



# Structure of an Inclusion Compound of 28,28,35,35-Tetramethyl-11-oxo-1,4,18,21- tetraoxa[4,1,4,1,1]paracyclophane with *para*-Xylene

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**Abstract.** The structure of the 2:3 complex between cyclophane **1** and *para*-xylene has been determined by a single crystal X-ray diffraction study at 143 K. One *para*-xylene molecule is enclosed within the cavity formed by two molecules of the host cyclophane; this ensemble displays crystallographic inversion symmetry. The other independent *para*-xylene molecule is located on a general position in the intermolecular cavities of the crystal lattice. The complex crystallizes in the triclinic space group  $P(-1)$  with  $a = 10.473(4)$ ,  $b = 13.589(4)$ ,  $c = 16.322(4)$  Å,  $\alpha = 67.01(3)$ ,  $\beta = 89.51(3)$ ,  $\gamma = 87.26(2)^\circ$ , and  $Z = 1$ . Refinement based on 7539 unique reflections led to a final  $R(F)$  value of 0.0609.

**Key words:** tetraoxaparacyclophane complex, preparation, crystal structure, clathrate.

## 1. Introduction

The synthesis of host molecules possessing cavities suitable for the complexation of guest molecules has been recognized as an important objective in organic chemistry during the past three decades. For various paracyclophanes, several structural studies have appeared; for tetraoxaparacyclophanes in particular, important work on the complexation of neutral molecules (e.g., benzene or *para*-xylene) is available [1–3]. Other interesting tetraazaparacyclophanes [4–7] and thiaparacyclophanes [8] with the ability to form inclusion compounds have also been reported.

## 2. Experimental

The detailed methods for the preparation of the host compound, **1**, according to Scheme 1 will be described elsewhere [**1**: m.p. 200–203 °C (from CH<sub>2</sub>Cl<sub>2</sub>); IR(KBr) 1650 cm<sup>-1</sup> (C=O), <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$ : 1.65 s (12H), 4.30 t (4H), 4.50

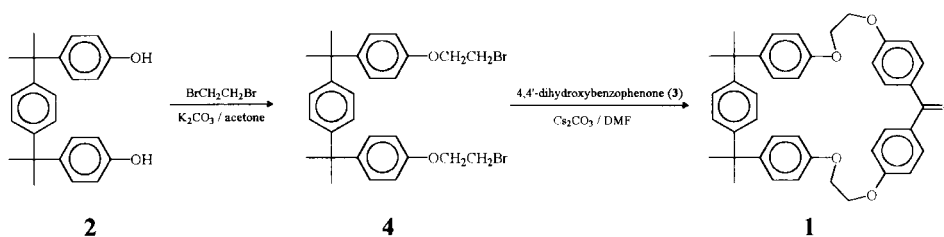
t (4H), 6.78, 7.67 dd (8H,  $J = 8.8$  Hz), 6.99, 7.13 dd (8H,  $J = 8.8$  Hz), 7.11 s (4H);  $^{13}\text{C}$  ( $\text{CDCl}_3$ )  $\delta$ : 195.1, 161.0, 155.5, 147.3, 142.9, 131.6, 130.9, 127.3, 125.6, 114.4, 113.7, 66.4, 65.6, 41.3, 30.2; UV:  $\lambda_{\text{max}}$  ( $\text{CH}_2\text{Cl}_2$ ) 284 nm ( $\log \epsilon = 4.35$ ), 277 nm ( $\log \epsilon = 4.34$ ); LSIMS: 613[M + 1] $^+$ .

Colourless single crystals of the host–guest complex were obtained from a *para*-xylene solution of **1** by slow evaporation. Data were collected on a Stoe STADI-4 diffractometer using the programs DIF4/REDU4 [9]. The structure was solved by direct methods using SHELXS86 [10] and refined anisotropically on  $F^2$  using SHELXL93 [11]. Methyl H atom positions were taken from difference syntheses, idealised and refined as rigid groups allowed to rotate but not tip. Other H atoms were treated by a riding model started from calculated positions. Crystallographic, experimental and computational details are given in Table I. Scattering factors were taken from *International Tables for Crystallography* (Vol. C). Fractional atomic coordinates and equivalent isotropic displacement parameters are given in Table II, with derived bond lengths and angles in Table III. Molecular graphics: Siemens XP [12].

Complete crystallographic data (excluding structure factors) have been deposited at the Fachinformationszentrum Karlsruhe, Germany, 76344 Eggenstein-Leopoldshafen, and can be obtained on quoting a full literature citation and the reference number CSD 408700. TGA measurements was taken with a Universal V1.3F TA Instruments.

### 3. Results and Discussion

The synthesis of host compound **1** began with diphenol derivatives **2** and **3** (Scheme 1). Reaction of **2** with excess 1,2-dibromoethylene in acetone in the presence of  $\text{K}_2\text{CO}_3$  gave the cyclization component **4**. Cyclization of this dibromide with the bisphenol **3** in DMF in the presence of caesium carbonate afforded the tetraoxaparacyclophane **1** (29%) [13]. Benzophenone and  $\alpha,\alpha'$ -diphenylene-1,4-diisopropylbenzene units organize and determine to a large extent the cavities of compound **1**. A similar effect was observed for diphenylmethane units by Diederich [1] and Koga [5].



Scheme 1.

Table I. Crystallographic data and refinement details

Empirical formula	$2 \times \text{C}_{41}\text{H}_{40}\text{O}_5 + 3 \times \text{C}_8\text{H}_{10}$
Formula weight	1543.94
Crystal system	Triclinic
Space group	$P(-1)$
Colour, habit	Colourless tablet
Crystal size	$0.6 \times 0.5 \times 0.1$ mm
Unit cell dimensions	$a = 10.473(4)\text{Å}$ , $\alpha = 67.01(3)^\circ$ $\beta = 13.589(4)\text{Å}$ , $\beta = 89.51(3)^\circ$ $c = 16.322(4)\text{Å}$ , $\gamma = 87.26(2)^\circ$
Volume	$2135.9(12)\text{Å}^3$
Z	1
Density	$1.200 \text{ mg/m}^3$
Absorption coefficient	$0.076 \text{ mm}^{-1}$
Temperature	143 K
Wavelength (MoK $\alpha$ )	$0.71073 \text{ Å}$
$\Theta$ range	$3.11$ to $25.03^\circ$
Limiting indices	$-12 \leq h \leq 12$ $-16 \leq k \leq 15$ $-19 \leq l \leq 4$
$F(000)$	826
Reflections collected	10078
Independent reflect. ( $R_{\text{int}}$ )	7539 (0.0365)
Data/parameters	7539/530
Goodness-of-fit on $F^2$	1.068
$R1, wR2 [I > 2\sigma(I)]$	0.0609, 0.1134
$R1, wR2$ [all data]	0.1192, 0.1419
Largest diff. peak and hole	0.197 and $-0.264 \text{ eÅ}^{-3}$

Tetraoxaparacyclophane **1** crystallizes from *para*-xylene with inclusion of the solvent. The molar ratios of *para*-xylene and tetraoxaparacyclophane molecules were estimated to be 3:2 on the basis of the  $^1\text{H}$  NMR measurements. This stoichiometry was confirmed by a single crystal X-ray structure analysis. Fig. 1a shows the host **1** (projected onto the least-squares plane); Fig. 1b shows the enclosed *para*-xylene guest within the intramolecular cavity formed by two molecules of **1**.

In the solid state, the two neighbouring tetraoxaparacyclophane molecules, related by an inversion centre, adopt the shape of a box-like cavity with ten aromatic rings as its wall. The cavity size is defined approximately by the distances between ring centres:  $10.4 \text{ Å}$  between rings C(22)—C(27) and  $11.4 \text{ Å}$  between rings C(40)—C(45) of both host molecules. This cavity accommodates one inversion-

Table II. Fractional atomic coordinates [ $\times 10^4$ ] and equivalent isotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ).  $U_{\text{eq}}$  is defined as one third of the trace of the orthogonalized  $U_{ij}$  tensor

Atom	$x$	$y$	$z$	$U(\text{eq})$
O(1)	3411(2)	9948(2)	2763(1)	48(1)
C(2)	4603(3)	10445(2)	2535(2)	46(1)
C(3)	4712(3)	10908(2)	1527(2)	49(1)
O(4)	5731(2)	10417(2)	1205(1)	50(1)
C(5)	5564(3)	9469(2)	1124(2)	39(1)
C(6)	4527(3)	8844(2)	1433(2)	41(1)
C(7)	4496(3)	7880(2)	1330(2)	44(1)
C(8)	5480(3)	7529(2)	917(2)	40(1)
C(9)	6499(3)	8188(2)	595(2)	41(1)
C(10)	6548(3)	9137(2)	700(2)	43(1)
C(11)	5435(3)	6516(2)	777(2)	45(1)
C(12)	4907(3)	5561(2)	1478(2)	39(1)
C(13)	4978(3)	5389(2)	2375(2)	39(1)
C(14)	4522(3)	4472(2)	3027(2)	36(1)
C(15)	3964(3)	3729(2)	2778(2)	35(1)
C(16)	3898(3)	3879(2)	1887(2)	42(1)
C(17)	4376(3)	4781(2)	1251(2)	44(1)
O(18)	3446(2)	2814(2)	3365(1)	42(1)
C(19)	3337(3)	2707(2)	4267(2)	40(1)
C(20)	2504(3)	1776(2)	4716(2)	46(1)
O(21)	2542(2)	1457(2)	5659(1)	48(1)
C(22)	1856(3)	2065(2)	6033(2)	38(1)
C(23)	1028(3)	2927(2)	5582(2)	38(1)
C(24)	410(3)	3480(2)	6045(2)	38(1)
C(25)	593(3)	3196(2)	6949(2)	38(1)
C(26)	1420(3)	2317(2)	7382(2)	46(1)
C(27)	2035(3)	1752(2)	6937(2)	47(1)
C(28)	-99(3)	3831(2)	7430(2)	42(1)
C(29)	-1535(3)	3790(3)	7307(3)	64(1)
C(30)	208(3)	3350(3)	8433(2)	66(1)
C(31)	326(3)	4986(2)	7073(2)	35(1)
C(32)	1536(3)	5245(2)	6737(2)	46(1)
C(33)	1967(3)	6263(2)	6490(2)	47(1)
C(34)	1221(3)	7082(2)	6586(2)	34(1)
C(35)	5(3)	6829(2)	6916(2)	37(1)
C(36)	-434(3)	5808(2)	7154(2)	38(1)
C(37)	1782(3)	8169(2)	6376(2)	40(1)
C(38)	2830(3)	8017(3)	7069(2)	55(1)
C(39)	776(3)	8997(2)	6447(2)	51(1)

Table II. Continued

Atom	x	y	z	U(eq)
C(40)	2296(3)	8615(2)	5424(2)	35(1)
C(41)	1479(3)	8756(3)	4714(2)	47(1)
C(42)	1870(3)	9205(3)	3843(2)	48(1)
C(43)	3105(3)	9529(2)	3654(2)	39(1)
C(44)	3941(3)	9394(2)	4337(2)	37(1)
C(45)	3529(3)	8932(2)	5216(2)	38(1)
O(46)	5851(3)	6476(2)	84(1)	64(1)
C(51)	46(5)	1273(4)	987(3)	83(1)
C(52)	-1226(5)	1571(5)	731(3)	98(2)
C(53)	-1760(5)	2563(5)	618(3)	94(2)
C(54)	-1047(5)	3308(4)	750(3)	83(1)
C(55)	222(5)	3015(4)	993(3)	81(3)
C(56)	750(4)	2028(4)	1111(2)	75(1)
C(57)	616(5)	182(4)	1138(3)	117(2)
C(58)	-1641(5)	4369(4)	680(3)	122(2)
C(61)	3758(3)	5364(3)	4926(2)	52(1)
C(62)	4654(4)	6041(2)	4417(2)	50(1)
C(63)	5902(3)	5658(3)	4502(2)	51(1)
C(64)	4278(6)	7162(3)	3779(3)	106(2)

symmetric molecule of *para*-xylene (independent atoms C(61)—C(64)), thus forming a 2:1 host-guest complex. The guest adopts a face-to-edge arrangement with the two aromatic rings of  $\alpha,\alpha'$ -diphenylene-1,4-diisopropylbenzene moieties of both host molecules. The shortest distance of the methyl units of *para*-xylene from the surrounding phenyl 'wall' is *ca.* 2.75 Å (H(64C) to the centre of ring C(40)—C(45); the shortest individual C···H distance is H(64C)···C(43) 2.67 Å, with C(64)···C(43) 3.32 Å). Further significant orientation-defining contacts are from the xylene ring H atom H(63) to the ring C(22')—C(27') (H···ring centre 2.91 Å) and from the host H atom H(14) to the xylene ring (H···ring centre 2.73 Å).

The other independent *para*-xylene molecules (atoms C(51)—(58)) are not associated with the above-mentioned 2:1 complexes, but instead are located between them in the crystal lattice in the regions  $z \approx 0$ . They interact only weakly through dispersion forces with surrounding molecules of the cyclophane host; significant specific interactions between host and guest molecules are not indicated. Figure 2 shows the crystal packing in projection onto the  $xz$  plane and, in particular, the locations of all *para*-xylene guests in the crystal lattice. The overall stoichiometry cyclophane:xylene is 2:3.

Table III. Bond lengths [Å] and angles [°]

O(1)—C(43)	1.379(3)	C(28)—C(29)	1.525(4)
O(1)—C(2)	1.425(3)	C(28)—C(31)	1.532(4)
C(2)—C(3)	1.519(4)	C(28)—C(30)	1.537(4)
C(3)—O(4)	1.434(3)	C(31)—C(32)	1.383(4)
O(4)—C(5)	1.364(3)	C(31)—C(36)	1.389(4)
C(5)—C(6)	1.378(4)	C(32)—C(33)	1.378(4)
C(5)—C(10)	1.391(4)	C(33)—C(34)	1.387(4)
C(6)—C(7)	1.386(4)	C(34)—C(35)	1.384(4)
C(7)—C(8)	1.391(4)	C(34)—C(37)	1.526(4)
C(8)—C(9)	1.390(4)	C(35)—C(36)	1.387(4)
C(8)—C(11)	1.483(3)	C(37)—C(38)	1.531(4)
C(9)—C(10)	1.369(4)	C(37)—C(40)	1.534(4)
C(11)—O(46)	1.230(3)	C(37)—C(39)	1.542(4)
C(11)—C(12)	1.482(4)	C(40)—C(45)	1.379(4)
C(12)—C(13)	1.392(4)	C(40)—C(41)	1.393(4)
C(12)—C(17)	1.393(4)	C(41)—C(42)	1.378(4)
C(13)—C(14)	1.388(4)	C(42)—C(43)	1.379(4)
C(14)—C(15)	1.381(4)	C(43)—C(44)	1.373(4)
C(15)—O(18)	1.373(3)	C(44)—C(45)	1.397(4)
C(15)—C(16)	1.390(4)	C(51)—C(56)	1.368(6)
C(16)—C(17)	1.373(4)	C(51)—C(52)	1.393(6)
O(18)—C(19)	1.427(3)	C(51)—C(57)	1.499(6)
C(19)—C(20)	1.507(4)	C(52)—C(53)	1.379(7)
C(20)—O(21)	1.427(3)	C(53)—C(54)	1.369(6)
O(21)—C(22)	1.379(3)	C(54)—C(55)	1.385(6)
C(22)—C(27)	1.378(4)	C(54)—C(58)	1.505(6)
C(22)—C(23)	1.381(4)	C(55)—C(56)	1.368(6)
C(23)—C(24)	1.394(4)	C(61)—C(63#1)	1.369(4)
C(24)—C(25)	1.385(4)	C(61)—C(62)	1.374(5)
C(25)—C(26)	1.389(4)	C(62)—C(63)	1.371(5)
C(26)—C(27)	1.383(4)	C(62)—C(64)	1.508(5)
C(43)—O(1)—C(2)	116.9(2)	C(7)—C(8)—C(11)	122.2(3)
O(1)—C(2)—C(3)	108.3(3)	C(10)—C(9)—C(8)	121.2(3)
O(4)—C(3)—C(2)	113.8(3)	C(9)—C(10)—C(5)	120.4(3)
C(5)—O(4)—C(3)	120.0(2)	O(46)—C(1)—C(12)	120.7(3)
O(4)—C(5)—C(6)	125.2(3)	O(46)—C(11)—C(8)	119.5(3)
O(4)—C(5)—C(10)	115.1(3)	C(12)—C(11)—C(8)	119.8(3)
C(6)—C(5)—C(10)	119.8(3)	C(13)—C(12)—C(17)	118.1(3)
C(5)—C(6)—C(7)	119.2(3)	C(13)—C(12)—C(11)	121.8(3)
C(6)—C(7)—C(8)	121.8(3)	C(17)—C(12)—C(11)	120.1(3)
C(9)—C(8)—C(7)	117.7(3)	C(14)—C(13)—C(12)	121.2(3)
C(9)—C(8)—C(11)	120.1(3)	C(15)—C(14)—C(13)	119.2(3)

Table III. Continued

O(18)—C(15)—C(14)	124.0(2)	C(34)—C(35)—C(36)	121.8(3)
O(18)—C(15)—C(16)	115.5(2)	C(35)—C(36)—C(31)	121.6(3)
C(14)—C(15)—C(16)	120.5(3)	C(34)—C(37)—C(38)	107.6(2)
C(17)—C(16)—C(15)	119.6(3)	C(34)—C(37)—C(40)	110.3(2)
C(16)—C(27)—C(12)	121.4(3)	C(38)—C(37)—C(40)	112.0(2)
C(15)—O(18)—C(19)	116.9(2)	C(34)—C(37)—C(39)	112.0(2)
O(18)—C(19)—C(20)	106.0(2)	C(38)—C(37)—C(39)	107.5(2)
O(21)—C(20)—C(19)	110.8(2)	C(40)—C(37)—C(39)	107.4(2)
C(22)—O(21)—C(20)	118.9(2)	C(45)—C(40)—C(41)	116.8(3)
C(27)—C(22)—O(21)	115.0(2)	C(45)—C(40)—C(37)	123.6(3)
C(27)—C(22)—C(23)	119.4(3)	C(41)—C(40)—C(37)	119.5(3)
O(21)—C(22)—C(23)	125.6(3)	C(42)—C(41)—C(40)	122.0(3)
C(22)—C(23)—C(24)	119.4(3)	C(41)—C(42)—C(43)	119.9(3)
C(25)—C(24)—C(23)	122.3(3)	C(44)—C(43)—O(1)	124.7(3)
C(24)—C(25)—C(26)	116.6(3)	C(44)—C(43)—C(42)	119.7(3)
C(24)—C(25)—C(28)	120.6(3)	O(1)—C(43)—C(42)	115.5(3)
C(26)—C(25)—C(28)	122.8(3)	C(43)—C(44)—C(45)	119.5(3)
C(27)—C(26)—C(25)	122.0(3)	C(40)—C(45)—C(44)	122.0(3)
C(22)—C(27)—C(26)	120.2(3)	C(56)—C(51)—C(52)	116.3(5)
C(29)—C(28)—C(31)	111.5(2)	C(56)—C(51)—C(57)	121.4(5)
C(29)—C(28)—C(25)	108.2(3)	C(52)—C(51)—C(57)	122.3(5)
C(31)—C(28)—C(25)	110.7(2)	C(53)—C(52)—C(51)	122.3(5)
C(29)—C(28)—C(30)	108.3(3)	C(54)—C(53)—C(52)	120.8(5)
C(31)—C(28)—C(30)	106.6(2)	C(53)—C(54)—C(55)	116.7(5)
C(25)—C(28)—C(30)	111.6(2)	C(53)—C(54)—C(58)	121.2(5)
C(32)—C(31)—C(36)	116.3(3)	C(55)—C(54)—C(58)	122.1(5)
C(32)—C(31)—C(28)	121.8(2)	C(56)—C(55)—C(54)	122.4(5)
C(36)—C(31)—C(28)	121.7(2)	C(51)—C(56)—C(55)	121.4(5)
C(33)—C(32)—C(31)	122.1(3)	C(63#1)—C(61)—C(62)	121.2(3)
C(32)—C(33)—C(34)	121.8(3)	C(63)—C(62)—C(61)	117.8(3)
C(35)—C(34)—C(33)	116.3(3)	C(63)—C(62)—C(64)	121.0(4)
C(35)—C(34)—C(37)	123.8(2)	C(61)—C(62)—C(64)	121.2(4)
C(33)—C(34)—C(37)	119.8(3)	C(61#1)—C(63)—C(62)	121.0(3)

Symmetry transformation used to generate equivalent atoms: #1  $-x + 1, -y + 1, -z + 1$ .

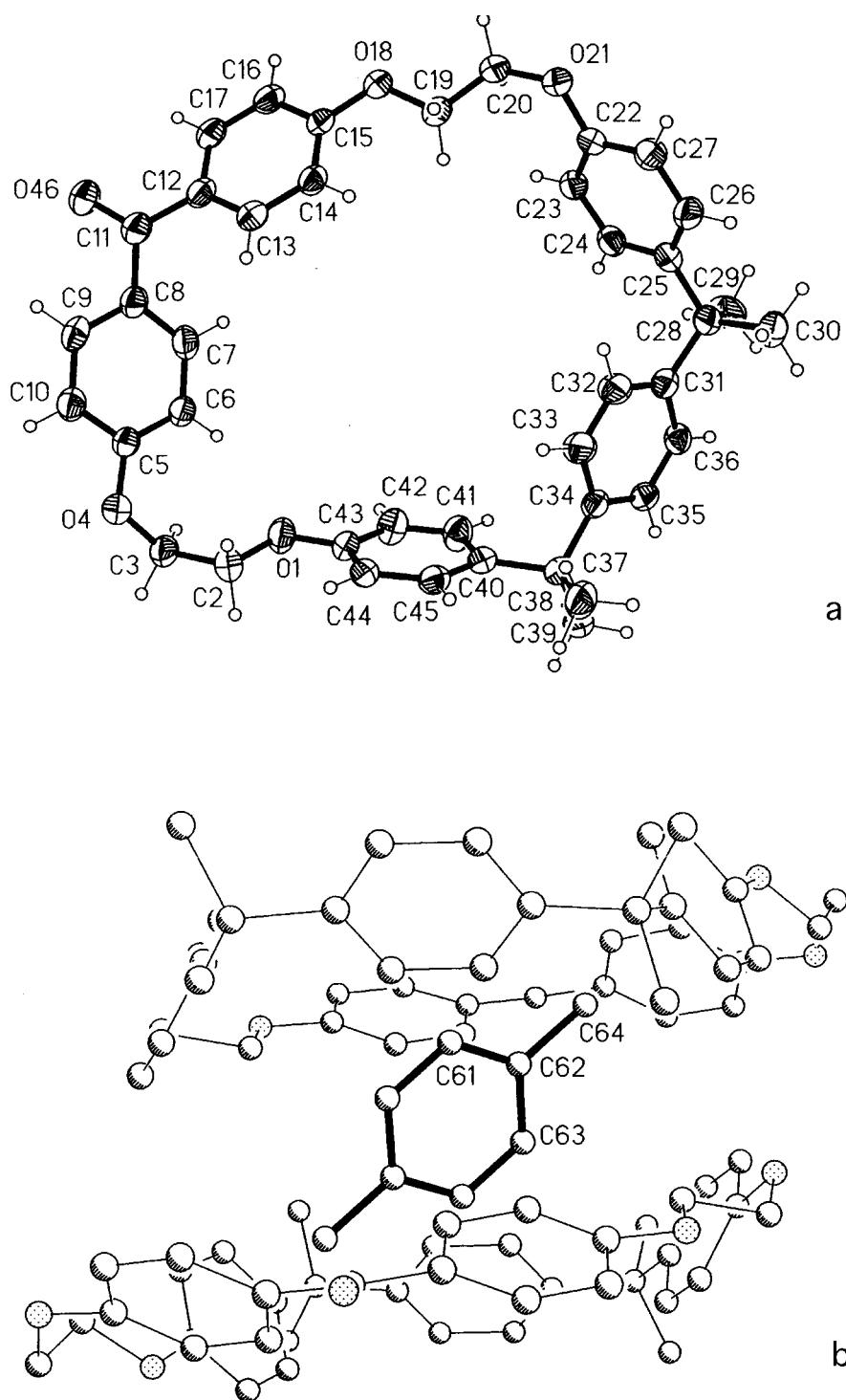


Figure 1. (a) View of the host molecule **1** projected onto its least-squares plane. Ellipsoids represent 50% probability levels. H atom radii are arbitrary. (b) Side view of the guest *para*-xylene molecule in the cavity formed by two host molecules.



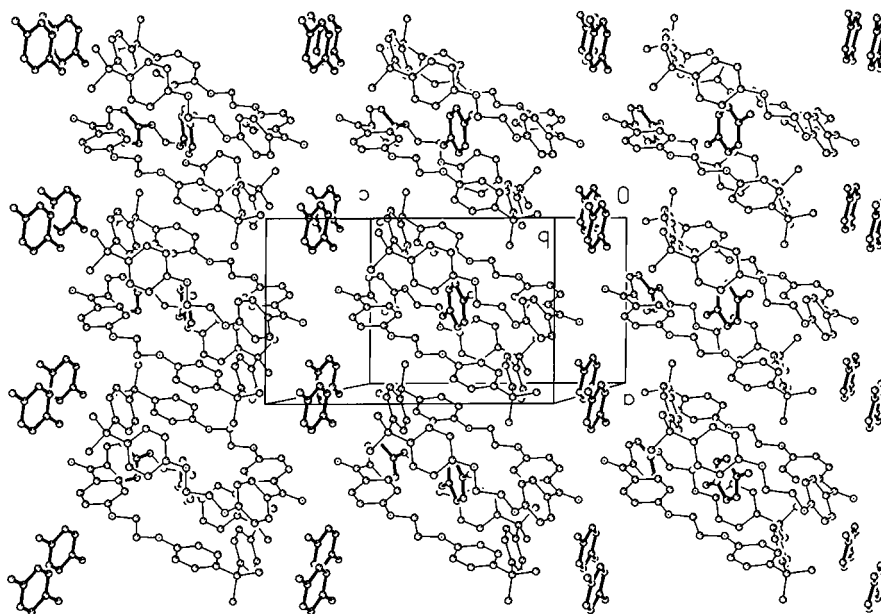


Figure 2. Packing diagram of the inclusion compound projected onto the  $xz$  plane. H atoms are omitted.

Thermogravimetry (TGA) measurements showed the release of the *para*-xylene molecules to occur gradually from 138 to 146 °C (two molecules) and 183 °C (one molecule). The final temperature is 45 °C higher than the boiling point of *para*-xylene. These results indicate that the release of *para*-xylene molecules depends on their position in the crystal lattice.

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### References

1. K. Krieger and F. Diederich: *Chem. Ber.* **118**, 3620 (1985).
2. J. Ratilainen, K. Airola, M. Nieger, M. Böhmer, J. Huuskonen, and K. Rissanen: *Chem. Eur. J.* **3**, 749 (1997).
3. N. K. Dalley, X. Kou, R. A. Bartsch, B. P. Czech, and P. Kus: *J. Incl. Phenom.* **29**, 323 (1997).
4. K. Odashima, A. Itai, Y. Iitaka, and K. Koga: *J. Am. Chem. Soc.* **102**, 2504 (1980).
5. K. Odashima, A. Itai, Y. Iitaka, Y. Arata, and K. Koga: *Tetrahedron Lett.* **21**, 4347 (1980).
6. I. Tabushi, K. Yamamura, H. Nonoguchi, K. Hirotsu, and T. Higuchi: *J. Am. Chem. Soc.* **106**, 2621 (1984).
7. H. Nonoguchi, K. Yamamura, I. Tabushi, T. Higuchi, and K. Hirotsu: *Bull. Chem. Soc. Jpn.* **65**, 805 (1992).

8. T. Takemura, K. Kozawa, T. Uchida, and N. Mori: *Chem. Lett.* **1984**, 1839.
9. Stoe et Cie., Darmstadt, Germany: Diffractometer control software.
10. G. M. Sheldrick, *Acta Crystallogr.* **A46**, 467 (1990).
11. G.M. Sheldrick, SHELXL93, a program for refining crystal structures, University of Göttingen, Germany (1993).
12. Siemens. XP, molecular graphics program, version 5.03. Siemens Analytical X-ray Instruments, Madison, USA (1994).
13. We have synthesized other tetraoxaparacyclophanes, and will report on them elsewhere.