

Crystal and Molecular Structure of the (1 : 1) Clathrate between a Calix[4]arene Containing One *p*-Nitrophenol Unit and Toluene

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(Received: 29 March 1989; in final form: 16 October 1989)

Abstract. *p*-(Methyl, *tert*-butyl, nitro, *tert*-butyl) calix[4]arene: toluene, C₃₇H₄₁NO₆. C₇H₈, *M_r* = 687.87, triclinic, *P* $\bar{1}$, *a* = 13.668(2), *b* = 12.187(2), *c* = 13.231(1) Å, α = 106.78(8), β = 77.88(1), γ = 114.00(1)°, *V* = 1916.8(8) Å³, *Z* = 2, *D_x* = 1.19 g cm⁻³, $\lambda(\text{CuK}\alpha)$ = 1.54178 Å, μ = 5.90 cm⁻¹, *F*(000) = 736, *T* = 293 K, final *R* = 0.068 for 6309 observed reflections. This macrocycle, having different substituents at the positions *para* to the hydroxyl groups, is the first one of its type to be studied. The general conformation of this calix[4]arene is compared to similar symmetrical ones. The *tert*-butyl groups are not disordered as is usual and toluene is retained between the macrocycles. Two calixarene molecules are positioned to permit a *tert*-butyl group of one to be inside the cavity of the second to establish CH₃- π interactions.

Key words. X-Ray crystal structure analysis, calixarene conformation.

Supplementary Data relating to this article are deposited with the British Library as Supplementary Publication No. SUP 82089 (41 pages).

1. Introduction

Calixarenes are cyclic molecules consisting of 4 to 8 phenolic units which are linked via methylene bridges (usually) in the position *ortho* to the phenolic hydroxyl group. Their ability to include various guests (cations or neutral molecules) explains the increasing interest in these compounds, which are usually prepared by direct condensation of alkyl phenols with formaldehyde [1]. Therefore, the first X-ray analysis published for *p-tert*-butylcalix[4]arenes [2] provided the definitive proof of the ring size of such a condensation product. The molecule was found to exist in the so called cone-conformation with one molecule of toluene included in the molecular cavity.

Later several X-ray structures of different calix[4]arenes [3, 6] with various substituents in the *para*-positions (e.g. *tert*-octyl, *iso*-propyl, hydrogen) were reported, showing the molecules always to be in the cone-conformation, although the solvent entrapped in the crystal lattice was not always situated within the cavity and

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solvent free crystals were obtained from *tert*-octylcalix[4]arene. Obviously the cyclic array of intramolecular hydrogen bonds between adjacent phenolic hydroxyl groups, which is not possible in other conformations like the partial cone, 1,2- or 1,3-alternate, is the most important factor in determining the conformation of calix[4]arenes.

These intramolecular hydrogen bonds, which may be deduced from spectroscopic studies in solution [1], were found also in the crystal structures reported for calixarenes with five [7], six [8, 9] or eight [10] phenolic units in the molecule, while intermolecular hydrogen bonding has never been observed for calixarenes in the solid state in contrast to the linear phenolic oligomers [11–13].

To elucidate the acidic properties of calix[4]arenes we have synthesized several compounds in which one *p*-nitrophenol unit is combined with various *p*-alkylphenol units. In this paper we report the X-ray structure of such a calixarene, which seemed interesting mainly for two reasons: (a) the 'intrinsic' acidity of a *p*-nitrophenol unit is higher than the acidity of the *p*-alkylphenol units (the single phenols differ by about three units in their *pK*-values) and this might have some influence on the cyclic array of hydrogen bonds; (b) the nitro group may act as an acceptor for hydrogen bonds, and thus intermolecular OH...O₂N bonds may be found in the solid state. Furthermore the structure reported here is the first one of a calix[4]arene having different substituents in the *p*-positions of the same molecule.

2. Experimental

2.1. SYNTHESIS

The compound was synthesized as already described for similar molecules [14]. Condensation of 2,6-dibromomethyl-4-nitrophenol with an excess of *tert*-butylphenol, in the presence of a stoichiometric amount of zinc carbonate gave a linear trimer [2,6-di-(2-hydroxy-5-*tert*-butyl-benzyl)-4-nitrophenol] which was cyclized by condensation with 2,6-dibromomethyl-4-methylphenol in dioxane using TiCl₄ as catalyst [15]. A detailed description will be published elsewhere [16].

2.2. X-RAY DATA COLLECTION AND STRUCTURE DETERMINATION

X-Ray diffraction was carried out on a single crystal at room temperature. A needle approximately 0.2 × 0.3 × 1.1 mm was used for data collection with an automatic Nonius CAD4 four-circle diffractometer (graphite monochromator, CuK_α radiation); lattice parameters were refined from 25 reflections in 11 ≤ θ ≤ 46°; the ω–2θ scan mode was used to collect intensities of reflections with θ < 73° (range of *hkl*: –16 ≤ *h* ≤ 16, –15 ≤ *k* ≤ 15, 0 ≤ *l* ≤ 16); from 8187 reflections collected, 6309 with *I* > 3σ(*I*) were considered as observed and used in the structure analysis and refinement; three standard reflections were monitored every 60 min to control the intensity and the same at 100 reflections interval to control the orientation of the crystal; Lorentz and polarisation corrections were applied and absorption was corrected with the program PSI and EAC of SDP [1.40 < *A*(θ) < 1.37]. The structure was determined by direct methods and refined on *F* by SHELX 76 [17]; of 656 independent parameters, 623 were refined, with the thermal parameters of

some H atoms being fixed at the values of the isotropic thermal parameters of the corresponding heavy atoms. An *E*-map showed clearly all non-H atoms of the molecule; H positions were determined by difference Fourier syntheses or by calculations.

Non H-atoms were refined first isotropically, then anisotropically; H atoms were refined isotropically with constant *U* for H of methyl and OH groups; $(\Delta/\sigma)_{\max} = 1.41$ for C152, $(\Delta/\sigma)_{\text{av}} = 0.046$; residual electron density in final difference Fourier synthesis = $0.69 \text{ e } \text{\AA}^{-3}$; unit weights were used, $R_w = 0.068$, $S = 1.13$. Atomic scattering factors are from SHELX 76.

3. Results and Discussion

Figure 1 shows the numbering scheme of the atoms of calixarene molecules and C(100) to C(106) correspond to the toluene molecule. The final coordinates with

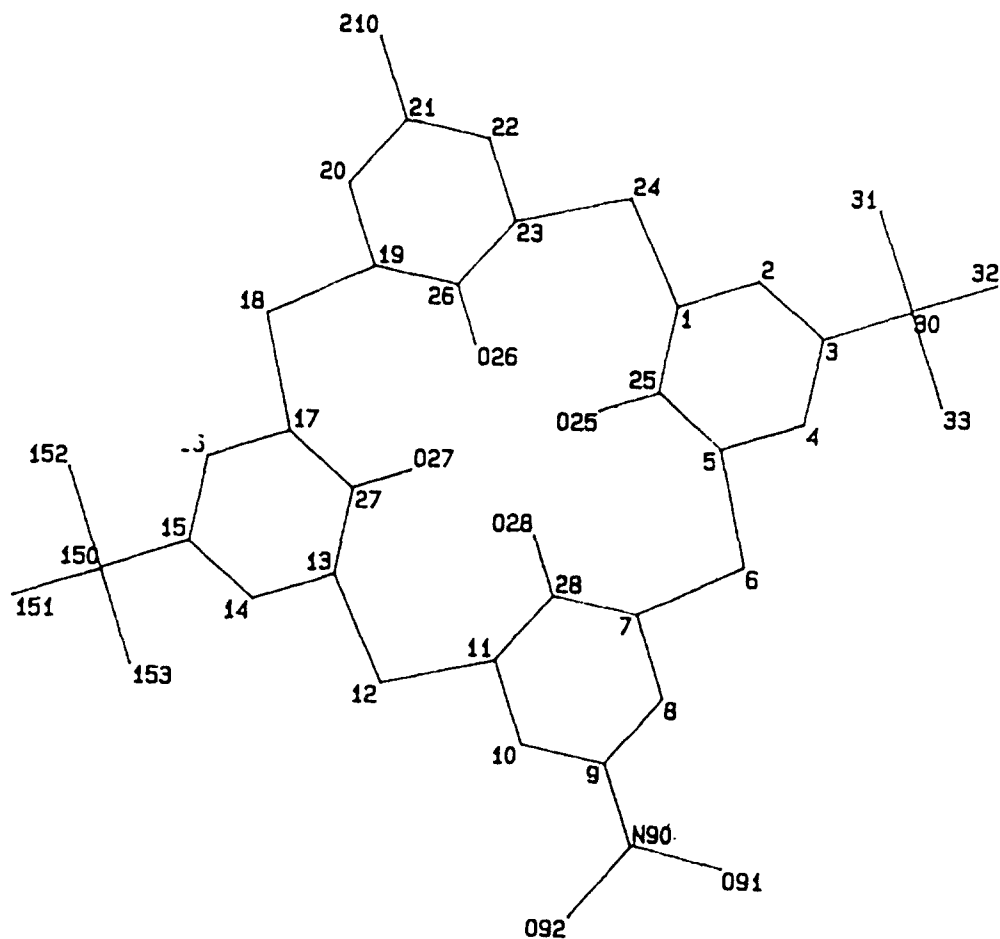


Fig. 1. Numbering scheme of the calixarene atoms.

Table I. Final atomic coordinates ($\times 10^4$) with e.s.d.'s in parentheses and equivalent isotropic thermal parameters (\AA^2)

Atom	x	y	z	B_{eq}^*	Atom	x	y	z	B_{eq}^*
O(25)	6141(2)	1975(3)	11239(2)	3.94(9)	C(20)	6388(3)	5265(4)	8851(3)	4.0(1)
O(26)	5117(2)	2742(2)	10238(2)	3.77(8)	C(21)	7016(4)	6215(4)	9609(4)	4.3(1)
O(27)	5160(2)	931(2)	8579(2)	3.77(8)	C(22)	7016(4)	5965(4)	10566(3)	3.9(1)
O(28)	6152(2)	156(2)	9545(2)	3.78(9)	C(23)	6403(3)	4806(3)	10785(3)	3.3(1)
O(91)	10946(5)	705(8)	8137(5)	16.4(4)	C(24)	6463(3)	4554(4)	11828(3)	3.6(1)
O(92)	10334(4)	53(6)	6622(5)	12.3(3)	C(25)	7182(3)	2849(3)	11414(3)	3.0(1)
N(90)	10222(4)	377(6)	7601(5)	8.2(2)	C(26)	5571(3)	3881(3)	10010(3)	3.2(1)
C(1)	7358(3)	4096(3)	11747(3)	3.0(1)	C(27)	5748(3)	1304(3)	7658(3)	3.0(1)
C(2)	8397(3)	4947(4)	11967(3)	3.3(1)	C(28)	7167(3)	264(3)	9067(3)	3.2(1)
C(3)	9259(3)	4584(3)	11856(3)	3.2(1)	C(30)	10405(3)	5531(4)	12097(3)	4.1(1)
C(4)	9039(3)	3320(4)	11510(3)	3.3(1)	C(31)	10408(6)	6749(6)	12754(9)	11.2(4)
C(5)	8016(3)	2436(3)	11285(3)	3.2(1)	C(32)	11119(5)	5713(9)	11076(6)	12.8(4)
C(6)	7835(4)	1064(4)	10901(3)	3.7(1)	C(33)	10929(5)	5036(7)	12670(6)	9.0(3)
C(7)	8009(3)	669(3)	9704(3)	3.4(1)	C(100)	6564(4)	6407(4)	5739(3)	10.2(4)
C(8)	9016(4)	704(4)	9210(3)	4.3(1)	C(101)	5868(4)	6383(4)	5252(3)	12.0(4)
C(9)	9163(4)	350(4)	8110(4)	4.6(2)	C(102)	6216(4)	7315(4)	4476(3)	12.0(5)
C(10)	8337(4)	-20(4)	7486(3)	4.0(1)	C(103)	7295(4)	7846(4)	4241(3)	11.5(4)
C(11)	7319(3)	-64(3)	7954(3)	3.3(1)	C(104)	8031(4)	7719(4)	4701(3)	8.6(3)
C(12)	6406(4)	-462(3)	7277(3)	3.5(1)	C(105)	7679(4)	7001(4)	5439(3)	9.3(3)
C(13)	6325(3)	617(3)	6990(3)	3.0(1)	C(106)	8473(9)	6890(9)	5931(8)	14.4(5)
C(14)	6815(3)	931(4)	6023(3)	3.3(1)	C(150)	7208(4)	2125(4)	4596(3)	4.1(1)
C(15)	6757(3)	1900(4)	5715(3)	3.3(1)	C(151)	8288(6)	2030(9)	4272(5)	10.8(4)
C(16)	6214(3)	2593(4)	6441(3)	3.3(1)	C(152)	7393(8)	3400(7)	4508(5)	11.0(4)
C(17)	5701(3)	2309(3)	7413(3)	3.0(1)	C(153)	6429(7)	1168(9)	3853(5)	14.5(4)
C(18)	5096(3)	3078(4)	8171(3)	3.6(1)	C(210)	7667(4)	7490(4)	9386(3)	6.4(2)
C(19)	5764(3)	4086(4)	9030(3)	3.3(1)					

$$B_{eq}^* = (4/3)[a^2B_{11} + b^2B_{22} + c^2B_{33} + ab \cos \gamma B_{12} + ac \cos \beta B_{13} + bc \cos \alpha B_{23}]$$

their e.s.d.'s and the isotropic thermal parameters are given in Table I. Selected bond distances and angles as well as torsion angles are listed in Tables II and III.

The aromatic C—C distances are normal and vary from 1.381(7) to 1.404(6) Å with an average value of 1.390(6) Å. The N—O distances are 1.20(1) and 1.236(8) Å in good agreement with the usual value; C—O bonds have values of 1.392(4), 1.389(4), 1.377(4) and 1.367(5) Å, the last being the distance for the *p*-nitrophenol unit. In the benzene ring, internal angles at the substituted C atoms deviate from the mean value (120°), being more than 120° at OH and NO₂ groups, and less than 120° at methyl and *tert*-butyl groups, these effects being connected with the σ -electron withdrawing or releasing characters of the substituents [18]. No particular dissymmetry is found around the C—O bonds as reported by Hirshfeld [19]; furthermore the positions of H-atoms of hydroxyl groups are not well defined on difference syntheses, perhaps because hydrogen bonds are of the 'flip-flop' type, which have been found in many calixarenes.

Angles at methylene bridges have values close to 112°. Some torsional angles show the geometry around the CH₂ bridges as well as the relative positions of the *tert*-butyl and nitro groups versus phenolic ring planes.

Some mean plane equations as well as some dihedral angles were also calculated; it is seen that angles between the ring plane and adjacent (—C—CH₂—C—) groups are nearly 90°; the nitro group is in the ring plane as commonly found in nitrophenols [20, 21].

Dihedral angles between the four phenol entities A, B, C, D have values of 69.2(2), 111.4(3), 112.7(4) and 73.5(4)°. The phenolic units A, B, C, D make angles of 124.7(2), 125.7(2), 130.6(4) and 123.9(4)° respectively with the least squares plane defined by the four bridging methylene groups which are alternately below and above the plane by about 0.02(1) Å.

Table II. Bond distances (Å) with e.s.d.s in parentheses

O(25)—C(25)	1.389(4)	C(8)—C(9)	1.390(6)	C(21)—C(210)	1.510(6)
O(26)—C(26)	1.377(4)	C(9)—C(10)	1.381(7)	C(22)—C(23)	1.385(6)
O(27)—C(27)	1.392(4)	C(10)—C(11)	1.384(6)	C(23)—C(24)	1.522(7)
O(28)—C(28)	1.367(5)	C(11)—C(12)	1.517(6)	C(23)—C(26)	1.396(5)
O(91)—N(90)	1.20(1)	C(11)—C(28)	1.404(5)	C(30)—C(31)	1.486(9)
O(92)—N(90)	1.236(8)	C(12)—C(13)	1.521(7)	C(30)—C(32)	1.505(8)
N(90)—C(9)	1.454(7)	C(13)—C(14)	1.392(5)	C(30)—C(33)	1.52(1)
C(1)—C(2)	1.390(5)	C(13)—C(27)	1.395(6)	C(100)—C(101)	1.371(9)
C(1)—C(24)	1.519(7)	C(14)—C(15)	1.393(7)	C(100)—C(105)	1.408(6)
C(1)—C(25)	1.382(5)	C(15)—C(16)	1.396(6)	C(101)—C(102)	1.428(7)
C(2)—C(3)	1.392(7)	C(15)—C(150)	1.534(5)	C(102)—C(103)	1.344(7)
C(3)—C(4)	1.390(6)	C(16)—C(17)	1.393(5)	C(103)—C(104)	1.361(9)
C(3)—C(30)	1.536(5)	C(17)—C(18)	1.527(6)	C(104)—C(105)	1.375(7)
C(4)—C(5)	1.386(5)	C(17)—C(27)	1.383(7)	C(105)—C(106)	1.45(1)
C(5)—C(6)	1.526(6)	C(18)—C(19)	1.522(5)	C(150)—C(151)	1.49(1)
C(5)—C(25)	1.391(7)	C(19)—C(20)	1.386(6)	C(150)—C(152)	1.50(1)
C(6)—C(7)	1.515(5)	C(19)—C(26)	1.392(6)	C(150)—C(153)	1.479(8)
C(7)—C(8)	1.382(6)	C(20)—C(21)	1.390(5)		
C(7)—C(28)	1.402(6)	C(21)—C(22)	1.386(7)		

Table III. Bond and torsion angles with e.s.d.s in parentheses

O(91)—N(90)—C(9)	119.4(5)	C(20)—C(19)—C(26)	117.7(3)
O(92)—N(90)—C(9)	117.9(6)	C(19)—C(20)—C(21)	122.0(4)
O(91)—N(90)—O(92)	122.7(2)	C(20)—C(21)—C(22)	118.6(4)
C(2)—C(1)—C(24)	119.7(4)	C(22)—C(21)—C(210)	121.4(3)
C(2)—C(1)—C(25)	118.5(4)	C(1)—C(22)—C(23)	121.7(3)
C(24)—C(1)—C(25)	121.7(3)	C(22)—C(23)—C(26)	118.1(4)
C(1)—C(2)—C(3)	122.1(4)	C(22)—C(23)—C(24)	120.0(3)
C(2)—C(3)—C(4)	117.0(3)	C(24)—C(23)—C(26)	121.9(3)
C(2)—C(3)—C(30)	121.8(4)	C(24)—C(23)—C(26)	121.9(3)
C(4)—C(3)—C(30)	121.2(4)	C(1)—C(24)—C(23)	112.0(3)
C(3)—C(4)—C(5)	122.9(5)	O(25)—C(25)—C(5)	118.7(3)
C(4)—C(5)—C(6)	120.1(4)	O(25)—C(25)—C(1)	119.6(4)
C(4)—C(5)—C(25)	117.7(4)	C(1)—C(25)—C(5)	121.7(3)
C(6)—C(5)—C(25)	122.2(3)	O(26)—C(26)—C(19)	119.3(3)
C(5)—C(6)—C(7)	112.7(4)	C(19)—C(26)—C(23)	122.0(3)
C(6)—C(7)—C(8)	120.3(4)	O(26)—C(26)—C(23)	118.6(4)
C(6)—C(7)—C(28)	121.5(4)	O(27)—C(27)—C(13)	118.7(4)
C(8)—C(7)—C(28)	118.1(3)	O(27)—C(27)—C(17)	119.0(3)
C(7)—C(8)—C(9)	119.4(4)	C(13)—C(27)—C(17)	122.2(3)
N(90)—C(9)—C(8)	118.9(5)	O(28)—C(28)—C(11)	118.5(4)
N(90)—C(9)—C(10)	118.9(4)	O(28)—C(28)—C(7)	118.9(3)
C(8)—C(9)—C(10)	122.1(4)	C(7)—C(28)—C(11)	122.6(4)
C(11)—C(10)—C(9)	120.2(1)	C(3)—C(30)—C(33)	110.5(4)
C(10)—C(11)—C(28)	117.7(4)	C(3)—C(30)—C(32)	109.8(4)
C(10)—C(11)—C(12)	120.5(3)	C(3)—C(30)—C(31)	112.5(5)
C(12)—C(11)—C(28)	121.8(4)	C(31)—C(30)—C(32)	109.7(6)
C(11)—C(12)—C(13)	113.4(3)	C(31)—C(30)—C(33)	108.7(6)
C(12)—C(13)—C(14)	120.2(4)	C(32)—C(30)—C(33)	105.5(6)
C(12)—C(13)—C(27)	122.2(3)	C(101)—C(100)—C(105)	116.2(4)
C(14)—C(13)—C(27)	117.6(4)	C(100)—C(101)—C(102)	123.7(4)
C(13)—C(14)—C(15)	122.6(4)	C(101)—C(102)—C(103)	115.8(5)
C(14)—C(15)—C(16)	117.0(3)	C(102)—C(103)—C(104)	123.6(5)
C(14)—C(15)—C(150)	120.7(4)	C(103)—C(104)—C(105)	119.7(4)
C(16)—C(15)—C(150)	122.2(4)	C(100)—C(105)—C(106)	120.0(5)
C(15)—C(16)—C(17)	122.6(4)	C(100)—C(105)—C(104)	121.0(1)
C(16)—C(17)—C(18)	120.7(4)	C(104)—C(105)—C(106)	119.0(1)
C(16)—C(17)—C(27)	117.8(4)	C(151)—C(150)—C(152)	105.1(6)
C(18)—C(17)—C(27)	121.5(3)	C(152)—C(150)—C(153)	110.3(7)
C(17)—C(18)—C(19)	113.8(4)	C(151)—C(150)—C(153)	109.1(5)
C(18)—C(19)—C(20)	119.8(4)	C(15)—C(150)—C(151)	111.6(5)
C(18)—C(19)—C(26)	122.5(3)	C(15)—C(150)—C(152)	113.0(4)
O(91)—N(90)—C(9)—C(10)	179.51(0.66)	C(11)—C(12)—C(13)—C(14)	95.82(0.44)
O(92)—N(90)—C(9)—C(10)	-0.67(0.85)	C(16)—C(17)—C(18)—C(19)	-96.70(0.46)
N(90)—C(9)—C(10)—C(11)	179.38(0.45)	C(17)—C(18)—C(19)—C(26)	-90.22(0.49)
C(4)—C(5)—C(6)—C(7)	-89.69(0.49)	C(22)—C(23)—C(24)—C(1)	-88.86(0.49)
C(5)—C(6)—C(7)—C(28)	-87.66(0.49)	C(23)—C(24)—C(1)—C(2)	-84.10(0.44)
C(10)—C(11)—C(12)—C(13)	-91.70(0.45)		

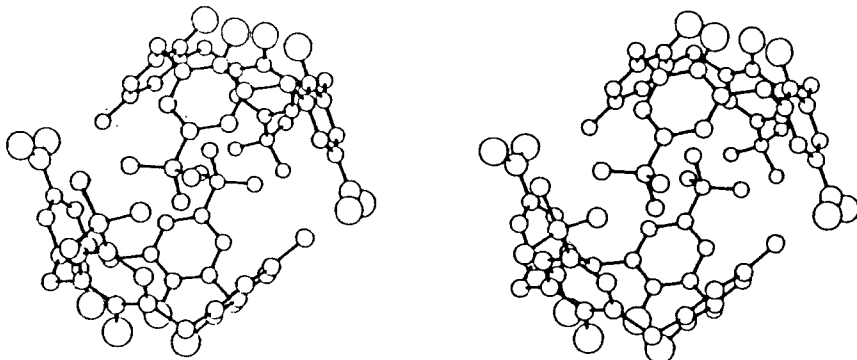


Fig. 2. Stereoscopic view of the symmetry centre derived calixarene molecules.

The intramolecular hydrogen bonding mainly determines the conformation of the macrocycle: [O(25)⋯O(26) = 2.672(5), O(26)⋯O(27) = 2.635(4), O(27)⋯O(28) = 2.613(5), O(28)⋯O(25) = 2.661(4) Å]. Steric effects due to *para*-substitution on the phenyl rings seem to play a limited role, even with an NO₂ group.

Two calixarene molecules around a center of symmetry are positioned to permit the *tert*-butyl groups of one molecule to be inside the macrocycle of the other (Figure 2). So there are CH₃-π interactions as is often found in calixarene structures. However usually these interactions are between the host and guest molecules; for the first time interactions between two calixarenes are found; with these relative positions, at least in the solid state, it is not possible to have inclusion compounds with the guest interacting inside a host cavity as sometimes observed in calixarenes [2, 5, 6]. The toluene molecules interact by van der Waals contacts with the pair of calixarenes. Figure 3 shows the molecular packing.

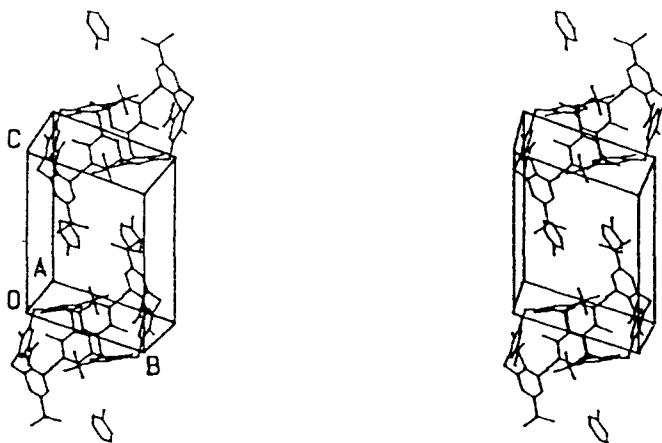


Fig. 3. Stereoscopic view of the structure along [100].

References

1. For a recent review see C. D. Gutsche: *Top. Curr. Chem.* **123**, 1 (1984).
2. G. D. Andreetti, R. Ungaro, and A. Pochini: *J. Chem. Soc., Chem. Commun.* 1005 (1979).
3. G. D. Andreetti, A. Pochini, and R. Ungaro: *J. Chem. Soc., Perkin Trans. 2* 1773 (1983).
4. R. Ungaro, A. Pochini, G. D. Andreetti, and V. Sangermano: *J. Chem. Soc., Perkin Trans. 2* 1979 (1984).
5. R. Ungaro, A. Pochini, G. D. Andreetti, and P. Domiano: *J. Chem. Soc., Perkin Trans. 2* 197 (1985).
6. D. Oehler: Thesis, Lyon (France), (1987).
7. M. Coruzzi, G. D. Andreetti, V. Bocchi, A. Pochini, and R. Ungaro: *J. Chem. Soc., Perkin Trans. 2* 1133 (1982).
8. R. Perrin and R. Lamartine: *Makromol. Chem., Makromol. Symp.* **9**, 69 (1987).
9. G. D. Andreetti, F. Ugozzoli, A. Casnati, E. Ghidini, A. Pochini, and R. Ungaro: *Gazzetta Chimica Italiana*, in press.
10. C. D. Gutsche, A. E. Gutsche, and A. I. Karaulov: *J. Incl. Phenom.* **3**, 447 (1985).
11. G. Casiraghi, M. Cornia, G. Sartori, G. Casnati, V. Bocchi, and G. D. Andreetti: *Makromol. Chem.* **183**, 2611 (1982).
12. E. Paulus and V. Böhmer: *Makromol. Chem.* **185**, 1921 (1984).
13. G. Casiraghi, M. Cornia, G. Ricci, G. Casnati, V. Bocchi, G. D. Andreetti, and L. Zetta: *Macromolecules* **17**, 19 (1984).
14. (a) V. Böhmer, W. Lotz, J. Pachta, and S. Tütüncü: *Makromol. Chem.* **182**, 2671 (1981). (b) V. Böhmer, E. Schade, and W. Vogt: *Makromol. Chem., Rapid Commun.* **5**, 221 (1984).
15. (a) V. Böhmer, F. Marschollek, and L. Zetta: *J. Org. Chem.* **52**, 3200 (1987). (b) H. Goldmann, W. Vogt, E. Paulus, and V. Böhmer: *J. Am. Chem. Soc.* **110**, 6811 (1988).
16. V. Böhmer, T. Fey, D. Büttner, and W. Vogt: unpublished results.
17. G. Sheldrick: SHELX-76, Program for Crystal Structure determination. University of Cambridge (1976).
18. A. Domenicano, A. Vaciago, and C. A. Coulson: *Acta Crystallogr.* **B31**, 221 (1975).
19. F. L. Hirshfeld: *Isr. J. Chem.* **2**, 87 (1964).
20. F. Iwasaki and Y. Kawano: *Acta Crystallogr.* **B33**, 2455 (1977).
21. F. Iwasaki, M. Sato, and A. Aihara: *Acta Crystallogr.* **B32**, 102 (1976).