-homomolecular and inter-heteromolecular hydrogen bonds, interhost—molecular interactions of the >C(δ +)= $O(\delta -)$ dipole, and four-centered interactions involving two hydroxyl and two carbonyl groups. Here, we present characteristic crystal structures of the inclusion crystals of host 1, principally focusing on a hydrogen bonding motif, along with that of guest-free 1, which was obtained as a polycrystalline solid by thermal guest release. For the latter, the crystal

Received:	May 15, 2011
Revised:	July 1, 2011
Published:	July 06, 2011

Гаb	le 1	l. (Crystal	lographic	Parameters	of	Inclusion	Comp	olexes	Derived	from	Host	: 1
-----	------	------	---------	-----------	------------	----	-----------	------	--------	---------	------	------	-----

	$(1)_2(benzene)_3$	(1)(acetone)	(1)(EtOH)	$(1)(CH_2Cl_2)$
T °C	-50	23	-50	-50
formula	$C_{84}H_{62}O_8$	C36H28O5	C35H28O5	$\mathrm{C}_{34}\mathrm{H}_{24}\mathrm{O}_4\mathrm{Cl}_2$
crystal system	monoclinic	triclinic	triclinic	monoclinic
space group	$P2_1/a(#14)$	$P\overline{1}(#2)$	$P\overline{1}(#2)$	$P2_1(#4)$
a/Å	15.775(5)	9.3492(4)	9.343(4)	9.3881(19)
b/Å	9.796(2)	11.2462(5)	11.137(6)	26.515(6)
c/Å	20.695(5)	14.0186(6)	14.234(6)	11.103(3)
$\alpha/^{o}$	90	74.5463(12)	112.231(18)	90
$\beta/^o$	94.896(11)	79.4118(14)	96.642(19)	97.768(10)
$\gamma/^{o}$	90	83.2828(15)	98.197(17)	90
$V/Å^3$	3186.3(14)	1392.87(11)	1338.8(10)	2738.5(10)
Ζ	2	2	2	4
$d_{\rm calc}/{\rm g~cm^{-3}}$	1.250	1.289	1.316	1.376
reflections collected	30516	13762	13289	44508
independent reflections	7276	6298	6090	12534
no. of reflections used	5497	6298	4372	7424
R_1	0.0431	0.0422	0.0658	0.0604
wR ₂	0.0107	0.1300	0.2158	0.0985



Figure 1. Molecular arrangement of the host molecules in $(1)_2$ -(benzene)₃. For clarity, all hydrogen atoms are omitted. The oxygen atoms related to hydrogen bonding are linked by blue dashed lines. The red benzene molecules are located on the crystallographic inversion center.

structure was determined from synchrotron powder X-ray diffraction data.



RESULTS AND DISCUSSION

Crystal Structures. Among the various solvents used for recrystallization (clathration) experiments on 1, acetone, dichloromethane, benzene, and ethanol gave single crystals suited for X-ray analysis. Their host-to-guest stoichiometry was 1:1, except for benzene, which afforded a rather uncommon 2:3 stoichiometry. Other solvents such as acetonitrile (1:1), chloroform (1:1), and pyridine (2:1) afforded inclusion crystals, but their crystal structures were not characterized because of their



Figure 2. Crystal structure of $(1)_2$ (benzene)₃ as viewed down the *b*-axis showing the channel embedded with guest molecules.

poor crystallinity. The guest molecules were not released to form guest-free crystals after standing for three weeks at room temperature except for $(1)(CH_2Cl_2)$, which collapsed within a few days. The crystal structures of $(1)_2$ (benzene)₃, (1)(acetone), (1)(EtOH), and $(1)(CH_2Cl_2)$ were elucidated (Table 1).

The crystal structure of $(1)_2(\text{benzene})_3$ is shown in Figure 1. The host molecules are linked by complementary intermolecular $>C=0\cdots$ HO – hydrogen bonds to form an infinite chain along the *a*-axis. The two $>C=0\cdots$ HO hydrogen bonds connecting the molecules show markedly different $O(H)\cdots O$ distances: one is 2.730 Å, while the other is 2.989 Å. These observations imply that a neighboring pair of host molecules, and hence the dimeric motif in $(1)_2(\text{benzene})_3$, is not in a centrosymmetric arrangement. The guest molecules are located in channel-type voids formed by the host chain parallel to the *b*-axis and show no specific modes of host–guest binding (Figure 2). Thus, the enclosure of benzene in $(1)_2(\text{benzene})_3$ occurs as a clathrate formation in terms of the original meaning (true clathrates).⁹ The structural unit observed in $(1)_2(\text{benzene})_3$, a cyclic dimer linked by two C=O···HO hydrogen bonds, is commonly Scheme 1. Diagrammatic Representation of a Supramolecular Network Based on the Dimeric Unit, Showing Hydrogen Bonding with Guest Molecules, Carbonyl–Carbonyl Interactions between Dimeric Units, and Four-Centered Quasi-Bifurcated Hydrogen Bonding^a



^a The hydrogen bonding with guest molecules is represented as $G \cdots HO$. (a) (1)₂(benzene)₃, (b) (1)(acetone), (c) (1)(EtOH), and (d) (1)(CH₂Cl₂).



Figure 3. Crystal structure of (1)(acetone) showing the carbonyl–carbonyl interaction between the dimers. The oxygen and carbon atoms related to the $(C=)0\cdots C(=O)$ interactions are linked by blue dashed lines. For clarity, all hydrogen atoms are omitted.

observed in all the crystals investigated in this work (Scheme 1). In the dimeric unit, two hydroxyl and two carbonyl groups are free for hydrogen bonding to other dimer or solvent molecules. These groups control the supramolecular network in the crystal structure.

The crystal structure of (1)(acetone) is shown in Figure 3. Two host molecules associate to form a centrosymmetric cyclic dimer (O(H)···O=C: 2.779 Å). Two guest molecules join this host unit as hydrogen bond acceptors resulting in a 1:1 host-guest stoichiometry (O(H)···O=C(CH₃)₂: 2.827 Å). The noncovalent carbonyl-carbonyl interaction due to the >C(δ +)=O(δ -) dipole is observed between the dimeric units, which makes an infinite linear chain of host molecules along the *b*-axis (Scheme 1b). The carbonyl groups of the neighboring molecules are in close contact with the antiparallel arrangement with zero torsional angle, indicating an all-planar antiparallel arrangement of the two C=O groups. The C···O distance is 3.147 Å, which is markedly shorter than the 3.6 Å distance accepted for carbonyl–carbonyl interactions.^{10,11} This type of carbonyl–carbonyl interaction is observed between cyclic dimers in all crystals except for $(1)_2$ (benzene)₃ (Scheme 1, Table 2). The host molecules provide a channel running along the *a*-axis, in which guest molecules are embedded by hydrogen bonding (Figure 4a).

The host lattice in the crystal structure of (1) (EtOH) is similar to that of (1)(acetone). The centrosymmetric dimeric unit, in which the $OH \cdots O = C < hydrogen bonds have an O(H) \cdots O$ distance of 2.776 Å, is linked further by carbonyl-carbonyl interactions to make a linear chain of host molecules along the *a*-axis: the guest molecule is connected to this chain by hydrogen bonding $(O(H) \cdots (H)OEt: 2.753 \text{ Å})$. Thus, the guest molecules are embedded in the channels running along the a-axis (Figure 4b). This packing motif of host molecules is similar to that of (1)(acetone). In (1)(EtOH), however, the OH and C=O groups involved in the formation of the dimeric unit participate further in hydrogen bonding between dimers of the neighboring chain. Thus, a centrosymmetric cyclic assembly of four host molecules is formed by an alternative arrangement of the hydroxyl and carbonyl groups (Figure 5, Scheme 1c). We discuss this hydrogen bonding motif, designated as a four-centered quasi-bifurcated hydrogen bonding motif, in the following section.

The crystallographic study of $(1)(CH_2Cl_2)$ has recently been reported by Adams et al.⁸ Our structural analysis of this solvate crystal is consistent with their results. Figure 6 shows the crystal structure of $(1)(CH_2Cl_2)$, which belongs to the chiral space group $P2_12_12_1$. Chirality in the crystallization of an achiral compound has arisen from helical arrangement of the chiral dimeric units formed by conformationally fixed molecules of 1. The guest molecules are included in channels made by the host lattice (Figure 4c). There are two crystallographically independent CH_2Cl_2 molecules in a unit cell. One of these is free of specific noncovalent interactions, while the other seems to interact with the host molecule through close contact of the chlorine atom to the aromatic ring ($Cl \cdot \cdot \cdot C$; 3.444 Å) within the sum of their van der Waals radii (Cl + C: 3.45 Å). The geometry

Table 2. S	Structural Parameters of	Carbon	yl–Carbonyl	Interactions in	Inclusion C	rystals Based or	1 1
------------	--------------------------	--------	-------------	-----------------	-------------	------------------	-----

compd	torsion ∕°	00 ∕Å	R ∕Å	α /°	β /∘	C=O ∕Å
(1)(EtOH)	0.00	2.863	3.048	69.68	110.32	1.209
(1)(acetone)	0.00	2.863	3.147	65.40	114.60	1.206
$(1)(CH_2Cl_2)$	0.28 0.28	2.853	3.121 3.120	66.06 66.11	113.83 113.99	1.208 1.210



Figure 4. Channel structure of the host lattice in (a) (1)(acetone), (b) (1)(EtOH), and (c) (1)(CH_2Cl_2) as viewed down the *a*-axis, showing the channel embedded with guest molecules.



Figure 5. Four-centered interaction between the host dimers in (1)(EtOH) showing alternative contact of the hydroxyl and carbonyl oxygen atoms. For clarity, all hydrogen atoms are omitted. The oxygen atoms related to hydrogen bonding are linked by blue dashed lines.

of the host dimer in $(1)(CH_2Cl_2)$ is not centrosymmetric; the $O(H) \cdots OH$ distances are 2.777 and 2.729 Å. Distortion from a parallelogram is also observed in the carbonyl–carbonyl interaction

(Table 2). Despite such deformations, the host molecules retain the arrangement of a linear chain linked by $OH \cdots O=C$ hydrogen bonds and $C=O \cdots C=O$ interactions, as observed in (1)(EtOH) and (1)(acetone). The host-guest hydrogen bond found in (1)(acetone) is replaced by a host—host hydrogen bond. Thus, the $OH \cdots OH$ hydrogen bonds bridge the linear chain of the host dimers (O(H)---OH: 2.921 Å).

Four-Centered Interactions through Quasi-Bifurcated Hydrogen Bonding. In the crystal structure of (1)(EtOH), the two >C=O···HO- hydrogen bonding motifs are aligned in a parallel and head-to-tail manner. The hydroxyl group appears to participate as a H-donor in a bifurcated hydrogen bond to the two carbonyl oxygen atoms, and at the same time, the carbonyl oxygen joins a bifurcated hydrogen bond as a H-acceptor for the two hydroxyl groups (Scheme 3c). However, judging from the C=O···(H)O distances, the interchain hydrogen bonding is appreciably weaker than that in the dimeric unit; the former is 2.776 Å, while the latter is 3.036 Å (Scheme 2a). Therefore, strictly speaking, the cyclic hydrogen bonding motif observed in



Figure 6. Crystal structure of (1)(CH₂Cl₂). The OH···O(H) hydrogen bonds are shown by blue dashed lines and the oxygen atoms related to the C=O···C=O interaction are linked by red dashed lines.

Scheme 2. (a) Schematic Representation of Four-Centered Quasi-Bifurcated Hydrogen Bonding in (1)(EtOH); Hydrogen Bonding (Red) and Dipole–Dipole Interaction (Blue)^{*a*}; (b) Generation of Dipole in >C=O···HO– Hydrogen Bonding System



^{*a*} Structural parameters: hydrogen bonding O---O distance, 2.776 Å. dipole–dipole contact O···O distance, 3.036 Å. (C=)O···O(=C): 3.818 Å. Dihedral angle: (C=O)···(O=C); 180°, C=O···O··O; 133.10°, C-O···O··O; 142.98°. (C=)O···O(H)···O(=C) angle: 98.00°.

Scheme 3. Search Fragment of Four-Centered Alignment of the Oxygen Atoms in Two $>C=O\cdots(H)O-Hydrogen$ Bonding Systems^{*a*}



^{*a*} (a) Definition of geometrical parameters, d_1 , d_2 , d_3 , and d_4 , for search data set A; (b) $d_1 = d_2$, $d_3 = d_4$: all-planar parallelogram arrangement of four oxygen atoms, affording four-centered quasi-bifurcated hydrogen bonding; (c) $d_1 = d_2 = d_3 = d_4$: true four-centered bifurucated hydrogen bonding. (b) and (c) are included in data set B.

(1)(EtOH) may not be regarded as typical four-centered bifurcated hydrogen bonding but could be designated as quasi-bifurcated hydrogen bonding. Thus, this motif may be interpreted by considering the dipolar interactions between the two $>C=O\cdots$ H-O- hydrogen bonding systems aligned in antiparallel orientation (Scheme 3b). Both the carbonyl and hydroxyl oxygen atoms involved in the hydrogen bonding should be highly polarized and therefore become favorable at the same time for dipole–dipole interactions between the $>C=O\cdots$ H-Osystems (Scheme 2b).

The motif of four-centered quasi-bifurcated hydrogen bonding has been overlooked so far despite its highly frequent occurrence in molecular crystals. Thus, in the Cambridge Structural Database (ver. 5.32, November 2010 + 1 update; 525,095 entries), we examined the structural fragments in which two hydrogen bonding systems of >C=O···(H)O- are closely aligned to make a four-membered cycle with the four oxygen atoms. The O · · · O distances, d_1 , d_2 , d_3 , and d_4 , were defined as depicted in Scheme 3a and were restrained within a range from 2.5 to 3.2 Å for d_1 and d_2 , and from 2.5 to 6.0 Å for d_3 and d_4 . The former includes both intramolecular and intermolecular contacts, whereas the latter is restricted only to the intermolecular one. The search for this data set (data set A) gave 56715 hits. In order to search all-planar antiparallel alignment of the two $(C=)O\cdots(H)O-$ fragments (Figure 3b,c), that is, a parallelogram arrangement of the four oxygen atoms, secondary search criteria were applied to data set A so that the $O \cdots O$ lengths of opposite sides were equal $(d_1 = d_2 \text{ and } d_3 = d_4)$ and the sum of the interior angles was 360° (data set B). The search for data set B gave 19354 hits.

The scatter plot of d_1 (= d_2) vs d_3 (= d_4) in data set B is shown in Figure 7a. The distance d_1 ranges mostly between 2.6 and 2.9 Å, whereas d_3 is scattered in longer distances over 4 Å. This result is reasonable because d_3 includes only intermolecular contact. In the histogram of Figure 7b, it is recognized that not only d_1 but also d_3 lies predominantly between 2.7 and 2.9 Å, the commonly accepted distance for $O \cdots (H)O$ hydrogen bonding. Favorable distance of d_3 is clearly shown in the histogram of the distribution of d_1 over d_3 . The search of structure for this fragment, cluster P, gives 655 hits, which is 3.4% of data set B. The structures occurring in cluster P should be designated as four-centered bifurcated hydrogen bonding. It is interesting to note that the appearance of diamond arrangement $(d_1 = d_2 = d_3 = d_4)$ as shown in Figure 9c, which should be designated as true four-centered bifurcated hydrogen bonding, is rather rare with only 5 hits in 655 hits. Thus, most four-centered bifurcated hydrogen bonding is in the alignment of a paralellogram of four oxgen atoms.

Scheme 3 indicates that the longer d_3 becomes, the wider allplanar antiparallel alignment spreads. This might reflect the occurrence of centrosymmetric crystals, which must necessarily comprise antiparallel >C=O···(H)O- fragments in packing structures. However, looking more closely at Figure 7a, the existence of another high scattering region, cluster Q, can be recognized at 2.6–2.9 Å for d_1 and at 3.3–4.0 Å for d_3 . In particular, for d_3 , pronounced appearance can be seen clearly from the histogram shown in Figure 7b. Cluster Q includes 2484 hits and is 12.9% of data set B. We assume that the structures scattered in cluster Q are not necessarily due to packing requirements from centrosymmetry but rather result from participation of particular intermolecular interactions, which exert a longrange force, that is, dipole-dipole interaction. Thus, the motif involved in the structure of cluster Q would be extracted as fourcentered quasi-bifurcated hydrogen bonding. The distance d_1 , that is, the hydrogen bonding distance, tends to shift to shorter distances in cluster Q as compared with that in cluster P.



Figure 7. (a) Scatter plots of d_1 vs d_3 : d_1 is the O(H)···O distance in a hydrogen bond and d_3 is that of an intermolecular contact. (b) Histogram showing distribution of d_3 (= d_4). (c) Scatter plots of d_3 vs the dihedral angle (ϕ_1) made by the C=O, C-C(=O), and O···O(=C) bonds.

This observation could support the participation of dipole–dipole interactions in a quasi-bifurcated hydrogen bonding system because it seems to be reasonable that the enhanced polarization of the carbonyl group due to dipole–dipole interaction should be advantageous also for hydrogen bonding (Scheme 2b). It would be reasonable to assume that dipole–dipole interaction gradually weakens beyond 4 Å, at which point the requirements for centrosymmetric packing become operative.

It is interesting to note that there is a gap between cluster P and Q, wherein neither hydrogen bonding nor close $O \cdots O$ contact is favorable. This observation could be rationalized based on preferential directions of approach between the oxygen atoms for dipole-dipole interaction: the hydroxyl oxygen should be positioned in the direction perpendicular to the carbonyl plane in contrast to hydrogen bonding in which the oxygen lies close to a carbonyl oxygen lone pair direction and hence in the carbonyl plane. We obtained another scatter plot, showing dependence of d_3 on dihedral angle (ϕ_1) made by the C=O, C(=O)-C, and $O \cdots O(=C)$ bonds (Figure 7c). In Figure 7c, high scattering region for d_3 responsible for dipole-dipole interaction is concentrated around $\phi_1 = \pm 90^\circ$, while d_3 responsible for hydrogen bonding is around 0° and 180° . Thus, it would be reasonable to assume that the low scattering of d_3 in 2.8–3.2 Å region could be caused by the closest limit of the $O \cdots O$ van der Waals contact in direction perpendicular to the carbonyl plane, because the

van der Waals radii of the carbonyl oxygen in the direction along π -orbital is 1.6–1.7 Å.¹² On the other hand, hydrogen bonding interaction would be unfavorable over 2.8 Å of the O···O distances because the van der Waals radii of the hydrogen bonding carbonyl oxygen is 1.4 Å in the carbonyl plane.¹²

Powder X-ray Diffraction Analysis of Solvent-Free 1. Upon heating $(1)(CH_2Cl_2)$ at 120 °C for 30 min, the guest CH_2Cl_2 molecules are released and the original single crystals become opaque. It was revealed based on X-ray diffraction studies that the resulting polycrystalline solid is a new crystalline phase (Figure 8). As is the case in many host molecules, the crystallization of 1 from solution always gave inclusion crystals but not guest-free crystals. Thus, this new guest-free phase could only be obtained by the desolvation process. Because the desolvation process gave the polycrystalline solid, the crystal structure of solvent-free 1 was analyzed from powder X-ray diffraction (XRD) data using the direct space strategy followed by the Rietveld refinement.¹³ Figure 9 shows the results of the final Rietveld refinement of desolvated crystals of 1. The crystal adopts an orthorhombic crystal system in space group $P2_12_12_1$. Thus, the solvent-free crystals of 1 are still in a chiral crystalline phase, which arises from helical arrangement of conformationally fixed molecules of 1.

The most characteristic feature of the desolvated crystals is the collapse of the dimeric unit of **1** found in solvate crystals. One of



Figure 8. Powder X-ray diffraction pattern of (a) $(1)(CH_2Cl_2)$ and (b) after desolvation of $(1)(CH_2Cl_2)$.



Figure 9. Rietveld refinement plot for desolvated 1.



Figure 10. X-ray crystal structure of guest-free crystal of 1.

the hydroxyl groups is connected to its translation-related molecules via $C=O\cdots H-O-$ hydrogen bonding ($O\cdots O: 2.81$ Å) to form an infinite one-dimensional (1-D) chain along the *c*-axis (Figure 10), and the other hydroxyl group forms a helical molecular arrangement along the *b*-axis. Taking into consideration that no particular heteromolecular interactions occur between 1 and CH_2Cl_2 in (1)(CH_2Cl_2) crystals, one might assume that topology with respect to the interhost–molecular interaction network is retained after the loss of solvent molecules. However, this is not true, as noted above; the dimeric unit is not maintained in desolvated crystals.

Phase Change with Guest Release. The phase changes that occur upon desolvation of other solvate crystals were monitored by powder XRD, thermal analysis (TG and TD), and temperature-dependent IR spectra. All the polycrystalline crystals resulting from guest release showed the same XRD and IR data as



Figure 11. TG and DTA profiles of $(1)_2$ (benzene)₃.



Figure 12. Temperature-dependent FT-IR spectra of $(1)_2$ (benzene)₃ in the 3100–3700 cm⁻¹ region recorded by lower shift with raising the temperature from 60 to 160 °C (5 °C min⁻¹).

those observed on the desolvated sample of **1**, for which the crystal structure has been determined by applying the Rietveld method. This result means that the desolvated crystals, not depending on the included guest molecules, are all in the same crystal structure, that is, in space group $P2_12_12_1$. The TD curves are characterized by an initial endotherm corresponding to guest release, followed by a second endotherm due to the melting of the host compound at 221 °C, as depicted in Figure 11 for $(1)_2$ (benzene)₃. In the temperature-dependent IR spectra, the temperature of guest release was evaluated from changes in the intensities of the OH absorption band, which showed good agreement with the values obtained from TD experiments. Figure 12 shows the results for $(1)_2$ (benzene)₃, which gives relatively simple results because of the involvement of only interhost hydrogen bonding.

On release of the solvent molecules, the chiral crystal lattice of $P2_1$ in (1)(CH₂Cl₂) is kept without conversion to racemic crystals. In the case of (1)₂(benzene)₃, (1)(acetone), and (1)(EtOH), however, their achiral space groups are converted to chiral $P2_12_12_1$ after the release of the guest molecules despite the absence of a 2_1 substructure. The solid-state transformation of a racemic compound into a conglomerate is rarely encountered, in contrast to the reverse conversion.¹⁴ Much more rarely encountered is the appearance of chiral crystals from achiral molecules.¹⁵ Thus, these results provide an example of the transformation of achiral host—guest inclusion crystals into chiral crystals of the host compound by guest elimination, wherein the resulting homochirality arises from freezing the conformation in achiral molecules.

CONCLUSIONS

As a new host compound for crystalline host-guest inclusion complexes, 2,2-bis(4-hydroxy-3-phenylphenyl)-1H-indene-1,3(2H)-dione (1) was prepared; it bears both hydrogen-bond donor and acceptor sites and adopts a scissors shape. Compound 1 forms crystalline inclusion complexes represented as (1)-(acetone), $(1)(CH_2Cl_2)$, (1)(EtOH), and $(1)_2(benzene)_3$. Their crystal structures were characterized as a supramolecular synthon with a cyclic head-to-tail dimer linked by $C=O\cdots HO$ complementary hydrogen bonding in all crystals. Another characteristic feature recognized in (1)(EtOH) is the occurrence of fourcentered quasi-bifurcated hydrogen bonding. This hydrogen bonding motif has been revealed to be quite general as probed in CSD research. The structures of desolvated polycrystalline solids were elucidated by ab initio structure determination from powder XRD data followed by Rietveld refinement. In the desolvated crystals, the complementary hydrogen bonds forming the dimeric unit of 1 in the solvated crystals, collapse, and a 1-D chain of 1 is formed by linkage of intermolecular >C= $O\cdots$ (H)O- hydrogen bonds at one site. In (1)(acetone) and (1)(EtOH), the formation of chiral crystals from achiral crystals was accomplished by thermal elimination of guest molecules from host-guest inclusion crystals.

EXPERIMENTAL SECTION

General Information. The ¹H NMR (500 MHz) and ¹³C NMR (125 MHz) spectra were recorded using a JEOL α -500 spectrometer. Chemical shifts are given in δ values (ppm) using TMS as the internal standard. Mass spectra were taken on a Shimadzu GCMS-QP5050A mass spectrometer. Elementary combustion analyses were recorded using a Yanaco CHN CORDER MT-6 analyzer. Column chromatography was carried out on silica gel (Merck 60N spherical).

Temperature-dependent FT-IR spectra were recorded on a JASCO FT/IR-6100 FTIR spectrometer equipped with an IR microscope, IRT-5000, for samples compressed in KBr disks. The temperature was raised 5 °C per minute from ca. 50 to 170 °C. Thermogravimetry (TG) and differential thermal analysis (DTA) were performed on a Rigaku TG-DTA system at a heating rate of 20 °C min⁻¹. Sample weights were ca. 5 mg. Platinum sample pans with loose lids were used in the TG experiments, and aluminum sample pans with crimped but vented lids were used in the TDA experiments.

Synthesis of Host Compound 1. 2,2-Bis(4-hydroxy-3-phenylphenyl)-1,3-indandione (1) was prepared by the reaction of ninhydrin with *o*-phenylphenol. Ninhydrin (1.8 g, 10 mmol) and 2-phenylphenol (3.4 g, 20 mmol) were heated at 80–90 °C along with a drop of H₂SO₄ in acetic acid (20 mL) for 6 h. Workup of the reaction mixture, including extraction with CH₂Cl₂, washing, drying (MgSO₄), and evaporation of the solvent under reduced pressure, yielded a crude product that was purified by column chromatography on silica gel (dichloromethane as eluent) to provide 1 in 70% yield. ¹H NMR (500 MHz, CDCl₃): δ 5.23 (2H, s), 6.92 (2H, d, *J* = 8.5 Hz), 7.15 (2H, d, *J* = 2.5 Hz), 7.21 (2H, dd, *J* = 8.5, 2.5 Hz), 7.35–7.41 (6H, m), 7.44–7.47 (4H, m), 7.88 (2H, m), 8.08 (2H, m). ¹³C NMR (125 MHz, CDCl₃): δ 66.3, 116.1, 124.2, 128.0, 128.2, 129.1, 129.2, 129.7, 130.4, 130.4, 136.2, 136.6, 141.5, 152.1, 200.2. Anal. (for the sample after loss of guest species): Found. C, 81.84%. H, 4.65%. Calcd for $C_{33}H_{22}O_4$; C, 82.14%. H, 4.60%.

Preparation of Clathrate Crystals of 1. Compound 1 was dissolved by heating in a minimum amount of the guest solvent. The solution was placed in a hot oil bath to prevent it from rapid cooling and to ensure crystallization of the inclusion compound. After storage for 12 h at room temperature, crystals were collected by suction filtration and dried. The host-to-guest stoichiometric ratios were determined by ¹H NMR and TG analysis.

Single-Crystal X-ray Crystallographic Studies. X-ray analysis was performed for a single crystal coated with adhesive immediately after it was taken out of solution. X-ray diffraction data were collected on a Rigaku RAXIS RAPID imaging plate area detector with graphite monochromated Mo–K α radiation ($\lambda = 0.7107$ Å). Diffraction data were collected at room temperature (23 °C) except for (1)(EtOH). The crystal structures were solved by the direct method using SIR92 and refined by the full-matrix least-squares method.¹⁶ Non-hydrogen atoms were refined anisotropically. Coordinates of hydrogen atoms bonded to each oxygen atom were determined from a difference Fourier map and refined isotropically. Other hydrogens were placed at calculated positions with C–H = 0.95 Å and refined using the riding model. All calculations were performed using the CrystalStructure 3.8 crystallo-graphic software package.^{17,18} Structural parameters are listed in Table 1.

Crystal data and other experimental details have been deposited at the Cambridge Crystallographic Data Centre (CCDC). $(1)_2$ (benzene)₃: CCDC-796554. (1)(acetone): CCDC-796557. (1)(EtOH): CCDC-796556. (1)(CH₂Cl₂): CCDC-796555.

Powder X-ray Diffraction. Synchrotron powder X-ray diffraction data for the polycrystalline sample of desolvated 1 were recorded at ambient temperature on beamline 4B2 (parallel beam optics) at the PF synchrotron facility at a wavelength of 1.196098(5) Å. The sample was loaded into a borosilicate glass capillary (2.0 mm diameter) and used for the diffraction measurement in the transmission mode. The powder XRD pattern was indexed using the program DICVOL04.¹⁹ Structure solution was carried out using the simulated annealing method incorporated in the program DASH.²⁰ The best structure obtained in the structure solution calculation was used as the initial structural model for Rietveld refinement, which was carried out using the GSAS program.²¹

Crystal data for desolvated 1: $C_{33}H_{22}O_4$, $P2_12_12_1$, a = 21.60117(18) Å, b = 12.83936(12) Å, c = 8.86864(6) Å, V = 2459.67(4) Å³, Z = 2, $D_{calc} = 1.303$ g/cm³, R(F*2) = 0.05861. CCDC-821644.

Database Searches. Database searches were carried out using CSD version 5.32 (November 2010 + 1 update; 525,095 entries)²² using the program ConQuest (ver. 1.12).²³ Data sets for the cyclic and alternate arrangements of oxygen atoms in carbonyl and hydroxyl groups were generated using criteria of the alternate O···O distances of 2.5···3.2 Å (d_1 and d_3) and 2.5···6.0 Å (d_2 and d_4), eliminating structures having: (a) a crystallographic *R* factor > 10% and (b) crystallographic disorder. To this data set, designated as data set A, secondary search criteria were applied to fill $d_1 = d_3$ and $d_2 = d_4$ and the sum of the internal angles being equal to 360° within errors to provide data set B. Data set A includes 56715 structural fragments (13 234 entries) and data set B includes 19354 fragments (8813 entries).

ASSOCIATED CONTENT

Supporting Information. X-ray crystallographic reports (CIF) are available free of charge via the Internet at http:// pubs.acs.org.

AUTHOR INFORMATION

Corresponding Author

*E-mail: kobayak@josai.ac.jp.

ACKNOWLEDGMENT

This work was supported by Grants-in-Aid for Scientific Research (C) from MEXT (Nos. 21550048 and 21550008). Part of this work was performed under the approval of the Photon Factory Program Advisory Committee (Proposal No. 2009G658).

REFERENCES

(1) Cruz-Cabeza, A. J.; Day, G. M.; Jones, W. Chem.—Eur. J. 2009, 15, 13033.

(2) (a) Desiraju, G. R. Angew. Chem., Int. Ed. Engl. **1995**, 34, 2311.(b) Desiraju, G. R. Crystal Engineering: Design of Organic Solids; Elsevier: Amsterdam, 1989.

(3) (a) Jeffrey, G. A. An Introduction to Hydrogen Bonding; Oxford University Press: Oxford, 1997. (b) Desiraju, G. R.; Steiner, T. The Weak Hydrogen Bond in Structural Chemistry and Biology; Oxford University Press: Oxford, 1999.

(4) MacNicol, D. D.; Downing, G. A. In *Comprehensive Supramolecular Chemistry*; Mac Nicol, D. D.; Toda, F.; Bishop, R., Eds.; Elsevier: Oxford, 1996; Vol. 6, p 421.

(5) (a) Caira, M. R.; Horne, A.; Nassimbeni, L. R.; Okuda, K.; Toda, F. J. Chem. Soc. Perkin Trans. 2 1995, 1063. (b) Apel, S.; Nitsche, S.; Beketov, K.; Seichter, W.; Seidel, J.; Weber, E. J. Chem. Soc. Perkin Trans. 2 2001, 1212. (c) Weber, E.; Csöregh, I.; Stensland, B.; Czugler, M. J. Am. Chem. Soc. 1984, 106, 3297. (d) Csöregh, I.; Czugler, M.; Weber, E.; Sjögren, A.; Cserzö, M. J. Chem. Soc., Perkin Trans. 2 1986, 507. (e) Csöregh, I.; Czugler, M.; Törnroos, K. W.; Weber, E.; Ahrendt, J. J. Chem. Soc., Perkin Trans. 2 1989, 1491. (f) Csöregh, I.; Czugler, M.; Weber, E.; Ahrendt, J. J. Incl. Phenom. 1990, 8, 309. (g) Czugler, M.; Weber, E. J. Incl. Phenom. 1991, 10, 355.

(6) (a) Weber, E.; Hens, T.; Gallardo, O.; Csoregh, I. J. Chem. Soc. Perkin Trans. 2 1996, 737. (b) Weber, E.; Finge, S.; Csoregh, I. J. Org. Chem. 1991, 56, 7281. (c) Weber, E.; Csöregh, I.; Ahrendt, J.; Finge, S.; Czugler, M. J. Org. Chem. 1988, 53, 5831. (d) Csöregh, I.; Czugler, M.; Ertan, A.; Weber, E.; Ahrendt, J. J. Incl. Phenom. 1990, 8, 275. (e) Csöregh, I.; Czugler, M.; Weber, E.; Ahrendt, J. J. Incl. Phenom. 1990, 8, 309. (f) Csöregh, I.; Gallarado, O.; Weber, E.; Finge, S.; Reutel, C. Tetrahedron: Asymmetry 1992, 3, 1555. (g) Csöregh, I.; Finge, S.; Weber, E. Bull. Chem. Soc. Jpn. 1991, 64, 1971.

(7) (a) Toda, F. Top. Curr. Chem. 1988, 149, 211. (b) Hart, H.; Lin, L. -T. W.; Ward, D. L. J. Am. Chem. Soc. 1984, 106, 4043. (c) Weber, E.; Skobridis, K.; Wierig, A.; Nassimbeni, L. R.; Johnson, L. J. Chem. Soc. Perkin Trans. 2 1992, 2123. (d) Jetti, R. K. R.; Kuduva, S. S.; Reddy, D. S.; Xue, F.; Mak, C. W.; Nangia, A.; Desiraju, G. R. Tetrahedron Lett. 1998, 39, 913. (e) Weber, E.; Nitsche, S.; Wierig, A.; Csoregh, I. Eur. J. Org. Chem. 2002, 856. (f) Jetti, R. K.; Xue, F.; Mak, C. W.; Nangia, A. G. W.; Yangia, A. J. Chem. Soc. Perkin Trans. 2 2000, 1223. (g) Hayashi, N.; Kuruma, K.; Mazaki, Y.; Imakubo, T.; Kobayashi, K. J. Am. Chem. Soc. 1998, 120, 3799. (h) Kobayashi, K. Bull. Chem. Soc. Jpn. 2003, 76, 247, and references cited therein.

(8) Recently, the preparation and crystallographic study of this compound have been reported.Poorheravi, M. R.; Loghmani-Khouzani, H.; Sadeghi, M. M. M.; Zendehdel, M.; Jackson, R. F. W.; Adams, H. *Anal. Sci. X-ray Struct. Anal. Online* **2007**, *23*, x227.

(9) (a) Atwood, J. L.; Davies, J. E. D.; MacNicol, D. D., Eds. *Inclusion Compounds*; Academic Press: London, 1984; Vol. 1–3. (b) Hart, H.; Lin, L. T. W.; Ward, D. L. *J. Am. Chem. Soc.* **1984**, *106*, 4043.

(10) (a) Gavezzotti, A. In *Structure Correlation*; Burgi, H.-B.; Dunitz, J. D., Eds.; VCH: Weinheim, 1994; Vol. 2, p 527. (b) Wan, C.-Q.; Mak,

T. C. W. Cryst. Growth Des. 2011, 11, 832and references therein.

(11) Allen, F. H.; Baalham, C. A.; Lommerse, J. P. M.; Raithby, P. R. Acta Crystallogr. **1998**, B54, 320.

- (12) Bondi, A. J. Phys. Chem. 1964, 68, 441.
- (13) Rietveld, H. M. J. Appl. Crystallogr. 1969, 2, 65.

(14) For example:(a) Yonemochi, E.; Oguchi, T.; Yamamoto, K.

J. Pharm. Pharmacol. 1997, 49, 384. (b) Toda, F.; Tanaka, K.; Miyamoto,

- H.; Koshima, H.; Miyahara, I.; Hirotsu, K. J. Chem. Soc., Perkin Trans. 2 1997, 1877.
 - (15) Matsuura, T.; Koshima, H. J. Photochem. Photobiol. 2005, 6, 7.
 (16) SIR92:Altomare, A.; Cascarano, G.; Giacovazzo, C.; Guagliardi,
- A.; Buria, M.; Polidori, G.; Camalli, M. J. Appl. Crystallogr. **1994**, 27, 435.
- (17) CrystalStructure 3.8: Crystal Structure Analysis Package; Rigaku and Rigaku/MSC (2000–2006): The Woodlands, TX.

(18) CRYSTALS Issue 11: Carruthers, J. R.; Rollett, J. S.; Betteridge, P. W., Kinna, D.; Pearce, L.; Larsen, A.; Gabe, E. Chemical Crystallography Laboratory: Oxford, UK, 1999.

(19) (a) Boultif, A; Louer, D. J. Appl. Crystallogr. 1991, 24, 987.
(b) Boultif, A.; Louer, D. J. Appl. Crystallogr. 2004, 37, 724.

(20) David, W. I. F.; Shankland, K.; van de Streek, J.; Pidcock, E.; Motherwell, W. D. S.; Cole, J. C. J. Appl. Crystallogr. **2006**, 39, 910.

(21) Larson, A. C.; Von Dreele, R. B. *General Structure Analysis System (GSAS)*; Los Alamos Laboratory Report No. LA-UR-86-748; Los Alamos National Laboratory: Los Alamos, NM, 1987; p 19.

(22) Allen, F. H. Acta Crystallogr. Sect. B: Struct. Sci. **2002**, B58, 380.

(22) Allen, F. H.; Kennard, O. Chem. Des. Autom. News 1993, 8 (1), 31.