357

Crystal Structure of a p-Benzylcalix[5]arene-pyridine Complex

PIERRE THUÉRY and MARTINE NIERLICH
CEA/Saclay, SCM (CNRS URA 331), Bât. 125, 91191 Gif-sur-Yvette, France.

BAHARI SOULEY, ZOUHAIR ASFARI and JACQUES VICENS
ECPM, Laboratoire de Chimie des Interactions Moléculaires Spécifiques (CNRS URA 405), 1 rue Blaise Pascal, 67008 Strasbourg, France.

Abstract. p-Benzylcalix[5]arene.3py (py = pyridine) (**1**) crystallizes in the triclinic space group $P\bar{1}$, $a = 10.641(3)$, $b = 13.975(3)$, $c = 24.052(12)$ Å, $\alpha = 94.60(4)$, $\beta = 91.51(4)$, $\gamma = 111.46(2)°$, $V = 3312(4)$ Å^3, $Z = 2$. Refinement led to a final conventional R value of 0.065 for 5457 reflections. The calixarene is in a distorted *cone* conformation. Two pyridine molecules are hydrogen bonded to phenolic oxygen atoms and one of them is included in the hydrophobic cavity of the neighboring calixarene molecule along the a axis.

Key words: calixarenes, crystal structure, supramolecular assembly.

1. Introduction

Calixarenes with an odd number of phenolic units are far less available than those with an even number, due to low synthetic yields. As a result, the investigation of calix[n]arenes with $n = 5$ or 7 has not reached the same development as that of compounds with $n = 4, 6$ or 8. However, a significant number of crystal structures of calix[5]arene and its derivatives have been described [1–17]. They comprise the structures of p-R-calix[5]arenes (R = H, tetramethylbutyl, *tert*-butyl) with included organic molecules or self-inclusion [1–3, 6, 7] or with complexed metal ions [17], p-sulfonato derivatives and some of their metal complexes [10, 14], π-metalated species [15] and various *lower rim* derivatives [11, 12, 13]. Recently, the structure of a complex of C60 has been reported, in which the fullerene molecule is encapsulated by two calix[5]arene iodo derivatives [16]. In this paper, we report the crystal structure of a complex between p-benzylcalix[5]arene and pyridine.

2. Experimental

2.1. SYNTHESIS

p-Benzylcalix[5]arene was synthesized as previously described [18]. Its recrystallization from pyridine yielded beautiful colorless crystals suitable for X-ray crystallography.

2.2. CRYSTAL STRUCTURE ANALYSIS

Crystal Data

p-Benzylcalix[5]arene.3py, $O_5N_3C_{85}H_{75}$, formula weight 1218.56, triclinic, space group $P\bar{1}$, $a = 10.641(3)$, $b = 13.975(3)$, $c = 24.052(12)$ Å, $\alpha = 94.60(4)$, $\beta = 91.51(4)$, $\gamma = 111.46(2)°$, $V = 3312(4)$ Å^3, $Z = 2$, $D_x = 1.222$, $\mu = 0.701$ cm^{-1}, $F(000) = 1292$.

Data Collection

The diffraction experiment was performed with an Enraf-Nonius CAD4 diffractometer using graphite monochromatized Mo$K\alpha$ radiation. The crystal (0.64 × 0.60 × 0.50 mm) was introduced in a glass capillary. The lattice parameters were determined from the least-squares refinement of the setting angles of 25 reflections ($8 < \theta < 12°$). The data were collected in the range $1 < \theta < 24°$ ($-12 < h < 12, -16 < k < 16, 0 < l < 27$), in the $\omega/2\theta$ scan mode, at 295 K. The intensity decay was estimated from three standard reflections, measured every 60 min (29.4% in 103 hours, linearly corrected). The data were corrected for Lorentz-polarization, but not for absorption effects.

Structure Analysis

The structure was solved by direct methods with SHELXS-86 [19] and refined by full-matrix least-squares on F. 5457 observations with $I > 2\sigma(I)$, out of 10486 unique reflections measured ($R_{\text{int.}} = 0.007$), were used. 808 parameters have been refined, with all non-hydrogen atoms anisotropic, apart from the ones of the non-bonded pyridine molecule, in which the nitrogen atom has not been identified. Hydrogen atoms bonded to carbon atoms were located at their ideal positions (C—H 0.95 Å, B 6 Å^2) and constrained to ride their parent carbon atom. The hydrogen atoms of the phenolic groups appeared on the last Fourier maps and were included as riding atoms (B 6 Å^2). Analytical scattering factors were taken from [20]. The final R values were $R = 0.065$ and $R_w = 0.066$ (unit weights), the goodness-of-fit parameter $S = 1.83$ and the maximum residual density 0.45 eÅ^{-3}. All calculations have been performed on a Vax 4000-200 computer, with the Enraf-Nonius MolEN system [21]. *ORTEPII* [22] drawings of the structure of **1** are represented in Figures 1 and 2, fractional atomic coordinates and equivalent
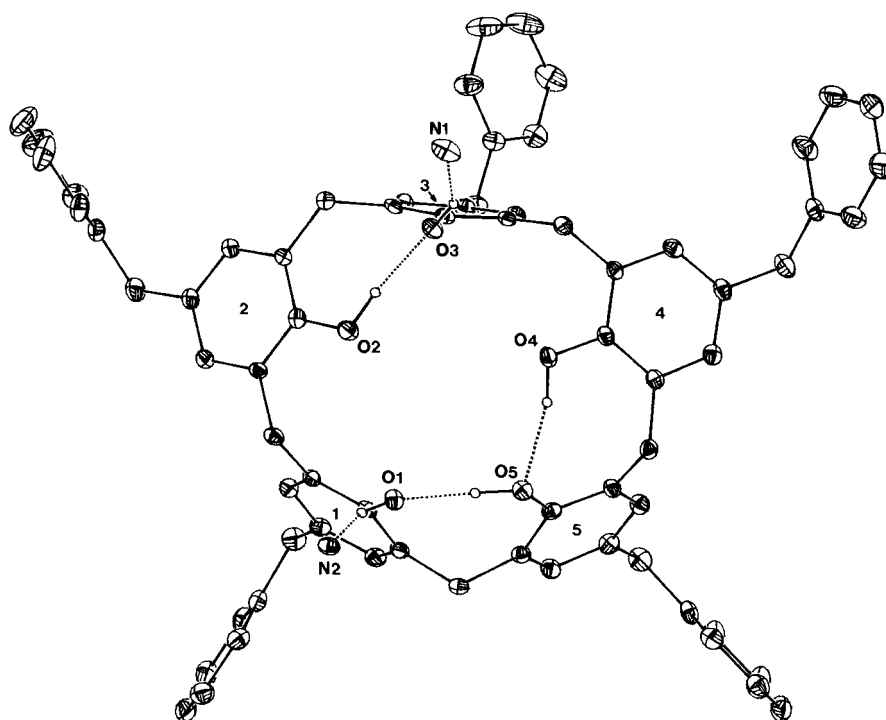
Figure 1. View of the molecular unit of **1** parallel to the oxygen atoms mean plane. Hydrogen bonds in dashed lines, phenolic hydrogen atoms represented as small spheres of arbitrary radius. Nitrogen atoms from the two nearer pyridine molecules only are represented. The numbering of phenolic rings is indicated. Non-bonded solvent molecule omitted.

isotropic displacement parameters are given in Table I and selected geometric parameters in Table II (all bond distances and angles lie in the usual range).

3. Results and Discussion

The *p*-benzylcalix[5]arene molecule does not possess any symmetry element. Its conformation is a distorted *cone*, as evidenced by the $(-+)_5$ sequence of ϕ and χ torsion angles, as defined by Ugozzoli and Andreetti [23]. The five carbon atoms of the methylene bridges define a plane within $\pm0.516(5)$ Å that cannot be considered as a proper reference plane. The oxygen atoms mean plane is better defined: the five oxygen atoms are in a plane within $\pm0.252(4)$ Å and the dihedral angles of the five phenolic rings with this plane are 66.5(1), 37.7(2), 88.7(1), 22.0(3) and 59.1(1)° for rings 1–5 respectively (see Figure 1 for the numbering scheme). Two rings (2 and 4) are tilted towards this plane whilst one (3) is nearly perpendicular to it. The two other rings (1 and 5) make dihedral angles typical of what is generally found in *cone* conformations, and ideal for hydrogen bonding [1]. Up to now, the majority of calix[5]arene derivatives appear to be in the *cone* conformation, but

Table I. Fractional atomic coordinates and isotropic or equivalent isotropic ($B_{eq.} = (4/3)\Sigma_i\Sigma_j\beta_{ij}\mathbf{a}_i.\mathbf{a}_j$) displacement parameters (Å^2) for non-hydrogen atoms, with ESD in parentheses. Starred atoms were refined isotropically.

Atom	x/a	y/b	z/c	$B_{iso.}, B_{eq.}$
O(1)	0.2618(3)	−0.0023(2)	0.4188(2)	3.88(8)
O(2)	0.0153(4)	−0.1015(3)	0.2992(2)	4.64(9)
O(3)	−0.0794(3)	0.0266(3)	0.2360(2)	4.40(9)
O(4)	0.2337(3)	0.2209(2)	0.3044(2)	4.31(9)
O(5)	0.3731(3)	0.2008(2)	0.4034(2)	3.96(8)
C(1)	0.3364(5)	−0.0599(4)	0.3987(2)	3.4(1)
C(2)	0.4763(5)	−0.0137(4)	0.4068(2)	3.5(1)
C(3)	0.5526(5)	−0.0676(4)	0.3841(2)	4.4(1)
C(4)	0.4941(5)	−0.1651(4)	0.3561(2)	4.0(1)
C(5)	0.3553(5)	−0.2090(4)	0.3501(2)	3.9(1)
C(6)	0.2727(5)	−0.1580(4)	0.3712(2)	3.3(1)
C(7)	0.5812(5)	−0.2237(4)	0.3346(3)	5.2(2)
C(8)	0.6347(5)	−0.2745(4)	0.3781(3)	4.1(1)
C(9)	0.7328(5)	−0.3136(4)	0.3626(3)	4.7(1)
C(10)	0.7800(6)	−0.3647(4)	0.3993(3)	5.9(2)
C(11)	0.7307(6)	−0.3784(4)	0.4512(3)	6.2(2)
C(12)	0.6358(6)	−0.3381(5)	0.4675(3)	6.0(2)
C(13)	0.5887(5)	−0.2856(4)	0.4306(2)	4.8(1)
C(14)	0.1203(5)	−0.2112(4)	0.3655(2)	3.7(1)
C(15)	0.0608(5)	−0.2524(4)	0.3068(2)	3.2(1)
C(16)	0.0119(5)	−0.1942(4)	0.2742(2)	3.5(1)
C(17)	−0.0442(5)	−0.2312(4)	0.2202(2)	3.5(1)
C(18)	−0.0460(5)	−0.3271(4)	0.1985(2)	4.3(1)
C(19)	0.0019(5)	−0.3871(4)	0.2301(2)	4.2(1)
C(20)	0.0528(5)	−0.3486(4)	0.2843(2)	4.1(1)
C(21)	0.0074(6)	−0.4890(4)	0.2047(3)	5.6(2)
C(22)	−0.1126(6)	−0.5575(4)	0.1678(2)	4.6(1)
C(23)	−0.0954(7)	−0.6101(5)	0.1195(3)	6.7(2)
C(24)	−0.2058(8)	−0.6757(6)	0.0862(4)	9.3(2)
C(25)	−0.3329(8)	−0.6856(6)	0.1004(4)	10.1(3)
C(26)	−0.3517(7)	−0.6341(5)	0.1472(4)	8.7(3)
C(27)	−0.2425(6)	−0.5714(4)	0.1808(3)	6.0(2)
C(28)	−0.0975(5)	−0.1684(4)	0.1846(2)	4.3(1)
C(29)	0.0095(5)	−0.0662(4)	0.1725(2)	3.6(1)
C(30)	0.0107(5)	0.0280(4)	0.1955(2)	3.5(1)
C(31)	0.1067(5)	0.1204(4)	0.1820(2)	3.6(1)
C(32)	0.2059(5)	0.1154(4)	0.1468(2)	3.7(1)
C(33)	0.2111(5)	0.0220(4)	0.1249(2)	3.9(1)
C(34)	0.1107(5)	−0.0671(4)	0.1375(2)	3.7(1)
C(35)	0.3229(5)	0.0188(4)	0.0888(2)	4.8(1)

Table I. Continued.

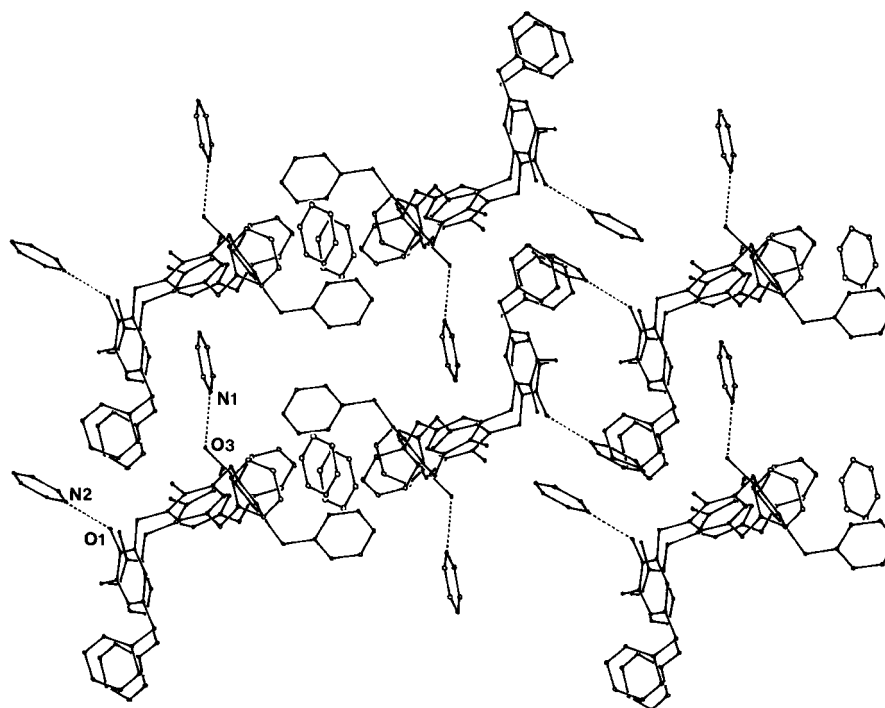| Atom	x/a	y/b	z/c	$B_{\text{iso.}}$, $B_{\text{eq.}}$
C(36)	0.3044(5)	0.0307(4)	0.0279(2)	4.3(1)
C(37)	0.4110(6)	0.0819(5)	−0.0029(3)	5.8(2)
C(38)	0.3959(7)	0.0908(5)	−0.0592(3)	7.7(2)
C(39)	0.2715(7)	0.0474(6)	−0.0852(3)	8.5(2)
C(40)	0.1642(7)	−0.0028(7)	−0.0569(3)	8.9(3)
C(41)	0.1792(6)	−0.0110(5)	−0.0002(3)	6.8(2)
C(42)	0.1016(5)	0.2233(4)	0.2050(2)	4.2(1)
C(43)	0.2355(5)	0.3063(3)	0.2238(2)	3.5(1)
C(44)	0.2971(5)	0.3033(3)	0.2748(2)	3.5(1)
C(45)	0.4142(5)	0.3844(4)	0.2970(2)	3.5(1)
C(46)	0.4717(5)	0.4657(4)	0.2644(2)	4.2(1)
C(47)	0.4169(5)	0.4699(4)	0.2122(2)	4.2(1)
C(48)	0.2968(5)	0.3891(4)	0.1932(2)	4.0(1)
C(49)	0.4888(6)	0.5573(4)	0.1771(3)	5.8(2)
C(50)	0.4010(6)	0.6057(4)	0.1499(2)	4.8(1)
C(51)	0.3473(7)	0.5748(5)	0.0962(3)	7.2(2)
C(52)	0.2667(8)	0.6198(5)	0.0715(3)	8.3(2)
C(53)	0.2406(7)	0.6959(5)	0.1004(3)	7.4(2)
C(54)	0.2894(7)	0.7275(5)	0.1532(3)	7.3(2)
C(55)	0.3687(6)	0.6821(5)	0.1783(3)	6.4(2)
C(56)	0.4721(5)	0.3890(4)	0.3554(2)	3.9(1)
C(57)	0.5556(5)	0.3229(4)	0.3627(2)	3.5(1)
C(58)	0.5060(4)	0.2336(4)	0.3897(2)	3.5(1)
C(59)	0.5894(5)	0.1802(4)	0.4040(2)	3.6(1)
C(60)	0.7180(5)	0.2138(4)	0.3851(2)	4.3(1)
C(61)	0.7680(5)	0.2979(4)	0.3543(2)	4.2(1)
C(62)	0.6861(5)	0.3528(4)	0.3448(2)	4.2(1)
C(63)	0.9091(5)	0.3325(5)	0.3337(3)	5.4(2)
C(64)	1.0150(5)	0.4191(4)	0.3703(2)	4.4(1)
C(65)	1.1504(6)	0.4476(4)	0.3583(3)	6.3(2)
C(66)	1.2505(6)	0.5258(5)	0.3895(3)	7.3(2)
C(67)	1.2177(6)	0.5789(5)	0.4336(3)	6.5(2)
C(68)	1.0852(6)	0.5545(5)	0.4462(3)	5.9(2)
C(69)	0.9854(5)	0.4745(4)	0.4146(2)	5.0(1)
C(70)	0.5441(5)	0.0900(4)	0.4390(2)	3.8(1)
N(1)	−0.3078(5)	0.0641(4)	0.2256(2)	6.7(1)
C(71)	−0.3334(7)	0.1482(6)	0.2214(4)	8.4(2)
C(72)	−0.4552(7)	0.1543(6)	0.2321(4)	9.0(2)
C(73)	−0.5575(7)	0.0729(5)	0.2456(3)	7.4(2)
C(74)	−0.5355(7)	−0.0144(6)	0.2490(3)	9.0(2)
C(75)	−0.4086(7)	−0.0158(5)	0.2385(3)	9.3(2)

Figure 2. View of the crystal packing. a axis vertical, c axis horizontal. Hydrogen bonds in dashed lines.

Table I. Continued.

Atom	x/a	y/b	z/c	$B_{iso.}, B_{eq.}$
N(2)	0.1146(4)	−0.0726(3)	0.5032(2)	4.0(1)
C(76)	−0.0390(6)	−0.1747(5)	0.5646(3)	5.5(2)
C(77)	0.0263(5)	−0.1630(4)	0.5156(2)	4.8(2)
C(78)	0.1358(5)	0.0084(4)	0.5407(2)	4.2(1)
C(79)	0.0736(5)	0.0024(5)	0.5896(2)	5.0(2)
C(80)	−0.0138(5)	−0.0902(5)	0.6022(3)	5.4(2)
C(81)	0.2552(9)	0.4085(7)	0.9521(4)	10.8(3)*
C(82)	0.1279(9)	0.3912(7)	0.9640(4)	10.0(3)*
C(83)	0.0591(9)	0.3231(7)	0.9969(4)	10.0(3)*
C(84)	0.121(1)	0.2663(8)	1.0189(5)	11.8(3)*
C(85)	0.249(1)	0.2767(8)	1.0095(5)	11.9(3)*
C(86)	0.322(1)	0.3503(8)	0.9750(5)	12.9(3)*

some *partial cone* or *1,2-alternate* conformations have also been reported [5, 11, 13]. The O···O contacts between oxygen atoms pertaining to adjacent phenolic groups span a wider range (2.707(4)–3.682(4) Å) than in the other R-calix[5]arenes

Table II. Selected geometric parameters (Å, °), with ESD in parentheses.

O···O and N···O contacts			
O(1)···O(2)	3.657(5)	O(2)···O(3)	2.866(6)
O(3)···O(4)	3.682(4)	O(4)···O(5)	2.860(5)
O(1)···O(5)	2.707(4)		
N(1)···O(3)	2.677(7)	N(2)···O(1)	2.628(5)

Hydrogen bonds					
O(1)—H(1)	1.09	N(2)···H(1)	1.56	O(1)—H(1)···N(2)	164.23
O(2)—H(2)	1.01	O(3)···H(2)	1.86	O(2)—H(2)···O(3)	173.72
O(3)—H(3)	0.95	N(1)···H(3)	1.83	O(3)—H(3)···N(1)	147.42
O(4)—H(4)	0.96	O(5)···H(4)	1.94	O(4)—H(4)···O(5)	160.07
O(5)—H(5)	1.00	O(1)···H(5)	1.71	O(5)—H(5)···O(1)	174.86

Torsion angles

Rings	ϕ	χ
1–2	−54.1(6)	84.9(6)
2–3	−116.3(5)	69.4(6)
3–4	−41.3(7)	105.8(6)
4–5	−104.2(5)	75.6(6)
5–1	−91.3(6)	85.2(6)

in the *cone* conformation (2.696–2.881 Å) [1, 2, 7]. The shorter contact, between O(1) and O(5), suggests a strong hydrogen bond, as well as the two other short ones, between O(2) and O(3) (2.86 Å) and O(4) and O(5) (2.84 Å): this is confirmed by the location of the hydrogen atoms from the Fourier maps. The cyclic hydrogen bonding array observed in calix[5]arenes in the *cone* conformation is disrupted by two strong hydrogen bonds between O(1) and O(3) and the nitrogen atoms from two pyridine molecules (O···N distances of 2.628(5) and 2.677(7) Å). This may be related to the departure of the conformation from a regular *cone* one. Such a pattern (three short O···O contacts and two longer ones) is also observed in the proton-depleted *p*-sulfonatocalix[5]arene [10, 14]. The pendant benzyl arms lie in rather unremarkable positions, probably largely determined by packing constraints. Three of the benzyl aromatic rings are nearly perpendicular to the oxygen mean plane (dihedral angles in the range 87.6(2)–90.6(1)°) and the two other rings are less inclined with respect to it (51.7(2)–53.5(2)°).

The most interesting feature of this structure resides in the inclusion of one of the pyridine molecules (corresponding to N(1)), hydrogen bonded to the calixarene, in the hydrophobic cavity of the neighboring calixarene along the *a* axis, and the inter- actions of the other hydrogen bonded pyridine molecule (corresponding to N(2)) with the adjacent calixarenes and with its own image by the symmetry centre, as evidenced in Figure 2. There are some examples of inclusion of organic molecules in calix[5]arenes, whose cavity, wider than that of calix[4]arenes, is particularly well adapted for that [1–3, 6]. The self-inclusion of one *tert*-butyl group has also

been reported [7]. The originality of the present structure is that the two pyridine molecules are complexed in two ways: by hydrogen bonding and by various possible interactions (π–π with the phenolic rings, π-CH_2 with the methylene bridges of the benzyl moieties, dipole-dipole). A similar situation has been described in the pyridine complex of *p-tert*-butylcalix[7]arene, in which one pyridine molecule is hydrogen bonded to a phenolic oxygen atom and the packing consists in a stacking of calixarene units, the complexed pyridine molecule being included in the cavity of the adjacent calixarene, as in our case [24]. Such an arrangement has been described as leading to 'supramolecular assemblies organized by feeble forces' [25]. It may give rise to the formation of dimers [25] or infinite chains, as in our case [24, 26, 27]. Three benzyl arms and their image by the symmetry centre form a sort of a cage including two other non hydrogen bonded pyridine molecules (one per molecular unit). The existence of such pyridine-calixarene or pyridine-pyridine contacts suggests that the presence of pyridine molecules plays a prominent role among the parameters governing the packing. The variety of possible interactions between pyridine and calixarenes (both polar molecules, able to form either acceptor or donor hydrogen bonds and possessing π-electron systems) may be at the origin of the well known efficiency of this solvent for the crystallization of calixarenes.

References

1. M. Coruzzi, G.D. Andreetti, V. Bocchi, A. Pochini, and R. Ungaro: *J. Chem. Soc. Perkin Trans. 2*, 1133 (1982).
2. M. Perrin and S. Lecocq: *J. Incl. Phenom.,* **11**, 171 (1991).
3. R.K. Juneja, K.D. Robinson, G.W. Orr, R.H. Dubois, K.A. Belmore, J.L. Atwood, J.A. Ripmeester, and C.I. Ratcliffe: *J. Incl. Phenom.* **13**, 93 (1992).
4. G. Barrett, M.A. McKervey, J.F. Malone, A. Walker, F. Arnaud-Neu, L. Guerra, M.J. Schwing-Weill, C.D. Gutsche, and D.R. Stewart: *J. Chem. Soc. Perkin Trans. 2*, 1475 (1993).
5. S. Usui, K. Deyama, R. Kinoshita, Y. Odagaki and Y. Fukazawa: *Tetrahedron Lett.* **34**, 8127 (1993).
6. J.L. Atwood, R.K. Juneja, P.C. Junk, and K.D. Robinson: *J. Chem. Crystallogr.* **24**, 573 (1994).
7. J.F. Gallagher, G. Ferguson, V. Böhmer, and D. Kraft: *Acta Crystallogr.* C**50**, 73 (1994).
8. M. Tabatabai, W. Vogt, V. Böhmer, G. Ferguson, and E.F. Paulus: *Supramol. Chem.* **4**, 147 (1994).
9. P.D. Beer, Z. Chen, M.G.B. Drew, and P.A. Gale: *J. Chem. Soc., Chem. Commun.* 1851 (1995).
10. J.W. Steed, C.P. Johnson, C.L. Barnes, R.K. Juneja, J.L. Atwood, S. Reilly, R.L. Hollis, P.H. Smith, and D.L. Clark: *J. Am. Chem. Soc.* **117**, 11426 (1995).
11. D.R. Stewart, M. Krawiec, R.P. Kashyap, W.H. Watson, and C.D. Gutsche: *J. Am. Chem. Soc.* **117**, 586 (1995).
12. R. Arnecke, V. Böhmer, G. Ferguson, and S. Pappalardo: *Tetrahedron Lett.*, **37**, 1497 (1996).
13. P.D. Beer, P.A. Gale, Z. Chen, and M.G.B. Drew: *Supramol. Chem.* **7**, 241 (1996).
14. C.P. Johnson, J.L. Atwood, J.W. Steed, C.B. Bauer, and R.D. Rogers: *Inorg. Chem.* **35**, 2602 (1996).
15. J.W. Steed, C.P. Johnson, R.K. Juneja, J.L. Atwood, and R.S. Burkhalter: *Supramol. Chem.* **6**, 235 (1996).
16. T. Haino, M. Yanase, and Y. Fukazawa: *Angew. Chem. Int. Ed. Engl.* **36**, 259 (1997).
17. P. Thuéry and M. Nierlich: *J. Incl. Phenom.* **27**, 13 (1997).
18. B. Souley, Z. Asfari, and J. Vicens: *Polish J. Chem.*, **66**, 959 (1992).
19. G.M. Sheldrick: SHELXS-86: *Program for the Solution of Crystal Structures*, University of Göttingen, Germany (1985).

20. *International Tables for X-ray Crystallography*, Vol. IV, Kynoch Press, Birmingham, England (1974). Present distributor: Kluwer Academic Publishers, Dordrecht, The Netherlands.
21. MolEN: *An Interactive Structure Solution Procedure*, Enraf-Nonius, Delft, The Netherlands (1990).
22. C.K. Johnson: ORTEPII, Report ORNL-5138, Oak Ridge National Laboratory, Tennessee, USA (1976).
23. F. Ugozzoli and G.D. Andreetti: *J. Incl. Phenom.* **13**, 337 (1992).
24. G.D. Andreetti, F. Ugozzoli, Y. Nakamoto, and S.I. Ishida: *J. Incl. Phenom.* **10**, 241 (1991).
25. J.L. Atwood, G.W. Orr, F. Hamada, S.G. Bott, and K.D. Robinson: *Supramol. Chem.* **1**, 15 (1992).
26. J.M. Harrowfield, M.I. Ogden, and A.H. White: *J. Chem. Soc. Dalton Trans.* 979 (1991).
27. C. Bavoux and M. Perrin: *J. Incl. Phenom.* **14**, 247 (1992).