# Molecular Inclusion in Functionalized Macrocycles. Part 5.† The Crystal and Molecular Structure of 25,26,27,28,29-Pentahydroxycalix[5]-arene–Acetone (1 : 2) Clathrate ‡

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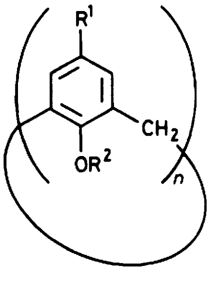
A phenol–formaldehyde cyclic pentamer, 25,26,27,28,29-pentahydroxycalix[5]arene (1), has been isolated after dealkylation of a fraction of cyclic products from the base-catalysed reaction of *p*-(1,1,3,3-tetramethylbutyl)phenol and formaldehyde. This compound, which is the first cyclic product with an odd number of phenolic units isolated in such reactions, is able to form an inclusion complex (1 : 2) with acetone. The symmetry of the macrocyclic molecule is $C_s$ and the acetone molecules interact with the OH crown and with the cavity with O · · · O and $CH_3$–phenyl contacts respectively.

MOLECULAR inclusion of organic guest molecules inside ordered matrices both natural such as cyclodextrins [4] or synthetic such as crown ethers [5] or other systems [6] is a well known phenomenon in chemistry. Studies in this field have increased in number recently taking in biomimetic chemistry and enzyme catalysis [7] as well as analytical chemistry.[8]



(1) $n = 5$, $R^1 = R^2 = H$
(2) $n = 4$, $R^1 = Bu^t$, $R^2 = H$
(3) $n = 4$, $R^1 = Bu^t$, $R^2 = CH_3CO$
(4) $n = 8$, $R^1 = Bu^t$, $R^2 = H$
(5) $n = 8$, $R^1 = Bu^t$, $R^2 = CH_3CO$
(6) $n = 4$, $R^1$ = 1,1,3,3,-tetramethylbutyl, $R^2 = H$
(7) $n = 8$, $R^1$ = octyl, $R^2 = H$

Among the synthetic matrices which are able to form inclusion complexes with several guest molecules, the cyclic oligomers between phenols and formaldehyde (1)—(7), recently named calix[5]arenes,[1] deserve special mention. They represent a class of functionalized macrocycles of well defined structure, with many possibilities of varying the number of phenolic units in the cyclic array and the nature of the substituents both on the aromatic nucleus ($R^1$) and on the phenolic OH ($R^2$) and therefore they are particularly attractive for the study of the influence of these parameters on the inclusion phenomena.

Two types of inclusion complexes have been shown by this class of functionalized macrocycle. Cage-like clathrates are formed by *p*-t-butylphenoxycalix[4]-arene (2) and aromatic molecules such as toluene,[9] benzene, *p*-xylene, and anisole [10] whereas channel-type clathrates are formed by calix[4]arene (3) and acetic acid [11] or by calix[4]arene (6) and aromatic molecules.[12]

We report here the crystal and molecular structure of a 2 : 1 clathrate between acetone and calix[5]arene (1) formally derived from phenol, but actually isolated after de-alkylation of a fraction of the cyclic products from the base-catalysed reaction of *p*-octylphenol and formaldehyde.[13] This compound is the first cyclic oligomer with an odd number of phenolic units isolated from the reaction mixtures from base-catalysed condensations of *para*-substituted phenols and formaldehyde, and this could also have some relevance for the mechanism of calixarene formation. In fact, only even numbered calixarenes ($n = 4$, 6, or 8) have been obtained so far as products from the reaction of *p*-t-butylphenol and formaldehyde in the presence of bases [1,3,9] and also in the analogous reaction of *p*-octylphenol only the cyclic tetramer [12] (6) and octamer [13] (7) have been identified. These facts suggested to Gutsche a possible reaction scheme in which cyclodimerization rather than the cyclization of linear monohydroxymethylated species was the major reaction pathway in the formation of calixarenes.[1] However calixarenes formed by five and seven phenolic units (not necessary identical) are known since being synthesized by Kämmerer *et al.* using a stepwise procedure.[14]

*X-Ray Structure Analysis*.—Crystals were colourless prisms elongated on [010]. Lattice parameters were refined by least-squares by use of 25 $(\theta,\chi,\phi)_{hkl}$ measurements taken on a Philips PW 1100 single crystal diffractometer. A crystal specimen of 0.3 × 0.7 × 0.4 mm was used for data collection.

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† Parts 1—4, refs. 9, 3, 11, and 2, respectively.

‡ We have adopted the nomenclature recently proposed by Gutsche *et al.* [1] and accepted by Chemical Abstracts, which has the advatage of being much simpler than the systematic names.[1,2] However, this nomenclature (which relates the shape of the molecules and the Greek name *chalix*) is fully appropriate for rings up to $n = 6$ but not completely so for octamers which have more rotational freedom, and much less so for derivatives of these macrocycles in which the OH groups are functionalised and the chalice structure destroyed.[1–3]

*Crystal data.* $C_{35}H_{30}O_5 \cdot 2C_3H_6O$, $M = 646.8$. Orthorhombic, $a = 22.916$ (7), $b = 10.341$ (3), $c = 14.723$ (5) Å, $U = 3\,489$ (2) Å$^3$, $Z = 4$, $D_c = 1.23$ g cm$^{-3}$, $F(000) = 1\,376$. Mo-$K_\alpha$ radiation, $\lambda = 0.71069$ A, $\mu$(Mo-$K_\alpha$) = 0.78 cm$^{-1}$. Absence spectra: $0kl$ $k + l \neq 2n$, $h0l$ $h \neq 2n$ define space group *Pnam* or $Pna2_1$, ($D_{2h}^{16}$, No. 62 non-standard setting or $C_{2v}^{9}$, No. 33) and the latter was confirmed by the analysis.

Intensity data were collected up to $\theta$ 29° by use of the $\omega$ scan with graphite-monochromatized Mo-$K_\alpha$ radiation. 1 443 significant reflections with $I > 2\sigma(I)$ [$\sigma(I)$ based on counting statistics] have been retained out of a total of 3 122 measured reflections. No corrections were made for absorption.

*Structure analysis and refinement.* The distribution of unitary structure factors was dubious and closer to the centrosymmetric theoretical model, but it was decided to start in the non-centrosymmetric space group $Pna2_1$ and check the correct assignment later. The structure was solved at the first trial by direct phase-determining methods using the SHELX system of programs.[15] The 257 reflections having the largest $|E|$ magnitudes were used. An $E$ map computed with that set of phases which gave the lowest residual revealed all the non-hydrogen atom positions in the asymmetric unit. The approximate atomic parameters were adjusted by several cycles of full-matrix least-squares calculations and, with anisotropic temperature factors for all atoms, $R$ was reduced to 0.097. The hydrogen atoms were clearly evident in a difference electron-density distribution but were included in the subsequent cycles of least-squares refinement in their geometrically constructed position with C–H 1.08 Å and with variable isotropic thermal parameters in order to reduce the number of refined parameters. The final $R$ value was 0.053 ($R_w$ 0.049). The final difference electron-density map showed the highest residual peaks of *ca.* 0.4 e Å$^{-3}$ near the hydroxy oxygen atoms and distributed in the two possible directions of the isodromic intramolecular hydrogen bonds system.

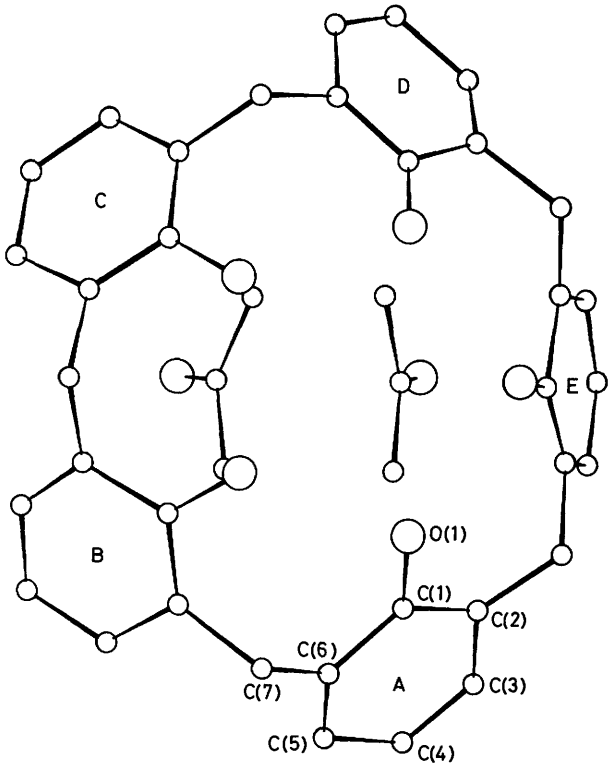

FIGURE 1 Atomic numbering

Plots of $|\Delta F|$ as a function of scattering angle, magnitude of $|F_o|$, and Miller indices revealed a linear trend. The number of observations (1 443) is rather limited with respect to the number of refined parameters (458) and

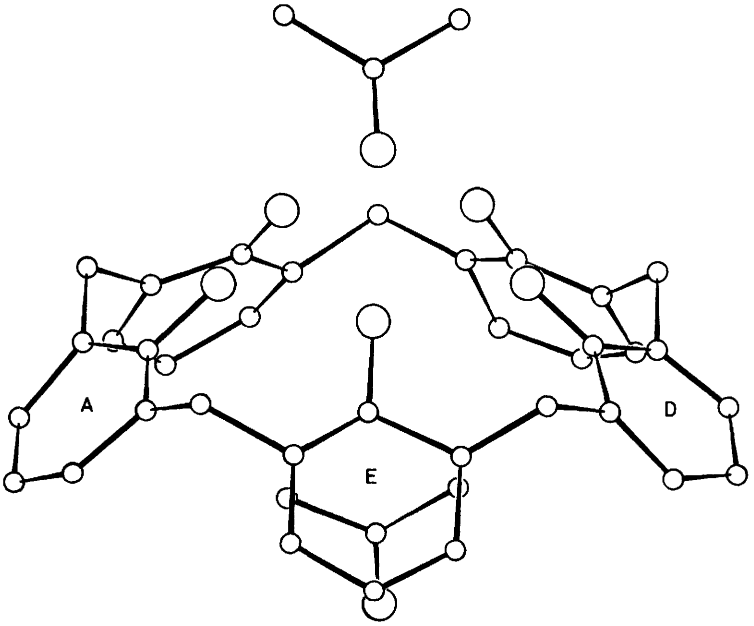

FIGURE 2 An illustration of the host–guest interactions in the crystal as viewed perpendicularly to the $C_s$ molecular plane

this affects the accuracy of the geometrical parameters, mainly bond distances.

At this stage, starting with the final co-ordinates, refinement of the space group *Pnam* was repeated, locating the acetone molecules and the pentamer on a plane of symmetry going through O(1),C(1); O(2),C(11); and C(4E),C(1E),O(1E),C(7B). Several cycles of full-matrix least-squares cycles led to a final $R$ of 0.065 ($R_w$ 0.061). On the basis of Hamilton's significance test the refinement in the space group $Pna2_1$ results in a significant improvement. Moreover some comment on the two sets of final data must be made. In the centrosymmetric space group, bond distances within the phenyl rings are less scattered around the theoretical value of 1.39 Å while thermal parameters are much more anisotropic, especially those of the guest acetone molecules. So the average geometry of the macrocycle can be assigned to the $C_s$ point group with slight but significance distortions caused by packing forces (see Figure 2) and for this reason the data have been assigned the $Pna2_1$ space group.

Calculations were carried out on a CDC Cyber 76 computer, (CINECA, Bologna). Observed and calculated structure factors and anisotropic thermal parameters are listed in Supplementary Publication No. SUP 23302 (13 pp.).* Scattering factors were taken from ref. 16. Atomic fractional co-ordinates are listed in Table 1 and various parameters connected with the molecular geometry are listed in Table 2.

*Molecular Geometry*.—The conformation of the molecule with $C_s$ symmetry, shown in Figures 1 and 2, is mainly determined by the intramolecular hydrogen bond system, as observed in the tetramer, so the molecular shape resembles a chalice and the proposed name is fully justified for this compound. The O · · · O contacts [O(1A) · · · O(1B) 2.848 (9), O(1B) · · · O(1C) 2.856(10), O(1C) · · · O(1D) 2.841(10), O(1D) · · · O(1E) 2.828(9), O(1E) · · · O(1A) 2.832(10) Å] are significantly longer than observed in the tetramer [2.670(9) Å], indicating a significant weakening of the hydrogen bonding. The angles at the methylene carbon atoms are 113.2 (7), 116.8(9), 114.4(9), 118.0(12), and 118.1(13)°, respectively, for atoms C(7A)—C(7E) to be compared with 113.1(6)° observed in the tetramer and the inclination of the phenolic units with respect of the five methylene carbon atoms mean plane are 139.4(6), 126.8(7), 128.3(8), 138.2(7), 126.5(8)°, respectively, for rings A—E, instead of 123(1)° in the tetramer. So the differences observed in the conformational parameters of the two macrocycles indicate a greater strain in the macro-ring in the pentamer and a less favourable situation for hydrogen bonding at least for units A and D, the ideal tilt of the phenolic units for the strongest O–H · · · O interaction being *ca.* 120°. Moreover one of the two molecules of acetone strongly interacts with the plane of the five OH groups with contacts O(1) · · · O(1A) 2.945(10), O(1) · · ·

TABLE 1

Fractional atomic co-ordinates (× $10^4$, hydrogens × $10^3$). Hydrogen atoms are numbered according to the atoms to which they are attached

| | *x/a* | *y/b* | *z/c* |
|---|---|---|---|
| C(1A) | 1 686(4) | 7 509(9) | 0(0) |
| C(2A) | 2 125(3) | 6 563(10) | −173(7) |
| C(3A) | 2 070(5) | 5 605(12) | −798(9) |
| C(4A) | 1 600(5) | 5 668(10) | −1 433(9) |
| C(5A) | 1 219(4) | 6 623(12) | −1 346(8) |
| C(6A) | 1 237(3) | 7 442(9) | −634(6) |
| C(7A) | 749(3) | 8 543(9) | −641(6) |
| O(1A) | 1 699(2) | 8 389(6) | 649(5) |
| C(1B) | 167(4) | 8 732(10) | 759(7) |
| C(2B) | 222(3) | 8 208(9) | −85(6) |
| C(3B) | −216(4) | 7 412(13) | −421(8) |
| C(4B) | −715(4) | 7 323(16) | 108(10) |
| C(5B) | −804(5) | 7 762(14) | 938(10) |
| C(6B) | −345(3) | 8 724(9) | 1 267(7) |
| C(7B) | −469(3) | 9 363(9) | 2 138(18) |
| O(1B) | 611(2) | 9 511(6) | 1 147(5) |
| C(1C) | 165(4) | 8 813(8) | 3 486(6) |
| C(2C) | −375(4) | 8 555(9) | 2 984(6) |
| C(3C) | −765(4) | 7 929(10) | 3 406(7) |
| C(4C) | −729(5) | 7 260(11) | 4 241(6) |
| C(5C) | −221(4) | 7 604(10) | 4 751(7) |
| C(6C) | 233(4) | 8 381(11) | 4 377(7) |
| C(7C) | 769(4) | 8 648(12) | 5 007(8) |
| O(1C) | 623(2) | 9 436(6) | 3 085(4) |
| C(1D) | 1 665(4) | 7 465(8) | 4 410(6) |
| C(2D) | 1 194(4) | 7 581(10) | 5 054(7) |
| C(3D) | 1 166(4) | 6 513(10) | 5 682(7) |
| C(4D) | 1 669(5) | 5 591(12) | 5 735(9) |
| C(5D) | 2 121(4) | 5 731(9) | 5 154(7) |
| C(6D) | 2 143(4) | 6 612(9) | 4 432(6) |
| C(7D) | 2 674(6) | 6 705(18) | 3 886(12) |
| O(1D) | 1 699(3) | 8 398(6) | 3 706(5) |
| C(1E) | 2 578(3) | 6 569(8) | 2 228(16) |
| C(2E) | 2 701(7) | 5 965(18) | 2 973(14) |
| C(3E) | 2 840(7) | 4 713(20) | 3 002(14) |
| C(4E) | 2 901(3) | 4 015(9) | 2 174(23) |
| C(5E) | 2 824(8) | 4 605(19) | 1 366(15) |
| C(6E) | 2 657(7) | 5 944(19) | 1 313(13) |
| C(7E) | 2 668(7) | 6 655(19) | 459(11) |
| O(1E) | 2 407(2) | 7 859(4) | 2 180(11) |
| O(1) | 1 773(3) | 286(7) | 2 133(19) |
| C(1) | 1 646(3) | 1 426(9) | 2 181(21) |
| C(2) | 1 603(10) | 2 169(29) | 3 066(17) |
| C(3) | 1 543(10) | 2 104(21) | 1 327(15) |
| O(2) | 227(3) | 3 833(8) | 2 127(19) |
| C(11) | 474(5) | 4 855(12) | 2 159(22) |
| C(12) | 527(21) | 5 357(34) | 3 042(25) |
| C(13) | 698(17) | 5 500(30) | 1 343(22) |
| H(3A) | 237(5) | 480(9) | −81(7) |
| H(4A) | 155(5) | 500(8) | −199(8) |
| H(5A) | 88(4) | 677(9) | −185(8) |
| H(71A) | 93(3) | 942(8) | −37(7) |
| H(72A) | 62(3) | 870(9) | −134(6) |
| H(3B) | −15(4) | 677(10) | −99(7) |
| H(4B) | −112(4) | 719(11) | −27(9) |
| H(5B) | −113(5) | 731(10) | 136(10) |
| H(71B) | −93(3) | 963(9) | 212(10) |
| H(72B) | −21(4) | 1 022(8) | 219(9) |
| H(3C) | −119(4) | 796(9) | 310(7) |
| H(4C) | −102(5) | 648(10) | 444(6) |
| H(5C) | −20(5) | 733(9) | 546(7) |
| H(71C) | 100(4) | 951(10) | 479(8) |
| H(72C) | 60(4) | 880(10) | 568(8) |
| H(3D) | 79(4) | 638(10) | 612(7) |
| H(4D) | 167(5) | 480(9) | 622(9) |
| H(5D) | 250(4) | 513(9) | 526(7) |
| H(71D) | 305(6) | 638(10) | 429(10) |
| H(72D) | 273(6) | 772(9) | 373(10) |
| H(3E) | 291(7) | 429(10) | 366(9) |
| H(4E) | 302(3) | 302(9) | 223(10) |
| H(5E) | 289(8) | 401(10) | 77(11) |
| H(71E) | 301(7) | 623(10) | 6(9) |
| H(72E) | 277(7) | 766(11) | 59(10) |

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* For details of Supplementary Publications see Notice to Authors No. 7 in *J. Chem. Soc., Perkin Trans. 2*, 1981, Index Issue.

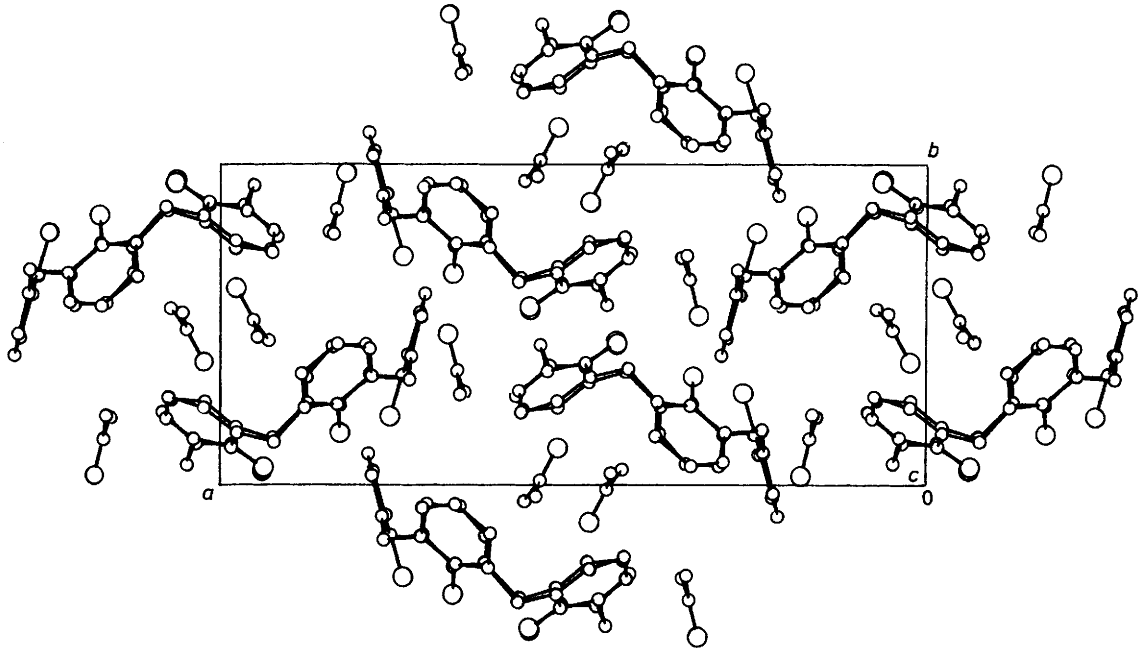

FIGURE 3 A view of the molecular packing along *c*

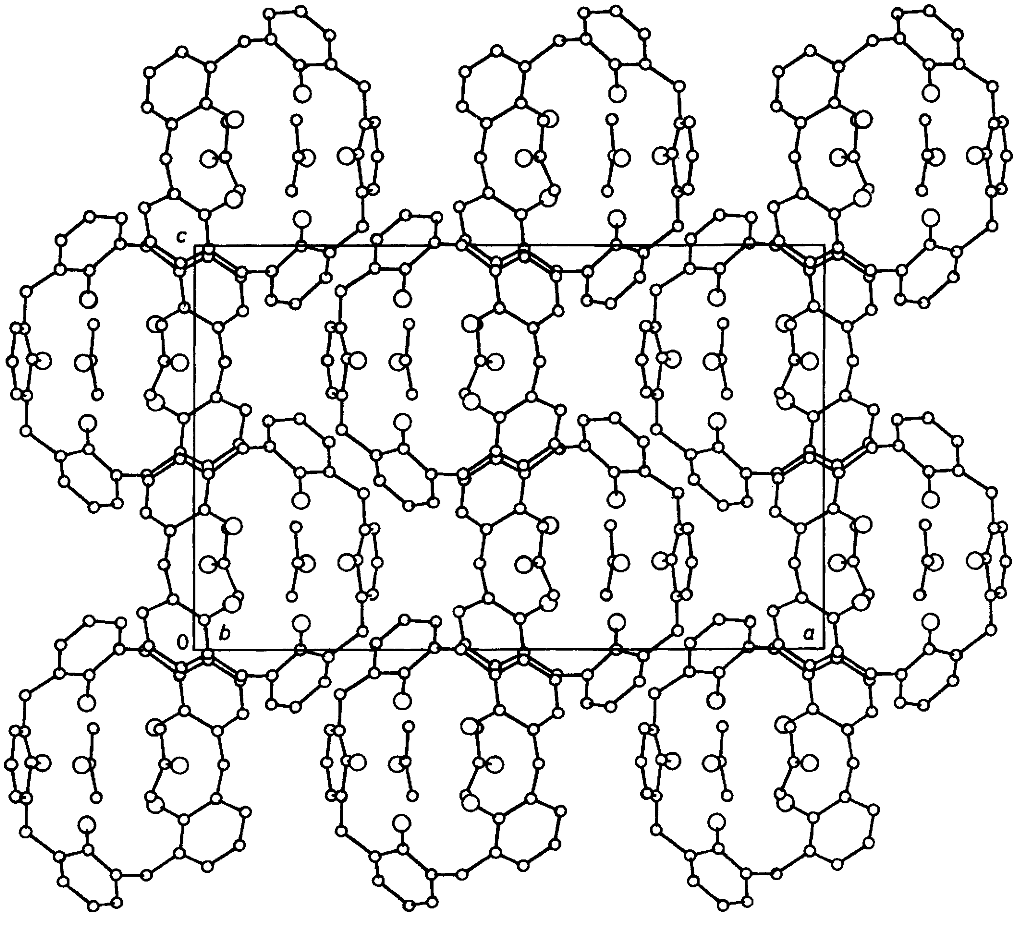

FIGURE 4 A view of the molecular packing along *b*

TABLE 2

Interatomic distances (Å), bond angles (°), and selected torsion angles (°) with standard deviations in parentheses

(*a*) Bond lengths

| | A | B | C | D | E |
|---|---|---|---|---|---|
| C(1)–C(2) | 1.43(1) | 1.36(1) | 1.47(1) | 1.44(1) | 1.30(1) |
| C(1)–C(6) | 1.39(1) | 1.39(1) | 1.39(1) | 1.41(1) | 1.51(3) |
| C(1)–O(1) | 1.32(2) | 1.42(1) | 1.37(1) | 1.42(1) | 1.40(1) |
| C(2)–C(3) | 1.36(1) | 1.39(1) | 1.27(2) | 1.44(1) | 1.34(3) |
| C(3)–C(4) | 1.43(1) | 1.39(1) | 1.41(1) | 1.49(2) | 1.42(3) |
| C(4)–C(5) | 1.33(1) | 1.32(2) | 1.43(1) | 1.35(2) | 1.35(3) |
| C(5)–C(6) | 1.35(1) | 1.53(2) | 1.43(1) | 1.40(1) | 1.44(3) |
| C(6)–C(7) | 1.59(1) | 1.47(3) | 1.56(2) | 1.47(2) | 1.46(3) |

| | | | |
|---|---|---|---|
| C(2A)–C(7E) | 1.56(2) | C(7A)–C(2B) | 1.50(1) |
| C(7B)–C(2C) | 1.52(2) | C(7C)–C(2D) | 1.48(2) |
| C(7D)–C(2E) | 1.54(3) | O(1)–C(1) | 1.22(1) |
| C(1)–C(2) | 1.52(4) | C(1)–C(3) | 1.46(3) |
| O(2)–C(11) | 1.20(1) | C(11)–C(12) | 1.41(5) |
| C(11)–C(13) | 1.47(4) | | |

(b) Bond angles

| | A | B | C | D | E |
|---|---|---|---|---|---|
| C(6)–C(1)–O(1) | 122(1) | 113(1) | 118(1) | 114(1) | 114(2) |
| C(2)–C(1)–O(1) | 126(1) | 122(1) | 121(1) | 118(1) | 125(2) |
| C(2)–C(1)–C(6) | 112(1) | 125(1) | 121(1) | 128(1) | 122(1) |
| C(1)–C(2)–C(3) | 124(1) | 120(1) | 116(1) | 113(1) | 123(1) |
| C(2)–C(3)–C(4) | 119(1) | 116(1) | 129(1) | 119(1) | 119(2) |
| C(3)–C(4)–C(5) | 118(1) | 129(1) | 112(1) | 119(1) | 121(1) |
| C(4)–C(5)–C(6) | 122(1) | 114(1) | 122(1) | 125(1) | 121(2) |
| C(1)–C(6)–C(5) | 125(1) | 114(1) | 118(1) | 113(1) | 113(2) |
| C(5)–C(6)–C(7) | 115(1) | 116(1) | 116(1) | 119(1) | 122(2) |
| C(1)–C(6)–C(7) | 119(1) | 129(1) | 126(1) | 127(1) | 124(2) |

| | | | |
|---|---|---|---|
| C(1A)–C(2A)–C(7E) | 114(1) | C(3A)–C(2A)–C(7E) | 122(1) |
| C(6A)–C(7A)–C(2B) | 113(1) | C(7A)–C(2B)–C(1B) | 119(1) |
| C(7A)–C(2B)–C(3B) | 122(1) | C(6B)–C(7B)–C(2C) | 116(1) |
| C(7B)–C(2C)–C(1C) | 116(1) | C(7B)–C(2C)–C(3C) | 126(1) |
| C(6C)–C(7C)–C(2C) | 114(1) | C(7C)–C(2D)–C(1D) | 122(1) |
| C(7C)–C(2D)–C(3D) | 125(1) | C(6D)–C(7D)–C(2E) | 118(1) |
| C(7D)–C(2E)–C(1E) | 119(2) | C(7D)–C(2E)–C(3E) | 117(1) |
| C(2A)–C(7E)–C(6E) | 118(1) | O(1)–C(1)–C(3) | 117(2) |
| O(1)–C(1)–C(2) | 124(2) | C(2)–C(1)–C(3) | 119(2) |
| O(2)–C(11)–C(12) | 114(2) | O(2)–C(11)–C(13) | 122(2) |

(c) Torsion angles

| | |
|---|---|
| C(1A)–C(2A)–C(7E)–C(6E) | 89(2) |
| C(5A)–C(6A)–C(7A)–C(2B) | 96(1) |
| C(6A)–C(7A)–C(2B)–C(3B) | −81(1) |
| C(5B)–C(6B)–C(7B)–C(2C) | 76(2) |
| C(6B)–C(7B)–C(2C)–C(3C) | −96(2) |
| C(5C)–C(6C)–C(7C)–C(2C) | 80(1) |
| C(6C)–C(7C)–C(2D)–C(3D) | −88(1) |
| C(5D)–C(6D)–C(7D)–C(2E) | 98(2) |
| C(6D)–C(7D)–C(2E)–C(3E) | −83(2) |
| C(1E)–C(6E)–C(7E)–C(2A) | −106(2) |
| C(3A)–C(2A)–C(7E)–C(6E) | −87(2) |
| C(1A)–C(6A)–C(7A)–C(2B) | −94(1) |
| C(6A)–C(7A)–C(2B)–C(1B) | 101(1) |
| C(1B)–C(6B)–C(7B)–C(2C) | −94(2) |
| C(6B)–C(7B)–C(2C)–C(1C) | 102(1) |
| C(1C)–C(6C)–C(7C)–C(2D) | −99(1) |
| C(6C)–C(7C)–C(2D)–C(1D) | 87(1) |
| C(1D)–C(6D)–C(7D)–C(2E) | −93(2) |
| C(6D)–C(7D)–C(2E)–C(1E) | 96(2) |
| C(5E)–C(6E)–C(7E)–C(2A) | 85(2) |

O(1B) 3.139(11), O(1) · · · O(1C) 3.114(9), O(1) · · · O(1D) 3.037(10), and O(1) · · · O(1E) 2.907(10) Å which are significantly shorter than the sum of the van der Waals radii. The dihedral angle formed by acetone with respect to the five OH planes is 126.1(7)° and the C–O-angle (baricentre of the five oxygens) is 139(1)°, these fulfilling the stereochemical requirements for the interaction of an oxygen doublet with the hydrogen bonds system. The second acetone molecule (see Figure 2) lies on the internal side of the chalice so that the methyl group points towards rings B and C with contacts H · · · C compatible with the sum of the van der Waals radii. It seems that this interaction could be responsible for the *Cs* symmetry of the macrocycle. The packing is shown in Figure 3 projected along [001] and in Figure 4 projected along [010].

## EXPERIMENTAL

*Instrumentation.*—Mass spectrum was recorded on a Varian CH5 spectrometer at 70eV (EI). I.r. spectrum was recorded on a Perkin-Elmer model 298 i.r. spectrophotometer. $^{1}$H and $^{13}$C (at 25.2 MHz) n.m.r. spectra were determined on a Varian XL 100 instrument. Chemical shifts are reported in p.p.m. from internal tetramethylsilane. M.p.s was determined in a capillary sealed *in vacuo* using a Büchi apparatus. H.p.l.c. analyses were performed using a Waters (model 6000 A pump, U6K injector and model 440 u.v. detector at 254 and 280 (nm) liquid–liquid chromatograph on a 30 cm × 3.9 mm i.d. high efficiency $\mu$-Bondapak $C_{18}$ column (Waters).

25,26,27,28,29-*Pentahydroxycalix*[5]*arene* (1).—Compound (1) was isolated after removal of the 1,1,3,3-tetramethylbutyl group, from the fraction of cyclic products derived from the base-catalysed reaction of *p*-1,1,3,3-tetramethylbutylphenol and formaldehyde. The reaction was performed by following Cornforth's procedure exactly.[13] From the mother liquors from which the compound called LOC by Cornforth crystallizes and which has been shown by us to be the cyclic tetramer,[12] a second crop of a powder has been collected (*ca.* 5% based on the total starting *p*-1,1,3,3-tetramethylbutylphenol).

This compound (350 mg) and $AlCl_3$ (267 mg, 2 mmol) were stirred in toluene (5 ml) at ambient temperature for 2 h under nitrogen. Water (20 ml) was then added and the organic phase separated and thoroughly washed with $H_2O$. Toluene was removed by rotary evaporator and diethyl ether added which caused the precipitation of a powder which was filtered and washed with diethyl ether. Crystallization from acetone gave prisms of the title *compound* (140 mg, 80%), m.p. 295—298 °C, $\nu_{max.}$ (KBr) 3 280, 1 600, 1 450, 1 480, and 760 cm$^{-1}$, $\delta_H$ ($CDCl_3$ )2.19 [s, 12 H, 2 $(CH_3)_2CO$], 3.88 (s, OH, $ArCH_2Ar$), 6.87 (t, 5 H, H-4), 7.24 (d, 10 H, H-3 + H-5, $AB_2$ $J_{AB}$ 8 Hz), and 8.95 (s, 5 H, OH); $\delta_C$ ($CDCl_3$) 31.2 ($ArCH_2Ar$), 121.4 (C-4), 126.5 (C-2 + C-6), 129.0 (C-3 + C-5), and 149.7 (C-1) p.p.m.; *m/e* 530 ($M^+$, 100%), 531 ($M + 1^+$, 39), 512 (10), 436 (12), 424 (28), 211 (28), and 119 (39), h.p.l.c., MeOH–$H_2O$ 9 : 1, flux 2.0 ml min$^{-1}$, $R_t$ 11.5 min.

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## REFERENCES

[1] C. D. Gutsche, B. Dhawan, K. Hyun No, and R. Muthukrishnan, *J. Am. Chem. Soc.*, 1981, **103**, 3782. We thank Prof. D. Gutsche for making available the manuscript of this paper before publication.

[2] V. Bocchi, D. Foina, A. Pochini, R. Ungaro, and G. D. Andreetti, *Tetrahedron*, 1982, **38**, 373.

[3] G. D. Andreetti, R. Ungaro, and A. Pochini, *J. Chem. Soc., Chem. Commun.*, 1981, 533.

[4] W. Saenger, *Angew. Chem. Int. Ed. Engl.*, 1980, **19**, 344; M. L. Bender and M. Komiyama, 'Cyclodextrin Chemistry,'

Spring-Verlag, Berlin, 1978; I. Tabushi, K. Yamamura, K. Fujita, and H. Kawakubo, *J. Am. Chem. Soc.*, 1979, **101**, 1019.

[5] F. Vögtle, *Pure Appl. Chem.*, 1980, **52**, 2405.

[6] D. D. MacNicol, J. J. McKendrick, and D. R. Wilson, *Chem. Soc. Rev.*, 1978, **7**, 65 and references therein.

[7] R. Popowitz-Biro, M. C. Chang, C. P. Tang, N. R. Shochet, M. Lahav, and L. Leiserowitz, *Pure Appl. Chem.*, 1980, **52**, 2693 and references therein; R. Breslow, *Acc. Chem. Res.*, 1980, **13**, 170.

[8] E. Smolková-Keulemansová and S. Krysl, *J. Chrom.*, 1980, **184**, 347.

[9] G. D. Andreetti, R. Ungaro, and A. Pochini, *J. Chem. Soc., Chem. Commun.*, 1979, 1006.

[10] Unpublished results.

[11] C. Rizzoli, G. D. Andreetti, R. Ungaro, and A. Pochini, *J. Mol. Struct.*, 1982, **82**, 133.

[12] G. D. Andreetti, International Symposium on Clathrate Compounds and Molecular Inclusion Phenomena, Jackranka, 1980.

[13] J. W. Cornforth, P. D'Arcy Hart, G. A. Nicholls, R. J. W. Rees, and J. A. Stock, *Brit. J. Pharmacol.*, 1955, **10**, 73.

[14] G. Happel, B. Mathiasch, and H. Kämmerer, *Makromol. Chem.*, 1975, **176**, 3317; H. Kämmerer and G. Happel, *ibid.*, 1980, **181**, 2049.

[15] G. M. Sheldrick, 1975, SHELX, Programs for Crystal Structure Determination, Univ. of Cambridge.

[16] 'International Tables for X-ray Crystallography,' Kynoch Press, Birmingham, 1974, vol. IV, pp. 99—101.