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Structure of Host-Guest Complexes of 1′,1″-Dimethyldispiro[1,6,20,25-tetraoxa[6.1.6.1]paracyclophane-13,4′:32,4″-bispiperidine] with Benzene and *p*-Xylene

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The molecular and crystal structures of the **1**-benzene (1/2) monohydrate **2** and of the **1**-*p*-xylene (1/1) complex **3** were determined by *X*-ray analysis. In both complexes the host molecules take the "face to face" conformation. In the **1**-benzene (1/2) monohydrate **2** one benzene ring is perfectly enclosed within the intramolecular cavity of the host. The second benzene ring is located in channel type intermolecular cavities of the crystal lattice. The water molecule in the crystal lattice forms hydrogen bonds to the piperidine-nitrogens of neighbouring **1**-molecules. – In the **1**-*p*-xylene (1/1) complex **3** the host molecules are stacked along the *a* axis and *p*-xylene molecules are sandwiched by two adjacent host molecules in the stack. The two methyl groups of a *p*-xylene molecule are inserted into the cavities of the two sandwiching hosts. – The requirements for a preference of intramolecular cavity inclusion over intermolecular lattice inclusion of apolar guests in crystalline complexes of apolar macrocyclic hosts are discussed.

Kristall- und Molekülstrukturen der Wirt-Gast-Komplexe von 1′,1″-Dimethyldispiro[1,6,20,25-tetraoxa[6.1.6.1]paracyclophan-13,4′:32,4″-bispiperidin] mit Benzol und *p*-Xylol

Die Molekül- und Kristallstrukturen des **1**-Benzol (1/2)-Monohydrats **2** und des **1**-*p*-Xylol (1/1)-Komplexes **3** wurden durch Röntgenstrukturanalyse bestimmt. In beiden Komplexen liegen die Wirtmoleküle in der „face to face"-Konformation vor. Im 1-Benzol (1/2)-Monohydrat **2** ist ein Benzolring perfekt im intramolekularen Hohlraum des Wirtmoleküls eingeschlossen. Der zweite Benzolring ist in kanalartigen intermolekularen Hohlräumen des Kristallgitters lokalisiert. Das Wassermolekül im Kristallgitter bildet Wasserstoffbrücken-Bindungen zu den Piperidin-Stickstoffatomen benachbarter **1**-Moleküle aus. – Im **1**-*p*-Xylol (1/1)-Komplex **3** stapeln die Wirtmoleküle entlang der *a*-Achse und die *p*-Xylolmoleküle sind zwischen zwei benachbarten Wirtmolekülen im Stapel eingelagert. Die beiden Methylgruppen eines *p*-Xylolmoleküls ragen in die Hohlräume der beiden umgebenden Wirtmoleküle. – Die Voraussetzungen für die Bevorzugung eines intramolekularen Hohlraumeinschlusses unpolarer Gastmoleküle gegenüber einem intermolekularen Gittereinschluß in kristallinen Komplexen unpolarer makrocyclischer Wirte werden diskutiert.

During the past decades, there has been considerable interest in the interactions between macrocyclic organic host molecules and neutral organic guests in solution as well as in the solid state[1-3]. Single-crystal *X*-ray analysis was used as method of choice to establish unequivocally whether in a crystalline complex the guest occupies *intramolecular cavities of*

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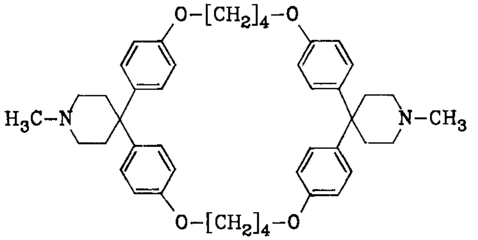
the host or whether the guest is located within *intermolecular cavities of the host lattice.* A considerable number of *X*-ray structural investigations involved complexes with benzene derivatives as guests. The *X*-ray analysis of crystalline host-guest complexes of the naturally occurring cyclodextrins as hosts and a variety of polar benzene derivatives have been reported[1,4-9]. In these complexes the guest molecules are located within the molecular cavity of the cyclodextrins.

Intramolecular cavity inclusion of neutral benzene derivatives has less often been observed for complexes formed by artificial macrocyclic hosts. Crystalline, stable 1:1 complexes of tetraaza[n.0.n.0]paracyclophanes as hosts and benzene as guest have been described already in 1955 by *Stetter* and *Roos*[10]. These complexes were thought for a long time to be of the intramolecular cavity inclusion type until recently *Hilgenfeld* and *Saenger* showed that benzene in these complexes is located between host molecules in the crystal lattice[11]. Intermolecular lattice inclusion of aromatic guests (hydroquinone and *p*-xylene) has also been observed in crystalline complexes formed by other hosts of the cyclophane type[12,13]. Intramolecular cavity inclusion has been demonstrated by *X*-ray analysis for the crystalline 1:1 complex of a protonated tetraaza[6.1.6.1]paracyclophane and durene, which was obtained from aqueous solution[14]. Both types of inclusion have been observed for the 1:1 complexes of two differently substituted calix[4]arenes and toluene as guest[15,16].

We found that the 1,6,20,25-tetraoxa[6.1.6.1]paracyclophane **1**[17] forms stable crystalline complexes with benzene derivatives. In this paper, we present the molecular and crystal structures of the **1**-benzene (1/2) monohydrate **2** and of the **1**-*p*-xylene (1/1) complex **3**.



1

2 = **1**–benzene–water (1/2/1)

3 = **1**–*p*–xylene (1/1)

Molecular and Crystal Structures of 2 and 3[18]

Crystal Preparation and X-Ray Structure Analysis

2: 100 mg (0.15 mmol) of **1** was dissolved in 50 ml of benzene, saturated with water. Upon standing of the solution at room temperature in a dessicator over pellets of potassium hydroxide, colourless prismatic crystals of **2** were obtained.

3: 100 mg (0.15 mmol) of **1** was dissolved in 20 ml of *p*-xylene and the solution was treated as described for **2**: colourless prismatic crystals of **3** were obtained.

Crystal and data collection parameters for **2** and **3** are listed in Table 1. Intensity data were collected on a CAD4 4-circle diffractometer by using a graphite-monochromated Mo-K_α irradiation and applying $\Theta/2\Theta$-scan technique. The structures were solved by conventional direct methods (MULTAN) and were refined by full-matrix least squares technique using anisotropic temperature factors for non-hydrogen atoms and isotropic temperature factors for hydrogen atoms. Atomic coordinates and thermal parameters for non-hydrogen atoms are given in Tables 2 and 3 (for the numbering of atoms cf. Figures 1, 2, and 5).

Molecular Geometry of the **1**-*Benzene (1/2) Monohydrate* **2**: The most striking feature of the structure of **2** is the complete incorporation of one benzene ring (A)

Table 1. Crystal and data collection parameters for **2** and **3**

Compound	**2**	**3**
Formula	$C_{44}H_{54}N_2O_4 \times 2C_6H_6 \times H_2O$	$C_{44}H_{54}N_2O_4 \times C_8H_{10}$
Molecular mass	849.2	781.1
Size of crystal [mm]	0.45 × 0.3 × 0.2	0.35 × 0.35 × 0.3
a [pm]	799.2 (1)	626.2 (1)
b [pm]	1002.8 (2)	1210.6 (2)
c [pm]	1473.6 (3)	1534.0 (2)
α [°]	90.85 (2)	107.74 (2)
β [°]	90.21 (2)	90.66 (2)
γ [°]	93.96 (2)	86.76 (2)
Space group	$P\bar{1}$	$P\bar{1}$
Z	1	1
Symmetry of complex in the crystal	C_i	C_i
d_r [gcm^{-3}]	1.197	1.173
Max. sin Θ/λ [nm^{-1}]	6.68	6.68
No. of reflections measured	5969	5470
No. of reflections with $I \geq 1.96\ \sigma(I)$	4121	3515
R	0.042	0.042

Table 2. Atomic coordinates and thermal parameters U_{equ} (in pm^2) for **2** (numbers in parentheses are estimated standard deviations in units of the last quoted digit)

Atom	x	y	z	Uequ.	Atom	x	y	z	Uequ.
O(1)	0.7843(1)	0.90943(8)	0.54849(5)	540(3)	C(17)	0.1417(1)	0.1810(1)	0.39750(8)	428(4)
C(2)	0.7991(2)	0.8948(1)	0.45266(8)	506(4)	C(18)	0.0366(2)	0.2751(1)	0.42823(8)	479(4)
C(3)	0.6982(2)	0.9980(1)	0.40961(8)	503(4)	C(19)	-0.0276(1)	0.3623(1)	0.36682(8)	460(4)
C(4)	0.7111(2)	0.9980(1)	0.30722(8)	555(4)	N(1')	-0.3509(1)	0.3421(1)	0.11527(7)	568(4)
C(5)	0.6115(2)	0.8855(1)	0.25926(8)	534(4)	C(2')	-0.3562(2)	0.3865(1)	0.20968(8)	517(4)
O(6)	0.4392(1)	0.89961(8)	0.27797(6)	590(3)	C(3')	-0.2282(1)	0.5013(1)	0.23039(8)	458(4)
C(7)	0.3257(1)	0.7953(1)	0.25588(8)	454(4)	C(5')	-0.0520(2)	0.4175(1)	0.11070(8)	459(4)
C(8)	0.3527(2)	0.6971(1)	0.19289(8)	518(4)	C(6')	-0.1833(2)	0.3048(1)	0.09142(8)	532(4)
C(9)	0.2300(2)	0.5949(1)	0.17698(8)	493(4)	C(1")	-0.4720(2)	0.2277(2)	0.0991(1)	897(6)
C(10)	0.0789(1)	0.5870(1)	0.22258(7)	396(3)	C(A1)	0.4145(2)	0.4955(2)	0.4199(1)	921(7)
C(11)	0.0545(2)	0.6894(1)	0.28436(8)	493(4)	C(A2)	0.4947(2)	0.3876(2)	0.4467(1)	873(6)
C(12)	0.1750(2)	0.7921(1)	0.30097(8)	512(4)	C(A3)	0.5808(2)	0.3926(2)	0.5265(1)	897(6)
C(13)	-0.0475(1)	0.4656(1)	0.21024(7)	390(3)	C(B1)	-0.1345(2)	-0.0076(2)	-0.0574(1)	793(6)
C(14)	0.0098(1)	0.3591(1)	0.27565(7)	376(3)	C(B2)	-0.1321(2)	-0.0896(2)	0.0155(1)	821(6)
C(15)	0.1139(2)	0.2613(1)	0.24727(7)	449(4)	C(B3)	0.0027(2)	-0.0822(2)	0.0728(1)	801(6)
C(16)	0.1793(2)	0.1741(1)	0.30701(8)	471(4)	O a)	-0.6065(3)	0.4171(2)	-0.0119(1)	838(8)

a) q = 0.50

within the cavity of the host molecule. The whole 1/2/1 (host : guest : water) complex sits on a center of symmetry and benzene ring A is located exactly at the middle of the intramolecular cavity. Benzene ring B and the water molecule are located outside the cavity between host molecules in the crystal lattice.

Host **1** in the complex takes a "face to face" conformation[19)] with the four benzene rings nearly perpendicular to the mean molecular plane of **1**. A least

Table 3. Atomic coordinates and thermal parameters U_{equ} (in pm^2) for **3** (numbers in parentheses are estimated standard deviations in units of the last quoted digit)

Atom	x	y	z	Uequ.	Atom	x	u	z	Uequ.
O(1)	0.7788(2)	0.08963(8)	0.46580(6)	554(4)	C(16)	0.4120(2)	0.8539(1)	0.39522(9)	487(5)
C(2)	0.9550(3)	0.1054(1)	0.41287(9)	511(5)	C(17)	0.2345(2)	0.8429(1)	0.44359(9)	421(5)
C(3)	0.9309(3)	0.0275(1)	0.3153(1)	576(6)	C(18)	0.0835(2)	0.7665(1)	0.3998(1)	486(5)
C(4)	0.7310(3)	0.0546(1)	0.2660(1)	549(5)	C(19)	0.1130(2)	0.7023(1)	0.30817(9)	458(5)
C(5)	0.7379(3)	0.1689(1)	0.2468(1)	531(5)	N(1')	0.2254(2)	0.7805(1)	0.03610(8)	506(4)
O(6)	0.5430(2)	0.18548(8)	0.19955(7)	570(4)	C(2')	0.0554(2)	0.7479(1)	0.0865(1)	485(5)
C(7)	0.5018(2)	0.2926(1)	0.18710(9)	441(5)	C(3')	0.1110(2)	0.6323(1)	0.10181(9)	416(5)
C(8)	0.6441(2)	0.3801(1)	0.2068(1)	511(5)	C(5')	0.4902(2)	0.6731(1)	0.10468(9)	421(5)
C(9)	0.5813(2)	0.4866(1)	0.1954(1)	486(5)	C(6')	0.4264(2)	0.7868(1)	0.0859(1)	483(5)
C(10)	0.3815(2)	0.5093(1)	0.16276(8)	362(4)	C(1″)	0.1690(3)	0.8899(1)	0.0190(1)	695(6)
C(11)	0.2441(2)	0.4183(1)	0.14099(9)	441(5)	C(A1)	0.1265(3)	0.4774(2)	0.5657(1)	752(7)
C(12)	0.3033(2)	0.3119(1)	0.1530(1)	482(5)	C(A2)	0.1866(3)	0.4259(1)	0.4751(1)	667(6)
C(13)	0.3180(2)	0.6319(1)	0.15735(8)	359(4)	C(A3)	0.0553(3)	0.4508(2)	0.4104(1)	759(7)
C(14)	0.2887(2)	0.7114(1)	0.25747(8)	350(4)	C(A2')	0.3852(4)	0.3460(2)	0.4484(2)	1069(11)
C(15)	0.4385(2)	0.7892(1)	0.30386(9)	446(5)					

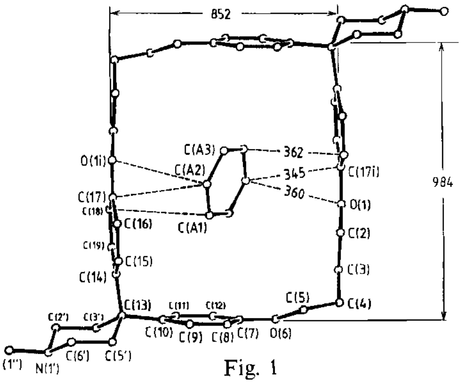


Fig. 1

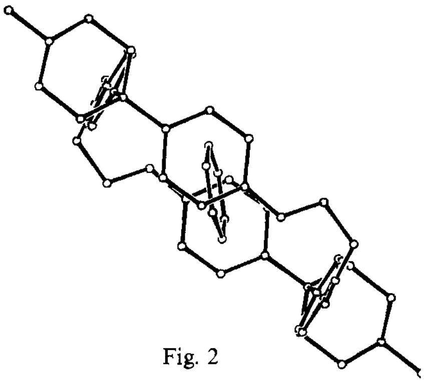


Fig. 2

Figure 1. Molecular structure of **2** in a view onto the least square plane of the host. Only the host and the benzene ring A in the intramolecular cavity are shown. Some short C···C host-guest contacts and characteristic extensions of the cavity are shown (for details see text)

Figure 2. View of the molecular structure of **2** parallel to the least square plane of the host. Only the host and the benzene ring in the intramolecular cavity are shown

square molecular plane of **1** can be defined passing through C(7), C(10), C(13), C(14), C(17), N(1′), and C(1″). Figure 1 is a view onto this plane and Figure 2a view parallel to this plane. The cavity of **1** is rectangularly shaped and the distances between least square planes including parallel benzene rings are 984 and 852 pm (Figure 1). The least square planes through the benzene ring of the shorter cavity site, through the benzene ring of the larger cavity site and through C(2′), C(3′),

Table 4. Bond lengths of **2** and **3** (in pm; numbers in parentheses are estimated standard deviations in units of the last quoted digit)

Host	2	3		2	3
O(1) - C(2)	142.4(1)	143.2(2)	C(13) - C(14)	154.1(1)	155.1(1)
O(1) - C(17i)	137.7(1)	138.2(1)	C(13) - C(3')	154.1(1)	154.3(1)
C(2) - C(3)	150.2(1)	151.8(2)	C(13) - C(5')	153.7(1)	154.6(2)
C(3) - C(4)	151.3(1)	152.6(2)	C(14) - C(15)	139.0(1)	139.6(1)
C(4) - C(5)	150.2(1)	151.0(2)	C(14) - C(19)	137.8(1)	138.3(2)
C(5) - O(6)	142.1(1)	143.7(2)	C(15) - C(16)	137.6(1)	138.8(2)
O(6) - C(7)	137.1(1)	137.8(1)	C(16) - C(17)	137.0(1)	137.8(2)
C(7) - C(8)	137.2(1)	138.3(2)	C(17) - C(18)	137.9(1)	138.0(2)
C(7) - C(12)	137.6(1)	137.8(2)	C(18) - C(19)	138.9(1)	139.2(2)
C(8) - C(9)	138.5(1)	138.8(2)	N(1') - C(2')	145.6(1)	146.2(2)
C(9) - C(10)	138.2(1)	138.6(2)	N(1') - C(6')	145.9(1)	145.8(2)
C(10) - C(11)	138.7(1)	139.3(2)	N(1') - C(1")	146.5(2)	145.1(2)
C(10) - C(13)	153.6(1)	154.2(1)	C(2') - C(3')	151.3(1)	151.0(2)
C(11) - C(12)	137.9(1)	138.6(2)	C(5') - C(6')	151.1(1)	152.1(2)

2 Benzene	A		B
C(A1) - C(A2)	135.8(2)	C(B1) - C(B2)	136.4(2)
C(A1) - C(A3i)	136.1(2)	C(B1) - C(B3ii)	136.0(2)
C(A2) - C(A3)	135.9(2)	C(B2) - C(B3)	136.3(2)

3 o - Xulene			
C(A1) - C(A2)	138.5(2)	C(A2) - C(A3)	137.4(2)
C(A1) - C(A3v)	137.5(2)	C(A2) - C(A2')	151.2(3)

i) : x' = 1 - x ; y' = 1 - y ; z' = 1 - z

ii) : x' = - x ; y' = - y ; z' = - z

v) : x' = - x ; y' = 1 - y ; z' = 1 - z

C(5'), C(6') of the spiropiperidine ring form angles of 89°, 81°, and 85°, respectively, with the least square molecular plane of **1**. The lone pairs of the four ether oxygens are directed outward of the cavity. The sequence of the torsional angles of the chains bridging the diphenylmethane units, C(17i)–O(1)–C(2)–C(3)–C(4)–C(5)–O(6)–C(7), is ap(antiperiplanar)–ap–sc(synclinal)–sc–ap. All hydrogen atoms of the tetramethylene bridges take staggered positions. With values of 150.2 and 151.3 pm, the C–C bond lengths of the tetramethylene bridges of **1** are short and comparable to the short C–C bond lengths observed for the methylene bridges of higher [n.n.]paracyclophanes[20]. The spiropiperidine rings take chair conformations and the methyl group C(1") at N(1') is in an equatorial position. As has been established for other piperidine derivatives before[21], the spiropiperidine rings of **1** are more puckered than the cyclohexane ring (see torsional angles in Table 5).

Table 5. Bond angles and torsional angles of **2** and **3** (in °, numbers in parentheses are estimated standard deviations in units of the last quoted digit)

Host	2	3		2	3		2	3
C(2) - O(1) - C(17i)	118.0(1)	117.4(1)	C(11) - C(10) - C(13)	122.4(1)	123.7(1)	C(15) - C(16) - C(17)	120.3(1)	120.5(1)
O(1) - C(2) - C(3)	107.6(1)	108.2(1)	C(10) - C(11) - C(12)	122.1(1)	121.6(1)	O(11) - C(17) - C(16)	115.6(1)	116.7(1)
C(2) - C(3) - C(4)	112.9(1)	115.1(1)	C(7) - C(12) - C(11)	120.2(1)	120.8(1)	O(11) - C(17) - C(18)	124.9(1)	124.4(1)
C(3) - C(4) - C(5)	115.1(1)	112.5(1)	C(10) - C(13) - C(14)	105.0(1)	106.4(1)	C(16) - C(17) - C(18)	119.5(1)	119.0(1)
C(4) - C(5) - O(6)	107.6(1)	107.8(1)	C(10) - C(13) - C(3')	111.0(1)	111.3(1)	C(17) - C(18) - C(19)	119.2(1)	119.7(1)
C(5) - O(6) - C(7)	118.3(1)	117.4(1)	C(10) - C(13) - C(5')	110.3(1)	110.5(1)	C(14) - C(19) - C(18)	122.6(1)	122.9(1)
O(6) - C(7) - C(8)	124.6(1)	124.4(1)	C(14) - C(13) - C(3')	111.5(1)	111.3(1)	C(2') - N(1') - C(6')	110.7(1)	110.3(1)
O(6) - C(7) - C(12)	116.1(1)	116.6(1)	C(14) - C(13) - C(5')	112.8(1)	112.6(1)	C(2') - N(1') - C(1")	110.4(1)	111.1(1)
C(8) - C(7) - C(12)	119.2(1)	119.0(1)	C(3') - C(13) - C(5')	104.7(1)	104.9(1)	C(6') - N(1') - C(1")	109.5(1)	110.6(1)
C(7) - C(8) - C(9)	119.8(1)	119.5(1)	C(13) - C(14) - C(15)	121.6(1)	123.8(1)	N(1') - C(2') - C(3')	112.3(1)	111.2(1)
C(8) - C(9) - C(10)	122.5(1)	122.8(1)	C(13) - C(14) - C(19)	121.8(1)	120.1(1)	C(13) - C(3') - C(2')	112.5(1)	113.8(1)
C(9) - C(10) - C(11)	116.2(1)	116.3(1)	C(15) - C(14) - C(19)	116.3(1)	116.0(1)	C(13) - C(5') - C(6')	113.6(1)	113.7(1)
C(9) - C(10) - C(13)	121.2(1)	119.9(1)	C(14) - C(15) - C(16)	122.0(1)	122.0(1)	N(1') - C(6') - C(5')	111.7(1)	111.9(1)

2 Benzene	A		B
C(A2) - C(A1) - C(A3i)	119.9(2)	C(B2) - C(B1) - C(B3ii)	119.9(1)
C(A1) - C(A2) - C(A3)	119.7(2)	C(B1) - C(B2) - C(B3)	120.1(1)
C(A1i) - C(A3) - C(A2)	120.4(2)	C(B1ii)-C(B3) - C(B2)	120.0(1)

3 p - Xylene			
C(A2) - C(A1) - C(A3v)	121.8(2)	C(A1) - C(A2) - C(A2')	122.0(2)
C(A1) - C(A2) - C(A3)	116.4(2)	C(A3) - C(A2) - C(A2')	121.5(2)
C(A1v)- C(A3) - C(A2)	121.8(2)		

	2	3		2	3
C(17i)- O(1) - C(2) - C(3)	175.9	177.1	C(10) - C(13) - C(14) - C(19)	80.7	72.4
C(2) - O(1) - C(17i)- C(16i)	-171.2	-176.2	C(3') - C(13) - C(14) - C(15)	144.5	135.5
C(2) - O(1) - C(17i)- C(18i)	8.5	3.5	C(3') - C(13) - C(14) - C(19)	-41.1	-48.9
O(1) - C(2) - C(3) - C(4)	176.9	-62.6	C(5') - C(13) - C(14) - C(15)	27.0	18.0
C(2) - C(3) - C(4) - C(5)	75.8	-68.8	C(5') - C(13) - C(14) - C(19)	-158.6	-166.4
C(3) - C(4) - C(5) - O(6)	63.1	-179.8	C(10) - C(13) - C(3') - C(2')	174.4	174.1
C(4) - C(5) - O(6) - C(7)	-167.9	-170.4	C(14) - C(13) - C(3') - C(2')	-67.4	-67.5
C(5) - O(6) - C(7) - C(8)	-21.7	-7.7	C(5') - C(13) - C(3') - C(2')	54.9	54.6
C(5) - O(6) - C(7) - C(12)	158.7	172.1	C(10) - C(13) - C(5') - C(6')	-175.5	-172.7
O(6) - C(7) - C(8) - C(9)	179.0	177.2	C(14) - C(13) - C(5') - C(6')	66.4	68.5
C(12) - C(7) - C(8) - C(9)	-1.4	-2.6	C(3') - C(13) - C(5') - C(6')	-55.0	-52.7
O(6) - C(7) - C(12) - C(11)	-178.8	-177.9	C(13) - C(14) - C(15) - C(16)	173.4	176.2
C(8) - C(7) - C(12) - C(11)	1.5	1.8	C(19) - C(14) - C(15) - C(16)	-1.3	0.4
C(7) - C(8) - C(9) - C(10)	-0.1	1.5	C(13) - C(14) - C(19) - C(18)	-173.5	-176.4
C(8) - C(9) - C(10) - C(11)	1.4	0.4	C(15) - C(14) - C(19) - C(18)	1.2	-0.4
C(8) - C(9) - C(10) - C(13)	-174.0	-176.3	C(14) - C(15) - C(16) - C(17)	0.5	-0.2
C(9) - C(10) - C(11) - C(12)	-1.3	-1.2	C(15) - C(16) - C(17) - C(18)	0.6	0.0
C(13) - C(10) - C(11) - C(12)	174.1	175.4	C(16) - C(17) - C(18) - C(19)	-0.8	-0.1
C(9) - C(10) - C(13) - C(14)	83.7	70.1	C(17) - C(18) - C(19) - C(14)	-0.1	0.3
C(9) - C(10) - C(13) - C(3')	-154.7	-168.5	C(6') - N(1') - C(2') - C(3')	56.4	58.6
C(9) - C(10) - C(13) - C(5')	-38.6	-52.4	C(1") - N(1') - C(2') - C(3')	177.8	-178.3
C(11) - C(10) - C(13) - C(14)	-91.5	-106.3	C(2') - N(1') - C(6') - C(5')	-55.5	-56.7
C(11) - C(10) - C(13) - C(3')	30.1	15.0	C(1") - N(1') - C(6') - C(5')	-177.5	179.9
C(11) - C(10) - C(13) - C(5')	146.2	131.2	N(1') - C(2') - C(3') - C(13)	-58.5	-60.1
C(10) - C(11) - C(12) - C(7)	-0.2	0.1	C(13) - C(5') - C(6') - N(1')	57.7	56.3
C(10) - C(13) - C(14) - C(15)	-93.7	-103.2			

Benzene guest A is perfectly enclosed within the intramolecular cavity of **1**. The plane of benzene forms an angle of 45° with the least square molecular plane of **1** and the intersect of these planes forms an angle of 10° with the normal to the least square plane through C(2′), C(3′), C(5′), and C(6′) of the spiropiperidine ring. As consequence of this orientation, short contacts exist between the carbon atoms C(A1) and C(A2) of the guest and carbon atoms of the aromatic rings of **1** located on the larger sides of the rectangular cavity (Figure 1; Table 6). With 345 pm, the shortest contact is observed between C(A2) of the guest and C(17) of **1**. Benzene guest A interacts via short H···C-contacts with the aromatic rings of the smaller side of the cavity of **1** (Table 6).

Table 6. Some short distances in **2** (in pm)

Short distances between host **1** and benzene ring A:					
C(17)...C(A2)	(x, y, z)	345.0	O(1)...C(A2)	$(1-x, 1-y, 1-z)$	359.7
C(18)...C(A1)	(x, y, z)	362.2	C(12)...H(A3)	$(1-x, 1-y, 1-z)$	302
C(17)...C(A1)	(x, y, z)	371.8	C(17)...H(A2)	(x, y, z)	302
C(18)...C(A2)	(x, y, z)	376.3	C(16)...H(A2)	(x, y, z)	313
C(16)...C(A2)	(x, y, z)	377.6	C(9)...H(A1)	(x, y, z)	315
C(12)...C(A3)	$(1-x, 1-y, 1-z)$	378.3	O(1)...H(A2)	$(1-x, 1-y, 1-z)$	309
C(7)...C(A3)	$(1-x, 1-y, 1-z)$	384.1	H(2′A)...H(A1)	$(-1+x, y, z)$	261
C(2′)...C(A2)	$(-1+x, y, z)$	369.4	H(2′B)...H(A2)	$(-1+x, y, z)$	264
C(2′)...C(A1)	$(-1+x, y, z)$	379.0			
Short distances between host **1** and benzene ring B:					
C(6′)...C(B3)	$(-x, -y, -z)$	363.8	C(11)...H(B3)	$(x, 1+y, z)$	299
C(6′)...C(B2)	$(-x, -y, -z)$	376.5	C(12)...H(B3)	$(x, 1+y, z)$	304
C(15)...C(B1)	$(-x, -y, -z)$	376.5	C(1″)...H(B2)	$(-1-x, -y, -z)$	310
C(6′)...C(B1)	(x, y, z)	384.1	C(1″)...H(B1)	$(-1-x, -y, -z)$	313
C(1″)...C(B2)	$(-1-x, -y, -z)$	375.1	H(1′A)...H(B6)	$(-1-x, -y, -z)$	265
C(1″)...C(B1)	$(-1-x, -y, -z)$	375.8			
Short distances between host molecules:					
C(3)...C(18)	$(1+x, 1+y, z)$	374.8	O(1)...C(12)	$(1-x, 2-y, 1-z)$	369.5
C(5′)...C(5′)	$(-x, 1-y, -z)$	375.0	O(1)...C(6)	$(1-x, 2-y, 1-z)$	370.9
C(12)...C(16)	$(x, 1+y, z)$	382.9	O(1)...C(2)	$(2-x, 2-y, 1-z)$	374.7
O(6)...C(16)	$(x, 1+y, z)$	358.3			
Short distances involving the water molecule:					
O...N(1′)	(x, y, z)	291.1	O...C(6′)	$(-1-x, 1-y, -z)$	356.4
O...N(1′)	$(-1-x, 1-y, -z)$	291.4	[O...O	$(-1-x, 1-y, -z)$	231.9]
O...C(1″)	(x, y, z)	279.3			

In the **2**-crystals the host molecules form band type structures along [110]. Short contacts between host molecules are given in Table 6. Figure 3 shows the crystal packing of **2** in the projection along *a* and depicts the position of benzene guest B and the water molecule in the crystal lattice, located both in [001]. Benzene guest B occupies intermolecular channel type cavities along the *a* axis. The van der Waals interactions of this guest with the neighbouring macrocycles are considerably weaker than the interactions between **1** and the intramolecularly enclosed benzene ring A (Table 6). The shortest intermolecular C···C-contact of guest B is 363.8 pm compared to 345 pm for the shortest intramolecular C···C-contact between **1** and benzene ring A. The C–C-bond lengths of both benzene guests are short with a mean value of 136 pm. This is a consequence of the considerable temperature factors of both guests. The thermal parameters U_{equ} of their carbon atoms are almost twice as large as U_{equ} of the aromatic carbon atoms of **1** (Table 2).

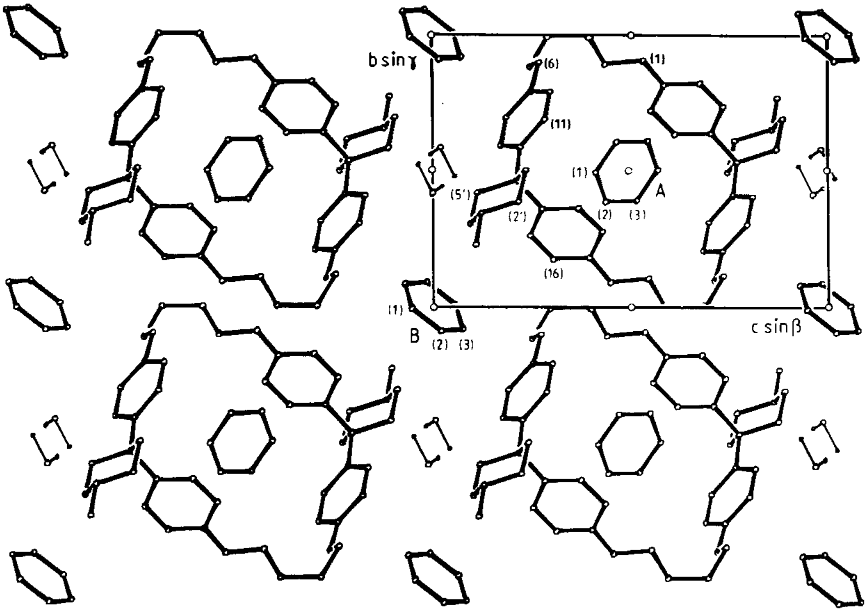


Figure 3. Crystal packing of **2** as shown in the projection along *a*

Two water molecules, each with occupancy 0.5 and related by an inversion center at 0.5, 0.5, 0, are located between the host molecules and the benzene rings **B**. The water molecules are presumably contributing significantly to the stability of the crystal lattice. Their position enables them to form hydrogen bonds to the tertiary nitrogens of the spiropiperidines of neighbouring bands (N···H—O-distance of 291 pm).

Molecular Geometry of the **1**-*p-Xylene (1/1) Complex* **3**: The most striking feature of the structure of **3** is a completely different location of the aromatic guest as compared to the location of the two benzenes in **2**. In **3**, host molecules form stacks along the *a* axis and the *p*-xylene molecules are sandwiched by two adjacent host molecules in the stacks.

Besides many similarities, the molecular geometries of host **1** in complexes **2** and **3** exhibit distinct differences. The least square molecular plane of **1** is defined as described above for **1** in complex **2**. Figure 4 is a view onto this plane and Figure 5 a view parallel to this plane. The cavity of the host in complex **3** is more

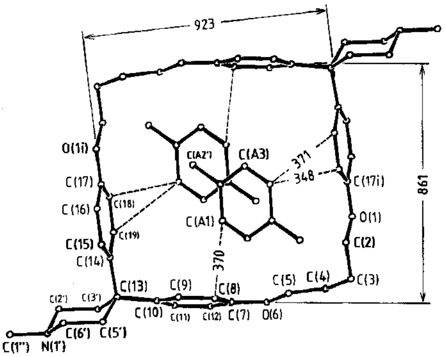


Fig. 4

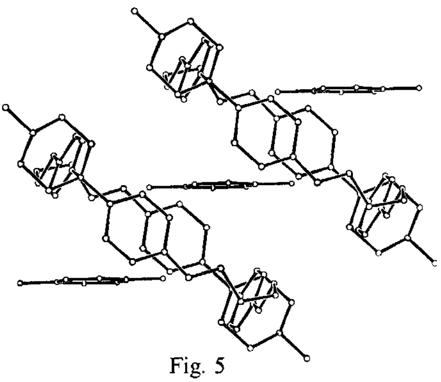


Fig. 5

Figure 4. Molecular structure of **3** in a view onto the least square plane of the host. The host and two *p*-xylenes, penetrating each with one methyl group from one side into the intramolecular cavity, are shown. Some short C···C host-guest contacts and characteristic extensions of the cavity are shown (for details see text)

Figure 5. Stacking feature of the host in **3** and position of the *p*-xylene in a view parallel to the least square plane of the host

quadratic than in complex **2**. The extensions of **1** between the least square planes passing through parallel benzene rings are 923 and 861 pm (Figure 4). The "face to face" conformation of host **1** in complex **3** is less ideal than in complex **2**. The least square planes through the benzene ring of the larger cavity and through the benzene ring of the smaller cavity site form angles of 69° and 77°, respectively, with the least square molecular plane of **1**. In **3**, the sequence of the torsional angles of the chains C(17i)–O(1)–C(2)–C(3)–C(4)–C(5)–O(6)–C(7) bridging the diphenylmethane units is ap–sc–sc–ap–ap, and all hydrogen atoms are staggered. The geometry of the spiropiperidine rings is very similar in both complexes. In **3**, the least square plane through C(2'), C(3'), C(5'), and C(6') of the piperidine ring forms an angle of 88° with the least square molecular plane of **1**. Bond lengths and bond angles of **1** in both complexes are very similar (Tables 4 and 5). C–C-, C–O-, and C–N-bond lengths of **1** in complexes **2** and **3** differ only by 2 pm at maximum.

The host molecules in the **3**-crystals are stacked along the *a* axis with the stacking axis forming an angle of 14° with the least square molecular planes of the **1**-molecules (Figure 5). Neighbouring **1**-molecules in the stack are laterally shifted to each other parallel to the molecular plane by 151 pm. Short contacts between host compounds in a stack and between host compounds in neighbouring stacks are shown in Table 7. The *p*-xylene molecules are sandwiched between two adjacent macrocycles in the stack. The two methyl groups of a *p*-xylene molecule are inserted into the cavities of the two sandwiching hosts. The plane of *p*-xylene forms an angle of 41° with the least square molecular plane of the host and the intersect of these planes forms an angle of 2° with the normal to the least square plane through C(2'), C(3'), C(5'), and C(6') of the spiropiperidine ring. The angle of 41° in **3** is similar to the angle of 45° between the plane of benzene guest A and the least square molecular plane of **1** in complex **2**.

Table 7. Some short distances in **3** (in pm)

Short distances between host **1** and *p*-xylene:					
C(18)...C(A1)	$(-x, 1-y, 1-z)$	348.4	O(6)...C(A2′)	(x, y, z)	383.1
C(8)...C(A1)	$(1-x, 1-y, 1-z)$	370.4	C(8)...H(A1)	$(1-x, 1-y, 1-z)$	303
C(19)...C(A1)	$(-x, 1-y, 1-z)$	370.5	C(9)...H(A1)	$(1-x, 1-y, 1-z)$	312
C(5)...C(A2′)	(x, y, z)	383.1	C(12)...H(A3)	(x, y, z)	313
C(19)...C(A3)	(x, y, z)	386.1	H(5B)...H(A2C)	(x, y, z)	254
C(18)...C(A3)	(x, y, z)	388.9	H(8)...H(A3)	$(1+x, y, z)$	260
Short distances between host molecules:					
C(1″)...C(1″)	$(-x, 2-y, -z)$	349.3	C(16)...O(1)	$(x, 1+y, z)$	366.0
C(2)...C(17)	$(1+x, -1+y, z)$	369.5	O(6)...C(1″)	$(1-x, 1-y, -z)$	366.0
C(5′)...C(2′)	$(1+x, y, z)$	373.7	O(1)...C(2)	$(2-x, -y, 1-z)$	373.9
C(7)...C(1″)	$(1-x, 1-y, -z)$	380.9	O(1)...O(1)	$(2-x, -y, 1-z)$	375.8
C(3)...C(17)	$(1+x, -1+y, z)$	382.1	C(7)...N(1′)	$(1-x, 1-y, -z)$	368.0
C(3)...C(18)	$(1+x, -1+y, z)$	383.4	C(8)...N(1′)	$(1-x, 1-y, -z)$	371.6

There exist expectedly less short C···C-contacts between *p*-xylene and **1** in **3** than between benzene ring A and host **1** in **2**. With 348 pm, the shortest C···C-contact is observed between C(A1) and C(18) (Table 7). *p*-Xylene interacts via short H···C-contacts with the benzene rings of the large cavity side. It is noticeable that in both complexes the guests located in the intramolecular cavities almost exclusively interact with the aromatic rings of **1** and not with the tetramethylene-bridges of the host. With a mean value of 138 pm, the aromatic C–C-bond lengths of *p*-xylene are longer than the C–C-bond lengths of the two benzene guests of complex **2** (Table 4). The thermal parameters U_{equ} of the carbon atoms of *p*-xylene are sligthly smaller than those of the carbon atoms of the two benzene guests in **2**, but still considerably larger than the thermal parameters of the aromatic carbon atoms of **1** in complex **3** (Table 3).

Discussion

In analogy to the solid state complexes formed by cyclodextrins, the guests in **2** and **3** are enclosed either completely (benzene) or to a significant extent (*p*-xylene) within the molecular cavity of host **1**. From its geometry, the molecular and crystal structure of **2** is analogous to the structure of the α-cyclodextrin-*m*-nitrophenol (1/2) complex[22], in which one guest molecule penetrates the intramolecular cavity whereas the second guest molecule is located between host molecules in the crystal lattice. The geometry of **3** is comparable to the geometry of the α-cyclodextrin-1-phenylethanol (1/1) tetrahydrate[7], in which the guest molecules are also sandwiched between adjacent macrocycles in the stacks of the cyclodextrin molecules.

There is much discussion about the conditions which lead to preference of intramolecular cavity inclusion of an apolar guest over intermolecular lattice inclusion in crystalline complexes formed by macrocyclic hosts having apolar cavities[11,13,16]. One essential requirement for intramolecular cavity inclusion is of course the geometric fit of the guest to the cavity of the host. Another important requirement in host-guest chemistry for intramolecular cavity inclusion of a guest in the crystalline state as well as in solution has been clearly recognized by *Cram* and coworkers[23,24]. A macrocyclic host should not have energetically favourable conformations in which the host fills its own cavity. Thus the host of the *Stetter* complexes would have to reorganize to an energetically less favourable conformation if the benzene guest in the solid state had to be enclosed within the intramolecular cavity[11]. Cyclodextrins possess enforced and organized cavities and intramolecular cavity inclusion is always observed[1,4]. Diphenylmethane units enforce and organize to a large extent the cavities of host **1** and of the host described by *Koga*[14]. The "face to face" conformation of these hosts seems to be energetically favourable.

These geometrical requirements however are not necessarily sufficient to guarantee intramolecular cavity inclusion in crystalline complexes of apolar hosts and guests[12,13,16]. Van der Waals contacts between macrocyclic host and guest might be of the same magnitude in crystals with the guest located in intermolecular cavities of the host lattice than in crystals with the guest located in the intramolecular cavity of the host. Furthermore, molecular packing effects can be more important than differences in van der Waals interactions in determining the location of the guest in the crystalline complex. Molecular cavity inclusion seems especially favoured to us if the crystals are grown from a solution, in which there exist already strong interactions between host and guest. In aqueous solution, hydrophobic interactions lead to the complexation of apolar guests in the apolar cavities of macrocyclic hosts[17,25] and the host-guest complexes can crystallize as a kind of preformed entity. Crystallization from aqueous solution has indeed led most often to molecular cavity inclusion[1,4-9,14].

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[18] Further information concerning the *X*-ray structure analyses of **2** and **3** may be requested from Fachinformationszentrum Energie Physik Mathematik, D-7514 Eggenstein-Leopoldshafen, with indication of the registry number CSD-51115, the authors' names, and the journal citation.

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