



# Molecular Structure and Mutual Recognition Between Host and Guest Molecules Found in the Crystal Structures of Oxacalix[4]arenes Complexed with Xylene Isomers

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(Received: 19 April 1999; in final form: 5 October 1999)

**Abstract.** The crystal structures of two complexes of oxacalix[4]arene derivatives {*p*-isopropyl-dihomooxacalix[4]arene (IOC-4) and *p*-*tert*-butyldihomooxacalix[4]arene(BOC-4)} with xylene isomers have been determined by X-ray diffraction method. Furthermore, in order to estimate the strength of the mutual interactions between host (IOC-4 and BOC-4) and guest (*o*-, *m*- and *p*-xylene), the heat of complex formation for the IOC-4 : xylene complexes was calculated using a molecular orbital method, and a differential scanning calorimetric investigation was performed for the BOC-4 : xylene complexes.

**Key words:** oxacalix[4]arene : xylene complex, X-ray structure analysis, heat of complex formation, differential scanning calorimetry.

## 1. Introduction

The base-catalyzed condensation of *p*-isopropylphenol and paraformaldehyde yields a series of cyclic phenol-methylene oligomers for which the name “calix-arene” has been suggested [1]. Under mild conditions, homologous compounds containing an extra oxygen in the macrocyclic ring, named as a dihomooxacalix-arene can be also isolated [2]. In general, the calix[*n*]arenes and oxacalix[*n*]arenes are capable of including organic and inorganic compounds into the cavities formed by the host molecules, i.e., calix[*n*]arenes and oxacalix[*n*]arenes [3]. We have been interesting in their complex formations with organic compounds, and we determined several crystal structures of calix[4]arene and dihomooxacalix[4]arene complexes with xylene, toluene and acetone [4–8]. Mutual molecular recognition

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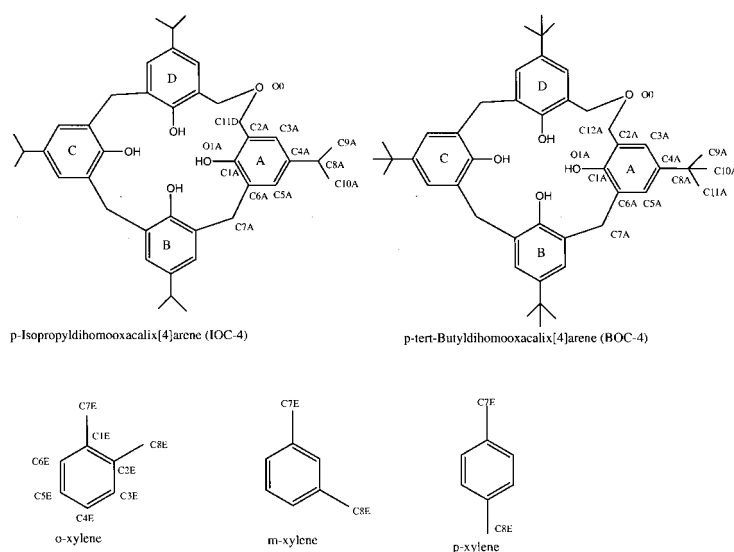


Figure 1. Chemical structures of host and guest molecules.

between host and guest molecules in the case of the oxalix[4]arene : xylene complex is of most interest to us, because the dihomooxalix[4]arene molecule has no four-fold molecular symmetry as found in the case of the calix[4]arene molecule [6, 8, 9], but has more conformational flexibility due to the extra addition of an oxymethylene group and it may uniquely interact with each of the three structural isomers (ortho-, meta- and para-forms) of the xylene molecule. Preliminary X-ray studies of *p*-isopropyldihomooxalix[4]arene (see Figure 1 and hereafter designated as IOC-4) complexed with *o*-xylene [6], and the crystal structure of *p*-tert-butylidihomooxalix[4]arene (Figure 1 and hereafter designated as BOC-4) complexed with *m*-xylene have been already reported [5, 19]. Here we describe the detailed crystal structures of IOC-4 complexed with *o*- and *m*-xylene, and of BOC-4 complexed with each of the three xylene isomers. Furthermore, in order to estimate the strength of the mutual molecular recognition and interaction between the host and guest molecules during the inclusion process, the computational analysis on the heat of complex formation and differential thermal analysis were performed and these results are discussed based on their molecular structure.

## 2. Experimental

*p*-tert-Butylidihomooxalix[4]arene(BOC-4) was purchased from ACROS (Geel, Belgium) and *p*-isopropyldihomooxalix[4]arene(IOC-4) was kindly provided by J. Vicens, EHIS, Strasbourg, France. Ortho-, meta-, and para-xylenes were of commercially high grades.

Table I. Crystal data

Host Guest	IOC-4 <sup>1</sup>		BOC-4 <sup>2</sup>		
	<i>o</i> -Xylene	<i>m</i> -Xylene	<i>o</i> -Xylene	<i>m</i> -Xylene	<i>p</i> -Xylene
Crystal system	Monoclinic		Orthorhombic		
Space group	P2 <sub>1</sub> /n	P2 <sub>1</sub> /n	Pbcm	Pbcm	Pbcm
Unit cell (Å)					
<i>a</i>	18.808(3)	19.175(3)	9.258(2)	9.322(1)	9.189(3)
<i>b</i>	24.714(4)	24.274(4)	19.484(6)	19.322(1)	19.218(8)
<i>c</i>	9.203(1)	9.213(2)	25.872(4)	25.931(1)	26.790(10)
$\beta$ (deg)	100.31(1)	101.31(2)			
No. of refs.	7487	7248	4387	4180	4444
No. of unique refs.	6348	6835	3983	3784	4026
No. of used refs. ( $F_o > 4\sigma$ )	3784	3554	2766	1616	2369
<i>Z</i>	4	4	4	4	4
<i>R</i> value (%)	9.9	9.4	6.0	6.9	8.2

<sup>1</sup>IOC-4: *p*-isopropylidihomooxalix[4]arene.

<sup>2</sup>BOC-4: *p*-*tert*-butylidihomooxalix[4]arene.

## 2.1. X-RAY STRUCTURE ANALYSIS OF IOC-4 COMPLEXED WITH XYLENE

IOC-4 (ca. 20 mg) was completely dissolved in *o*-, *m*- and *p*-xylene upon heating, respectively, and after a few days, colorless rod-like crystals of the *o*- and *m*-xylene complexes were obtained by slow evaporation at room temperature. However, the IOC-4: *p*-xylene complex has not been obtained so far as a single crystal. Unit cell constants were obtained by the least-squares refinement based on  $2\theta$  values (ca.  $45^\circ < 2\theta < \text{ca. } 60^\circ$ ) of 25 reflections. The X-ray diffraction data were collected on a Rigaku AFC-5R diffractometer by use of the  $\omega - 2\theta$  scan mode ( $2\theta_{\text{max}} = 126^\circ$ ) and graphite-monochromated  $\text{CuK}\alpha$  radiation ( $\lambda = 1.5418 \text{ \AA}$ ). Three standard reflections were monitored every 200 reflections and checked for intensity decrease during the data collection. No corrections for absorption and extinction were applied, because of the small crystals. The crystal data are listed in Table I.

The structure of the IOC-4: *o*-xylene (1 : 1) complex was first solved by direct method using the program SHELX86(10) and that of the *m*-xylene complex was solved by the molecular replacement method, because of the isomorphous crystal with the *o*-xylene complex as shown in Table I. Positional and thermal parameters were refined by the block-diagonal least squares method with HBL5 [11]. Non-H atoms and H-atoms were refined with anisotropic and isotropic temperature factor, respectively. All computations were carried out on an ACOS 930 computer at the Crystallographic Research Center, Institute for Protein Research, Osaka University.

## 2.2. MOLECULAR ORBITAL CALCULATION FOR ESTIMATION OF THE HEAT OF COMPLEX FORMATION IN THE CASE OF IOC-4 : XYLENE COMPLEXES

The calculation of the heat of complex formation for IOC-4 : *o*-xylene and IOC-4 : *m*-xylene was carried out with the widely used molecular orbital calculation program package MOPAC [12] which contains four different semi-empirical molecular orbital methods, i.e., MINDO/3, MNDO, AM1, and PM3. This time, we used the PM3-type Hamiltonian [13] in the electronic part of the molecular orbital calculation to obtain the heat of complex formation ( $\Delta H_f$ ) as follows;

$$\Delta H_f = E_{\text{tot}} - \sum_A E_{\text{el}}^A + \sum_A \Delta H_f^A,$$

where  $E_{\text{tot}}$  is the total electronic energy of the complex molecule,  $E_{\text{el}}^A$  is the electronic energy for atom A calculated by the molecular orbital method and  $\Delta H_f^A$  is the standard heat of formation for atom A obtained experimentally. Using the atomic coordinates of the complexes (IOC-4 : *o*-xylene and IOC-4 : *m*-xylene) obtained from their crystal structure analyses, the heat of complex formation was calculated at every 30° rotation of xylene (see Figure 4) around the normal axis passing through the center of the guest xylene ring. All the computations were performed with an Indigo II computer (Silicon Graphics, Inc. Mountain View, CA, USA) at Fujisawa Pharmaceutical Co., Osaka, Japan.

## 2.3. X-RAY STRUCTURE ANALYSIS OF BOC-4 COMPLEXED WITH XYLENE

Crystallizations of BOC-4 complexed with the three xylene isomers were tried with similar procedures as the case of IOC-4 : xylene complexes. X-ray data collection, unit cell constants refinement and absorption collection for the BOC-4 : xylene complexes were achieved with almost the same methods and equipments as with the IOC-4 : xylene complexes. The crystal data are listed in Table I. The crystal structure of BOC-4 : *o*-xylene was first solved by the direct method using the program SHELX86 and two other complex structures were solved by the molecular replacement method, because they are isomorphous crystals with the *o*-xylene complexes as shown in Table I. Because of disordered xylene molecules, the three structures were refined by several cycles of constrained full-matrix least squares calculation first with isotropic and then with anisotropic temperature factors for all non-H atoms and with isotropic temperature factor for all H atoms using the program SHELXL93 [14]. All calculations were carried out on a Micro VAX II (DEC, Maynard, MA, USA) and Indy (Silicon Graphics Inc., Mountain View, CA, USA) workstation at the Information Science Center, Osaka University of Pharmaceutical Sciences [18].

#### 2.4. DIFFERENTIAL SCANNING CALORIMETRY(DSC) FOR BOC-4 : XYLENE COMPLEXES

A Perkin–Elmer Differential Scanning Calorimeter Model DSC-7 (Perkin–Elmer Corporation, Norwalk, CT, USA) was used for measurement of the temperature changes in the sample due to endothermic or exothermic enthalpic transitions such as the liberation of the guest molecule (xylene) from the host cavity, the re-arrangement of the host molecule (BOC-4) and the melting of BOC-4. The crystals (ca. 4–6 mg) of BOC-4 complexed with *o*-, *m*- and *p*-xylene, respectively, were powdered and sealed in an aluminium container, and under a nitrogen gas flow, the temperature was raised from 40 °C to 340 °C with a rate of 10 °C/min. Heat flow (mW) was recorded as a function of temperature (°C). The area enclosed by the DSC curve peak and the back ground line (the dotted line in Figure 9) is directly proportional to the enthalpy change ( $\Delta H$ ) and the mass of sample ( $m$ );

$$\text{Area} = k \cdot \Delta H \cdot m,$$

where  $k$  is the calibration coefficient.

### 3. Results and Discussion

#### 3.1. CRYSTAL AND MOLECULAR STRUCTURE OF IOC-4 : XYLENE COMPLEX

The final positional and equivalent isotropic thermal parameters ( $B_{\text{eq}}$ ) of non H atoms are listed in Table II. The bond lengths, bond angles and torsion angles are all normal. Because of isomorphous crystals, the crystal and molecular structures are very similar in the two crystals (IOC-4 : *o*-xylene and IOC-4 : *m*-xylene). Figure 2 shows the crystal packing of IOC-4 : *o*-xylene projected on the *ab*-plane, in which the guest xylene molecule is pointing towards and deeply embedded into the host cavity, and a similar packing diagram was obtained for the IOC-4 : *m*-xylene complex (not shown here). The molecular structures of IOC-4 : *o*-xylene and IOC-4 : *m*-xylene are depicted in Figure 3(a), (b). The host IOC-4 molecule adopts the so-called “cone” conformation [17] which is one of the possible calix[n]arene conformations and mainly stabilized by intramolecular cyclic four O—H—O hydrogen bonds [in IOC-4 : *o*-xylene: O1A—O1B = 2.679(7) Å, O1B—O1C = 2.711(6) Å, O1C—O1D = 2.677(6) Å, O1D—O1A = 3.075 (7) Å; in IOC-4 : *m*-xylene: O1A—O1B = 2.695(7) Å, O1B—O1C = 2.745(6) Å, O1C—O1D = 2.788(7) Å, O1D—O1A = 3.176(6) Å]. The intermolecular interactions between host and guest molecules in this case are mainly due to the van der Waals forces, but some very interesting short contacts were obtained between the phenol ring plane (host) and methyl carbon atom C7E (guest) which are probably attributed to C-H/ $\pi$  (aromatic ring) interaction. Furthermore, the weak C-H/ $\pi$  interactions were also observed between the guest methyl carbon atom C7E and the host phenol oxygen atom O1[in IOC-4 : *o*-xylene: C7E–phenol B ring plane = 3.80(2) Å, C7E–phenol C ring plane = 3.95(2) Å, and C7E–O1D = 3.67(2) Å; in IOC-4 : *m*-xylene:

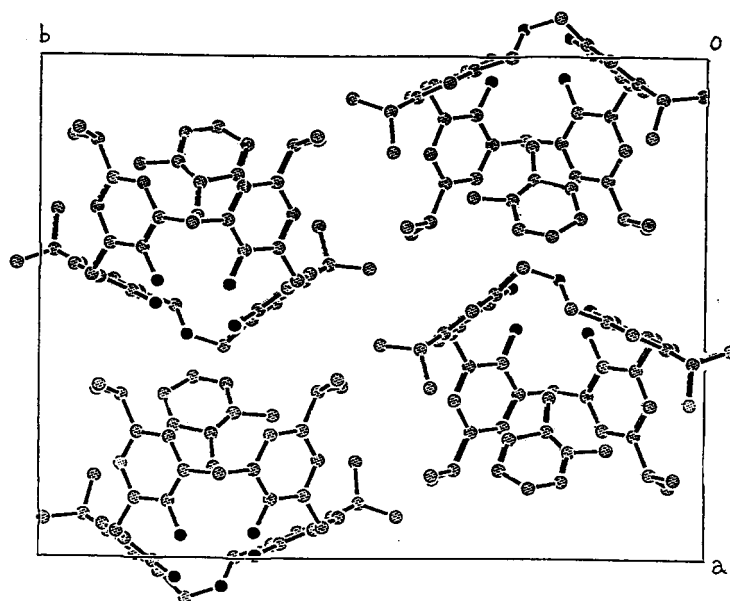


Figure 2. Crystal packing diagram along [001] of the IOC-4:*o*-xylene complex.

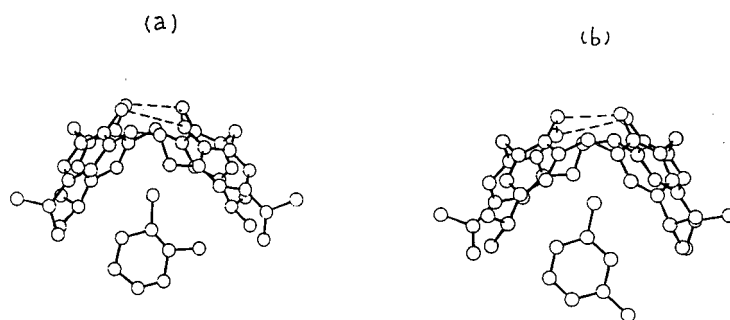


Figure 3. Molecular structures of IOC-4:xylene complexes. (a) IOC-4:*o*-xylene complex. (b) IOC-4:*m*-xylene complex. Broken line depicts hydrogen bond.

C7E–phenol B ring = 3.68(1) Å, C7E–phenol C ring plane = 3.96(1) Å and C7E–O1D = 3.62(1) Å]. The importance of C–H/ $\pi$  (aromatic ring) interaction has been suggested even though the interaction energy (ca. 4.8 kJ/mol) is rather weak compared with a typical hydrogen bond [15] and some evidences have been observed [16].

### 3.2. MOLECULAR ORBITAL CALCULATION FOR ESTIMATION OF THE HEAT OF COMPLEX FORMATION IN THE CASE OF IOC-4 : XYLENE COMPLEXES

The computer-simulated molecular structures of the IOC-4:*o*-xylene complex are displayed in Figure 4 for each 30° rotation around the axis which is normal to the

Table II. Fractional atomic coordinates and equivalent temperature factors ( $B_{eq}$ ). (a) IOC-4:*o*-xylene complex. (b) IOC-4:*m*-xylene complex.  $B_{eq} = (4/3)\Sigma_i \Sigma_j B_{ij} \mathbf{a}_i \mathbf{a}_j$  ( $\text{\AA}^2$ )

(a)	<i>o</i> -Xylene complex				(b)	<i>m</i> -Xylene complex			
	$x (\times 10^4)$	$y (\times 10^4)$	$z (\times 10^4)$	$B_{eq} (\text{\AA}^3)$		$x (\times 10^4)$	$y (\times 10^4)$	$z (\times 10^4)$	$B_{eq} (\text{\AA}^3)$
O0	10556(5)	7223(4)	7497(10)	5.4(3)	O0	10614(2)	2224(15)	7466(6)	5.8(12)
O1A	10377(2)	7937(2)	4875(5)	5.6(13)	O1A	10427(2)	2967(2)	4833(4)	6.7(13)
C1A	10064(3)	8275(3)	5780(6)	4.8(2)	C1A	10130(3)	3291(2)	5726(5)	5.0(2)
C2A	10257(3)	8182(3)	7281(7)	5.2(2)	C2A	10293(3)	3196(2)	7239(6)	5.2(2)
C3A	9927(3)	8532(3)	8241(7)	5.7(2)	C3A	9979(3)	3517(2)	8183(6)	6.0(2)
C4A	9484(3)	8949(3)	7717(3)	5.4(2)	C4A	9508(3)	3930(3)	7661(6)	6.2(2)
C5A	9338(4)	9032(3)	6198(7)	5.5(2)	C5A	9383(3)	4022(2)	6137(6)	5.8(2)
C6A	9623(3)	8708(2)	5200(6)	4.3(16)	C6A	9671(3)	3719(2)	5160(5)	4.8(16)
C7A	9468(3)	8836(3)	3675(7)	4.6(2)	C7A	9520(3)	3853(2)	3503(5)	5.5(2)
C8A	9162(5)	9317(3)	8772(9)	7.1(3)	C8A	9149(4)	4263(3)	8709(7)	8.3(3)
C9A	9244(7)	9922(4)	8424(13)	9.6(4)	C9A	9210(5)	4881(4)	8440(9)	12.6(4)
C10A	8393(7)	9159(6)	8772(15)	10.3(5)	C10A	8398(5)	4100(4)	8549(8)	11.3(4)
O1B	9556(2)	7856(2)	2072(4)	5.1(13)	O1B	9601(2)	2853(15)	1986(4)	5.5(11)
C1B	8874(3)	8063(2)	1995(6)	4.1(15)	C1B	8926(3)	3075(2)	1910(5)	4.6(16)
C2B	8817(3)	8559(2)	2728(6)	4.3(16)	C2B	8861(3)	3564(2)	2651(5)	4.8(16)
C3B	8136(3)	8777(3)	2652(6)	4.5(2)	C3B	8188(3)	3782(2)	2604(5)	5.0(2)
C4B	7509(3)	8529(2)	1901(6)	4.4(16)	C4B	7566(3)	3514(2)	1871(5)	4.9(2)
C5B	7599(3)	8046(2)	1187(6)	4.5(2)	C5B	7659(3)	3034(2)	1123(5)	5.0(2)
C6B	8262(3)	7812(2)	1200(6)	4.3(16)	C6B	8328(3)	2803(2)	1133(5)	4.7(16)
C7B	8317(4)	7282(2)	0317(6)	4.6(2)	C7B	8370(3)	2274(2)	0230(5)	5.4(2)
C8B	6765(3)	8777(3)	1786(7)	5.3(2)	C8B	6833(3)	3745(2)	1817(6)	5.5(2)
C9B	6584(6)	9109(5)	0339(11)	7.7(3)	C9B	6663(4)	4190(3)	0640(8)	8.5(3)
C10B	6661(6)	9135(6)	3063(12)	9.6(4)	C10B	6737(4)	3983(4)	3252(8)	9.4(3)
O1C	9493(2)	6761(15)	2154(4)	4.7(11)	O1C	9533(2)	1734(15)	2125(4)	6.0(13)
C1C	8823(3)	6532(2)	2065(6)	4.2(15)	C1C	8868(3)	1509(2)	2023(5)	4.7(16)
C2C	8230(3)	6777(2)	1192(6)	4.4(16)	C2C	8284(3)	1759(2)	1111(5)	5.0(2)
C3C	7548(3)	6539(3)	1117(6)	4.9(2)	C3C	7616(3)	1533(2)	1074(5)	5.3(2)

Table II. Continued

(a)	<i>o</i> -Xylene complex				(b)	<i>m</i> -Xylene complex			
	$x (\times 10^4)$	$y (\times 10^4)$	$z (\times 10^4)$	$B_{\text{eq}} (\text{\AA}^3)$		$x (\times 10^4)$	$y (\times 10^4)$	$z (\times 10^4)$	$B_{\text{eq}} (\text{\AA}^3)$
C4C	7451(3)	6074(2)	1900(6)	4.7(2)	C4C	7514(3)	1072(2)	1884(5)	5.4(2)
C5C	8043(3)	5840(2)	2726(7)	4.7(2)	C5C	8110(3)	0827(2)	2713(6)	5.3(2)
C6C	8747(3)	6048(2)	2843(6)	4.3(15)	C6C	8781(3)	1032(2)	2804(5)	5.0(2)
C7C	9378(8)	5771(6)	3792(14)	4.4(4)	C7C	9418(3)	0750(2)	3776(5)	4.9(2)
C8C	6686(3)	5843(3)	1802(8)	6.0(2)	C8C	6747(3)	0865(3)	1787(7)	6.7(2)
C9C	6438(6)	5561(5)	0346(12)	9.1(4)	C9C	6624(4)	0579(4)	3160(8)	10.7(3)
C10C	6589(6)	5489(6)	3049(13)	9.5(4)	C10C	6521(4)	0505(4)	0471(8)	10.7(3)
C11C	9944(5)	6742(4)	5079(10)	5.2(3)	O1D	10022(2)	1719(15)	5074(4)	5.8(12)
C1D	9706(7)	6375(6)	6017(14)	4.4(4)	C1D	9771(3)	1368(2)	5993(5)	4.7(16)
C2D	9426(7)	5890(6)	5436(14)	4.4(4)	C2D	9461(3)	0876(2)	5400(5)	4.9(2)
C3D	9183(8)	5522(6)	6340(16)	4.9(4)	C3D	9204(3)	0518(2)	6322(5)	5.3(2)
C4D	9188(8)	5617(6)	7863(15)	5.1(4)	C4D	9204(3)	0629(2)	7811(6)	5.7(2)
C5D	9483(8)	6112(6)	8400(2)	5.2(5)	C5D	9511(3)	1127(2)	8352(5)	5.7(2)
C6D	9731(7)	6495(6)	7530(15)	4.6(4)	C6D	9777(3)	1499(2)	7479(5)	4.9(2)
C7D	9981(10)	7041(8)	8150(2)	5.8(5)	C7D	10036(3)	2047(3)	8095(6)	6.3(2)
C8D	8907(9)	5216(7)	8840(2)	6.2(5)	C8D	8905(3)	0239(3)	8804(6)	6.8(2)
C9D	9167(15)	4643(8)	8650(3)	7.8(8)	C9D	9136(3)	0347(3)	8666(7)	9.1(3)
C10D	8086(14)	5262(14)	8580(4)	11.2(12)	C10D	8144(5)	0259(4)	8554(11)	12.7(4)
C11D	1079(4)	7775(3)	7900(8)	5.5(2)	C11D	10848(3)	2777(2)	7884(6)	6.4(2)
C1E	7532(5)	7399(4)	6009(10)	9.1(2)	C1E	2740(3)	2692(3)	0820(6)	6.7(2)
C2E	7125(7)	7065(6)	6467(14)	3.6(3)	C2E	2350(3)	2265(3)	1256(6)	7.4(2)
C3E	6543(5)	7173(4)	7190(11)	10.4(2)	C3E	1761(4)	2391(3)	1946(7)	8.6(2)
C4E	6415(6)	7674(5)	7312(14)	12.6(3)	C4E	1601(4)	2938(4)	2134(7)	9.8(3)
C5E	6763(8)	8111(6)	6790(2)	16.2(3)	C5E	2003(4)	3351(4)	1763(8)	10.9(3)
C6E	7376(8)	7966(6)	6150(2)	17.4(5)	C6E	2551(4)	3235(3)	1062(7)	8.8(3)
C7E	8191(7)	7364(5)	5201(14)	13.3(3)	C7E	3358(4)	2582(3)	0066(8)	9.1(3)
C8E	7173(8)	6494(7)	6506(16)	16.7(4)	C8E	1328(5)	1940(5)	2386(10)	13.2(4)



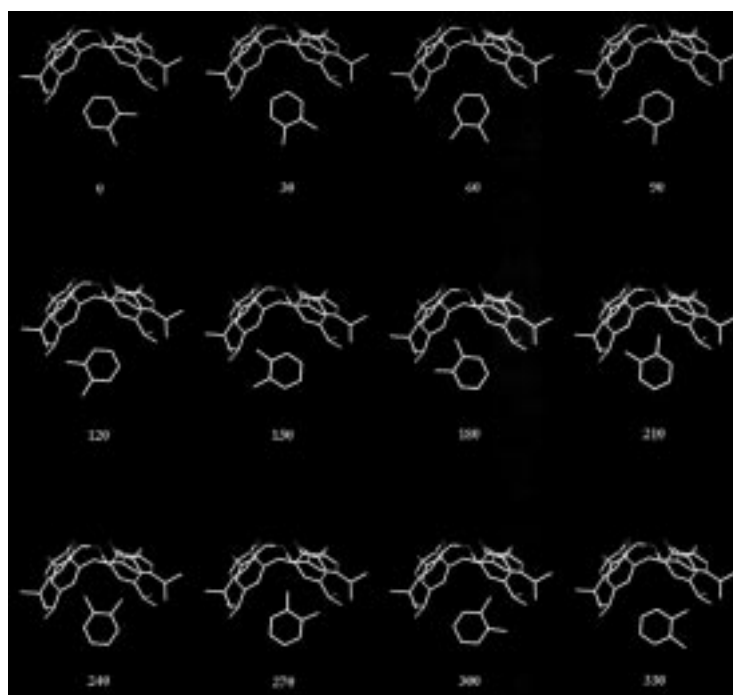


Figure 4. Computer-simulated structure of the IOC-4 : *o*-xylene complex for each 30° rotation around the normal axis passing through the center of the xylene ring.

*o*-xylene ring plane and also passes through the center of the *o*-xylene ring. The starting model in this calculation was obtained from the crystal structure of the IOC-4 : *o*-xylene complex or the IOC-4 : *m*-xylene complex. The heat of complex formation at every 30° rotation angle was calculated and plotted as a function of rotation angle. Figures 5 and 6 show the heat of complex formation as a function of rotation angle for IOC-4 : *o*-xylene and for IOC-4 : *m*-xylene, respectively. In the case of the IOC-4 : *o*-xylene complex, the minimum point representing the most stable complex formation is very close to the rotation angle of 258° which just corresponds to the orientation of the *o*-xylene molecule found in the crystal structure of the IOC-4 : *o*-xylene complex. We are very interested in this finding, because the molecular recognition between host and guest molecules should start with mutual contacts and settle down in the most stable state after rolling and fluctuation. In the case of the IOC-4 : *m*-xylene complex as shown in Figure 6, three lowest troughs appeared with similar values of the heat of complex formation, of which one minimum region (around 230°–300°) involves the rotation angle of the *m*-xylene found in the crystal structure of the IOC-4 : *m*-xylene complex.

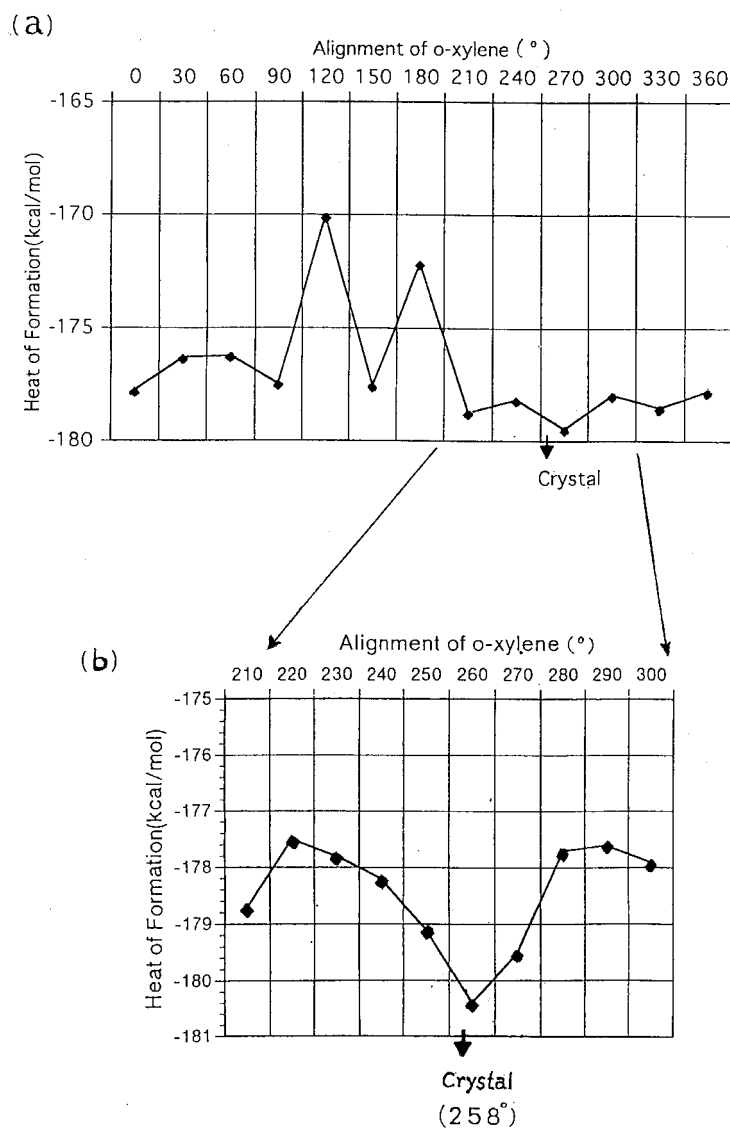


Figure 5. Heat of complex formation of the IOC-4:o-xylene complex as a function of the rotation angle of o-xylene. (a) For each 30° rotation. (b) For each 10° rotation in the range of 210° to 300°.

### 3.3. CRYSTAL AND MOLECULAR STRUCTURE OF BOC-4 : XYLENE COMPLEXES

The final positional and equivalent isotropic temperature factors ( $B_{eq}$ ) of non H atoms are given in Table III. The bond lengths, bond angles and torsion angles are all normal [18].

Table III. Fractional atomic coordinates ( $\times 10^4$ ) and equivalent temperature factors ( $B_{eq}$ ) of BOC-4 : xylene complexes

BOC-4 : <i>o</i> -Xylene complex					BOC-4 : <i>m</i> -Xylene complex					BOC-4 : <i>p</i> -Xylene complex				
	$x (\times 10^4)$	$y (\times 10^4)$	$z (\times 10^4)$	$B_{eq} (\text{\AA}^2)$		$x (\times 10^4)$	$y (\times 10^4)$	$z (\times 10^4)$	$B_{eq} (\text{\AA}^2)$		$x (\times 10^4)$	$y (\times 10^4)$	$z (\times 10^4)$	$B_{eq} (\text{\AA}^2)$
O(0)	4568(3)	190(2)	2500	5.28(1)	O(0)	4571(16)	148(3)	2500	5.64(2)	O(0)	4345(4)	273(2)	2500	6.23(1)
O(1A)	7065(2)	11(1)	3086(1)	5.93(1)	O(1A)	7042(4)	-25(2)	3092(1)	5.99(1)	O(1A)	6870(3)	78(2)	3051(1)	7.33(1)
C(1A)	6182(3)	255(2)	3479(1)	4.93(1)	C(1A)	6158(6)	229(2)	3476(2)	4.75(1)	C(1A)	6004(4)	309(2)	3443(2)	6.20(1)
C(2A)	4691(3)	202(2)	3416(1)	4.99(1)	C(2A)	4685(6)	167(3)	3413(2)	5.00(1)	C(2A)	4487(4)	258(2)	3390(2)	6.18(1)
C(3A)	3806(3)	460(2)	3800(1)	5.21(1)	C(3A)	3796(6)	439(3)	3789(2)	4.95(1)	C(3A)	3619(4)	492(2)	3775(2)	6.26(1)
C(4A)	4339(3)	755(2)	4253(1)	5.02(1)	C(4A)	4303(6)	743(6)	4237(2)	4.71(1)	C(4A)	4178(4)	755(2)	4219(2)	6.03(1)
C(5A)	5833(3)	789(2)	4295(1)	4.99(1)	C(5A)	5796(6)	782(2)	4286(2)	4.71(1)	C(5A)	5693(4)	792(2)	4251(2)	6.33(1)
C(6A)	6768(3)	546(2)	3919(1)	4.73(1)	C(6A)	6736(5)	530(2)	3814(2)	4.46(1)	C(6A)	6614(4)	573(2)	3874(2)	5.95(1)
C(7A)	8388(3)	615(3)	3990(1)	5.28(1)	C(7A)	9330(5)	603(3)	3984(2)	5.17(1)	C(7A)	8245(4)	636(2)	3938(2)	6.59(1)
C(8A)	3312(4)	1034(2)	4660(1)	5.78(1)	C(8A)	3279(6)	1032(3)	4637(2)	5.17(1)	C(8A)	3176(5)	999(2)	4635(2)	7.04(1)
C(9A)	4077(6)	1169(4)	5171(2)	8.47(2)	C(9A)	4036(9)	1185(6)	5147(3)	8.24(3)	C(9A)	3993(8)	1137(5)	5126(2)	11.32(3)
C(10A)	2613(7)	1691(3)	4457(2)	9.69(2)	C(10A)	2576(12)	1685(5)	4427(4)	8.72(3)	C(10A)	2379(9)	1657(4)	4462(3)	11.22(3)
C(11A)	2116(5)	500(3)	4768(2)	8.37(2)	C(11A)	2074(10)	499(5)	4739(4)	8.38(3)	C(11A)	2035(9)	408(4)	4748(3)	10.70(2)
C(12A)	4048(4)	-139(2)	2954(1)	5.61(1)	C(12A)	4057(7)	-181(3)	2950(2)	6.03(2)	C(12A)	3839(5)	-71(2)	2944(1)	6.50(1)
O(1B)	9915(2)	472(1)	3028(1)	5.90(1)	O(1B)	9863(4)	466(2)	3028(2)	5.61(1)	O(1B)	9749(3)	496(1)	3000(1)	7.28(1)
C(1B)	9787(3)	1129(1)	3237(1)	4.66(1)	C(1B)	9713(5)	1130(2)	3237(2)	4.35(1)	C(1B)	9638(4)	1156(2)	3209(2)	6.25(1)
C(2B)	9026(3)	1214(1)	3694(1)	4.68(1)	C(2B)	8963(5)	1210(2)	3694(2)	4.42(1)	C(2B)	8909(4)	1242(2)	3659(2)	6.16(1)
C(3B)	8841(3)	1875(2)	3883(1)	5.11(1)	C(3B)	8765(5)	1877(3)	3883(2)	4.72(1)	C(3B)	8759(5)	1909(2)	3852(2)	6.68(1)
C(4B)	9398(3)	2447(2)	3638(1)	4.99(1)	C(4B)	9297(5)	2457(3)	3633(2)	4.65(1)	C(4B)	9378(5)	2488(2)	3620(2)	6.93(1)
C(5B)	10219(3)	2325(2)	3196(1)	5.11(1)	C(5B)	10107(5)	2340(2)	3193(2)	4.62(1)	C(5B)	10150(5)	2373(2)	3182(2)	6.71(1)
C(6B)	10437(3)	1679(1)	2988(1)	4.64(1)	C(6B)	10347(5)	1690(2)	2985(2)	4.25(1)	C(6B)	10322(4)	1722(2)	2975(2)	6.33(1)
C(7B)	11340(4)	1588(2)	2500	5.04(1)	C(7B)	11253(7)	1605(4)	2500	4.45(2)	C(7B)	11212(6)	1629(3)	2500	7.04(2)
C(8B)	9160(4)	3172(2)	3841(2)	6.38(1)	C(8B)	9015(6)	3185(3)	3844(2)	5.67(2)	C(8B)	9147(7)	3225(2)	3839(2)	8.78(2)
C(9B)	8618(13)	3614(3)	3394(3)	15.43(4)	C(9B)	9339(21)	3737(5)	3425(6)	16.88(8)	C(9B)	8760(22)	3708(5)	3452(4)	23.26(11)
C(10B)	10678(9)	3453(4)	3989(4)	14.19(4)	C(10B)	9890(27)	3313(7)	4311(8)	19.81(12)	C(10B)	10824(13)	3500(4)	3923(5)	18.44(5)
C(11B)	8124(15)	3187(4)	4297(5)	17.76(6)	C(11B)	7357(12)	3287(6)	3916(8)	15.42(7)	C(11B)	8544(18)	3213(5)	4361(4)	18.70(5)
C(1E)	5324(8)	2299(4)	2500	10.25(3)	C(1E)	5395(13)	2194(7)	2500	9.51(4)	C(1E)	4801(10)	2463(4)	2124(5)	18.43(18)
C(2E)	4847(9)	2547(5)	2064(6)	17.86(6)	C(2E)	4900(10)	2471(6)	2060(3)	8.82(3)	C(2E)	4061(9)	3080(4)	2218(4)	8.49(5)
C(3E)	3863(16)	3129(6)	2042(9)	24.27(15)	C(3E)	3985(11)	2999(6)	2039(4)	10.17(4)	C(3E)	3864(7)	3306(4)	2706(4)	7.36(15)
C(4E)	3556(36)	3358(12)	2500	31.12(39)	C(4E)	3523(16)	3269(7)	2500	10.46(5)	C(4E)	4407(12)	2914(5)	3100(4)	11.37(6)
C(7E)	6396(10)	1712(4)	2500	12.63(4)	C(7E)	6399(19)	1650(8)	2500	15.05(9)	C(5E)	5146(12)	2297(5)	3007(5)	28.19(32)
C(8E)	5250(64)	2257(32)	1550(17)	38.31(43)	C(8E)	3680(16)	3213(9)	1513(6)	18.72(7)	C(6E)	5343(9)	2071(4)	2507(5)	27.08(22)
										C(7E)	4870(19)	2188(7)	1587(5)	32.54(32)
										C(8E)	4221(21)	3136(8)	3606(64)	34.08(41)

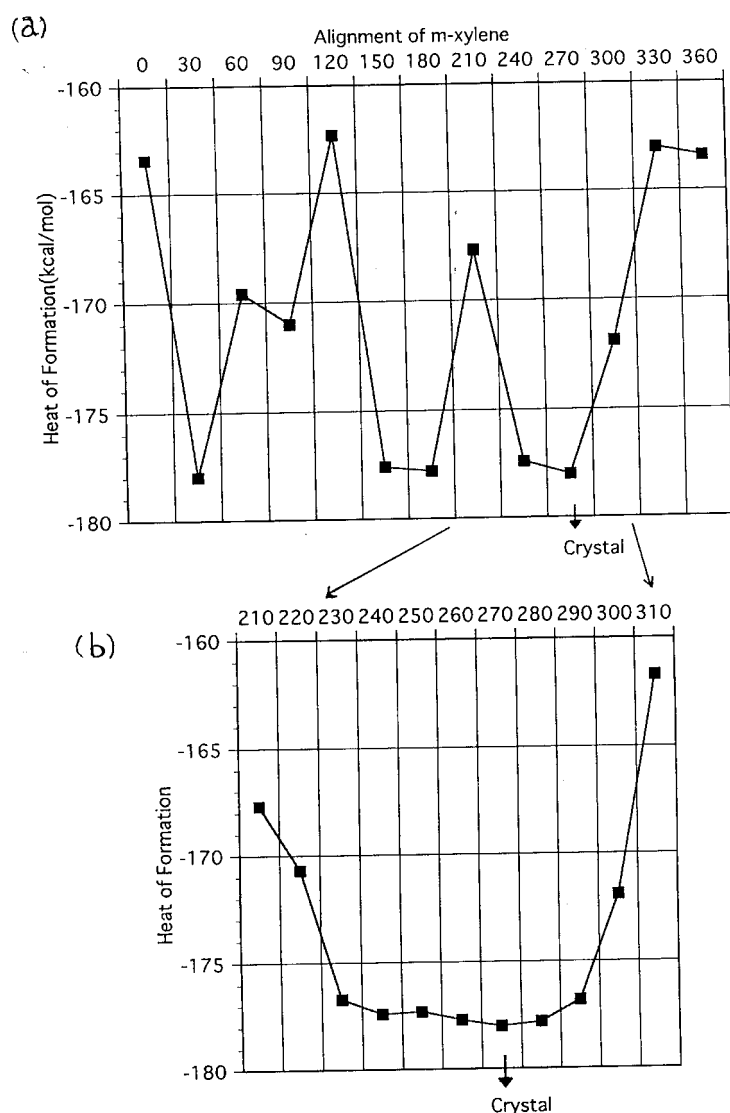


Figure 6. Heat of complex formation of the IOC-4: *m*-xylene complex as a function of rotation angle of the *m*-xylene. (a) For each 30° rotation. (b) For each 10° rotation in the range of 210° to 310°.

The structures of BOC-4 complexed with the three xylene isomers are very similar to each other, because their crystals are isomorphous. The BOC-4 molecule shows the “cone” conformation which is stabilized with four strong cyclic O—H—O hydrogen bonds (see Table IV), and the guest xylene molecule occupied the cavity created by the host BOC-4 molecule. Similarly to the case of the IOC-4: xylene complexes, the introduction of the —CH<sub>3</sub>—O—CH<sub>3</sub>— linkage between the A and D rings widens the “cone” shaped cavity and forms the “ellipsoidal”

Table IV. Hydrogen bonds, short contacts and dihedral angles found in BOC-4 : xylene complexes

	<i>o</i> -Xylene	<i>m</i> -Xylene	<i>p</i> -Xylene
Hydrogen bonds (distance Å)			
O1A—O1B	2.791(8)	2.799(4)	2.769(9)
O1A—O1D	3.032(8)	3.071(4)	2.955(9)
O1B—O1C	2.730(8)	2.739(4)	2.679(9)
CH—O interaction (distance Å)			
C7E—O0	3.42(2)	3.37(1)	4.45(5)
C8E—O0	4.63(5)	6.51(1)	6.25(5)
CH— $\pi$ interaction (distance Å)			
C7E—A phenol ring plane	3.64(2)	3.61(1)	5.31(4)
C7E—B phenol ring plane	3.80(2)	3.74(1)	6.24(4)
C8E—A phenol ring plane	3.45(5)	5.13(1)	4.85(4)
C8E—B phenol ring plane	3.46(5)	4.74(1)	4.18(4)
Dihedral angle (deg)			
The mass plane – A plane	54.1(4)	57.1(3)	68.2(9)
The mass plane—B plane	55.8(9)	52.5(3)	45.4(9)

cavity which rather nicely fits to the molecular dimensions of the guest xylene molecule, and also indicates the possible CH/O interaction between the Oo atom and the C7E methylgroup of the guest molecule (Table IV). From the requirement of the space group Pbcm, the mirror planes parallel to the *ab*-plane pass through at  $c = 1/4$  and  $3/4$ , and as a result of X-ray analysis, a mirror plane passes through the Oo oxygen atom and the C7B carbon atom in the BOC-4 molecule, and also passes C1E, C4E and C7E in *o*- and *m*-xylene but no atom in *p*-xylene lies on a mirror plane (Figures 7 and 8). Therefore, this mirror plane divides the BOC-4 molecule and also the *o*- and *m*-xylene molecule into two identical parts. This mirror symmetry causes the methyl group C8E of *o*- or *m*-xylene to take two possible positions at both sides of the mirror plane with equal probability. As well as the case of the IOC-4 : xylene complexes, one methyl group C7E of the xylene molecule deeply penetrates into the cavity formed by the host BOC-4 molecule and interacts with the phenol ring by C-H/ $\pi$  interaction (Table IV). Furthermore, in the case of the BOC-4 : *o*-xylene complex, the second methyl group C8E interacts rather strongly with the A and B phenol rings with distances of 3.45(5) Å and 3.46(5) Å, as shown in Table IV. When considered with the data in Table IV, the host-guest interaction becomes weaker in the order of BOC-4 : *o*-xylene, BOC-4 : *m*-xylene and BOC-4 : *p*-xylene. The dihedral angles formed between the plane

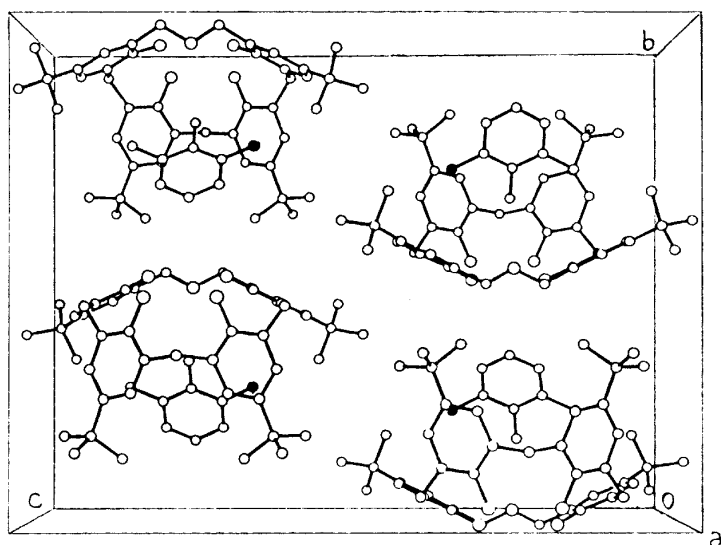


Figure 7. Perspective view of the crystal packing of the BOC-4:*o*-xylene complex. Methyl group with black circle is a mirror image of C8E with 50% occupancy.

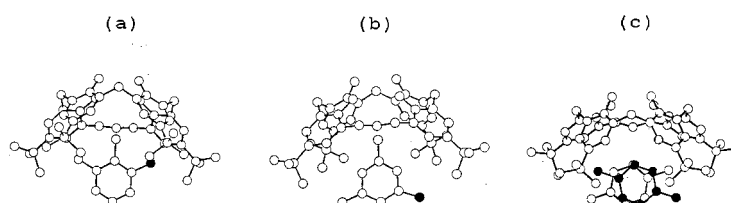


Figure 8. Molecular structures of BOC-4:xylene complexes along the axis roughly perpendicular to the xylene ring plane. (a) BOC-4:*o*-xylene complex. (b) BOC-4:*m*-xylene complex. (c) BOC-4:*p*-xylene complex. The black circle is a mirror image of C8E with 50% occupancy. *p*-Xylene occupies two disordered positions related by mirror plane.

composed of the central points of four phenol rings and each of the A and B rings are also shown in Table IV.

#### 3.4. DIFFERENTIAL SCANNING CALORIMETRY (DSC) FOR BOC-4 : XYLENE COMPLEXES

Differential scanning calorimetry (DSC) is a very useful complementary tool to investigate the energy transition of molecular recognition for inclusion compounds. The DSC curves of BOC-4:xylene complexes using a Perkin-Elmer DSC instrument is a recording of heat flow, in mW, as a function of temperature as shown in Figure 9. The thermal data for BOC-4:xylene complexes obtained from the DSC curves shown in Figure 9 are summarized in Table V. An endothermic curve peak is represented by peak area as A or C in the upward direction (increase

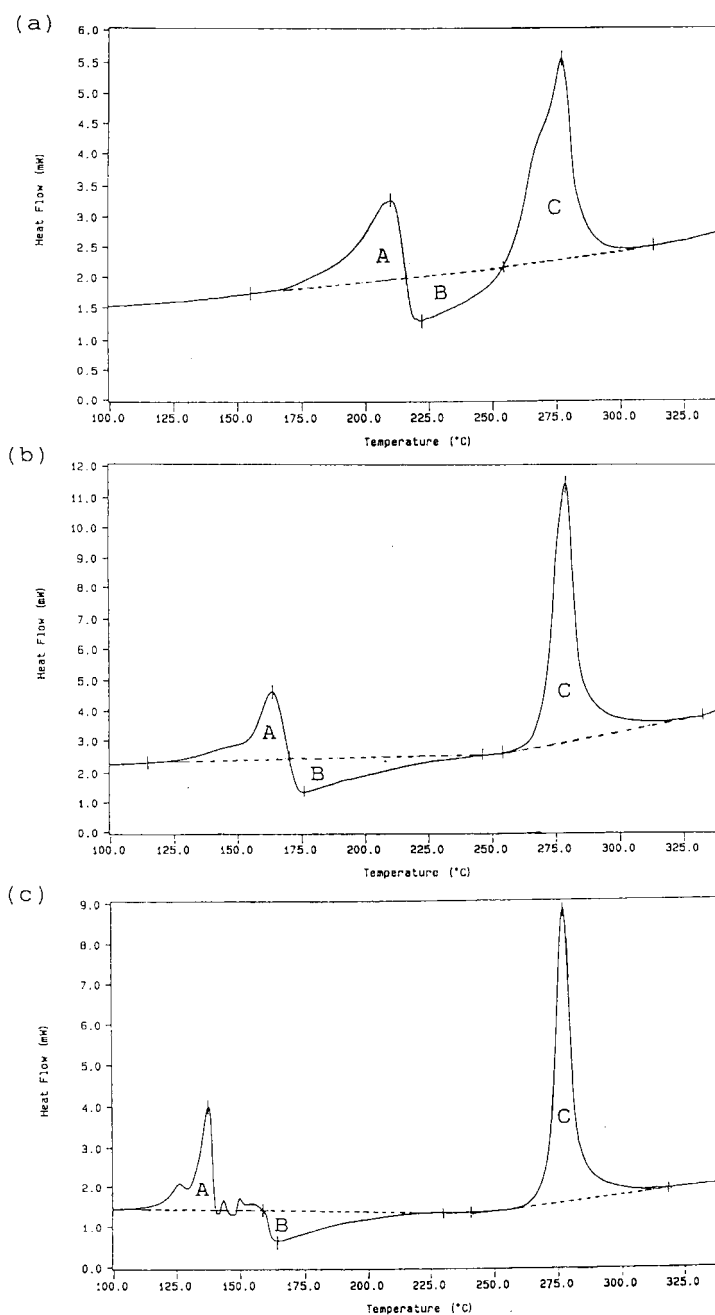


Figure 9. Heat flow as a function of temperature measured by differential scanning calorimeter. (a) BOC-4: *o*-xylene complex. (b) BOC-4: *m*-xylene complex. (c) BOC-4: *p*-xylene complex.

Table V. Differential scanning calorimetric data of BOC-4 : xylene complex crystals

Sample name	BOC-4 : <i>o</i> -xylene	BOC-4 : <i>m</i> -xylene	BOC-4 : <i>p</i> -xylene
Sample weight (mg)	4.90	5.78	4.18
Area	A	A	A
Temp. range (°C)	155.6–216.6	114.8–170.4	100.0–158.8
Peak temp. (°C)	210.7	163.8	137.7
$\Delta H$ (Joule/g)	30.783	32.358	31.998
Endo or exotherm	Endo	Endo	Endo
Area	B	B	B
Temp. range (°C)	216.6–255.0	170.6–246.4	159.0–229.8
Peak temp. (°C)	222.3	175.9	164.8
$\Delta H$ (Joule/g)	–23.402	–34.546	–28.689
Endo or exotherm	Exo	Exo	Exo
Area	C	C	C
Temp. range (°C)	254.6–314.2	253.8–332.6	240.6–318.2
Peak temp. (°C)	278.3	279.4	277.7
$\Delta H$ (Joule/g)	65.800	104.421	89.783
Endo or exotherm	Endo	Endo	Endo

in enthalpy), while an exothermic curve peak as B is recorded in the downward direction. Using the area enclosed by the DSC curve peak and the background curve (shown by the dotted line in Figure 9) and the mass of the used sample, the enthalpy change ( $\Delta H$  [Joule/g]) can be estimated as shown in Table V. The DSC profiles for each xylene isomer complexed with BOC-4 have the following characteristics: (a) As the temperature is increased, the curve peak appears in the order of A (endothermic), B (exothermic) and C (endothermic). (b) The endothermic curve peak A is probably due to the liberation of the guest xylene molecule first from the cavity created by the host BOC-4 molecule and then from the crystal lattice. The BOC-4 : *o*-xylene complex crystal with the highest peak temperature (210.7 °C) should have the strongest host-guest interaction among the three complex crystals. This was already borne out from the results of their crystal structure analyses. (c) The exothermic peak B having a negative enthalpy change is probably due to some structural transition from a metastable open structure after liberation of the guest xylene molecule to a stable compact structure. (d) The curve peak C is probably a melting temperature with a few degrees differences among three inclusion complexes.



### Acknowledgements

We are grateful to Dr. J. Vicens, EHICS, Strasbourg, for his generous supply of BOC-4 sample, and also to Prof. R. Matsuo and Mr. T. Maekawa, Faculty of Science, Osaka University, for their kind support and helpful discussion of DSC measurement. We are indebted to Prof. T. Ishida, Osaka University of Pharmaceutical Sciences, for his kind offer to use the X-ray diffractometer.

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