

## STRUCTURAL STUDY OF THE 1:2 METHANOL COMPLEX OF 1,1,2,2-TETRAKIS(4-HYDROXYPHENYL)ETHANE

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**Key Words:** Tetrakis(hydroxyphenyl)ethane, <sup>13</sup>C CPIMAS NMR, X-ray crystallography, inclusion complex, hydrogen bond

**Abstract:** The structure of the 1:2 inclusion complex of 1,1,2,2-tetrakis(4-hydroxyphenyl)ethane with methanol has been revealed by <sup>13</sup>C CPIMAS NMR and X-ray crystallography. This inclusion complex exhibits O—H·····O hydrogen bonding interactions.

Phenolic alkane compounds have proved to be versatile as hosts in the formation of crystalline inclusion complexes usually with concomitant hydrogen bond formation between host and guest molecules.<sup>1</sup> Recently, we have reported that 1,1,2,2-tetrakis(4-hydroxyphenyl)ethane (1) forms crystalline 1:2 or 1:4 inclusion complexes with various n-donors, such as alcohols, carbonyl compounds and so on.<sup>2</sup> From the IR spectra of each complex, it is suggested that hydrogen bonding exists between 1 and the guest compound,<sup>2</sup> but it is not clear how 1 and guest molecule interact to form the complex. The objective of this study was to clarify the details of specific interaction between 1 and guest molecules, by investigating the structure of the 1:methanol (1:2) complex (2) using <sup>13</sup>C CP/MAS (cross polarization/magic angle spinning) NMR and X-ray crystallography, which provides useful information to design characteristic host molecules.

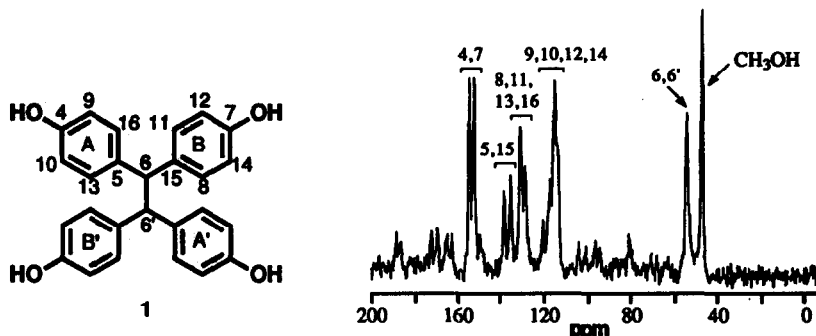


Fig. 1. <sup>13</sup>C CP/MAS NMR spectrum of 2 in the solid state at 300 K.

The <sup>13</sup>C CP/MAS NMR spectrum of 2 (Fig. 1) suggests that this complex exist as a centrosymmetrical conformer in the solid state.<sup>3</sup> This structure has been established by X-ray crystallographic study.<sup>4</sup> One asymmetric unit contains a half molecule of 1 and one methanol. Three hydrogen bonds are observed between one methanol molecule and three 1 molecules. One phenolic oxygen of an asymmetric unit forms two hydrogen bonds, with two methanol molecules, with one methanol molecule as hydrogen donor (O—O : 2.74 Å) and with another as hydrogen acceptor (O—O : 2.77 Å). Another phenolic oxygen forms one hydrogen bond with one methanol as hydrogen donor (O—O : 2.82 Å). The <sup>13</sup>C CP/MAS NMR spectrum of 2, showing two peaks of nearly equal intensity for C(4) and C(7) split by 2.1 ppm, is consistent with the presence of two types of associative patterns between the phenolic hydroxyl groups of the 1 molecule and the methanol molecules.

In conclusion, as shown in the packing diagram (Fig. 2), each phenolic hydroxyl group of **1** associates strongly with the neighboring methanol molecules and forms three-dimensional networks of hydrogen-bonded molecules. This result suggests that these hydrogen bonds support the highly stable crystal structure of **2**.

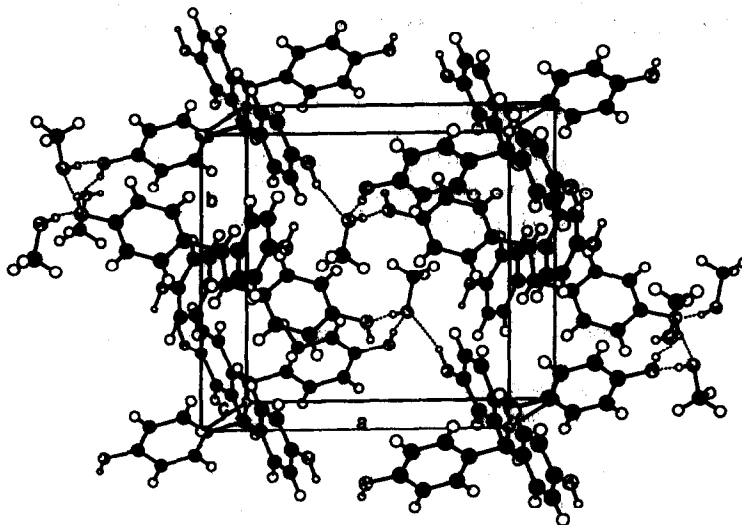


Fig. 2. Packing diagram in the crystal of **2**.

The four phenol rings of **1** play an important role in forming the cavities between them. The methyl group of the methanol molecule exists in a certain position in this cavity [between A and A' (or B')] in formula **1**] where the van der Waals repulsion is minimized. Furthermore, the methyl hydrogens of methanol possess a slight positive charge, and the carbons of the phenol ring possess a slight negative charge. These suggest the existence of electrostatic interaction, which contributes to stabilizing the crystal, between the methyl and phenol groups.

#### Acknowledgment

We wish to thank Dr. Shoichi Saito, Faculty of Pharmaceutical Sciences, University of Tokyo, for X-ray crystallographic analysis. We also thank Mr. Hitoshi Matsumoto for the NMR spectra measurements. We acknowledge the helpful discussions with Dr. Mamoru Aizawa and Dr. Yutaka Ohnishi.

#### References and Notes

1. I. Goldberg, Z. Stein, A. Kai, and F. Toda, *Chem. Lett.*, 1987, 1617; I. Goldberg, Z. Stein, K. Tanaka, and F. Toda, *J. Incl. Phenom.*, 6, 15 (1988); I. Goldberg, Z. Stein, K. Tanaka, and F. Toda, *J. Incl. Phenom. Mol. Recognit. Chem.*, 10, 97 (1991).
2. H. Suzuki, *Tetrahedron Lett.*, 33, 6319 (1992).
3. The  $^{13}\text{C}$  CP/MAS NMR spectra were obtained on a Bruker AMX400 FT NMR spectrometer at a carbon frequency of 100.6 MHz, with a sample spinning speed of 3.5 KHz.
4. The crystal used for measurement was prepared by slow crystallization of **1** in methanol. Measurement was done at room temperature.  
 Crystal Data -  $\text{C}_{14}\text{H}_{15}\text{O}_3$ ,  $M = 231.27$  (1/2 molecule), Monoclinic,  $a = 12.133(6)$ ,  $b = 11.751(7)$ ,  $c = 8.943(5)$  Å,  $\beta = 107.02(4)$  degree,  $V = 1219(1)$  Å<sup>3</sup>, Space Group  $P2_1/c$  (alt. $P2_1/c$ , No.14),  $Z = 4$ ,  $D_x = 1.43$  g/cm<sup>3</sup>.  
 Colorless plate. Crystal Size  $0.5 \times 0.6 \times 0.2$  mm<sup>3</sup>. Linear Absorption Coefficient 6.32 /cm (Cu K $\alpha$ ).  
 Data Collection - a Mac Science MXC18 4-circle diffractometer was used. max  $h, k, l$  13, 13, 10.  
 2307 reflections measured, 2029 unique, 2009 were used in analysis.  
 Structure analysis - the Mac Science Crystan-G program was used. Direct method, full-matrix least-squares refinement with all atoms. Hydrogen atom positions were calculated by difference Fourier synthesis.  
 Final residuals  $R = 0.045$ ,  $R_w = 0.064$ .