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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 pxylene inclusion complexes of the title host molecules, each pxylene 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-1,6diol (la) and 1,1,4,4-tetraphenylbut-2-yne-diol (lb) form crystalline complexes 1,2) with various kinds of guest compounds. In all the complexes, there are strong 1-3) hydrogen bonds between hydroxyl group of la or lb and the guest molecules. Recently, we found by means of IR and crystal structure analyses that 1,1,2,2tetraphenylethane-1,2-diol (lc) forms stable inclusion complex without forming such hydrogen bond. It was also found that 1,1,6,6-tetraphenylethane (2,2), 1,1,4,4-tetraphenylbut-2-yne (2b), and 1,1,2,2-tetraphenylethane (2c) can include some guest molecules in the same manner.

$$\frac{1}{2} \begin{array}{c} Ph_{2}C^{-}(-C \equiv C^{-}) n \stackrel{-CPh_{2}}{|} 2 \\ OH \\ OH \\ \end{array} \begin{array}{c} 2 \\ Ph_{2}C^{-}(-C \equiv C^{-}) n \stackrel{-CPh_{2}}{|} 2 \\ Ph_{2}C^{-}(-C \equiv C^{-}) n \stackrel{-CPh_{2}}{|} 2 \\ H \\ H \\ H \\ \end{array} \begin{array}{c} n=1 \\ C: n=0 \\ \end{array}$$

$$\frac{3}{2} m - xylene \\ \frac{4}{2} p - xylene \\ \frac{5}{2} o - chlorotoluene \\ \frac{6}{2} p - chlorotoluene \\ \frac{7}{2} - methylquinoline \\ \frac{8}{2} 8 - methylquinoline \\ \frac$$

Inclusion complxes of lg were prepared by recrystallization of lg from the various solvent molecules shown in Table 1. The vOH band of lg (3550 cm<sup>-1</sup>) 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 lg 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 lg 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 lg does not differ much from that of a 2:1 p-xylene complex of lg, because hydrogen bond is absent in these cases.

No.	Guest	Crystal	H:G	Mp θ <sub>m</sub> ∕°C	$vOH/cm^{-1}$
0		pisms		189	3550
1	acetone	prisms	1:2	<sub>nc</sub> 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

Table 1. Crystal, molar ratio, melting point, and vOH of the complex of 10

a) nc means not clear.

Table 2. Decomposition point and  $\Delta H$  of the complex of  $l_{c}$  and  $l_{c}$  with p-xylene and pyridine

Guest	łę		t ,	28		
	Decomposition point/°C	∆H/kcal mol <sup>-1</sup>	Decomposition point/°C	∆H/kcal mol <sup>-1</sup>		
p-xylene pyridine	112-114 103	130 500	96 98	125 225		

Because  $l_{\chi}$  includes one of isomers selectively, the inclusion phenomena with  $l_{\chi}$  can be used for a separation of isomers. For example,  $l_{\chi}$  (l.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  $l_{\chi}$  and 4 (0.98 g). Heating of the complex at 150 °C gave pure 4 (0.12 g, 15%). When  $l_{\chi}$  (l.0 g) was dissolved in a 1:1 mixture of o- (5) and p-chlorotoluene (6) (l.0 g) by heating, and the solution was kept at room temperature for 3 h, a 2:1 complex of  $l_{\chi}$  and 6 was formed

(0.7 g), which upon heating gave pure § (0.19 g, 38%). When  $\downarrow c$  (5.0 g), and a 50:50 mixture of 7 and 8 (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  $\downarrow_{C_1}^c$  and 7 was obtained (6.4 g). Heating of the complex at 120 °C under 5 mmHg gave pure 7 (1.8 g, 90%).

In order to know how the quest molecules are included by the host molecule, the X-ray crystal structural analyses of the 2:1 p-xylene inclusion complexes with both 1c and 2c 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 intensi-4) ties. The experimental details are given in Table 3. The structure of 1c complex was solved by direct method, crystal of 2c complex being apparently isomorphous to that of ic. 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 lc. 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 1c and 2c 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'-tetraisopropyloxamide and  $\alpha$ -methylnaphthalene. Other inclusion

Formula	2:1 lc:p-xylene	2:1 2c:p-xylene	
Formula wt	838 <b>~</b>	774	
SP. GP.	ΡĪ	ΡĪ	
	6 143(2)	5 941(1)	
a/A b	0.197(2)	9,341(1)	
d	9.197(3)	9,209(1)	
c	20.997(5)	20.81(3)	
α/°	95.13(2)	95.92(1)	
β	91.42(2)	90,34(5)	
Ŷa	104.54(3)	106.14(7)	
Volume/Å <sup>3</sup>	1142	1082	
Z	1	1	
Dm., Dc./gcm <sup>-3</sup>	1.22, 1.20	1,15, 1,14	
radiation	ΜοΚα	ΜοΚα	
$\theta/2\theta$ scan range	<b>1.4 + 0.7tan</b> θ	$1.6 + 0.7 \tan \theta$	
20 max	55	50	
NREF, NOBS	5199, 2227( $I > 3 \sigma$ ( $I$ ))	4080, 656( $I \ge 2\sigma(I)$ )	
Linear decay corr. 28% = 80%			
R, Rw	0,070, 0,045	0.070, 0.042	

Table 3. Crystal data

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Fig. 1. A stereo-view of 2:1 lc:p-xylene complex.

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

Guest	H:G	2a Mp θ ∕°C	H:G	2b мр θ ∕°С	H:G M	£ <sub>θ</sub> ∕°c
cyclopentanone			1:2	nc	1:1	nc
dioxane	1:1	nc <sup>a)</sup>	1:1	nc	1:1	nc
acetonitrile			1:2	115-125	1:2	nc
dimethvlsulfoxide	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-xvlene			1:1	nc	1:1	nc
pyridine			1:2	nc	1:1	nc
quinoline					1:1 10	7-124

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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