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Crystal Structural Study on 2:1 Complexes of Equatorial Isomers of 3,5-Dimethylcyclohexanone and 3,5-Dimethylcyclohexanol with 1,1,6,6-Tetraphenylhexa-2,4-diyne-1,6-diol

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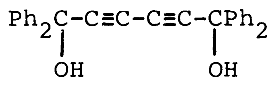
Selective inclusion of the diequatorial isomer of 3,5-dimethylcyclohexanone and the triequatorial isomer of 3,5-dimethylcyclohexanol by 1,1,6,6-tetraphenylhexa-2,4-diyne-1,6-diol was observed. The crystal structure of these complexes was studied.

It has been reported that 1,1,6,6-tetraphenylhexa-2,4-diyne-1,6-diol (**1**) includes equatorial isomer (**2**) selectively but not axial isomer (**3**) of 3,5-dimethylcyclohexanone.1) Recently, we also found that **1** includes equatorial isomer (**4**) selectively but not axial isomers (**5**, **6**) of 3,5-dimethylcyclohexanol. In order to know the reason for the selectivity, X-ray crystal structure of these complexes was studied.

A 2:1 complex (**7**) of *cis*-3,5-dimethylcyclohexanone (**2**) with **1** was prepared according to the reported method.1) A 2:1 complex (**8**) of *cis,cis,cis*-3,5-dimethylcyclohexanol (**4**) with **1** was prepared by a selective complexation of a commercially available mixture of **4** (63.2%), *trans,cis,trans*- (**5**) (21.9%), and *trans,trans,cis*-3,5-dimethylcyclohexanol (**6**) (14.9%) with **1**. For example, when a solution of this mixture (1 g, 7.8 mmol) and **1** (1.6 g, 3.9 mmol) in ether-petroleum ether (1:1) (10 ml) was kept at room temperature for 24 h, a 2:1 complex of **4** and **1** (**8**) was obtained as colorless prisms, which upon two recrystallizations from ether-petroleum ether (1:1) gave pure crystals (1.14 g, 69%, mp 90-91 °C). Heating of the crystals in vacuo gave **4** of 99.7% purity (0.41 g, 65%). The purity of **4** was determined by gas



$Ph_2C(OH)-C\equiv C-C\equiv C-C(OH)Ph_2$

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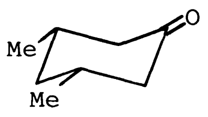

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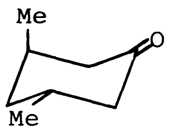

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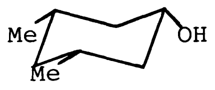

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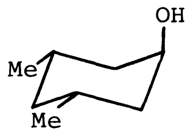

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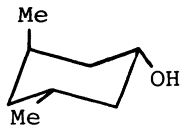

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chromatography. $NaBH_4$ reduction of pure **2** obtained from **7** by distillation gave a mixture of **4** and **5**. Complexation of this mixture with **1** by the same procedure as described above also gave **8**.

Each crystal of **7** (0.39x0.35x0.50 mm^3) and **8** (0.41x0.45x0.85 mm^3) was enclosed in a 0.5 mm diameter thin-walled Lindemann-grass capillaries to minimize loss by sublimation. The cell dimensions and X-ray diffractions were collected on Rigaku AFC-5 diffractometer using Cu-$K\alpha$ (λ=1.5418 Å) radiation. Intensity data were collected up to $2\theta=125^\circ$ by ω-2θ method with scan speed of 6°/min in ω and background counts for 5 s for both sides of scan range. The crystal data obtained are shown in the reference 2. The structure of **7** was solved by interpretation of Patterson map and that of **8** was done by the direct method (MULTAN-78).$^{3)}$ The refinements of both complexes were carried out by the block-diagonal least-squares procedure applying a weighting scheme of $w=(\sigma^2(F_o)-0.3885|F_o| + 0.0311|F_o|^2)^{-1}$ for **7** and $w=(\sigma^2(F_o)-0.5998|F_o| + 0.0453|F_o|^2)^{-1}$ for **8**, respectively. All hydrogen atoms were found on the difference Fourier-maps at the expected positions for both complexes. All the computations were done on a FACOM M-140F at the Computer Center and IBM 3080-GX3 at the Information Retrieval Center of Shimane University, using the computer program system, UNICS.$^{4)}$

The molecular structures of **7** and **8** are shown in Figs. 1 and 2, and the molecular packings in **7** and **8** in Figs. 3 and 4, respectively. The structures of host molecules in both complexes are very similar with each other. Each host molecules are constructed with a linear diacetylene linkage, a hydrophilic hydroxyl group, and two hydrophobic benzene rings whose dihedral angles are 88.6° and 89.3° for **7** and **8**, respectively. The two hydroxyl groups of each host molecule are in *trans* conformation with each other, and participate in the host-guest hydrogen bonding. The hydrogen bond scheme, however, is different from each other. In **7**,

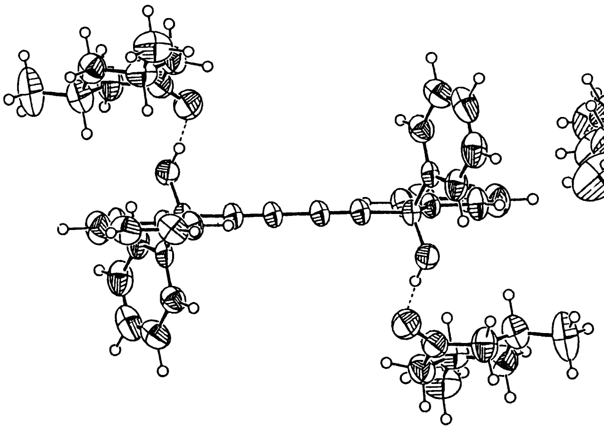

Fig. 1. Molecular structure of 7, ORTEP drawing,[5)] 50% probability.

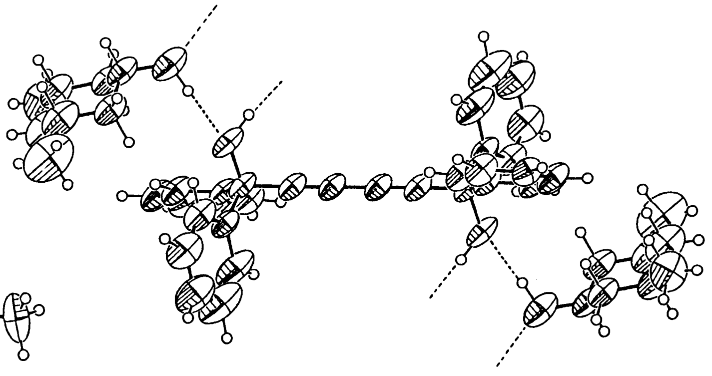

Fig. 2. Molecular structure of 8, ORTEP drawing,[5)] 50% probability.

the hydroxyl group of 1 acts as the hydrogen donor toward the carbonyl oxygen atom of 2, OH···O = 2.770(2) Å, whereas in 8, the hydroxyl group of 1 plays two roles, firstly as the hydrogen acceptor from the hydroxyl group of 4, O···HO = 2.686(3) Å, secondly as the donor toward the hydroxyl oxygen atom of another 4, OH···O = 2.904(3) Å.

The molecular structures of 2 and 4 in 7 and 8, respectively, are similar with each other. The cyclohexane ring of both complexes is in chair form and the two methyl groups are at equatorial positions.

In contrast to the above mentioned discussion on the host-guest molecular structures and the crystal data,[2)] the crystal structures of 7 and 8 are somewhat different from each other as shown in Figs. 3 and 4, respectively. 7 and 8 are not isomorphous. The difference depends mainly upon the scheme of hydrogen bond.

Roughly speaking, the crystal structure of 8 could be obtained by sliding the host-guest structural unit of 7 by one unit toward the a-axis. Nevertheless, in both crystal structures, the host-guest molecules seem to be so stabilized in the crystalline state as to gain much favorable hydrogen bondings between the host and guest molecules, and closest van der Waals contacts. If so, one can easily suppose that the both crystal structures would be less stable when the guest configuration is changed from equatorial to axial at one of two methyl groups, because the guests with less bulky shape would fit well in the narrow space formed by two benzene rings.

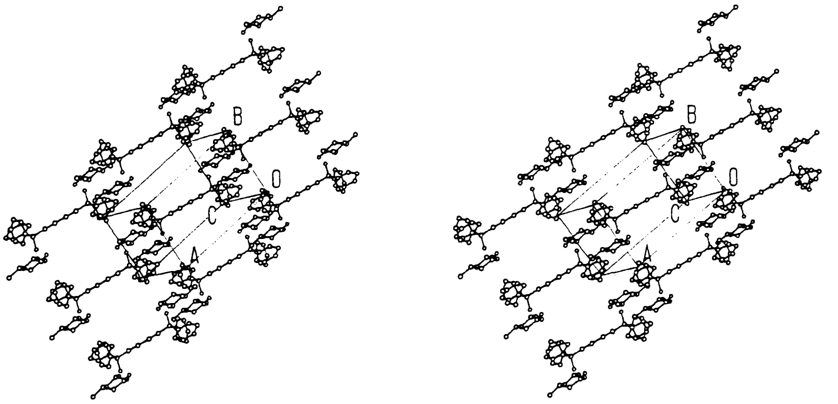

Fig. 3. Stereodrawing[6)] of molecular packing in 7.

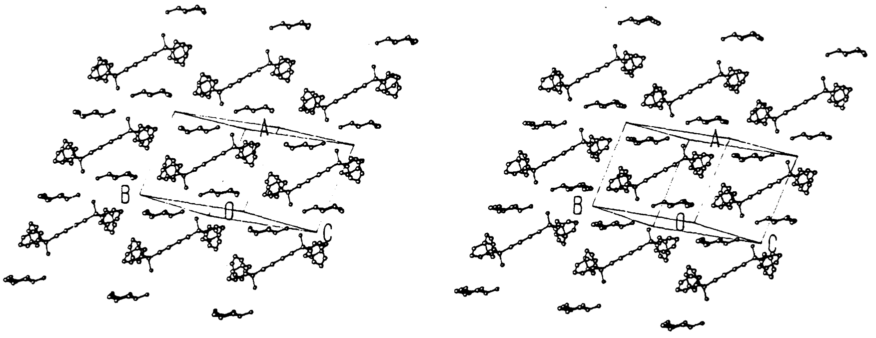

Fig. 4. Stereodrawing[6)] of molecular packing in 8.

References

1) K. Tanaka and F. Toda, Nippon Kagaku Kaishi, 1986, 932.

2) Crystal data of $C_{30}H_{22}O_2 \cdot 2C_8H_{14}O$ (7) are as follows: FW=666.9, triclinic, space group $P\bar{1}$, a=13.149(4), b=8.806(4), c=8.546(4) Å, α=100.10(3)°, β=81.10(2)°, γ=98.48(3)°, V=961.8(5) Å^3, D_x=1.151 Mg m^{-3}, μ=5.70 cm^{-1}, total number of reflections=2801 ($F_o>3\sigma(F_o)$), R/wR=0.060/0.060, F(000)=358.
Crystal data of $C_{30}H_{22}O_2 \cdot 2C_8H_{16}O$ (8) are as follows: FW=670.9, triclinic, space group $P\bar{1}$, a=10.596(8), b=12.256(6), c=11.734(4) Å, α=138.32(3)°, β=81.39(9)°, γ=103.81(9)°, V=983(1) Å^3, D_m=1.11(1) Mg m^{-3}, D_x=1.127 Mg m^{-3}, μ=5.57 cm^{-1}, total number of reflections=2768 ($F_o>3\sigma(F_o)$), R/wR=0.069/0.070, F(000)=362.

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