ISOLATION AND CRYSTAL STRUCTURE OF ALCOHOL INCLUSION COMPLEXES

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ABSTRACT. Some host compounds which include various kinds of alcohol were designed and X-ray crystal structures of their alcohol complexes were studied.

1. INTRODUCTION

If one can take out ethanol from its solution obtained by fermentation of biomass without wasting a large amount of energy, it would become a kind of revolution of energy.

Inclusion phenomena can be used for the isolation of ethanol from its aqueous solution. We have been working towards this goal, and we have found some good host compounds which include ethanol. In order to design a good host molecule, it is also important to study the crystal structures of alcohol inclusion complexes. An X-ray crystal structural study of some alcohol inclusion complexes resulted in several interesting findings. We now review these.

2. DESIGN OF HOST MOLECULES WHICH INCLUDE ALCOHOLS

In 1968, we have found that 1,1,6,6-tetraphenylhexa-2,4-diyne-1,6-diol (1a) includes various kinds of guest compounds in a 1:2 ratio and forms stable crystalline complexes.[1] However, 1a includes a few kinds of alcohol, MeOH, EtOH, and *t*-BuOH in a 1:1 ratio and their complexes are not stable. Recently, we found that the diacetylenic diol (1b) which has the much more bulky 2,4-dimethylphenyl group than phenyl shows a high ability of inclusion. 1b includes MeOH, EtOH, *i*-PrOH, and *t*-BuOH in a 1:2 ratio and forms stable crystalline complexes. 1,1-Bis(2,4-dimethylphenyl)prop-2-yn-1-ol (2b) showed also a high inclusion ability for ethanol, even though its phenyl-analog (2a) does not include any kind of alcohol.

By reference to the X-ray crystal structure of 1a in its

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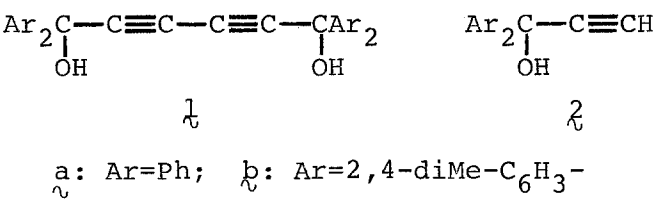
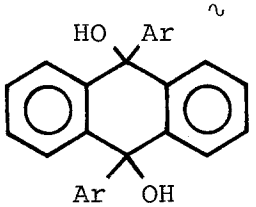
acetone complex,[2,3] we designed 9,10-dihydroxy-9,10-diphenyl-9,10-dihydroanthracene (3) which has a similar arrangement of four benzene rings to that of 1a. 3 formed stable complexes with various kinds of guest compound including alcohols.

Two structural modifications of 3 leads to 9-(1-propynyl)-9-fluorenol derivatives (4) and 2,5-diaryl-1,4-hydroquinones (5).



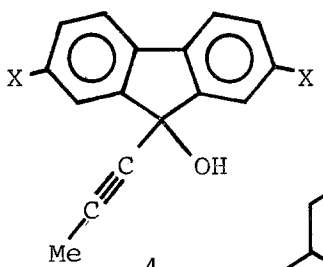
1 2

a: Ar=Ph; b: Ar=2,4-diMe-C_6H_3-



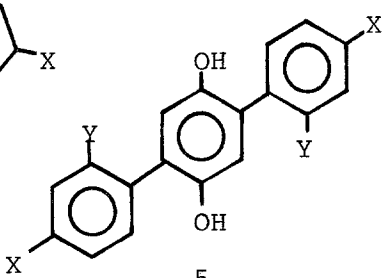
3

a: Ar=Ph
b: Ar=*o*-Me-C_6H_4-
c: Ar=*m*-Me-C_6H_4-
d: Ar=*p*-Me-C_6H_4-
e: Ar=2,4-diMe-C_6H_3-



4

a: X=H
b: X=Cl
c: X=Br



5

a: X=Y=Me
b: X=Cl, Y=H

3. FORMATION OF INCLUSION COMPLEXES WITH ALCOHOLS

The high inclusion abilities of 1b and 2b for alcohols compared with those of 1a and 2a, respectively, could be due to the sterically bulky 2,4-dimethylphenyl group. The alcohol molecules are probably surrounded by the bulky groups in the inclusion complex and the complex is stabilized. This bulky group seems to work as a kind of cap or lid. These data would be helpful for the design of new host molecules.

However, this cap or lid theory cannot be simply applied to all other host molecules. Although the inclusion ability of 3b and 3c is very similar to that of 3a, the ability of 3d becomes very high. The alcohols which can be included are shown in parentheses; 3a (MeOH, EtOH), 3b (MeOH, EtOH, *n*-PrOH), 3c (MeOH, EtOH), 3d (MeOH, EtOH, *n*-PrOH, *i*-PrOH, *i*-BuOH, *t*-BuOH, $HO(CH_2)_4OH$), 3e (*n*-BuOH).

9-(1-Propynyl)-9-fluorenols (4) include various kinds of alcohol shown in parentheses; 4a (MeOH, EtOH, *n*-PrOH, *i*-PrOH, *t*-BuOH, $PhCH_2OH$), 4b (EtOH, *n*-PrOH, *i*-PrOH, *n*-BuOH, *t*-BuOH, *p*-Cresol), 4c (MeOH, EtOH, *n*-PrOH, *i*-PrOH, *n*-BuOH, *t*-BuOH, $PhCH_2OH$, PhOH, *p*-Cresol). Halogeno-substituents of 4b and

4c may work as a lid.[4]

2,5-Diaryl-1,4-hydroquinones (5a and 5b) also include various kinds of alcohol shown in parentheses; 5a (MeOH, EtOH, *t*-BuOH, $HO(CH_2)_2OH$, $HO(CH_2)_4OH$), 5b (MeOH, EtOH, *n*-PrOH, *i*-PrOH, *n*-BuOH, *s*-BuOH, *i*-BuOH, *t*-BuOH, cyclohexanol, $PhCH_2OH$, PhOH, $HO(CH_2)_2OH$, $HO(CH_2)_4OH$).[4]

4. ISOLATION OF ETHANOL FROM AQUEOUS SOLUTION

Because 1-5 do not include water, these would be useful for the extraction of ethanol from aqueous solution. For example, when a mixture of 4a (12.3 g, 56 mmol) and 80% ethanol (10 ml, equivalent to 137 mmol of ethanol) was kept at room temperature for 12 h, opaque 4 turned to a 1:1 ethanol complex of transparent crystals gradually without dissolving. By filtration, 14.8 g (56 mmol, 100% based on 4a) of the 1:1 ethanol complex of 4a was obtained. By heating the complex, anhydrous ethanol (1.8 g, 72% based on the complex) distilled out. The remaining 4a can be used again.[4]

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

5. X-RAY CRYSTAL STRUCTURE OF ALCOHOL INCLUSION COMPLEXES

X-Ray crystal structural analyses of the complexes of 3a with MeOH (1:2), EtOH (1:1), and $HO(CH_2)_4OH$ (1:1) were carried out.[5,6] It was found that the structure of the 1:2 MeOH complex is very similar to that of the 1:1 $HO(CH_2)_4OH$ complex, but these two are completely different from the structure of the 1:1 EtOH complex,[6,7] In the crystal lattice, $HO(CH_2)_4OH$ behaves like two moles of MeOH, but MeOH and EtOH behave like different kinds of alcohols.

In all cases, a hydrogen bond between the hydroxyl groups of 4a and the alcohol is important for the formation of the complex. The host molecule 4a itself is not bound to each other by a hydrogen bond in the crystalline state. When alcohol is included in 4a, a hydrogen bond between the two appears.[7]

The crystal structure of the 1:2 EtOH complex of 5a is completely different from that of 3:1 MeOH complex of unsubstituted 1,4-benzoquinone.[8] The two aryl groups of 5 could play a special role in the formation of a different kind of complex.

A network structure of a 1:1 $HO(CH_2)_4OH$ complex of 5b is also very interesting.[6]

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