

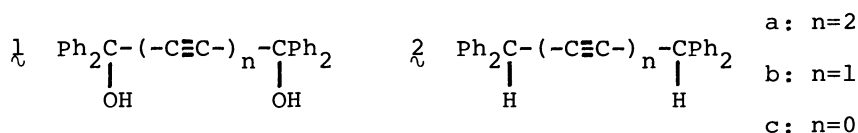
INCLUSION COMPLEXES OF 1,1,2,2-TETRAPHENYLETHANE-
1,2-DIOL AND 1,1,2,2-TETRAPHENYLETHANE

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The title compounds were found to be good host molecule for various organic guests. In the crystal structures of the 2:1 p-xylene inclusion complexes of the title host molecules, each p-xylene molecule is surrounded by four phenyl groups of the two neighboring host molecules. Application of such inclusion phenomena to the separation of isomers was also reported.

Previously, it has been reported that 1,1,6,6-tetraphenylhexa-2,4-diyne-1,6-diol ($1a$) and 1,1,4,4-tetraphenylbut-2-yne-diol ($1b$) form crystalline complexes with various kinds of guest compounds. In all the complexes, there are strong hydrogen bonds between hydroxyl group of $1a$ or $1b$ and the guest molecules. Recently, we found by means of IR and crystal structure analyses that 1,1,2,2-tetraphenylethane-1,2-diol ($1c$) forms stable inclusion complex without forming such hydrogen bond. It was also found that 1,1,6,6-tetraphenylhexa-2,4-diyne ($2a$), 1,1,4,4-tetraphenylbut-2-yne ($2b$), and 1,1,2,2-tetraphenylethane ($2c$) can include some guest molecules in the same manner.



- 3 m-xylene 4 p-xylene 5 o-chlorotoluene 6 p-chlorotoluene
7 2-methylquinoline 8 8-methylquinoline

Inclusion complexes of $\beta\text{-CD}$ were prepared by recrystallization of $\beta\text{-CD}$ from the various solvent molecules shown in Table 1. The νOH band of $\beta\text{-CD}$ (3550 cm^{-1}) did not change much by forming inclusion complex except in the case of #7, #8, #12, #13, and #14 (Table 1). This indicates the absence of hydrogen bond between $\beta\text{-CD}$ and guest molecules. In the exceptional cases, however, hydrogen bond may play an important role. In order to compare the stability of the complexes with and without hydrogen bond, DSC (differential scanning calorimetry) data of the 2:1 p-xylene (#10) and 1:2 pyridine complex (#12) of $\beta\text{-CD}$ were measured (Table 2) and the latter complex with hydrogen bond was found to be much more stable than the former one. However, stability of a 1:1 pyridine complex of $\alpha\text{-CD}$ does not differ much from that of a 2:1 p-xylene complex of $\alpha\text{-CD}$, because hydrogen bond is absent in these cases.

Table 1. Crystal, molar ratio, melting point, and νOH of the complex of $\beta\text{-CD}$

No.	Guest	Crystal	H:G	Mp $\theta_m/^\circ\text{C}$	$\nu\text{OH}/\text{cm}^{-1}$
0	---	prisms	---	189	3550
1	acetone	prisms	1:2	nc ^{a)}	3550
2	cyclopentanone	needles	1:2	nc	3550
3	γ -butyrolactone	prisms	1:2	98-110	3450
4	tetrahydrofuran	prisms	1:1	nc	3450
5	dioxane	prisms	1:1	nc	3520, 3450
6	carbon tetrachloride	needles	1:1	nc	3540
7	dimethylsulfoxide	prisms	1:2	136-138	3250
8	dimethylformamide	needles	1:2	nc	3280
9	benzene	prisms	1:1	nc	3540
10	p-xylene	prisms	2:1	nc	3530
11	p-chlorotoluene	prisms	2:1	nc	3550
12	pyridine	needles	1:2	nc	3220
13	2-methylquinoline	prisms	1:1	nc	3560, 3170
14	quinoline	prisms	1:2	92-93	3300

a) nc means not clear.

Table 2. Decomposition point and ΔH of the complex of $\beta\text{-CD}$ and $\alpha\text{-CD}$ with p-xylene and pyridine

Guest	$\beta\text{-CD}$		$\alpha\text{-CD}$	
	Decomposition point/ $^\circ\text{C}$	$\Delta\text{H}/\text{kcal mol}^{-1}$	Decomposition point/ $^\circ\text{C}$	$\Delta\text{H}/\text{kcal mol}^{-1}$
p-xylene	112-114	130	96	125
pyridine	103	500	98	225

Because $\beta\text{-CD}$ includes one of isomers selectively, the inclusion phenomena with $\beta\text{-CD}$ can be used for a separation of isomers. For example, $\beta\text{-CD}$ (1.0 g) was dissolved in a 1:1 mixture of m- (3) and p-xylene (4) by heating, and the solution was kept at room temperature for 3 h to form a 2:1 complex of $\beta\text{-CD}$ and 4 (0.98 g). Heating of the complex at 150°C gave pure 4 (0.12 g, 15%). When $\beta\text{-CD}$ (1.0 g) was dissolved in a 1:1 mixture of o- (5) and p-chlorotoluene (6) (1.0 g) by heating, and the solution was kept at room temperature for 3 h, a 2:1 complex of $\beta\text{-CD}$ and 6 was formed

(0.7 g), which upon heating gave pure ξ (0.19 g, 38%). When λ_C (5.0 g), and a 50:50 mixture of λ and ξ (3.9 g) were dissolved in acetone (3 ml) and the solution was kept at room temperature for 12 h, a 1:1 complex of λ_C and λ was obtained (6.4 g). Heating of the complex at 120 °C under 5 mmHg gave pure λ (1.8 g, 90%).

In order to know how the guest molecules are included by the host molecule, the X-ray crystal structural analyses of the 2:1 p-xylene inclusion complexes with both λ_C and λ_C were carried out. The diffraction data were collected on a CAD4 diffractometer at room temperature. Since both compounds decomposed readily during the data collection, a linear decay correction was applied to the relative intensities. The experimental details are given in Table 3.⁴⁾ The structure of λ_C complex was solved by direct method, crystal of λ_C complex being apparently isomorphous to that of λ_C . The asymmetric unit contains only half of the guest molecule, i.e. the guest molecule has a center of inversion which coincides with the crystallographic i. There appears no strong interaction between the host and guest molecules. In fact, the conformation of the host molecule in these complexes are exactly the same as that of free molecule λ_C .⁵⁾ From the molecular diagram in Fig. 1, it is clear that the four phenyl rings from the two neighboring host molecules form a pocket like space with a center of inversion at the center, and the pocket suits p-xylene better than m-xylene. This may be the reason why host λ_C and λ_C can selectively include p-xylene. It is also obvious that no hydrogen bond is involved between the host and the guest molecules. Similar packing mechanism was found in the complex of N,N,N',N'-tetraisopropylloxamide and α -methylnaphthalene.⁶⁾ Other inclusion

Table 3. Crystal data

	2:1 λ_C :p-xylene	2:1 λ_C :p-xylene
Formula	$C_{14}H_{10}$	$C_{14}H_{10}$
Formula wt	838	774
SP. GP.	$P\bar{1}$	$P\bar{1}$
a/Å	6.143(2)	5.941(1)
b	9.197(3)	9.269(1)
c	20.997(5)	20.81(3)
$\alpha/^\circ$	95.13(2)	95.92(1)
β	91.42(2)	90.34(5)
γ	104.54(3)	106.14(7)
Volume/Å ³	1142	1082
Z	1	1
Dm., Dc./gcm ⁻³	1.22, 1.20	1.15, 1.14
radiation	MoK α	MoK α
$\theta/2\theta$ scan range	1.4 + 0.7tan θ	1.6 + 0.7tan θ
$2\theta_{max}$	55	50
NREF, NOBS	5199, 2227 ($I \geq 3\sigma(I)$)	4080, 656 ($I \geq 2\sigma(I)$)
Linear decay corr.	28%	80%
R, Rw	0.070, 0.045	0.070, 0.042

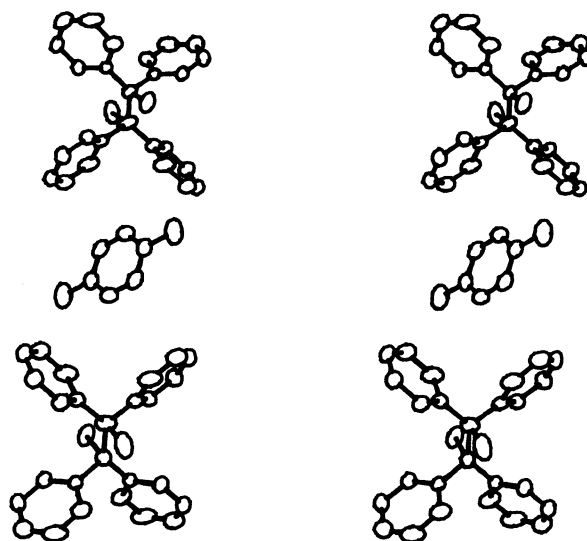


Fig. 1. A stereo-view of 2:1 $\text{1,2-dichloroethane:p-xylene}$ complex.

Table 4. Molar ratio and melting point of the complexes of 2a , 2b , and 2c

Guest	Host					
	H:G	2a Mp θ_m /°C	H:G	2b Mp θ_m /°C	H:G	2c Mp θ_m /°C
cyclopentanone	---		1:2	nc	1:1	nc
dioxane	1:1	nc ^{a)}	1:1	nc	1:1	nc
acetonitrile	---		1:2	115-125	1:2	nc
dimethylsulfoxide	2:1	154-163	1:2	134-151	2:1	nc
dimethylformamide	---		1:2	nc	1:1	nc
benzene	1:2	nc	1:2	nc	1:1	nc
p-xylene	---		1:1	nc	1:1	nc
pyridine	---		1:2	nc	1:1	nc
quinoline	---		---		1:1	107-124

a) nc means not clear.

complexes with 2a , 2b , and 2c are listed in Table 4. The interactions between host and guest molecules are of pure van der Waal's type with favorable packing environment.

References

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