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DIVERSE MODE OF CRYSTAL STRUCTURES IN THE HOST-GUEST COMPLEXES OF DIOLS

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Abstract Crystal structures have been determined by X-ray diffraction method for the host-guest complexes with *cis*-1,4-diphenylcyclohexane-1,4-diol as the host molecule. The guest molecules are methanol, *cis*-2-betene-1,4-diol, *trans*-2-betene-1,4-diol, and *trans*-cyclohexane-1,4-diol in complexes **1** to **4**, respectively. The host-guest interaction in these crystals are based on the hydrogen bond network between the hydroxyl groups of each component molecule. In these crystal structures, hydroxyl group behaves multifunctionally to form the diverse mode of host-guest interactions in these complexes.

INTRODUCTION

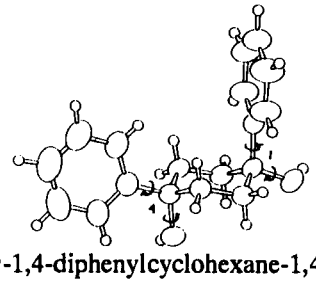
Atoms are assembled by the interatomic interactions into molecule, the chemistry of which is called molecular chemistry. The important interatomic interactions to form the backbone of the molecule are the covalent bond and the ionic bond. On the other hand, molecules are assembled by the intermolecular interactions into supramolecule, the chemistry of which is called supramolecular chemistry. The important intermolecular interactions to form the supramolecule are the hydrogen bond, the van der Waals interaction, and the metal-ligand coordination. It is well known that the assembly of the molecules reveals quite a novel functions the sole molecule can never has.

Especially important characteristics of the hydrogen bond for the formation of supramolecule are as follows. (i) Hydrogen bond is distinctly directional and specific interaction between the proton donor and proton acceptor. (ii) Hydrogen bond includes bifunctional behavior of the electronegative atoms as the proton donor and the proton

acceptor. When the 2nd lone paired electrons act as the proton acceptor, the electronegative atoms bearing hydrogen atom such as the hydroxyl group behaves as trifunctional group. (iii) Hydrogen bond is a soft interatomic interaction easy to form and easy to break.

In order to understand the role of the hydrogen bond in the process to form the supramolecule, this paper deals with the diverse mode of crystal structures in the host-guest complexes of diol as the host molecule.

The host molecule in the present work is cis-1,4-diphenylcyclohexane-1,4-diol. The molecule has the following structural characteristics. (i) This molecule has the rigid cyclohexane ring in chair form as the main component. (ii) In this molecule, two phenyl and two hydroxyl groups are cis on 1 and 4 positions of cyclohexane, respectively. (iii) Therefore, 1 and 4 positions of cyclohexane ring have different geometrical conformations. (iv) And the highest symmetry of this molecule is Cs. (v) The geometrical variation is only possible through the rotation around the 4 bonds of 1 and 4 substituents, however, the conformation of the axial phenyl is rather limited. (vi) This molecule has the hydrophobic and the hydrophilic sides. Two phenyl groups make the hydrophobic and two hydroxyl groups make the hydrophilic side, respectively.



cis-1,4-diphenylcyclohexane-1,4-diol

The crystal structure determinations have been carried out on the four complexes shown in the scheme-1. The guest molecules are methanol in complex **1**, *cis*-2-butene-1,4-diol in complex **2**, *trans*-2-butene-1,4-diol in complex **3**, and *trans*-cyclohexane-1,4-diol in complex **4**. All the guest molecules include one or two hydroxyl groups, therefore, it is difficult to say which is the guest and which is the host in these complexes. So, let say the *cis*-1,4-diphenylcyclohexane-1,4-diol, the common component in these complexes, as the host.

EXPERIMENTAL

Table I summarizes the crystal data and experimental conditions for the crystal structure determination of complexes **1** - **4**. In complex **3**, water molecule was found in the

crystal lattice as the third component. The space groups of these crystals are $P2_1$, $P2_1/n$, $P2_1/a$, and $P2_12_12_1$, so all the crystal structure include 2-fold screw axis as the translational symmetry operation. All the diffraction measurement were made on a Rigaku AFC-5R diffractometer with Ni-filtered CuKα radiation and 18 KW anode generator. The X-ray data were collected at 25°C using the ω–2θ scan technique to a maximum 2θ value of 120.0°. The data were corrected for conventional absorption, Lorentz and polarization effects.

Scheme-1

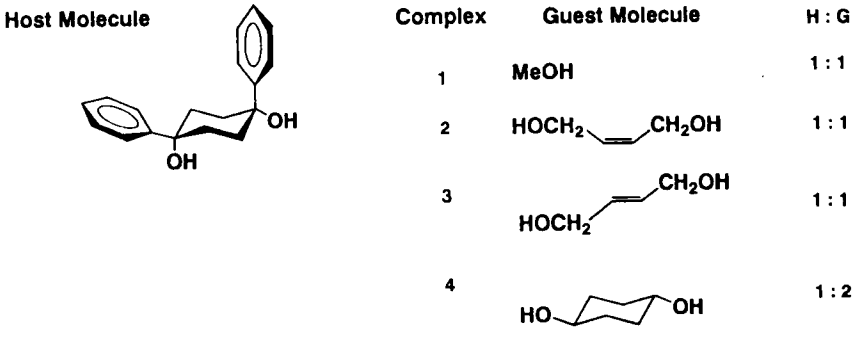


TABLE I Crystal data and experimental conditions for host-guest complexes of *cis*-1,4-diphenylcyclohexane-1,4-diol.

Parameter	1	2	3	4
Guest	CH_3OH	*cis*-2-butene-1,4-diol	*trans*-2-butene-1,4-diol, H_2O	*trans*-cyclohexane-1,4-diol
Formula	$C_{19}H_{24}O_3$	$C_{22}H_{28}O_4$	$C_{22}H_{30}O_5$	$C_{30}H_{44}O_6$
FW	300.40	356.46	374.48	500.67
Crystal system	monoclinic	monoclinic	monoclinic	orthorhombic
Space group	$P2_1$	$P2_1/n$	$P2_1/a$	$P2_12_12_1$
a/Å	7.589(2)	9.565(1)	7.479(2)	18.095(2)
b/Å	10.057(2)	9.371(1)	35.328(2)	25.374(3)
c/Å	11.033(2)	21.633(1)	7.801(1)	6.189(2)
β/°	93.81(1)	98.27(1)	100.58(1)	
V/Å^3	840.2(3)	1918.8(2)	2026.0(5)	2841.8(7)
Z	2	4	4	4
Dc/gcm^{-3}	1.187	1.234	1.228	1.170
μ(CuKα)/cm^{-1}	6.29	6.71	6.96	6.42
F(000)	324	768	808	1088
No.of independent reflections	1450	3265	3341	2483
No.of observed reflections	1341	3059	3087	748
R	0.039	0.055	0.046	0.079
R_w	0.043	0.049	0.044	0.080

Crystal structure analysis was proceeded by the use of teXsan crystallographic software package.[1] Non-hydrogen atoms were refined anisotropically. All the hydrogen atoms concerning the hydrogen bonds were located on the difference Fourier maps, while the other hydrogen atoms were located by the geometrical calculations and were included in the final stage of refinement with isotropic temperature factors. The quality of the crystal of complex **4** is rather low, and only non-hydrogen atoms were identified and included in the refinement. The final R and R_W of these complexes are small enough to discuss about the crystal structures in detail. The function minimized was $\sum w(|F_o| - |F_c|)^2$, where $w = 4F_o^2/s^2(F_o^2)$ with p-factor of 0.01.

MOLECULAR AND CRYSTAL STRUCTURES

Complex 1 Figure 1 shows the molecular structure of complex **1**, which is composed of the host, *cis*-1,4-diphenylcyclohexane-1,4-diol, and methanol in 1/1 ratio. The hydroxyl group of methanol connects to the oxygen of equatorial hydroxyl group of the host acting as proton donor. Almost all the hydrogen bond distances found in this work are in a range from 2.6 to 2.9 Å. The plane of the axial phenyl group faces to the base plane of cyclohexane ring, while the equatorial phenyl ring is perpendicular to the axial one. If the molecule is projected along the equatorial phenyl ring, the right drawing in Fig. 1 is obtained. The figure shows the simple and unique structure of this host molecule.

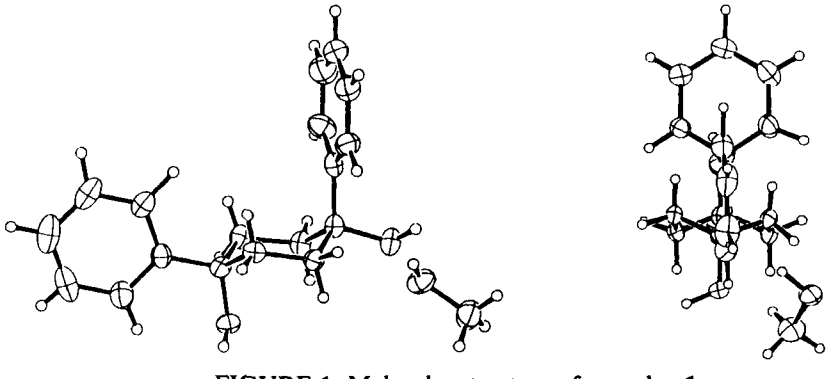


FIGURE 1 Molecular structure of complex **1**.

How is the interaction between the host and guest molecules in a crystal lattice? Figure 2 shows the crystal structure of complex **1** projected along the b-axis, so the 2-fold screw axis passes through the corner of the unit cell and perpendicular to the figure sheet. Around the 2-fold screw axis, six hydroxyl groups are close together and make an infinite helical loop through the hydrogen bonds. Around the helical loop of the hydroxyl groups, hydrophobic part of the host molecules make a kind of column.

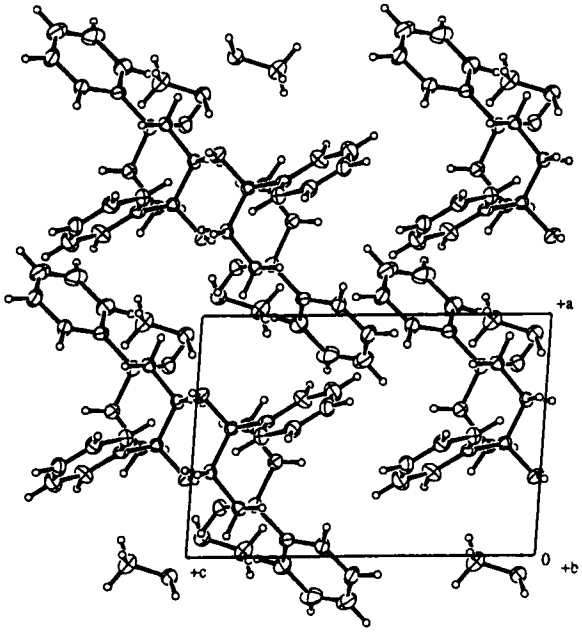
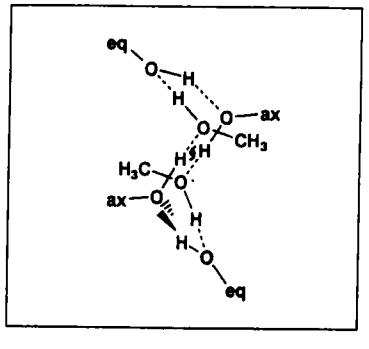
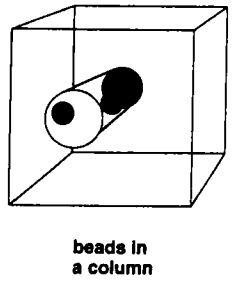


FIGURE 2 Crystal structure of complex **1**.

The mode of the hydrogen bond network in complex **1** is simplified in box-1. Here, six hydroxyl groups are shown around the crystallographic 2-fold screw axis. They make an infinite loop by connecting in the order to donate proton; ax-OH, MeOH, eq-OH, ax-OH, MeOH, eq-OH, then to ax-OH 1 unit cell over the first ax-OH. No direct interaction is found between the methanols in this helical loop. Schematically, the mode can be described as *the beads in a column* shown in scheme-2.



Box-1 Hydrogen bond network in **1**.



Scheme-2 Host-guest interaction in **1**.

Complex 2 The second complex is composed of the host and *cis*-2-butene-1,4-diol in 1/1 ratio. The molecular structure of this complex is shown in Fig. 3. Hydroxyl groups on both ends of the guest molecule connect to the eq-OH of the host molecule through the hydrogen bond, one of which acts as proton donor and the other as proton acceptor, respectively. The conformation of two phenyl groups are observed in the same mode in complex **1**, the ring plane of ax-Ph faces to and that of eq-Ph perpendicular to the base plane of cyclohexane ring.

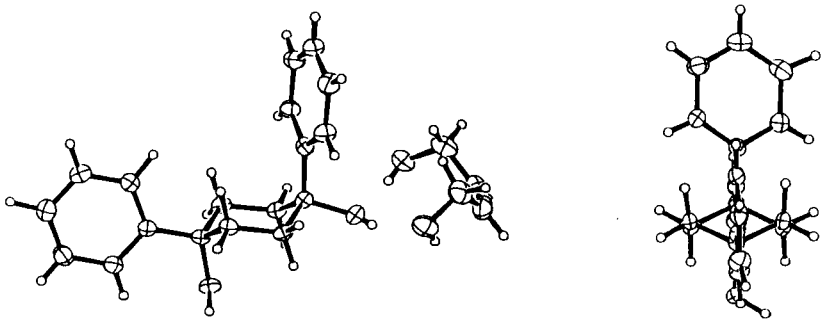


FIGURE 3 Molecular structure of complex **2**.

The crystal structure of the second complex **2** is also very unique as shown in Fig. 4. The pairs of host and guest molecules are connected together by the axial hydroxyl group of the host molecule. Then the guest molecules make a kind of string bridged by the hydroxyl group of the host molecule. A pair of strings are surrounded by the hydrophobic part of the host molecules.

The mode of the host-guest interaction is again simplified and shown in box-2. Hydroxyl groups on both ends of the guest molecule connect to the eq-OH in identical host molecule, and ax-OH of the host molecule connect them together. So, the host-guest interaction can be said as *the strings in a column*.

Complex 3 During the crystal structure determination of complex **3**, the water molecule was found as the third component of the host-guest complex between the host and *trans*-2-butene-1,4-diol. The molecular structure of complex **3** is shown in Fig. 5. One of two hydroxyl groups of guest molecule connects to the eq-OH and water molecule connect to the ax-OH of the host molecule by hydrogen bond. The conformation of two phenyl groups of the host molecule are conserved uniquely as found in complexes **1** and **2**.

The crystal structure of complex **3** is shown in Fig. 6. Hydroxyl groups of host, guest, and water molecules get together in a layer region and connected to each other by the hydrogen bonds. The hydrophilic layer is sandwiched by the hydrophobic part of the host molecules.

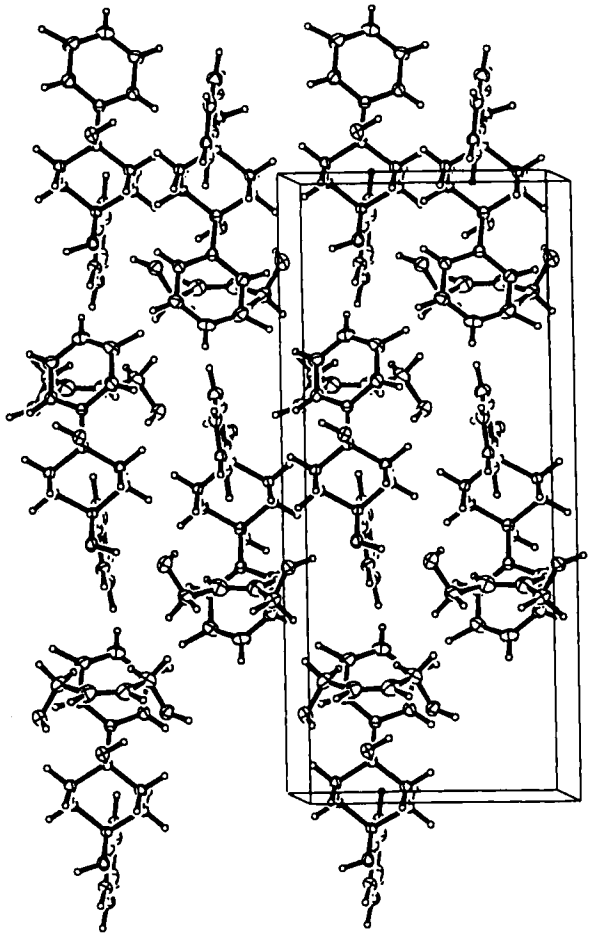
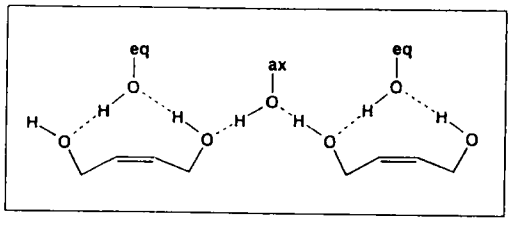
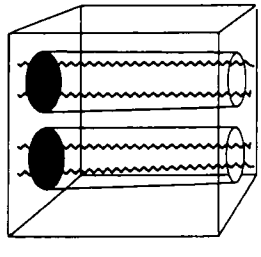


FIGURE 4 Crystal structure of complex **2**.



Box-2 Hydrogen bond network in **2**.



Scheme-2 Host-guest interaction in **2**.

The mode of hydrogen bond network is rather complicated in this complex. As shown in box 3, both ends of hydroxyl groups of guest molecule connect indirectly to the identical host molecule by the assist of water molecule. The direct interaction is found

between the neighboring guest molecules through the hydrogen bond. One of two hydroxyl groups of guest molecule act trifunctionally. In spite of rather complicated hydrogen bonding in the hydrophilic region, the crystal structure is simply said as *layer*.

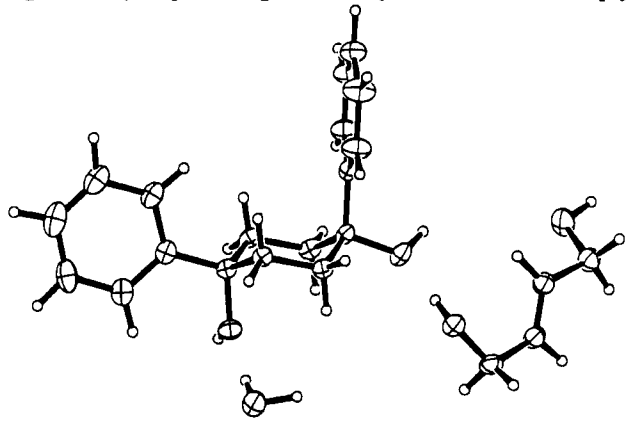


FIGURE 5 Molecular structure of complex **3**.

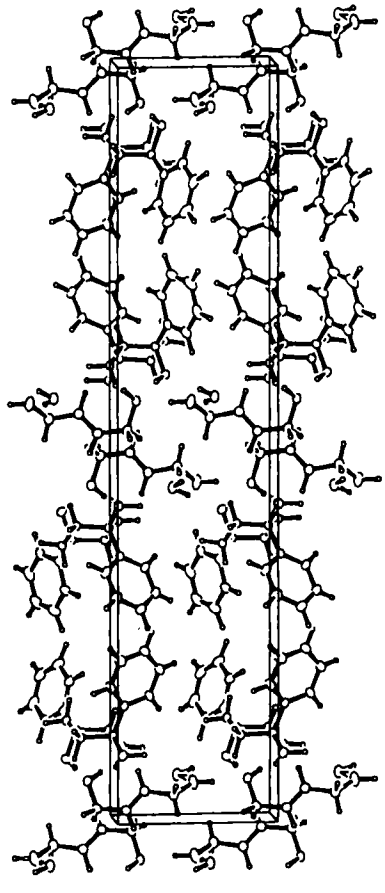
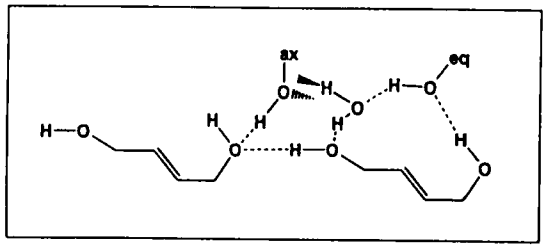
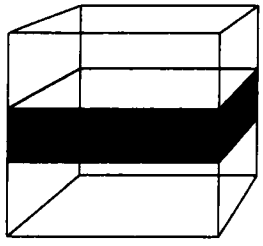


FIGURE 6 Crystal structure of complex **3**.



Box-3 Hydrogen bond network in 3.



Scheme-3 Host-guest interaction in **3**.

Complex 4 The last complex is composed of the host molecule and *trans*-cyclohexane-1,4-diol in 1/2 ratio. The two guest molecules are bonding to the two hydroxyl groups in the host molecule, respectively, as shown in Fig. 7. The conformation of eq-Ph ring deviate from the perpendicular position to the cyclohexane base plane. This is the only exception among the present structures.

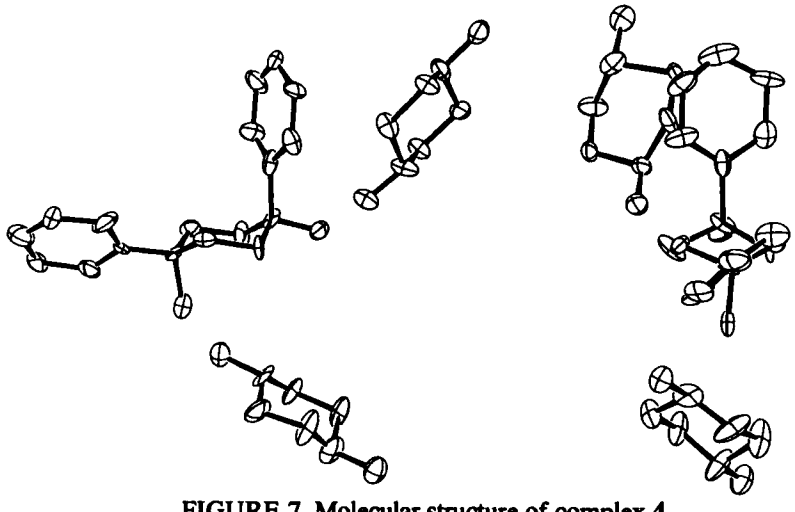


FIGURE 7 Molecular structure of complex **4**.

The hydrogen bond network in this crystal is very simple as shown in Fig. 8. The infinite hydrogen bonds are formed between a hydroxyl group of host molecule and two hydroxyl groups from two guest molecules. So, there exists two crystallographically independent hydrogen bond networks. In this crystal structure two host molecules are surrounded by ten guest molecules and stack along c-axis.

The hydrogen bond network in this crystal is very simple as shown in box-4. The crystal structure of complex **4** is described as *tube* (scheme-5).

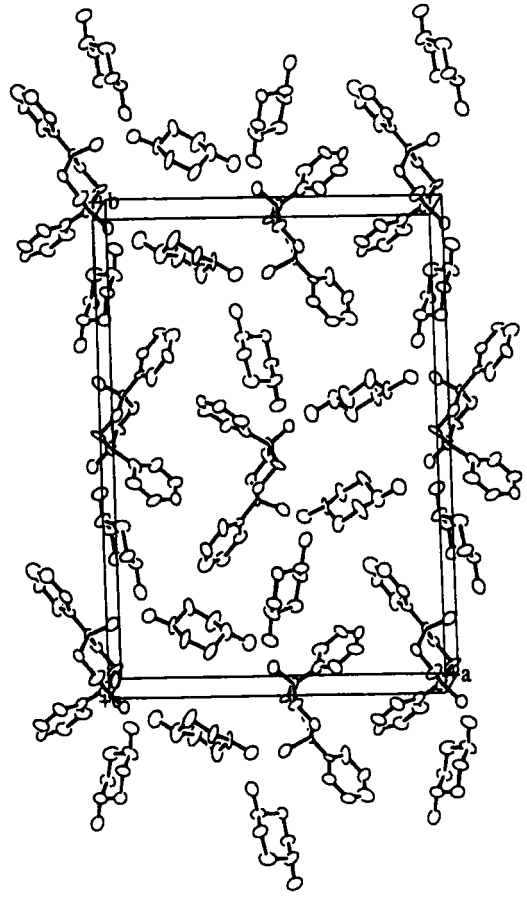
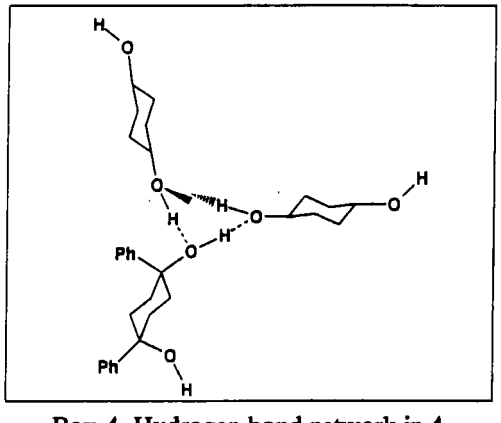
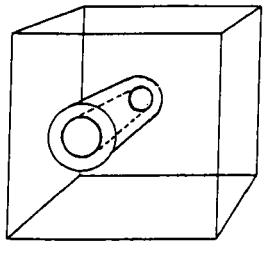


FIGURE 8 Crystal structure of complex **4**.

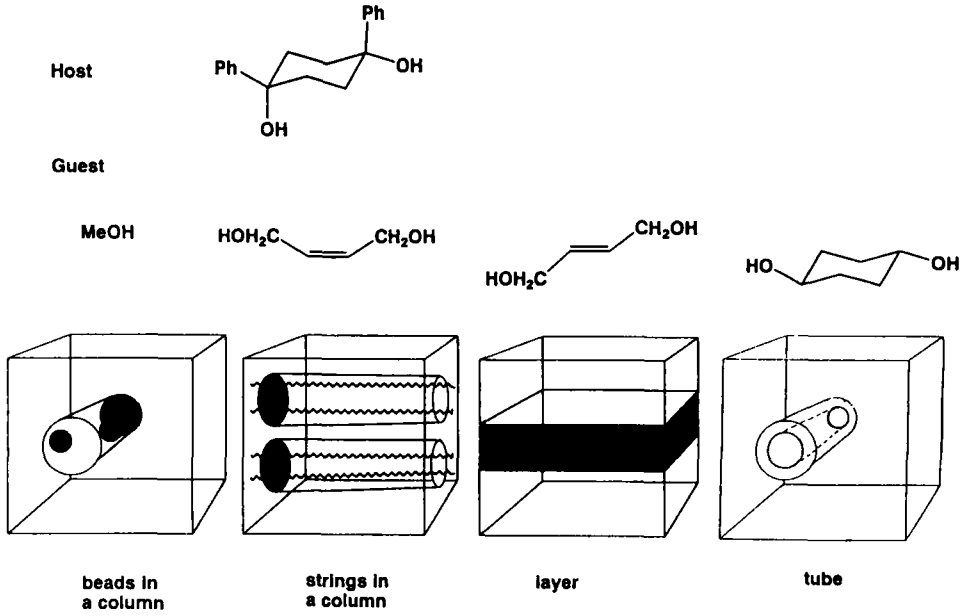


Box-4 Hydrogen bond network in 4.



Scheme-5. Host-guest interaction in 4.

The crystal structure determinations of the host-guest complexes of *cis*-1,4-diphenylcyclohexane-1,4-diol revealed the diverse mode of intermolecular interactions. Crystal structure determinations of four complexes with common host molecule revealed four different faces of these complexes (Scheme-6). When the size of the bead or the length of the string are modified, how the crystal structure will be modified? Our next step is concerned on this point because the number of the structures shown here is too small to characterize the function of the present host molecule. However, the combination of the hydrophobic interaction between the phenyl groups with rather rigid conformation in the host molecule and the hydrogen bond between the multifunctional hydroxyl groups are very interesting.



Scheme-6 Diverse mode of host-guest interaction of *cis*-1,4-diphenylcyclohexane-1,4-diol.

REFERENCES

1) teXsan, Crystal Structure Analysis Package, Molecular Structure Corporation (1985 & 1992).