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NOVEL HOST MOLECULES WHICH FORM INCLUSION COMPLEXES WITH ALCOHOLS. EXTRACTION OF ETHANOL FROM ITS AQUEOUS SOLUTION BY THE COMPLEXATION

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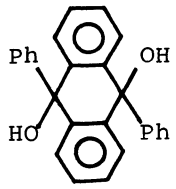
9,10-Dihydroxy-9,10-diphenyl-9,10-dihydroanthracene, 2,5-diarylhydroquinones, and 9-hydroxy-9-(1-propynyl)fluorene and its 2,7-dihaloanalogs were found to form inclusion complexes with various alcohols. By using the complexation, ethanol was extracted from aqueous solution of various concentration.

During the course of our recent studies on molecular inclusion phenomena of acetylenic diols,[1,2] we found that 9,10-dihydroxy-9,10-diphenyl-9,10-dihydroanthracene (1),[3] 2,5-bis(2,4-dimethylphenyl)hydroquinone (2),[4] 2,5-di(4-chlorophenyl)hydroquinone (3),[4] and 9-hydroxy-9-(1-propynyl)fluorene (4)[5] and its 2,7-dichloro- (5)[5] and 2,7-dibromo-analog (6)[5] form crystalline inclusion complexes with various guest molecules. The most striking result is the complexation of these hosts with various alcohols involving ethanol. By using the complexation, we succeeded to extract ethanol from aqueous solution of various concentration.

Complexes were prepared by recrystallization of the host in alcohols. Melting points of these complexes are shown in Table 1. The most complexes of the host of high melting point, 1 (mp 252-254 °C), 2 (188-189 °C), 3 (188-190 °C), 5 (172-173 °C), 6 (168-169 °C), did not show clear melting point even in sealed capillary, because alcohols evaporate during the measurement. Only the complexes of 4 (mp 103-104 °C) showed relatively clear melting points. Nonetheless, all complexes appeared as colorless transparent crystals.



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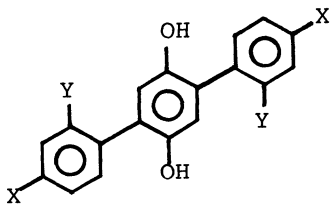
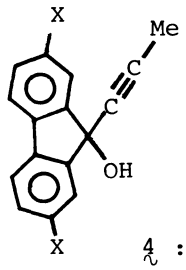


2 : X=Y=Me

3 : X=Cl; Y=H



4 : X=H

5 : X=Cl

6 : X=Br

Table 1. Melting points (°C) of the complex of 1-6 with alcohols[a)]

Alcohols	1	2	3	4	5	6
MeOH	nc	nc	nc	51-58	—	nc
EtOH	nc	nc	nc	32-45	nc	nc
n-PrOH	—	—	nc	48-54	nc	nc
i-PrOH	—	—	nc	45-51	nc	nc
n-BuOH	—	—	nc	—	nc	nc
s-BuOH	—	—	nc	—	—	—
i-BuOH	—	—	nc	—	—	—
t-BuOH	—	nc	nc	62-69	nc	nc
	—	—	117-120	—	—	—
$PhCH_2OH$	—	—	nc	75-76	—	102-105
PhOH	—	—	nc	—	—	—
$HO(CH_2)_2OH$	—	nc	178-187	—	—	—
$HO(CH_2)_3OH$	—	—	—	—	—	—
$HO(CH_2)_4OH$	nc	nc	nc	—	—	—
$HO(CH_2)_5OH$	—	—	—	—	—	—

a) All melting points were measured in sealed capillaries, and nc shows that melting point is not clear. Line — shows that no complexation occurs. All ratios of host and guest molecules were determined by NMR spectra. Although 1-3 include monools and diols in 1:2 and 1:1 ratio, respectively, 4-6 include only monools in 1:1 ratio.

Because 1-3 which have two hydroxyl groups include two monools and 4-6 which

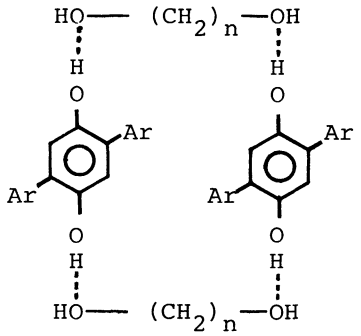


Fig. 1. An imaginary structure of the 1:1 complex of 2,5-diarylhydroquinone and α,ω-polymethylenediol.

have one hydroxyl group include one monool, each hydroxyl group of 1-6 is probably binding to one alcohol through hydrogen bond. In the IR spectra, all complexes show the presence of strongly hydrogen-bonded hydroxyl group. However, 1-3 form 1:1 complex with α,ω-polymethylenediol of an even methylene number (Table 1). Bridged-structure such as depicted in Fig. 1, for example, would be the reason to form the complex of 1:1 ratio. The diol of an odd methylene number would be sterically unfavorable to form such the complex shown in Fig. 1.

Because 1-6 do not include water, these would be useful for extraction of ethanol from aqueous solution. When a mixture of 4 (12.3 g, 56 mmol) and 80% ethanol[6] (10 ml, equivalent to 137 mmol of ethanol) was kept at room temperature for 12 h, opaque 4 turned to 1:1 ethanol complex of transparent crystals gradually without dissolving. By filtration, 14.8 g (56 mmol, 100% based on 4) of 1:1 ethanol complex of 4 was obtained. By heating the complex, unhydrous ethanol (1.8 g, 72% based on the complex) distilled out. The remained 4 can be used again.

In 50% ethanol solution (10 ml, equivalent to 86 mmol ethanol), 4 (1 g, 4.5 mmol) was dissolved by heating, and the solution was kept at room temperature for 12 h, in obtaining 1:1 ethanol complex of 4 (0.96 g, 3.6 mmol, 80% based on 4). However, it was necessary to use organic solvent for dissolving 4 in diluted ethanol solution.[7] A solution of 4 (2 g, 9 mmol) in ether-petroleum ether (1:1, 10 ml) was mixed with 15% ethanol solution (10 ml, equivalent to 26 mmol ethanol). The mixture was kept at room temperature for 12 h, in obtaining 1:1 ethanol complex of 4 (2.3 g, 18.6 mmol, 72% based on 4). By heating the dried complexes prepared from 4 and 50% or 15% ethanol solution, anhydrous ethanol was obtained in 70-80% yield.

Other host compounds can also be used for the ethanol extraction. For example, 2 (5 g, 15.5 mmol) was dissolved in 80% ethanol solution (50 ml, equivalent to 685

mmol of ethanol) by heating and the solution was kept at room temperature for 12 h, in obtaining 1:2 ethanol complex of 2 (5.1 g, 12.5 mmol, 81% based on 2). By heating the complex, unhydrous ethanol (1.1 g, 24.5 mmol, 98% based on the complex) distilled out. The remained 2 can be used again.

By the similar method as above, other alcohols can also be extracted from their aqueous solutions.

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6) All ethanol contents are shown in v/v%.
7) Because 4 is not soluble in 15% ethanol solution, organic solvent was used.

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