

Molecular Inclusion in Functionalized Macrocycles. Part 12★. Crystal and Molecular Structure of a *p*-(1,1,3,3)-Tetramethylbutylcalix[8]arene Octapodand

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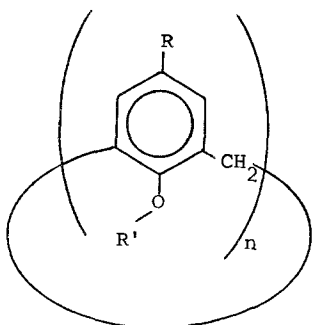
Abstract. The title compound was obtained as colourless transparent prismatic crystals (from acetone/methanol 1:1), space group $P\bar{1}$ $a = 16.647(2)$, $b = 16.447(2)$, $c = 14.269(3)$ Å, $\alpha = 108.56(3)$, $\beta = 105.63(3)$, $\gamma = 87.23(3)^\circ$, $Z = 1$, $D_{\text{calc}} = 1.03$ g cm⁻³. Refinement was carried out using 2863 reflections, with $I > \sigma(I)$. The molecule, which lies on a center of symmetry, possesses a roughly ellipsoidal shape with two sets of four phenolic nuclei following a helical arrangement. The polyether chains of two adjacent phenolic units partially fill the intramolecular cavity. No guest molecules are present.

Key words: X-ray crystal structure analysis; cyclic octamer from *p*-octylphenol and formaldehyde; cation ligand.

Supplementary Data relating to this article are deposited with the British Library as Supplementary Publication SUP 82025 (22 pages).

1. Introduction

In a previous paper [2] we have reported the crystal and molecular structure of a *p-t*-butylcalix[6]arene hexapodand (1), which belongs to a series of new lipophilic cation ligands recently synthesized using calixarenes as building blocks [3].



(1): $n = 6$; $R = \text{Bu}'$; $R' = \text{CH}_2\text{CH}_2\text{OCH}_3$

(2): $n = 8$; $R = (1,1,3,3)\text{-tetramethylbutyl}$; $R' = \text{CH}_2\text{CH}_2\text{OCH}_3$

★ For part 11 see [1].

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The extraction abilities of these ligands toward alkali and ammonium cations depend on the nature of the R group, on the length of the polyetheral chain (R') and the number (*n*) of phenolic units present in the cyclic calixarene array [4]. The last (matrix) effect is mainly linked with the conformational mobility of the macroring and the consequent possibility for the ether chains to cooperate in complexing the cations.

It was of interest, therefore, to determine the structure of an octapodand in the solid state and compare the results with those obtained with the hexapodand (1). The octapodand (2) was obtained from *p*-(1,1,3,3)-tetramethylbutylcalix[8]arene by introducing a short ether chain (R') = CH₂CH₂OCH₃. Its crystal structure is reported in this paper.

2. Experimental

The synthesis and characterization of podand (2) have been reported in [3]. Colourless transparent prismatic crystals were obtained from acetone/methanol (1 : 1).

3. Crystal data

C₁₄₄H₂₂₄O₁₆. Formula weight = 2211.3. Triclinic, *a* = 16.647(2), *b* = 16.477(2), *c* = 14.269(3) Å, α = 108.56(3)°, β = 105.63(3)°, γ = 87.23(3)°, *U* = 3563.6(1.3) Å³, *Z* = 1, *D_c* = 1.03 g cm⁻³, Space group *P* $\bar{1}$ (No. 2).

4. Structure determination

A single colourless transparent crystal suitable for X-ray analysis (0.4 × 0.5 × 0.5 mm) was used for intensity measurements.

Lattice parameters were determined from 22(*θ*, *χ*, *φ*)_{*hkl*} measurements on a Siemens AED single crystal diffractometer on line to a General Automation Jumbo 220 microcomputer [5].

The intensities *I*_{*hkl*} were collected, at room temperature with the *θ* – 2*θ* step scanning mode in the range 3° ≤ *θ* ≤ 70° using nickel filtered CuK_α radiation and analyzing the reflection profiles with a modified version of the Lehman and Larsen procedure [5, 6]. One standard reflection was recorded every 50 measurements to monitor specimen decomposition and instrumental stability.

A total of 11410 ± *h* ± *k* + *l* reflections were collected of which only the 2863 reflections with *I* > σ(*I*) (σ(*I*) based on counting statistics) were retained as 'observed' and used for the refinement. If the significance level is set to 3σ(*I*) the number of observed reflections is lowered to 1100, which is about three times the number of parameters to be refined considering only isotropic thermal motion.

No corrections were made for absorption. The structure was solved at the first trial by direct methods using the SHELX system of computer programs [7] leading to the approximate positioning of carbon atoms of the four independent phenolic rings. Successive cycles of difference electron density maps made it possible to locate all non-hydrogen atoms.

The approximate atomic parameters were refined using several cycles of block matrix least-squares calculations, first with isotropic and then with anisotropic temperature factors. The C–C distance in the butyl groups were constrained at 1.54 Å. Nevertheless, due to the upper limit of 80 anisotropic atoms in the SHELX program, it was necessary, before the anisotropic refinements, to subtract the contribution to the observed structure factors of the 112 hydrogen atoms that were placed in their calculated position with C–H = 1.08 Å.

Table I. Fractional atomic coordinates ($\times 10^4$), with standard deviations in the least significant digits in parentheses. For hydrogen atoms, whose coordinates were calculated, the standard deviations are omitted.

<i>Calix[8]arene from p-1,1,3,3-tetramethylbutyl octapodand</i>			
	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>
C(1)	3424(14)	8423(15)	5365(14)
C(2)	2623(14)	8830(11)	5243(14)
C(3)	1972(13)	8323(13)	4459(17)
C(4)	2006(14)	7512(16)	3842(16)
C(5)	2832(16)	7148(11)	3979(14)
C(6)	3507(12)	7631(17)	4748(18)
C(7)	4159(18)	8890(26)	6050(24)
C(8)	4282(41)	9159(45)	6944(34)
C(9)	4879(25)	8315(21)	6342(42)
C(10)	4504(21)	9517(22)	5641(29)
C(11)	4240(18)	8620(25)	7864(20)
C(12)	3443(16)	8037(19)	7366(15)
C(13)	4049(33)	9391(19)	8716(31)
C(14)	4913(20)	8114(39)	8397(30)
O(15)	1380(8)	7058(7)	3019(8)
C(16)	900(11)	6533(11)	3275(13)
C(17)	51(14)	6354(14)	2475(20)
O(18)	90(9)	5861(10)	1473(14)
C(19)	87(15)	6308(20)	801(17)
C(20)	2952(14)	6261(12)	3206(17)
C(1')	2731(10)	4732(12)	4688(15)
C(2')	2836(10)	5498(11)	4482(13)
C(3')	2863(10)	5489(11)	3480(14)
C(4')	2789(9)	4703(12)	2756(14)
C(5')	2745(10)	3931(15)	2939(14)
C(6')	2701(11)	3927(11)	3959(19)
C(7')	2680(12)	4807(13)	5800(15)
C(8')	3306(26)	4434(39)	6295(25)
C(9')	1822(17)	4373(19)	5595(22)
C(10')	2650(18)	5737(13)	6482(19)
C(11')	4290(14)	4626(19)	6784(25)
C(12')	4645(17)	4642(22)	5901(22)
C(13')	4668(17)	3867(20)	7133(24)
C(14')	4611(36)	5450(20)	7681(33)
O(15')	2837(8)	4654(8)	1750(9)
C(16')	2025(15)	4645(15)	1094(15)
C(17')	2188(16)	4953(19)	218(19)
O(18')	2437(14)	4250(15)	-332(18)
C(19')	2517(27)	4311(33)	-1154(42)
C(20')	2692(12)	3061(12)	2185(15)
C(1'')	322(13)	2809(10)	1515(14)
C(2'')	1110(13)	3121(12)	1988(16)
C(3'')	1718(11)	2740(14)	1576(18)
C(4'')	1565(14)	2064(11)	595(16)
C(5'')	769(14)	1730(13)	169(15)
C(6'')	114(12)	2163(13)	605(15)
C(7'')	-408(10)	3166(11)	1969(13)
C(8'')	-509(23)	2810(25)	2691(37)
C(9'')	-311(17)	4139(12)	2426(29)
C(10'')	-1281(12)	2943(22)	1216(20)

Table I (continued)

	x/a	y/b	z/c
C(11'')	-359(13)	2069(11)	2976(14)
C(12'')	468(13)	1633(14)	2911(17)
C(13'')	-1064(15)	1378(22)	2367(26)
C(14'')	-383(19)	2343(22)	4102(16)
O(15'')	2257(7)	1736(7)	237(9)
C(16'')	2424(15)	2101(14)	-456(14)
C(17'')	3164(17)	1742(19)	-709(21)
O(18'')	3289(16)	2143(16)	-1351(18)
C(19'')	4036(32)	2468(63)	-1023(58)
C(20'')	638(10)	923(10)	-745(14)
C(1''')	-1657(13)	492(11)	-2158(17)
C(2''')	-898(14)	580(10)	-1444(13)
C(3''')	-210(11)	904(10)	-1642(17)
C(4''')	-287(13)	1075(12)	-2527(14)
C(5''')	-1021(12)	1009(9)	-3201(14)
C(6''')	-1730(11)	674(11)	-3082(14)
C(7''')	-2480(11)	124(11)	-2022(13)
C(8''')	-3237(10)	723(12)	-2273(17)
C(9''')	-2295(12)	126(13)	-907(12)
C(10''')	-2720(12)	-803(12)	-2723(14)
C(11''')	-3315(10)	1624(9)	-1673(12)
C(12''')	-4063(9)	1942(11)	-2343(13)
C(13''')	-2555(8)	2214(12)	-1459(14)
C(14''')	-3504(12)	1721(14)	-652(14)
O(15''')	403(8)	1444(7)	-2615(8)
C(16''')	838(13)	893(13)	-3276(15)
C(17''')	1386(15)	1411(15)	-3526(20)
O(18''')	1761(17)	973(17)	-4022(24)
C(19''')	2279(28)	1392(22)	-4430(31)
C(20''')	-1106(11)	1250(11)	-4168(11)
H(1)	2538	9470	5717
H(2)	4115	7357	4848
H(3)	4565	9794	7364
H(4)	3837	9024	7309
H(5)	5010	7888	5654
H(6)	4702	7943	6762
H(7)	5430	8712	6816
H(8)	4382	9252	4817
H(9)	5169	9618	5983
H(10)	4204	10122	5835
H(11)	3550	7486	6762
H(12)	2938	8391	7049
H(13)	3282	7826	7938
H(14)	4595	9818	9088
H(15)	3882	9165	9274
H(16)	3537	9729	8384
H(17)	5486	8499	8759
H(18)	5022	7530	7833
H(19)	4702	7950	8970
H(20)	1205	5937	3268
H(21)	817	6854	4029
H(22)	-213	6961	2446

Table I (continued)

	x/a	y/b	z/c
H(23)	-350	6010	2715
H(24)	119	5863	70
H(25)	620	6754	1108
H(26)	-480	6656	698
H(27)	2829	5648	3279
H(28)	2986	6170	2434
H(1')	2898	6103	5090
H(2')	2648	3340	4128
H(3')	3096	4412	6940
H(4')	3276	3794	5760
H(5')	1341	4700	5194
H(6')	1707	4406	6316
H(7')	1815	3710	5132
H(8')	2146	6052	6094
H(9')	3234	6076	6631
H(10')	2548	5739	7199
H(11')	4394	5170	5632
H(12')	4475	4046	5280
H(13')	5317	4723	6170
H(14')	4434	3832	7755
H(15')	5340	3956	7389
H(16')	4498	3279	6499
H(17')	4356	6000	7462
H(18')	5284	5497	7872
H(19')	4418	5433	8340
H(20')	1737	4006	784
H(21')	1633	5081	1497
H(22')	2665	5461	520
H(23')	1625	5162	-211
H(24')	2725	3712	-1586
H(25')	2972	4819	-987
H(26')	1925	4454	-1598
H(27')	2131	2781	1594
H(28')	3227	2732	1979
H(1'')	1249	3664	2682
H(2'')	-533	1975	213
H(3'')	-189	3292	3395
H(4'')	-1175	2851	2590
H(5'')	-232	4409	1857
H(6'')	229	4313	3081
H(7'')	-862	4387	2665
H(8'')	-1319	3179	580
H(9'')	-1745	3240	1605
H(10'')	-1392	2256	933
H(11'')	981	2097	3330
H(12'')	478	1376	2117
H(13'')	528	1118	3240
H(14'')	-927	815	2608
H(15'')	-1112	1209	1558
H(16'')	-1648	1626	2510
H(17'')	-271	1798	4379
H(18'')	-989	2585	4160
H(19'')	93	2841	4559

Table I (continued)

	x/a	y/b	z/c
H(20'')	1909	1956	-1141
H(21'')	2515	2789	-109
H(22'')	3076	1057	-1086
H(23'')	3684	1872	-31
H(24'')	4141	2790	-1534
H(25'')	4473	1963	-996
H(26'')	4124	2923	-263
H(27'')	574	286	-702
H(28'')	400	913	-1531
H(1''')	-828	409	-756
H(2''')	-2313	558	-3674
H(3''')	-3784	386	-2289
H(4''')	-3274	735	-3036
H(5''')	-2123	771	-393
H(6''')	-1786	-289	-758
H(7''')	-2844	-103	-787
H(8''')	-2855	-827	-3515
H(9''')	-3266	-1024	-2587
H(10''')	-2208	-1210	-2558
H(11''')	-4160	2604	-1952
H(12''')	-4615	1554	-2483
H(13''')	-3942	1893	-3065
H(14''')	-2016	2006	-988
H(15''')	-2680	2865	-1063
H(16''')	-2436	2188	-2176
H(17''')	-2987	1501	-164
H(18''')	-4062	1342	-793
H(19''')	-3598	2388	-280
H(20''')	1206	471	-2898
H(21''')	399	516	-3971
H(22''')	1805	1812	-2827
H(23''')	1015	1810	-3937
H(24''')	2605	913	-4888
H(25''')	2726	1836	-3802
H(26''')	1887	1736	-4900
H(27''')	-1043	648	-4006
H(28''')	-1401	1132	-4975

With the contribution of the hydrogens the R factor reduced by about 0.03. At this stage a refinement was carried out using only the data with I above $3\sigma(I)$. The R factor with these calculations decreased by about 0.09, a value which is found frequently in the analysis of organic compounds with a density of 1.2–1.5 g cm⁻³, which gives a relative good scattering efficiency.

In our case, with a calculated density of 1.03 the scattering is dramatically reduced, and so is the number of observed reflections. It was decided to include in the refinement the largest number of reflections in order to have a ratio (number of reflections/number of parameters) sufficiently reliable for the least-squares methods. Several cycles using the 2863 data at the $\sigma(I)$ level were computed and this strategy gave quite a high traditional R value of about 0.15. This is however preferable, because the geometrical parameters are more reliable and lead to a sufficiently good description of the molecular conformation.

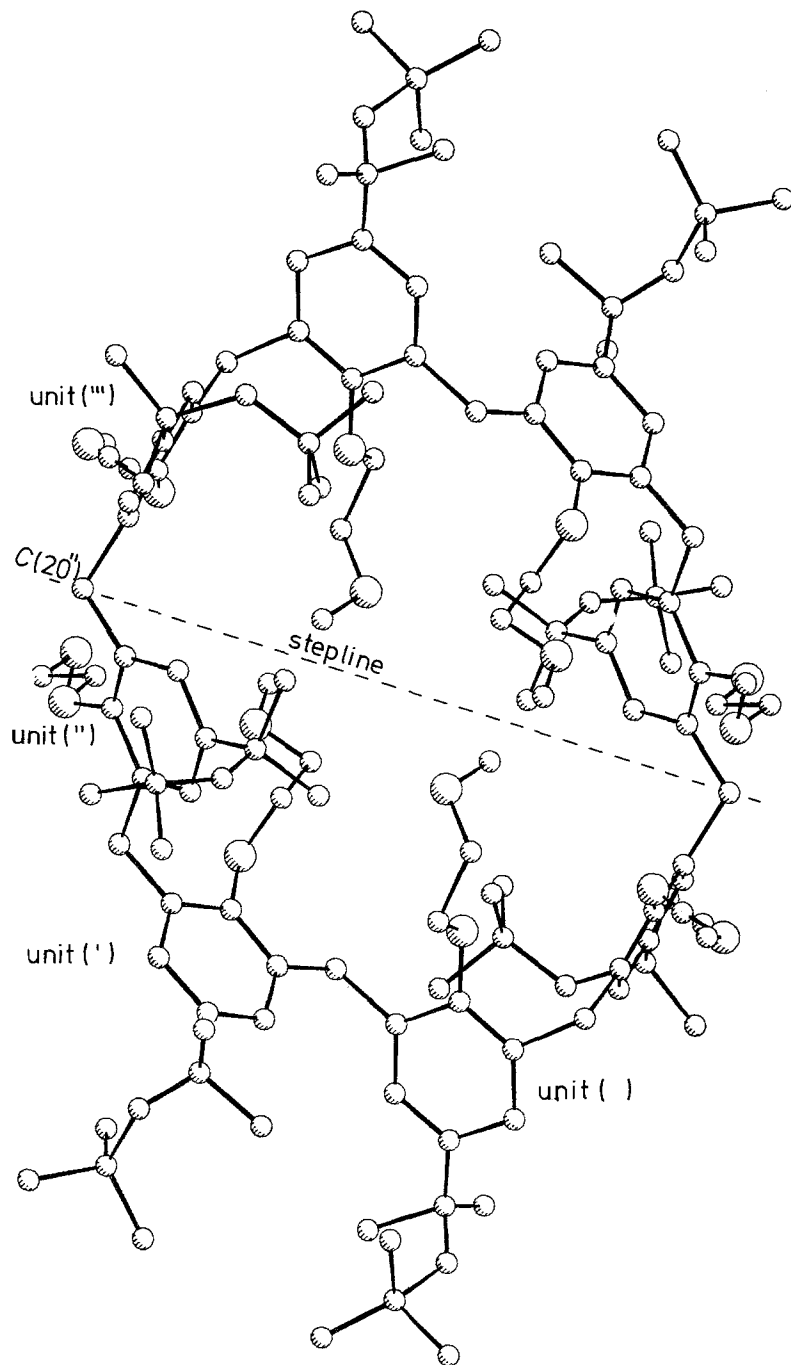


Fig. 1. View of the molecule projected on the mean molecular plane.

Table II. Bond distances (Å), Bond angles (°) and selected torsion angles (°) with standard deviations in parentheses

Bond distances (Å)	'	"	'''	
C(1)—C(2)	1.46(3)	1.41(3)	1.34(3)	1.37(3)
C(1)—C(6)	1.35(3)	1.39(3)	1.36(2)	1.42(3)
C(1)—C(7)	1.42(3)	1.58(3)	1.53(3)	1.61(3)
C(2)—C(3)	1.40(3)	1.44(3)	1.34(3)	1.42(3)
C(3)—C(4)	1.35(3)	1.36(2)	1.45(3)	1.35(3)
C(4)—C(5)	1.46(3)	1.38(3)	1.36(3)	1.32(3)
C(4)—O(15)	1.37(2)	1.44(3)	1.40(3)	1.38(3)
C(5)—C(6)	1.40(3)	1.48(4)	1.45(3)	1.40(3)
C(5)—C(20)	1.57(3)	1.48(3)	1.51(2)	1.52(3)
C(7)—C(8)	1.17(6)	1.33(5)	1.39(6)	1.60(3)
C(7)—C(9)	1.54(5)	1.54(4)	1.52(3)	1.54(3)
C(7)—C(10)	1.54(6)	1.54(3)	1.54(2)	1.54(2)
C(8)—C(11)	1.82(8)	1.60(5)	1.39(5)	1.48(2)
C(11)—C(12)	1.54(4)	1.54(5)	1.53(3)	1.54(2)
C(11)—C(13)	1.54(5)	1.53(5)	1.54(3)	1.54(2)
C(11)—C(14)	1.54(6)	1.54(4)	1.54(3)	1.53(3)
O(15)—C(16)	1.39(3)	1.42(3)	1.40(3)	1.41(2)
C(16)—C(17)	1.53(3)	1.58(4)	1.43(4)	1.46(4)
C(17)—O(18)	1.42(3)	1.30(4)	1.35(5)	1.13(4)
O(18)—C(19)	1.38(4)	1.25(7)	1.28(7)	1.46(6)
C(20)—C(3')	1.47(3)	1.64(3)	1.62(2)	1.58(3)
<i>Bond angles (°)</i>				
C(6)—C(1)—C(7)	118(2)	120(3)	115(2)	117(2)
C(2)—C(1)—C(7)	121(2)	118(2)	122(7)	122(2)
C(2)—C(1)—C(6)	121(2)	122(2)	123(2)	121(2)
C(1)—C(2)—C(3)	114(2)	121(2)	118(2)	118(2)
C(2)—C(3)—C(4)	128(2)	116(2)	124(2)	121(2)
C(3)—C(4)—O(15)	126(2)	119(2)	118(2)	117(2)
C(4)—C(5)—C(20)	119(2)	127(2)	117(2)	120(2)
C(6)—C(5)—C(20)	122(2)	113(2)	125(2)	118(2)
C(4)—C(5)—C(6)	119(2)	120(2)	119(2)	122(2)
C(1)—C(6)—C(5)	122(2)	116(2)	119(2)	118(2)
C(1)—C(7)—C(10)	114(3)	113(2)	116(2)	113(2)
C(1)—C(7)—C(9)	114(3)	103(2)	110(2)	108(2)
C(1)—C(7)—C(8)	125(3)	113(2)	114(2)	109(2)
C(9)—C(7)—C(10)	107(3)	107(2)	108(2)	108(2)
C(8)—C(7)—C(10)	111(5)	108(2)	99(2)	109(2)
C(8)—C(7)—C(9)	82(4)	113(2)	110(3)	111(2)
C(7)—C(8)—C(11)	131(5)	136(5)	142(4)	126(2)
C(8)—C(11)—C(14)	130(3)	120(3)	105(3)	113(2)
C(8)—C(11)—C(13)	99(3)	109(3)	112(3)	114(1)
C(8)—C(11)—C(12)	105(3)	106(2)	118(2)	105(1)
C(13)—C(11)—C(14)	107(3)	108(3)	107(2)	108(1)
C(12)—C(11)—C(14)	107(3)	108(3)	108(2)	108(1)
C(12)—C(11)—C(13)	107(3)	107(2)	107(2)	108(1)
C(4)—O(15)—C(16)	113(1)	110(2)	114(2)	115(2)
O(15)—C(16)—C(17)	108(2)	103(2)	108(2)	109(2)
C(16)—C(17)—O(18)	114(2)	100(2)	104(2)	109(3)
C(17)—C(18)—C(19)	117(2)	112(4)	109(4)	116(3)
C(5)—C(20)—C(3')	117(2)	111(2)	114(2)	110(2)
C(20)—C(3')—C(2')	124(2)	119(2)	111(2)	118(2)

Table II (continued)

		'	"	'''
<i>Selected torsion angles (°) concerning the ether chains</i>				
C(3)—C(4)—O(15)—C(16)	-95(3)	-94(2)	-97(2)	106(2)
C(4)—O(15)—C(16)—C(17)	157(2)	159(2)	177(2)	164(2)
O(15)—C(16)—C(17)—O(18)	66(2)	79(2)	-178(2)	177(2)
C(16)—C(17)—O(18)—C(19)	-99(2)	172(3)	127(5)	174(3)
<i>Selected torsion angles (°) concerning the methylene groups</i>				
C(4)—C(5)—C(20)—C(3')	-93(3)	-89(3)	-140(2)	-144(2)
C(5)—C(20)—C(3')—C(2')	-13(3)	-20(3)	-86(2)	-101(4)
<i>Selected torsion angles (°) concerning the butyl chains</i>				
C(1)—C(7)—C(8)—C(11)	54(8)	70(6)	-26(7)	-67(2)
C(10)—C(7)—C(8)—C(11)	-164(5)	-57(6)	97(6)	170(2)
C(9)—C(7)—C(8)—C(11)	-59(6)	-174(4)	-151(5)	52(2)
C(7)—C(8)—C(11)—C(12)	-44(7)	-58(6)	40(7)	170(2)
C(7)—C(8)—C(11)—C(13)	-154(6)	-173(5)	-85(6)	52(2)
C(7)—C(8)—C(11)—C(14)	85(8)	63(6)	160(5)	-73(2)
C(6)—C(1)—C(7)—C(8)	-122(5)	61(4)	96(3)	-50(2)
C(2)—C(1)—C(7)—C(8)	144(2)	-84(3)	-117(3)	66(6)

The final difference electron-density map showed the highest residual peak of $0.51 e \text{ \AA}^{-3}$ and the average C—C distance was $1.47(5) \text{ \AA}$ which is comparable with the value observed in structures with *R* factors around 0.05. Finally, the scattering factors were calculated with an analytical approximation [8]. All the calculations were performed on the GOULD-SEL 32/77 of Centro di Studio per la Strutturistica Diffraattometrica del C.N.R. Parma.

5. Discussion

Table I gives the atomic fractional coordinates for the C and O atoms, while bond distances, bond angles and selected torsion angles are reported in Table II. Unfortunately, due to the quite limited numbers of observed reflection, the e.s.d. of the geometrical parameters are rather high.

The molecule possesses a centre of symmetry which coincides with the crystallographic centre of symmetry at $(0, 1/2, 0)$. The macrocyclic molecule shows a roughly ellipsoidal shape and can be considered as formed by two molecular fragments of four phenolic units, each one in an almost helical arrangement (Figure 1).

The methylene carbon atoms of the four phenolic units practically lie in a plane from which the centre of symmetry deviates by $1.86(1) \text{ \AA}$ and the mean plane described by the remaining centrosymmetrically related four phenolic units by $3.72(1) \text{ \AA}$. On the other hand, if the oxygen atoms of the same four phenolic units are considered, they form an average plane with out of plane distances of about 0.45 \AA , which passes almost through the centre of symmetry (at -0.3 \AA). This plane will be considered in this paper as the mean molecular plane and Figure 1 shows the molecule projected on it.

The conformation of the macrocycle can be described by the dihedral angles (in this paper the notation $(), (') \dots$ is used, to indicate the phenolic units shown in Figure 1) formed by the four phenolic units with respect to the mean molecular plane: $21.3(5)^\circ$, $119.5(5)^\circ$, $45.5(5)^\circ$, $86.6(5)^\circ$ for the unprimed, primed, double primed and triple primed groups respectively.

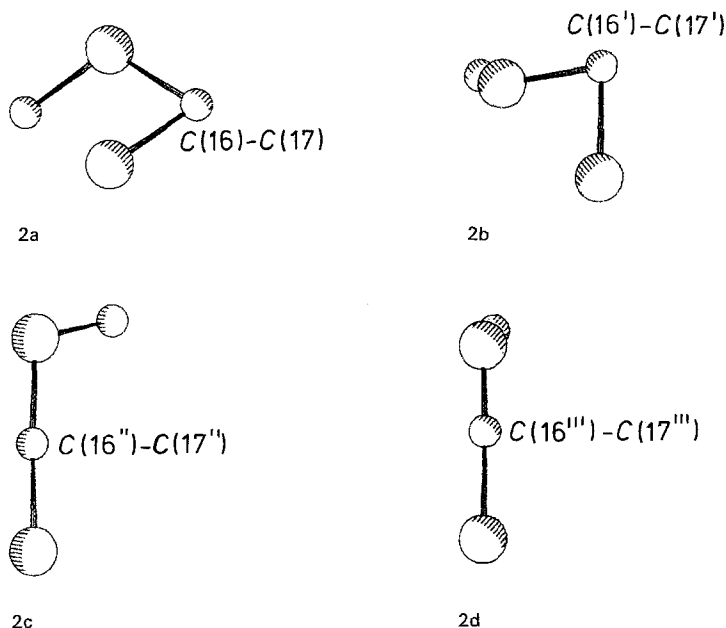


Fig. 2. Conformation of the ether chains: (a) View along C(16)–C(17); (b) View along C(16')–C(17'); (c) View along C(16'')–C(17''); (d) View along C(16''')–C(17''').

Moreover the relative dihedral angles formed by the mean square planes between the phenolic rings: (')–(') = $98.3(6)^\circ$, ('')–(') = $78.4(7)^\circ$, (''')–(') = $117.6(5)^\circ$ and (''')–('') = $95.1(5)^\circ$, describe a helical arrangement of the phenolic units in the macromolecular ring with a discontinuity between the units ('') and ('''); the butyl chains attached to the adjacent units ('') and (''') point outside the macroring and the ether chains point inside, while in the two successive phenolic units (''') and (''') the butyl chains point, at least in part, inside the macroring and the ether chains lie almost perpendicular to the mean molecular plane.

The disposition of the phenolic units responsible for the helical conformation of the macroring is comparable with that observed in the structure of *p-t*-butylphenol–formaldehyde cyclic octamer [9], where the angles between the rings and the mean molecular plane are in the range $40.0(5)$ to $60.2(5)^\circ$, and the dihedral angles between the mean phenolic planes are in the range $81.7(5)$ to $86.4(5)^\circ$.

In other cyclic oligomers investigated by us [10, 11] the macromolecular conformation is determined, to a large extent, by intramolecular hydrogen bonds. They influence some structural parameters, for example, the bond angles at the methylene carbon atoms that change from the theoretical value of 109.5° , to a mean value of 112° to 113° , while the torsion angles involving the methylene carbon atoms range around $\pm 90^\circ$.

In the present case, due to the functionalization of OH groups, the intramolecular hydrogen bonds are absent, so that the conformation of the macroring appears to be mainly influenced by steric interactions between the polyether chains. The torsion angles involving bridging methylenes are $-93(3)^\circ$, $-89(3)^\circ$, $-140(2)^\circ$, $-144(2)^\circ$, showing that the torsion angles

around the bridges joining ()—(') and (')—(") do not deviate significantly from $+90^\circ$ as observed in the presence of intramolecular hydrogen bonds, while in the two successive bridges joining (")—(") and (")—()— the two torsion angles deviate strongly from $\pm 90^\circ$. This situation is quite different from that observed in the *p-t*-butylcalix[6]arene hexapodand (1) where all the torsion angles involving methylene carbon atoms deviate significantly from $\pm 90^\circ$.

The structural parameters describing the butyl chains are listed in Table II, and reveal significant differences with respect to the butyl chains observed in other macrocycles investigated by us [10].

In particular the calculated torsion angles C(6)—C(1)—C(7)—C(8)' $-122(5)^\circ$, $61(4)^\circ$, $96(3)^\circ$, $-50(2)^\circ$ and C(1)—C(7)—C(8)—C(11)' $54(8)^\circ$, $70(6)^\circ$, $-26(7)^\circ$, $-67(2)^\circ$, can be compared with the corresponding ones observed in [12] which are $-55.5(6)^\circ$, $129.3(7)^\circ$, $-110.2(8)^\circ$, $111.5(5)^\circ$ and $-75.5(6)^\circ$, $-71.1(8)^\circ$, $-57.6(6)^\circ$ respectively.

The polar polyether chains in the units () and (') lie almost in the mean molecular plane. They point 'inside' the macroring, thereby partially filling the intramolecular cavity, while in the units (") and (") the chains lie almost perpendicular to the mean molecular plane and do not seem to affect the intramolecular cavity.

The conformation of the chains which are illustrated in Figure 2, can be better described by analyzing the torsion angles involved. In fact the four chains reveal, at least in part, a similar conformation, with the atom O(15) that lies almost in the mean plane of the phenolic ring and with the bonds O(15)—C(16) almost perpendicular to it. A similar situation has been observed in (1).

The most important relative differences in the conformation of the ether chains are in the fragments C(17)—O(18)—C(19). They are probably due to steric interactions between the chains. In fact in the chains () and (') the torsion angles O(15)—C(16)—C(17)—O(18), $66(2)^\circ$ and $79(2)^\circ$ reveal a *gauche* conformation while in the chains (") and (") the torsion angles $-178(2)^\circ$ and $177(2)^\circ$ reveal a *trans* conformation. This situation is different from that observed in the hexapodand (1) where the O—CH₂—CH₂—O conformation is *gauche* in the

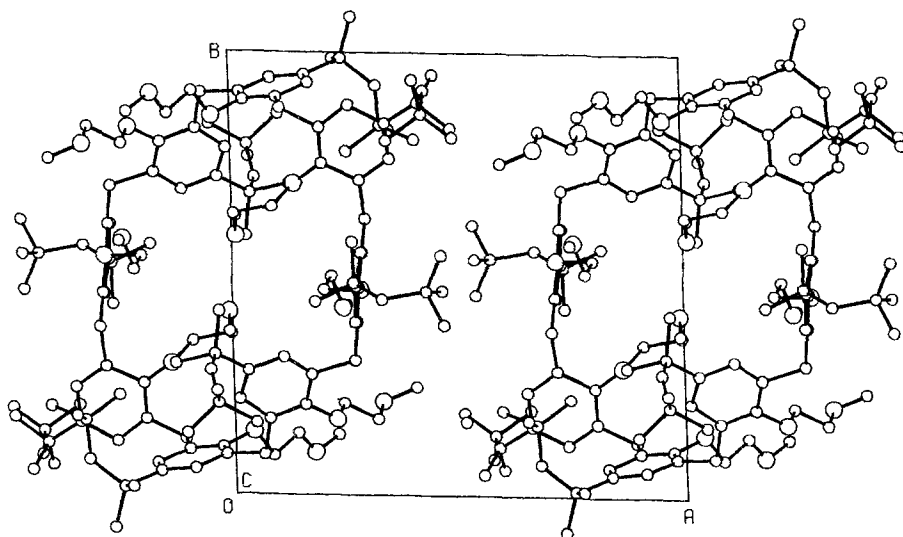


Fig. 3. Molecular packing projected along [001].

three ether chains. Moreover the torsion angles C(16)—C(17)—O(18)—C(19), $-99(2)^\circ$, $172(3)^\circ$, $127(5)^\circ$, $174(3)^\circ$ describe an identical conformation in the units (') and (") while the conformation of () and (") are different, by analogy with the structure of the hexapodand (1).

The intramolecular cavity is mainly filled by the ether chains of () and (') and their centrosymmetric units, while the butyl chains seems to play a negligible role. Under these conditions it can be concluded that the macrocycle assumes the observed topology in order to maximize the crystal density minimizing the molecular volume. A systematic search for cavities in the unit cell with the aid of a suitable computer program has not revealed the presence of an intermolecular cavity so that the low value of the crystal density, $D_c = 1.03 \text{ g cm}^{-3}$, can be explained in terms of a large number of intra- or intermolecular spacings of small dimensions rather than a small number of wide cavities.

Therefore, it is interesting to speculate on what the possible volume (fitted to an ellipsoidal shape) of the intramolecular cavity may be, if the atoms C(17)—O(18)—C(19) and their bonded hydrogen atoms H(22)—H(23)··H(26), of the most flexible part of the ether chains, are removed.

Under these conditions an 'ellipsoidal cavity', with the axes in the macroring plane of 3.3 by 5.4 Å can be calculated. In solution the rotation of the polar chains outside the cavity leaves a significant space available for intramolecular inclusion of small molecules. Further work is in progress to isolate molecular complexes of macrocycles (1) and (2) suitable for study by X-ray diffraction techniques.

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