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Structure of p-tert-Butylhexahomotrioxacalix[3]arene

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Abstract. 7,15,23-Tri-*tert*-butyl-25,26,27-trihydroxy-2,3,10,11,18,19-hexahomo-3,11,19-trioxacalix[3]-arene, $C_{36}H_{48}O_6$, $M_r = 576.4$, orthorhombic, *Pnma*, $a = 9.348$ (1), $b = 16.604$ (2), $c = 21.992$ (3) Å, $V = 3413.5$ (8) Å^3, $Z = 4$, $D_x = 1.12$ g cm^{-3}, graphite-monochromated Cu $K\alpha$, $\lambda = 1.54178$ Å, μ(Cu $K\alpha$) $= 5.65$ cm^{-1}, $F(000) = 1248$, $T = 288$ K, final $R = 0.054$ for 1858 reflections. There is a mirror plane and pseudo C_{3v} symmetry in the molecule. This inclusion molecule adopts a cone conformation and its cavity is too shallow to capture guest molecules.

Introduction. It is well known that calixarenes are cyclic phenol-methylene oligomers which are capable of including small molecules (Gutsche, 1989). The title compound, *p-tert*-butylhexahomotrioxacalix-[3]arene, is one of the calixarenes which can be made from the condensation of *p-tert*-butylphenol and paraformaldehyde (Dhawan & Gutsche, 1983). The X-ray structure analysis reported here was undertaken to determine the molecular conformation.

Experimental. Colorless pillar crystals from *m*-xylene solution evaporation at room temperature. Crystal $0.1 \times 0.1 \times 0.5$ mm. Cell dimensions: least squares on 25 reflections, $47 < 2\theta < 54°$. Systematic absences (0*kl*, $k + l = 2n$; *hk*0, $h = 2n$) indicated the space group to be *Pnma* or *Pn2$_1$a*; the final structure was refined as *Pnma*. Rigaku AFC-5 automated diffractometer, $2\theta_{max} = 120°$ ($-10 \le h \le 0$, $0 \le k \le 19$, $0 \le l \le 25$), ω–2θ-scan mode. A total of 3156 reflections collected, 2870 unique reflections measured, 2105 considered observed [$|F_o| > 3\sigma(F_o)$]. Three standard reflections (11$\overline{2}$, 31$\overline{1}$ and 1$\overline{5}$0) monitored every 200 reflections; intensity decreased less than 3% during the data collection. No corrections for absorption and extinction. Structure solved by direct methods with *SHELXS*86 (Sheldrick, 1985). Positional and thermal parameters refined by full-matrix least-squares method with *SHELX*76 (Sheldrick, 1976); H atoms, except those of the disordered C(11*B*) methyl group, located on difference Fourier maps using programs of *The Universal Crystallographic Computing System—Osaka* (1979); non-H atoms refined with anisotropic temperature factors and H-atom positions refined with fixed isotropic temperature factors. Final $R = 0.054$, $wR = 0.058$ for 1858 reflections, $S = 0.981$ for 271 parameters; function mini-

Table 1. *Atomic coordinates and equivalent isotropic thermal parameters for non-*H *atoms with e.s.d.'s in parentheses*

$$B_{eq} = (4/3)\Sigma_i\Sigma_j\beta_{ij}\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq} (Å^2)
O(A)	0.6669 (2)	0.0935 (13)	0.4027 (9)	4.13 (6)
O(1A)	0.9311 (2)	0.1570 (13)	0.3515 (10)	4.79 (7)
C(1A)	0.8935 (3)	0.1008 (2)	0.3089 (15)	3.96 (9)
C(2A)	0.8097 (3)	0.0359 (2)	0.3253 (14)	3.81 (9)
C(3A)	0.7716 (3)	−0.0190 (2)	0.2811 (2)	4.26 (9)
C(4A)	0.8152 (4)	−0.0128 (2)	0.2211 (16)	4.52 (10)
C(5A)	0.9034 (4)	0.0518 (2)	0.2077 (16)	4.53 (10)
C(6A)	0.9447 (3)	0.1086 (2)	0.2498 (2)	4.26 (9)
C(7A)	0.7599 (4)	0.0276 (2)	0.3894 (15)	4.33 (9)
C(8A)	0.6304 (4)	0.0997 (2)	0.4650 (16)	5.01 (11)
C(9A)	0.7680 (4)	−0.0718 (2)	0.1710 (2)	5.82 (12)
C(10A)	0.8956 (5)	−0.1145 (3)	0.1445 (2)	8.10 (2)
C(11A)	0.6550 (6)	−0.1301 (3)	0.1936 (2)	9.80 (2)
C(12A)	0.6979 (5)	−0.0220 (3)	0.1187 (2)	8.70 (2)
C(13A)	1.0372 (4)	0.1784 (2)	0.2325 (2)	5.15 (11)
O(1B)	0.7586 (3)	0.2500	0.4426 (14)	4.66 (10)
C(1B)	0.6198 (5)	0.2500	0.4633 (2)	3.89 (13)
C(2B)	0.5523 (3)	0.1778 (2)	0.4744 (15)	3.96 (9)
C(3B)	0.4117 (4)	0.1792 (2)	0.4954 (14)	4.07 (9)
C(4B)	0.3379 (5)	0.2500	0.5060 (2)	3.93 (13)
C(9B)	0.1833 (5)	0.2500	0.5312 (2)	4.98 (15)
C(10B)	0.1006 (4)	0.1766 (3)	0.5097 (2)	8.30 (2)
C(11B)	0.1936 (7)	0.2500	0.6013 (3)	9.60 (3)
O(C)	0.9587 (3)	0.2500	0.2448 (16)	4.57 (9)

mized $\Sigma w(|F_o| - k|F_c|)^2$, $w = [\sigma^2(F_o) - 0.00535|F_o| + 0.00128|F_o|^2]^{-1}$. Maximum Δ/σ in final refinement cycle 0.95. Maximum and minimum peak heights on a final $\Delta\rho$ map 0.52 and −0.18 e Å^{-3}. Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV). All computations carried out on an ACOS 930 computer at the Research Center for Protein Engineering, Institute for Protein Research, Osaka University.

Discussion. The final positional and thermal parameters are given in Table 1.* Selected bond lengths, angles and torsion angles for non-H atoms are listed in Table 2. The three phenol-methylene units are designated as *A*, *B* and *A'*. There is a mirror plane in the molecule, and unit *A'* is related to *A* by the mirror operation $(x, -y + \frac{1}{2}, z)$, and six atoms, O(*C*), O(1*B*), C(1*B*), C(4*B*), C(9*B*) and C(11*B*), are on the mirror plane as shown in Fig. 1. The molecule also has pseudo C_{3v} symmetry. The four torsion angles, φ_1, φ_2, φ_3 and φ_4, between the adjacent aromatic rings adopt *gauche$^-$-trans-trans-gauche$^+$* conformations in all connections as listed in Table 2. It is notable that the observed geometry should be stabilized by intramolecular hydrogen bonding [O(1*A*)···O(1*B*) = 2.999 (4), O(1*A*)···O(1*A'*) =

Table 2. *Selected bond lengths* (Å)*, angles* (°) *and torsion angles* (°) *with e.s.d.'s in parentheses*

O(A)—C(7A)	1.428 (4)	C(4A)—C(9A)	1.539 (5)
O(A)—C(8A)	1.415 (4)	C(5A)—C(6A)	1.377 (5)
O(C)—C(13A)	1.423 (5)	C(6A)—C(13A)	1.496 (5)
O(1A)—C(1A)	1.369 (4)	C(8A)—C(2B)	1.502 (5)
C(1A)—C(2A)	1.381 (5)	O(1B)—C(1B)	1.376 (5)
C(1A)—C(6A)	1.390 (5)	C(1B)—C(2B)	1.377 (5)
C(2A)—C(3A)	1.379 (5)	C(2B)—C(3B)	1.394 (5)
C(2A)—C(7A)	1.490 (5)	C(3B)—C(4B)	1.383 (6)
C(3A)—C(4A)	1.385 (5)	C(4B)—C(9B)	1.548 (7)
C(4A)—C(5A)	1.386 (5)		

O(A)—C(7A)—C(2A)	108.3 (3)	C(3A)—C(4A)—C(9A)	123.4 (3)
O(A)—C(8A)—C(2B)	108.3 (3)	C(4A)—C(5A)—C(6A)	123.7 (3)
O(1A)—C(1A)—C(2A)	119.9 (3)	C(5A)—C(4A)—C(9A)	120.8 (3)
O(1A)—C(1A)—C(6A)	119.2 (3)	C(5A)—C(6A)—C(13A)	121.4 (3)
C(1A)—C(2A)—C(3A)	118.5 (3)	C(6A)—C(13A)—O(C)	107.5 (3)
C(1A)—C(2A)—C(7A)	119.8 (3)	C(7A)—O(A)—C(8A)	113.6 (2)
C(1A)—C(6A)—C(5A)	117.9 (3)	C(8A)—C(2B)—C(1B)	120.3 (3)
C(1A)—C(6A)—C(13A)	120.6 (3)	C(8A)—C(2B)—C(3B)	121.2 (3)
C(2A)—C(1A)—C(6A)	120.9 (3)	O(1B)—C(1B)—C(2B)	119.4 (4)
C(2A)—C(3A)—C(4A)	123.2 (3)	C(1B)—C(2B)—C(3B)	118.4 (3)
C(3A)—C(2A)—C(7A)	121.7 (3)	C(2B)—C(3B)—C(4B)	122.7 (3)
C(3A)—C(4A)—C(5A)	115.8 (3)	C(3B)—C(4B)—C(9B)	121.7 (4)

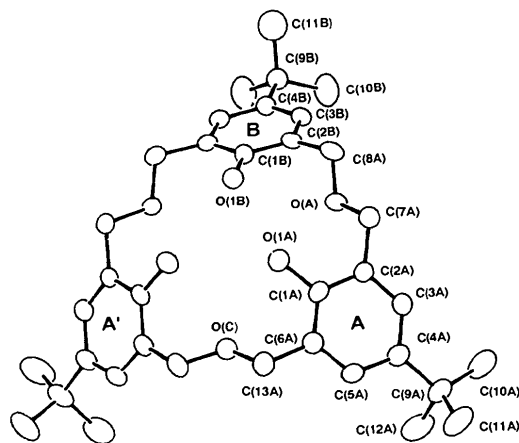| φ_1	C(1A)—C(6A)—C(13A)—O(C)	−58.3 (4)
φ_2	C(6A)—C(13A)—O(C)—C(13A')	177.7 (3)
φ_3	C(13A)—O(C)—C(13A')—C(6A')	−177.7 (3)
φ_4	O(C)—C(13A')—C(6A')—C(1A')	58.3 (4)
φ_1	C(1B)—C(2B)—C(8A)—O(A)	−62.5 (4)
φ_2	C(2B)—C(8A)—O(A)—C(7A)	171.2 (3)
φ_3	C(8A)—O(A)—C(7A)—C(2A)	−170.5 (3)
φ_4	O(A)—C(7A)—C(2A)—C(1A)	64.5 (4)

Fig. 1. *ORTEP*II drawing (Johnson, 1976) of the title compound. Thermal ellipsoids are at the 50% probability level.

3.088 (3) Å]. The dihedral angles between the aromatic rings are 61.4 (1) and 65.8 (1)° for *A–B* and *A—A'*, respectively. The dihedral angles between aromatic rings and the horizontal plane formed by the three centroids of each aromatic ring are 38.3 (1)° for *A* and 34.4 (1)° for *B*, and the distances between the centroids are 6.872 (*A–B*) and 6.834 Å (*A–A'*). The distance between the plane O(1*A*)–O(1*B*)–O(1*A'*) and the plane C(4*A*)–C(4*B*)–C(4*A'*), the depth of the cone structure, is 2.496 (6) Å. These values indicate

that the cone cavity is too shallow to include an organic solvent molecule such as xylene. This shallow cavity is shown from the upper and side directions in Fig. 2.
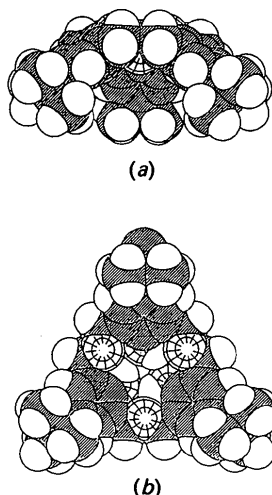
Fig. 2. Space-filling molecular model in different orientations (a) and (b), drawn with PLUTO (Motherwell & Clegg, 1978). C shaded, O spark, H other.

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Structure of 6,6-Dimethyl-1-phenyl-7-thiatricyclo[3.2.1.1³,⁸]nonane 7,7-Dioxide

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Abstract. $C_{16}H_{20}O_2S$, $M_r = 276.4$, orthorhombic, $P2_12_12_1$, $a = 6.175$ (2), $b = 11.102$ (2), $c = 19.862$ (3) Å, $V = 1362$ (6) Å^3, $Z = 4$, $D_x = 1.348$ g cm^{-3}, $\lambda(Mo\ K\alpha) = 0.71069$ Å, $\mu = 2.2$ cm^{-1}, $F(000) = 592$, $T = 296$ K, $R = 0.066$ for 972 observed diffractometer data. The three five-membered rings adopt an envelope conformation with a 5-exo-phenyl substituent and a 5-endo-isopropylsulfonyl group, with reference to the norbornane moiety. The structure of the title compound is compared with that of its cyano analogue and with that of its precursor connected to an efficient radical clock.

Introduction. Aiming to check for the presence of elusive radicals during organic reactions, free-radical clocks of ever increasing efficiency have been designed and synthesized (Surzur, 1982). A new kind of radical clock based on the 5-exo-substituted-5-endo-isopropylsulfonyl-2-norbornene structure (Fig. 1) has recently been described and the X-ray structures of (1a) and (1b) (Vacher, Samat, Allouche, Laknifli, Baldy & Chanon, 1988) were undertaken in order to explain the enhancement for the cyclization rate of the α-sulfonyl-C-centred intermediate radical (2b) as compared to (2a).