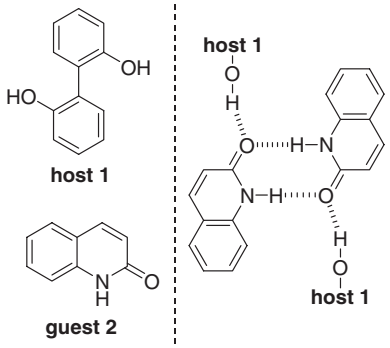
New Approach for the Recovery of Bisphenol A from Water Using Inclusion Complex with Quinoline Derivatives

Bunpei Hatano,* Akiko Aikawa, Hideyuki Tagaya, and Hiroki Takahashi†
Department of Chemistry and Chemical Engineering, Faculty of Engineering, Yamagata University, Jonan, Yonezawa, 922-8510
†*Graduate School of Human and Environmental Studies, Kyoto University, Yoshida, Kyoto 606-8501*

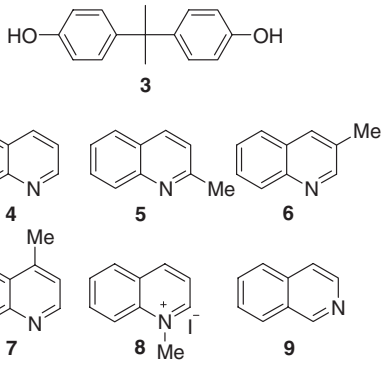
(Received June 29, 2004; CL-040761)

The simple inclusion complex of bisphenol A (**3**) with quinoline (**4**) was obtained from the several solutions, and this method was useful for the recovery of **3** from the water solution.

In recent years, the treatment of bisphenol derivatives has been studied because of its activity regarding environmental hormones. However, there are a few reports of the recovery of bisphenol derivatives as compared to those for the decomposition of them.[1,2] The development of the simple recovery method is useful in the field of ecological chemistry as well as in environmental chemistry. In a previous report on host–guest inclusion compound, we revealed that the simple host compound 2,2′-dihydroxybiphenyl (**1**) efficiently included 2-quinolone (**2**), and **2** was arranged in the inclusion crystal of **1** in a different manner from the crystal of **2** itself.[3]



We found that the 1:1 complex of 4,4′-isopropylidenebisphenol (bisphenol A) (**3**) with quinoline (**4**) was readily obtained from the various solutions of toluene, tetrahydrofuran, or acetone. This complexation of **3** was also performed by quinoline derivatives (**6** and **7**) and isoquinoline (**9**), giving the corresponding complexes in good yields. Furthermore, we revealed that this application was useful for the recovery of **3** from the water solution.



A typical procedure is as follows: **3** (2.0 mmol) and **4** (2.0 mmol) were dissolved in toluene (3 mL) and hexane (ca. 0.3 mL) at 50 °C. After storage at room temperature, the inclusion complex was collected by filtration. These results are summarized in Table 1.

When **3** and two molar amounts of **4** were dissolved in toluene and hexane, the 1:1 inclusion complex of **3** with **4** was readily obtained as colorless prisms in 84% yield (Entry 1). Furthermore, in both cases of mix ratio 1:1 and 2:1, the 1:1 inclusion complex of **3** was obtained in 68% and 59% yields, respectively (Entries 2 and 3). It is interesting to note that the complexation of **3** was independent of the solvent in preparation. The complexation of **3** with **4** can also be achieved in AcOEt, THF, and acetone; in EtOH the longer crystallization time led to the complex of **3** in 81% yield (Entries 4–7). Although it was reported that the hosts bearing the bisphenol functions generally included various solvents such as diethyl ether, acetone, DMF, and DMSO,[4] the complex of **3** with the solvent was not observed at all. These facts indicate that the complexation of **3** with **4** is performed by the tight interaction between **3** and **4**.

The complexation of **3** can be applied to other quinoline derivatives (**6** and **7**) and isoquinoline (**9**) (Table 2). A similar treat-

Table 1. Inclusion complex of **3** with **4** in several solvents

Entry	Solvent	Mix Ratio (**3**:**4**)	Inclusion Ratio (**3**:**4**)[a]	Yield/%
1	toluene : hexane	1:2	1:1	84
2	toluene : hexane	1:1	1:1	68
3	toluene : hexane	2:1	1:1	59
4	AcOEt : hexane	1:1	1:1	87
5	THF : hexane	1:1	1:1	88
6	acetone : hexane	1:1	1:1	97
7	EtOH : hexane	1:1	1:1	81

[a]The inclusion ratios were determined by ^{1}H NMR.

Table 2. Inclusion complex of **3** with quinoline derivatives (**5**–**8**) and isoquinoline (**9**)[a]

Entry	Guest	Inclusion Ratio (**3**:Guest)[b]	Yield/%
1	**5**	—	—
2	**6**	1:1	75
3	**7**	1:1	66
4	**8**	—	—
5	**9**	1:1	68

[a]Typical conditions: **3** (1.0 mmol), **5**–**9** (2.0 mmol), toluene (3.0 mL) and hexane (0.5 mL). [b]The inclusion ratios were determined by ^{1}H NMR.

ment of **3** with **6** and **7** led to the corresponding 1:1 inclusion complexes of **3** in good yields, though the complex of **3** with 2-methylquinoline (**5**) was not observed at all (Entries 1–3). In contrast, the substitution of an imino nitrogen significantly affects the formation of the complex: the 1-methylquinoline iodonium salt (**8**) did not induce the complex of **3** (Entry 4). These facts suggest that the imino group of the quinoline derivatives plays an important role in the formation of the complex. The complexation of **3** with **8** can also be carried out, thus providing the 1:1 inclusion complex in good yield (Entry 5).

The crystal structure of **3** with **4** was studied by X-ray analysis and the results are shown in Figures 1.[5] It is noteworthy that the molecule **3** has two different hydrogen bonds: one hydrogen bond is formed between the imino nitrogen of **4** and the OH hydrogen of **3** [N(1)···O(1) = 2.711 Å], and the other hydrogen bond is formed between the OH groups of two molecules of **3** [O(1)···O(2) = 2.758 Å]. The molecule **4** is intercalated in the channels of **3** molecules as depicted in Figure 1. These facts suggest that the inclusion complex of **3** with **4** is stabilized through tightly enclosed hydrogen bonding network.

This formation of inclusion complex of **3** with **4** was effectively applied to the recovery of **3** from the water solution (Figure 2). When the aq HCl solution (1.0 M, 4.0 mL) of **4** (1.1 mmol) was added to the aq NaOH solution (0.1 M, 45.0 mL) of **3** (1.0 mmol), **3** was recovered in 87% yield as a 1:1 inclusion crystal with **4**.[6,7] Finally, this method has some advantages of simplicity in procedures.

In conclusion, we found that 4,4′-alkylidenebisphenol

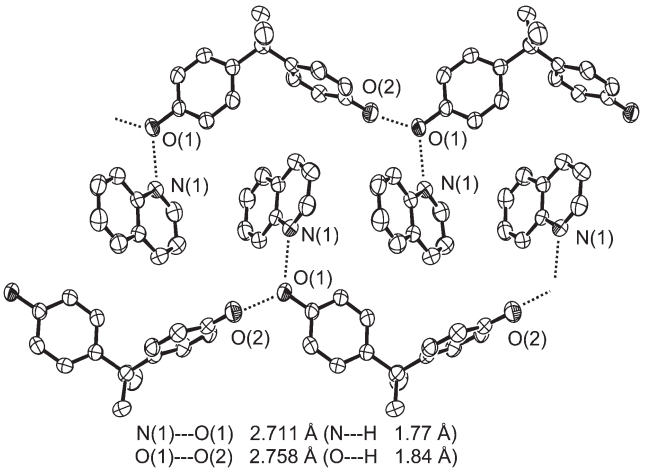


Figure 1. X-ray structure of inclusion crystal of **3** with **4**.

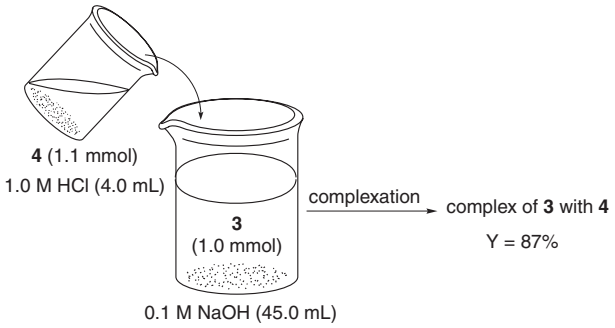


Figure 2. Recovery of **3** from the water solution using the inclusion complex of **3** with **4**.

(bisphenol A) (**3**) readily forms an inclusion complex with quinoline derivatives (**4**, **6**, and **7**) or isoquinoline (**9**). The X-ray structural analysis revealed that the molecule **4** was intercalated in the channels of **3** molecules through hydrogen bonding network. Furthermore, this method was useful for the recovery of **3** from the water solution. Further detailed applications using the inclusion complex are now in progress.

This work was partly supported by the Yamagata University Research Institute Promotion Foundation.

References and Notes

1 For decomposition of bisphenol derivatives, see: N. Watanabe, S. Horikoshi, H. Kawabe, Y. Sugie, J. C. Zhao, and H. Hidaka, *Chemosphere*, **52**, 851 (2003); S. Fukahori, H. Ichiura, T. Kitaoka, and H. Tanaka, *Environ. Sci. Technol.*, **37**, 1048 (2003); S. Tanaka, Y. Nakata, T. Kimura, Yustiawati, M. Kawasaki, and H. Kuramitz, *J. Appl. Electrochem.*, **32**, 197 (2002); J. Sajiki, *Environ. Int.*, **27**, 315 (2001); S. Tanaka, Y. Nakata, H. Kuramitz, and M. Kawasaki, *Chem. Lett.*, **1999**, 943.

2 For recovery of bisphenol derivatives, see: H. Kitano, T. Hirabayashi, M. Ide, and M. Kyogoku, *Macromol. Chem. Phys.*, **204**, 1419 (2003); M. Del Olmo, A. Zafra, A. Gonzalez-Casada, and J. L. Vilchez, *Int. J. Environ. Anal. Chem.*, **69**, 99 (1998).

3 B. Hatano, S. Hirano, T. Yanagihara, S. Toyota, and F. Toda, *Synthesis*, **2001**, 1181.

4 F. Toda, S. Hirano, S. Toyota, M. Kato, Y. Sugio, and T. Hachiya, *CrystEngComm*, **2002**, 171; S. Apel, S. Nitsche, K. Beketov, W. Seichter, J. Seidel, and E. Weber, *J. Chem. Soc., Parkin Trans. 2*, **2001**, 1212.

5 Crystal Date of the inclusion crystal of **3** with **4**: $C_{24}H_{23}NO_2$ $M = 357.45$, monoclinic, space group $P21/a$ (#14), $a = 10.9526(8)$, $b = 11.2656(4)$, $c = 15.9731(12)$ Å, $\beta = 91.142(4)°$, $V = 1970.5(2)$ Å^3, $Z = 4$, $D_{calcd} = 1.205$ (gcm^{-3}), No. of used refraction = 21292, $R = 0.044$, $R_w = 0.0520$, Temperature = 23 °C. CCDC deposition number: 211913.

6 The typical conditions: The aq HCl solution (1.0 M, 4.0 mL) of **4** (1.1 mmol) was added to the aq NaOH solution (0.1 M, 40.0 mL) of **3** (1.0 mmol) at 95 °C, and the aq NaOH (0.1 M, ca. 5.0 mL) was added until the mixture became slightly clear. After storage for one day at room temperature, **3** was recovered in 87% yield as a 1:1 inclusion crystal with **4**.

7 The solubility of the inclusion complex of **3** with **4** in water is less than 1 mM at 25 °C.

Published on the web (Advance View) September 4, 2004; DOI 10.1246/cl.2004.1276