

symmetric case). However, practically this extinction rule is not determinant because these satellites with  $h_2$  even are, like those with  $h_2$  odd, extremely weak (at least for the weak indices  $h_2$  considered). Fortunately, the other satellites  $h_1$ ,  $h_2$ ,  $h_3$ ,  $\pm 1$  are generally very sensitive to a change from a symmetric to an antisymmetric pattern of atomic displacements. In the latter case, the  $R$  factor becomes very high: 0.54. So, although the structure we have described belongs to the superspace group  $PP_1^a$  as it almost obeys the symmetry of  $PP_1^{2,1/a}$  we can conclude that the soft mode in the high-temperature phase is symmetric with respect to the screw axis, in agreement with Takeuchi *et al.* (1981).

The authors are indebted to Professor P. M. de Wolff for critically reading the first version of this paper and particularly for fundamental remarks concerning the choice of the superspace group. They thank Dr Vettier, for private communications, and Drs Currat and Bernard for helpful discussions.

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## Molecular Inclusion Phenomena in (2*R*,5*R*,8*R*,11*R*)-1,4,7,10-Tetrabenzyl-2,5,8,11-tetraethyl-1,4,7,10-tetraazacyclododecane

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(Received 12 April 1982; accepted 14 June 1982)

#### Abstract

The title compound,  $C_{44}H_{60}N_4$ , crystallizes in various different forms including different solvent molecules. The typical form is the tetragonal  $P4_3$  with a small aromatic molecule in 1:1 molecular ratio. The X-ray structure analyses reveal that the host molecules in the

tetragonal system form a triangular cavity, which is most suitable for the size and shape of the mesitylene molecule. [Crystal data for the mesitylene inclusion complex:  $P4_3$ ,  $a = 12.110$  (3),  $c = 32.579$  (11) Å,  $Z = 4$ ;  $R = 6.9\%$  for 1203 reflection data.] For a smaller solvent molecule the crystal is metastable, and for a larger solvent molecule a different crystal form appears.

This phenomenon can be used to recognize the different molecules in a mixed solvent.

### Introduction

A systematic investigation of the structures of the chiral cyclens\* has been performed in our Institute, and the structures of all the stereoisomers of tbt-cyclen have been clarified. The 12-membered ring forms a square, but the conformation is affected by the chiralities of the asymmetric C atoms (Sakurai, Watanabe, Tsuboyama & Tsuboyama, 1981). For many isomers, the benzyl groups are situated above or below the 12-membered ring, and the molecule has a more or less globular form. On the other hand, for the highest symmetrical  $C_4$  type [(*RRRR*) or (*SSSS*)] the molecule was found to have an open structure in which the benzyl groups are extended from the 12-membered ring (Fig. 1*a*). The structure analysis was performed on the racemic crystal (Sakurai, Kobayashi, Tsuboyama & Tsuboyama, 1978). Single crystals of either the (*RRRR*) or the (*SSSS*) forms always contain solvent molecules. This means that, because of the open structure of the molecule, the close-packed structure cannot be formed unless the solvent molecule occupies the vacant space formed by the free molecule. Above all, the crystal form or the lattice parameters depend on the kind of solvent molecule. In order to clarify these phenomena a systematic structure analysis was performed, and the mutual relation between the guest and host molecules was determined.

### Experimental

The host molecule was prepared by the method described previously (Tsuboyama, Tsuboyama, Higashi & Yanagita, 1970). Single crystals were grown by slow evaporation of the solution. When the resultant crystals are placed in the atmosphere, most gradually become opaque at room temperature, which means that they contain solvent molecules as guests. From the chemical analysis the host-guest ratio was determined.

Preliminary X-ray diffraction data were obtained photographically with Cu  $K\alpha$  radiation. Intensity data were measured on a Rigaku automated four-circle diffractometer with graphite-monochromatized Mo  $K\alpha$  radiation. Some of the metastable crystals were sealed in glass capillaries with saturated solvent.

Thermal gravimetry and differential thermal analysis (TG-DTA) measurements were made on a Rigaku

\* Abbreviations: cyclen: 1,4,7,10-tetraazacyclododecane; tbt-cyclen: (*RRRR*)-cyclen: (2*R*.5*R*.8*R*.11*R*)-1,4,7,10-tetrabenzyl-2,5,8,11-tetraethylcyclen.

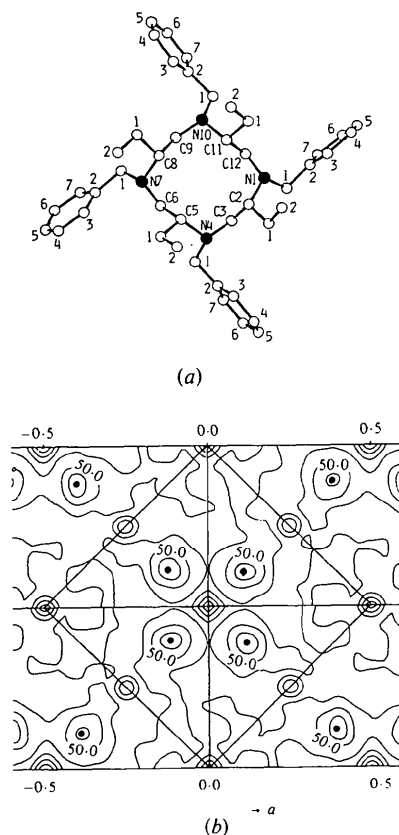


Fig. 1. (a) The model of the host molecule. (b) *R*-factor map in Cheshire group (Hirshfeld, 1968)  $Z'422$ .  $a' = \frac{1}{2}(a + b)$ ,  $b' = \frac{1}{2}(-a + b)$ . The minimum positions are shown by filled circles (*m*-xylene inclusion crystal).

8076 D1 DTA meter in an argon atmosphere. The small crystals were selected and weighed (each was 2–5 mg).  $\alpha$ - $\text{Al}_2\text{O}_3$  was used for the reference material and the temperature was raised at the rate 10 or 20 K  $\text{min}^{-1}$ .

Experimental results are summarized in Table 1. There are three different crystal systems, *viz* tetragonal, orthorhombic and monoclinic. The tetragonal form is obtained from various small aromatic solvents. The lattice parameters depend on the kind of guest molecule. Stable crystals were obtained from *m*-xylene solution, and the structure analysis was attempted for these data. The direct-phasing method was not successful. Since the structure of the host molecule was determined from the racemic crystal, it was used for the trial model and the structure was solved from the *R*-factor map (Sakurai, Ito & Kobayashi, 1968) shown in Fig. 1. The structure was successfully refined from this trial model, and the guest molecule was obtained by a difference Fourier synthesis. In this structure, a disordered configuration of the guest molecule was observed and a certain fraction of the methyl group appears at the 5th site of the benzene ring. Since the

Table 1. *Experimental results*

(a) Diffractometer data and desorption temperature

Guest	Space group	Lattice constants				<i>Z</i>	DTA (K)
		<i>a</i> (Å)	<i>b</i> (Å)	<i>c</i> (Å)	$\beta$ (°)		
Benzene	<i>P4</i> <sub>1</sub> or <i>P4</i> <sub>3</sub>	12.05		30.97	4	381	
Toluene	<i>P4</i> <sub>1</sub>	12.05		31.89	4	380	
<i>m</i> -Xylene	<i>P4</i> <sub>1</sub>	12.07		32.20	4	391	
Mesitylene	<i>P4</i> <sub>1</sub>	12.11		32.58	4	398	
<i>p</i> -Xylene	<i>P222</i>	23.56	12.08	49.98	12	406	
Cyclohexane (1/2)	<i>P2</i> <sub>1</sub>	21.94	27.29	18.32	94.1	340	
					10	449	

(b) Photographic data (space group *P4*<sub>1</sub> or *P4*<sub>3</sub>)

Guest	Lattice constants		Guest	Lattice constants	
	<i>a</i> (Å)	<i>c</i> (Å)		<i>a</i> (Å)	<i>c</i> (Å)
Ethylbenzene	11.92	32.8	Bromobenzene	12.01	31.9
<i>o</i> -Xylene	11.85	33.0	1.2 Dibromobenzene	12.05	32.2
Chlorobenzene	12.01	31.6	1.3 Dibromobenzene	11.89	33.2
1.2-Dichlorobenzene	11.97	31.7	Tetralin	11.93	33.8

Table 2. *Crystal data and results of the analysis (tetragonal, P4<sub>3</sub>, Z = 4)*

	Mesitylene C <sub>10</sub> H <sub>10</sub> N <sub>4</sub> ·C <sub>9</sub> H <sub>12</sub>	<i>m</i> -Xylene C <sub>10</sub> H <sub>10</sub> N <sub>4</sub> ·C <sub>8</sub> H <sub>10</sub>	Toluene C <sub>10</sub> H <sub>10</sub> N <sub>4</sub> ·C <sub>7</sub> H <sub>8</sub>
Crystal Formula	C <sub>19</sub> H <sub>20</sub> N <sub>4</sub> ·C <sub>9</sub> H <sub>12</sub>	C <sub>18</sub> H <sub>18</sub> N <sub>4</sub> ·C <sub>8</sub> H <sub>10</sub>	C <sub>17</sub> H <sub>16</sub> N <sub>4</sub> ·C <sub>7</sub> H <sub>8</sub>
Formula weight	765.18	751.15	737.13
Lattice constants			
<i>a</i> = <i>b</i> (Å)	12.110 (3)	12.070 (2)	12.046 (2)
<i>c</i> (Å)	32.579 (11)	32.201 (18)	31.892 (6)
<i>U</i> (Å <sup>3</sup> )	4777.8	4691.2	4627.7
<i>D<sub>m</sub></i> (floatation) (Mg m <sup>-3</sup> )	1.068	1.064	1.062
<i>D<sub>x</sub></i> (Mg m <sup>-3</sup> )	1.064	1.063	1.058
Total number of reflection data	1203	1863	1124
$\omega$ -scan rate (° min <sup>-1</sup> )	4	4	4
X-ray-tube setting	45 kV–30 mA	40 kV–20 mA	40 kV–20 mA
<i>R</i> factor (%) (block-diagonal least squares)	6.9	8.1	12.2
Analytical data (%)			
Observed C	83.52	83.38	83.19
H	9.27	9.27	9.26
N	7.46	7.67	7.73
Calculated C	83.20	83.15	83.10
H	9.48	9.39	9.30
N	7.32	7.46	7.60

average molecular shape resembled mesitylene, an attempt was made to grow the crystals from mesitylene solution. The resultant crystals were stable and did not decompose during X-ray exposure in the atmosphere. The crystal structure is similar to that obtained from *m*-xylene. A similar analysis was performed for the less stable toluene inclusion crystal. These results are summarized in Table 2. As a representative of the series, atomic parameters for the mesitylene inclusion crystal are given in Table 3.\*

\* Lists of structure factors, hydrogen coordinates and anisotropic thermal parameters for the mesitylene complex have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38000 (14 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 3. *Atomic parameters*

The numbering of the atoms is shown in Fig. 1(a). Positional parameters are multiplied by 10<sup>4</sup>. The equivalent isotropic temperature factor is defined by  $B_{eq} = \frac{1}{3} \sum_i \sum_j \beta_{ij} (\mathbf{a}_i \cdot \mathbf{a}_j)$ .

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B<sub>eq</sub></i> (Å <sup>2</sup> )
N(1)	3109 (13)	3454 (12)	0	4.3 (0.6)
N(4)	1334 (14)	6029 (14)	-5 (6)	4.8 (0.6)
N(7)	-1214 (13)	4271 (14)	-97 (6)	4.2 (0.6)
N(10)	488 (13)	1628 (13)	-15 (6)	4.1 (0.6)
C(2)	2552 (18)	4449 (16)	-185 (8)	4.7 (0.7)
C(3)	2086 (18)	5188 (18)	173 (9)	6.0 (0.9)
C(5)	327 (19)	5604 (17)	-211 (8)	4.8 (0.8)
C(6)	-449 (17)	5080 (17)	95 (7)	4.9 (0.8)
C(8)	-629 (17)	3244 (18)	-245 (7)	4.8 (0.8)
C(9)	-321 (17)	2431 (18)	138 (7)	4.4 (0.7)
C(11)	1580 (17)	2096 (17)	-182 (7)	4.5 (0.7)
C(12)	2281 (15)	2604 (16)	163 (7)	4.0 (0.7)
C(21)	3422 (20)	5104 (19)	-456 (8)	5.8 (0.9)
C(22)	3895 (29)	4431 (24)	-804 (9)	10.4 (1.3)
C(51)	-223 (21)	6448 (20)	-494 (9)	7.0 (1.0)
C(52)	510 (23)	6839 (27)	-856 (10)	9.8 (1.3)
C(81)	-1331 (19)	2614 (18)	-572 (8)	5.4 (0.9)
C(82)	-1525 (29)	3269 (28)	-974 (10)	11.0 (1.4)
C(111)	2271 (21)	1185 (19)	-420 (8)	6.4 (0.9)
C(112)	1576 (26)	597 (25)	-751 (9)	8.9 (1.2)
C(11)	3992 (17)	3706 (21)	287 (8)	6.2 (0.9)
C(12)	4751 (18)	2667 (19)	372 (8)	5.5 (0.8)
C(13)	5091 (19)	2073 (18)	43 (8)	5.6 (0.8)
C(14)	5937 (20)	1224 (21)	90 (9)	7.0 (1.0)
C(15)	6318 (21)	1040 (22)	501 (8)	7.1 (1.0)
C(16)	5953 (23)	1685 (23)	839 (9)	8.0 (1.1)
C(17)	5163 (20)	2524 (24)	774 (8)	7.2 (1.0)
C(41)	1036 (17)	6884 (18)	307 (8)	5.0 (0.8)
C(42)	2017 (20)	7599 (18)	426 (9)	6.4 (0.9)
C(43)	2579 (23)	8168 (23)	94 (10)	8.5 (1.1)
C(44)	3474 (19)	8911 (18)	190 (10)	7.6 (1.0)
C(45)	3701 (25)	9079 (24)	627 (10)	9.7 (1.3)
C(46)	3173 (32)	8604 (32)	947 (13)	14.0 (1.8)
C(47)	2338 (28)	7810 (25)	844 (10)	10.2 (1.3)
C(71)	-2217 (16)	3985 (18)	166 (8)	5.0 (0.8)
C(72)	-2956 (19)	4960 (19)	180 (8)	5.6 (0.8)
C(73)	-3193 (20)	5582 (22)	-168 (9)	7.6 (1.0)
C(74)	-4014 (24)	6487 (21)	-117 (10)	8.2 (1.1)
C(75)	-4452 (21)	6700 (21)	276 (9)	7.4 (1.1)
C(76)	-4276 (24)	6087 (21)	619 (9)	7.8 (1.1)
C(77)	-3513 (18)	5232 (19)	559 (8)	6.1 (0.9)
C(101)	714 (16)	819 (16)	310 (8)	4.9 (0.8)
C(102)	-252 (15)	-12 (16)	353 (6)	3.4 (0.7)
C(103)	-976 (20)	-295 (21)	13 (7)	6.2 (0.9)
C(104)	-1823 (21)	-1134 (20)	43 (9)	7.2 (1.0)
C(105)	-1928 (24)	-1611 (22)	436 (9)	8.0 (1.1)
C(106)	-1217 (20)	-1395 (18)	773 (9)	6.3 (0.9)
C(107)	-396 (21)	-555 (19)	729 (8)	6.1 (0.9)
C(11')	6982 (22)	-822 (23)	-1138 (9)	7.2 (1.0)
C(2')	6140 (24)	-1563 (25)	-1099 (9)	8.3 (1.1)
C(3')	5006 (24)	-1084 (27)	-1073 (10)	9.0 (1.2)
C(4')	4796 (23)	72 (25)	-1076 (9)	7.8 (1.0)
C(5')	5749 (23)	860 (25)	-1139 (9)	8.0 (1.0)
C(6')	6777 (22)	415 (24)	-1168 (9)	7.1 (1.0)
C(7')	8233 (23)	-1176 (26)	-1169 (11)	9.9 (1.3)
C(8')	3975 (27)	-1936 (30)	-1021 (11)	11.6 (1.5)
C(9')	5440 (32)	2042 (25)	-1175 (10)	11.2 (1.5)

### Discussion of the structure

The structure consists of a layer array of host molecules. The molecular packing in the layer is shown in Fig. 2. The molecular shape is almost identical to that in the racemic crystal. The layer involves close contacts between the benzyl groups. Since the ethyl groups stand vertically from the molecular plane, the next host molecular layer is supported by the ethyl groups. Therefore, the structure resembles a multi-storey building, where the ceiling is supported by the pillars of the ethyl groups, and a vacant room remains above the benzyl groups. To achieve a good close-packed crystal therefore, this space must be filled by the guest molecule (Fig. 3). The cavity in the molecular packing of the host is calculated as shown in Fig. 4. It has a triangular form, which explains all the inclusion phenomena. If the guest molecule fits this cavity, the

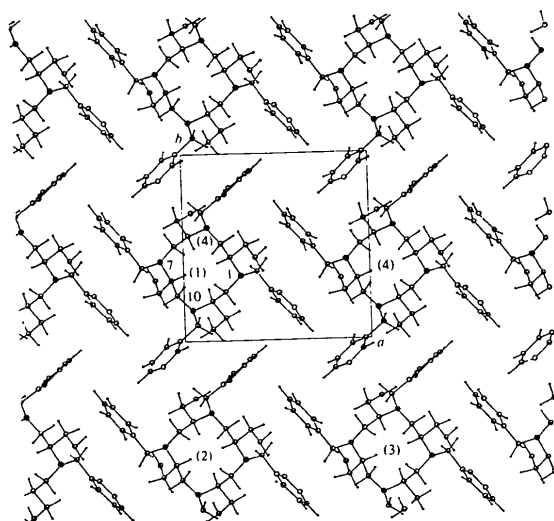


Fig. 2. Packing of the host molecules in the tetragonal layer.

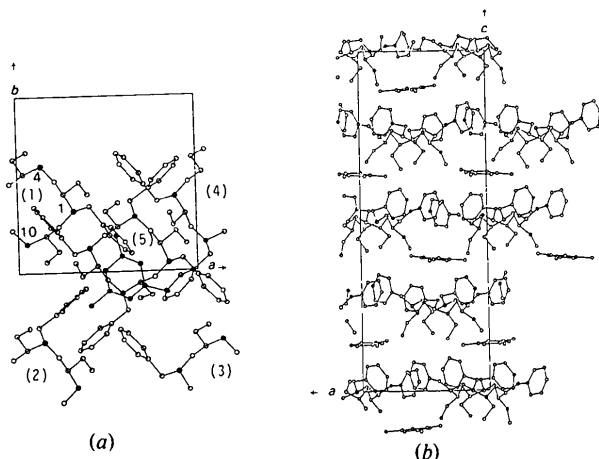


Fig. 3. Crystal structures (mesitylene inclusion crystal): (a) projection along the *c* axis (the projection is limited to two molecular layers), (b) projection along the *b* axis.

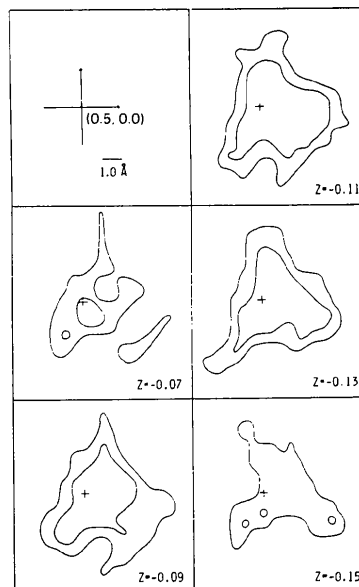


Fig. 4. Cavity in the host molecular layer packing. Sections are perpendicular to the *c* axis, and the *x*, *y* coordinates of the point '+' are 0.5, 0. The outermost lines are drawn at 1.2 Å from the surface of the van der Waals radii of the host molecule. The contour lines are drawn at every 0.5 Å.

crystal is most stable. If it is smaller, the crystal is disordered and metastable. If the guest molecule does not conform to this cavity, the crystal form changes. The *p*-xylene molecule is longer than this space, and the cyclohexane molecule is not planar and does not fit it. Therefore, the crystals for these guest molecules have quite different forms.

The electron density maps for the guest molecules are shown in Fig. 5. The mesitylene molecule appears clearly, which shows that the molecular shape is most suitable for the cavity. On the other hand, the *m*-xylene molecule appears clearly, but with a small residual density at the 5th position. For the toluene, the molecular shape is not clearly recognized. The cavity in the tetragonal form is made up of five molecules. The top and the floor of the cavity are the benzyl groups, and the side is formed by the ethyl groups. The interatomic distances between the guest and the host molecules are shown in Fig. 6 and Table 4. These are all within normal van der Waals distances.

The geometry of the host molecule is almost the same as that found in the racemic crystal. The torsion angles of the benzyl group show some flexibilities about the minimum-energy position (Sakurai *et al.*, 1978), but the observed values are essentially the same for all the structures studied (Table 5).

DTA results are shown in Fig. 7. These curves consist of two peaks. The higher-temperature one at about 473 K is common to all the crystals, and corresponds to the melting point of the host molecular crystal. The lower one is for the desorption of the guest molecule. The main feature of this figure is consistent

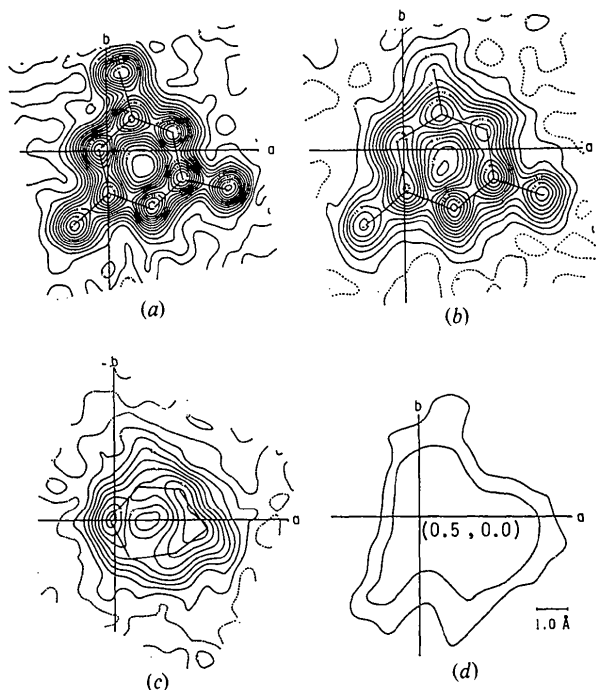


Fig. 5. Electron density map for the guest molecule. The  $x, y$  coordinates of the intersection of the  $a$  and  $b$  axes are at 0.5, 0. (a) Mesitylene. (b) *m*-Xylene. (c) Toluene. (d) The cavity after the guest molecule is removed.

with the above view. If the molecular shape is less suitable for the vacant space, the desorption temperature is low. For the *m*-xylene and mesitylene cases, the desorption peak is accompanied by a small secondary peak, about 15 K below the desorption temperature. The disordered structure of the *m*-xylene suggests that the molecular orientation has threefold potential against the rotation about the axis perpendicular to the molecular plane. The secondary peak may be due to the rotational transition of the guest molecule.

When the crystals are grown from the mixture of *p*-xylene and *m*-xylene, two different crystalline forms are obtained in the same batch. One has the tetragonal-pyramidal shape including *m*-xylene, and the other is the prismatic form including *p*-xylene (Fig. 8). Therefore, this cyclen molecule can be used to separate *p*-xylene and *m*-xylene from the mixture.

Although the symmetry is completely different in these two forms, a comparison of the lattice parameters suggests some similarities between the molecular packing. For the *p*-xylene crystal, the  $a$  axis is twice, the  $b$  axis is the same as and the  $c$  axis is  $\frac{1}{2}$  times the corresponding axial lengths in the *m*-xylene crystal. Therefore, the host molecule may also form a layer structure with six molecular layers in the unit cell.

For the cyclohexane crystal, the host-guest molecular ratio is 2:1, and the structure is completely different. The DTA analysis shows that the resultant

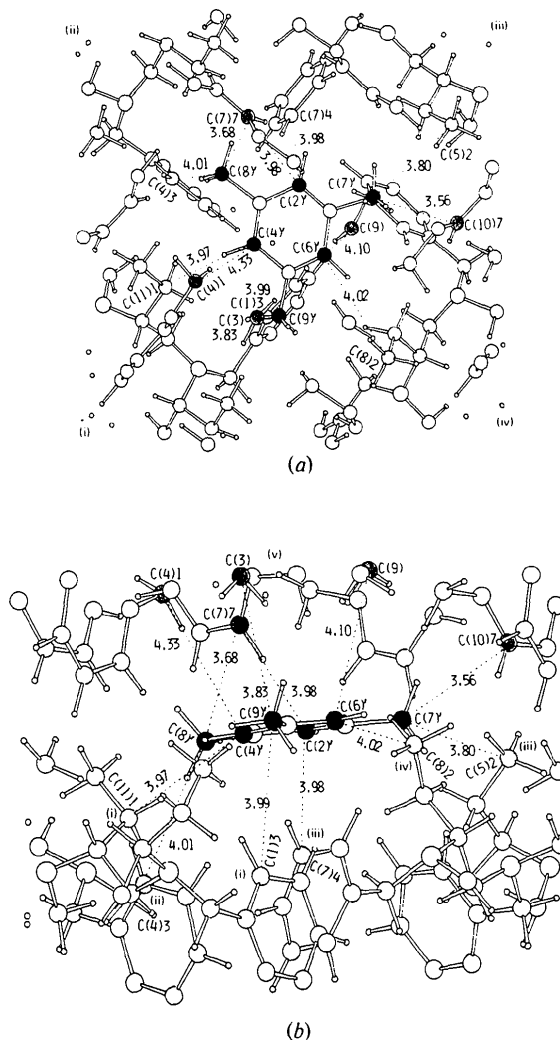


Fig. 6. The packing of the guest molecule (mesitylene inclusion crystal). For the sake of clarity, the  $-c$  axis is taken upward. Lower-case roman numerals represent the symmetry operation (cf. Table 4). (a) The  $-c$ -axis projection. (b) The  $b$ -axis projection.

Table 4. Distances (Å) between the guest and the host molecule

Guest...Host		Guest...Host	
C(2)'...C(7)4 <sup>iii</sup>	3.98 (5)	C(7)'...C(5)2 <sup>iii</sup>	3.80 (4)
C(2)'...C(7)7 <sup>v</sup>	3.98 (4)	C(7)'...C(10)7 <sup>v</sup>	3.56 (4)
C(4)'...C(11)1 <sup>i</sup>	3.97 (5)	C(8)'...C(4)3 <sup>ii</sup>	4.01 (4)
C(4)'...C(4)1 <sup>v</sup>	4.33 (5)	C(8)'...C(7)7 <sup>v</sup>	3.68 (3)
C(6)'...C(8)2 <sup>iv</sup>	4.02 (5)	C(9)'...C(1)3 <sup>i</sup>	3.99 (4)
C(6)'...C(9) <sup>v</sup>	4.10 (4)	C(9)'...C(3) <sup>v</sup>	3.83 (5)

Symmetry code

- |                          |                                  |
|--------------------------|----------------------------------|
| (i) $x, y, z$            | (iv) $1 + x, y, z$               |
| (ii) $x, -1 + y, z$      | (v) $1 - y, x, -\frac{1}{2} + z$ |
| (iii) $1 + x, -1 + y, z$ |                                  |

Table 5. Torsion angles ( $^{\circ}$ ) about benzyl groups (mean values)

	Racemic crystal ( <i>R</i> )	Mesitylene	<i>m</i> -Xylene	Toluene
$C(n+1)-N(n)-C(n)1-C(n)2$	-158	-160	-160	-158
$N(n)-C(n)1-C(n)2-C(n)7$	-144	-143	-144	-142

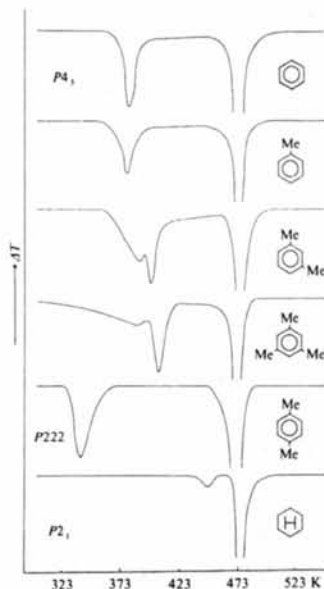


Fig. 7. The DTA curve.

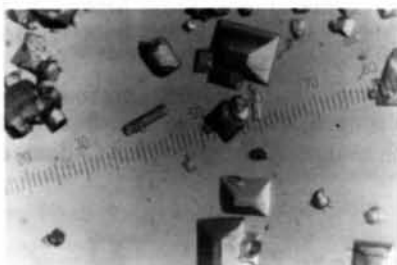


Fig. 8. Crystals obtained from the mixture of *p*-xylene and *m*-xylene. The tetragonal form contains *m*-xylene, and the rod form contains *p*-xylene. One unit of the scale is 0.042 mm.

inclusion crystal is quite stable. The guest molecules escape from the crystal lattice only about 25 K below the melting point.

For the tetralin (1,2,3,4-tetrahydronaphthalene) inclusion crystal, although the molecule is larger than the cavity, the crystal is tetragonal  $P4_3$ . In this case the cyclohexane part of the guest molecule will be inserted between the host molecular layer and the interlayer host molecular interaction becomes weak. The observed *c* axis is about 1.2 Å longer than that observed for the mesitylene, and the crystal is disordered in the direction perpendicular to the *c* axis.

Compared with other typical clathrate compounds, where the cavity is made up by the hydrogen bonds or the skeleton of the host molecule itself (MacNicol, McKendrick & Wilson, 1978), the cavity of the present crystal is made up by the side packing of the host molecule. Thus, the structure is more flexible, and has a possibility of forming a variety of crystalline forms depending on the kind of guest molecule.

The calculations were performed by a FACOM M-200 computer of this Institute using the UNICS III program system (Sakurai & Kobayashi, 1979). The authors express their sincere thanks to Mr Y. Abe of this Institute for his advice on the TG-DTA measurements.

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