

these are the only non-bonded interatomic distances less than 3.3 Å.

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Structure of *p*-*tert*-Butylbishomooxalix[4]arene–*m*-Xylene (1:1) Complex

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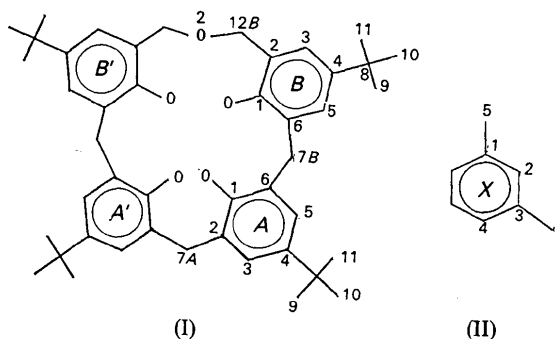
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Abstract. 7,13,19,25-Tetra-*tert*-butyl-27,28,29,30-tetrahydroxy-2,3-dihomo-3-oxalix[4]arene–*m*-xylene, C₄₅H₅₈O₅.C₈H₁₀, *M_r* = 787.03, orthorhombic, *Pbcm*, *a* = 9.328 (1), *b* = 19.348 (3), *c* = 25.939 (5) Å, *V* = 4681.4 (3) Å³, *Z* = 4, *D_x* = 1.114 g cm⁻³, graphite-monochromated Cu *Kα* radiation, λ = 1.54178 Å, μ = 5.10 cm⁻¹, *F*(000) = 1704, *T* = 283 K, final *R* = 0.077 for 1446 reflections. The complex has mirror symmetry in which the plane passes through two atoms: the O and the C atoms linking the phenyl rings. CH···O, CH₃–π and CH₃–CH₃ interactions are shown to exist between the host and guest. The methyl group of the guest that penetrates into the cavity of the host shows strong CH···O interactions of 3.393 (3) and 3.617 (3) Å.

Introduction. Calixarenes (Gutsche & Muthukrishnan, 1978) are a class of synthetic macrocycles having phenolic residues in a cyclic array with methylene groups at positions *ortho* to the hydroxy group (Andreotti, Pochini & Ungaro, 1983). Some are able to form inclusion complexes with several organic guest molecules. This inclusion behaviour depends on the size of the macroring (Andreotti, Ungaro & Pochini, 1979). In order to elucidate the

particular host–guest interaction in the oxalix[4]arene, we synthesized *p*-*tert*-butylbishomooxalix[4]arene (I) and carried out an X-ray structure determination of the 1:1 complex with *m*-xylene (II).



Experimental. A colourless needle crystal (0.1 × 0.1 × 0.5 mm) suitable for X-ray data collection was mounted on a Rigaku AFC-5 diffractometer. Data were collected using ω–2θ scan technique (2θ_{max} = 126°) and graphite-monochromated Cu *Kα* radiation. Unit-cell parameters were refined based on 2θ values (48 < 2θ < 60°) of 24 reflections. A total of

Table 1. Atomic coordinates and equivalent isotropic thermal parameters (\AA^2) of the non-H atoms with e.s.d.'s in parentheses

	x	y	z	B_{eq}
O2	0.4574 (9)	0.5154 (5)	0.75000*	5.4 (3)
O1A	0.9869 (6)	0.5470 (3)	0.6972 (2)	4.9 (2)
C1A	0.9720 (8)	0.6131 (4)	0.6772 (3)	4.0 (3)
C2A	1.0353 (8)	0.6689 (4)	0.7010 (3)	3.5 (2)
C3A	1.0112 (8)	0.7340 (4)	0.6803 (3)	4.2 (3)
C4A	0.9301 (8)	0.7458 (5)	0.6360 (4)	4.2 (3)
C5A	0.8756 (8)	0.6878 (4)	0.6116 (4)	4.1 (3)
C6A	0.8972 (8)	0.6211 (4)	0.6305 (3)	3.8 (3)
C7A	1.1220 (12)	0.6611 (6)	0.75000*	4.0 (4)
C8A	0.9019 (10)	0.8196 (4)	0.6149 (4)	5.5 (3)
C9A	0.9233 (2)	0.8730 (6)	0.6556 (6)	15.5 (8)
C10A	0.9944 (2)	0.8339 (7)	0.5716 (7)	21.2 (9)
C11A	0.7483 (15)	0.8288 (6)	0.6013 (9)	18.8 (9)
O1B	0.7068 (6)	0.4972 (3)	0.6903 (2)	5.4 (2)
C1B	0.6153 (9)	0.5228 (4)	0.6528 (3)	4.2 (3)
C2B	0.4692 (9)	0.5173 (4)	0.6590 (3)	4.5 (3)
C3B	0.3782 (8)	0.5445 (5)	0.6214 (3)	4.4 (3)
C4B	0.4307 (9)	0.5748 (4)	0.5768 (4)	4.3 (3)
C5B	0.5787 (9)	0.5785 (4)	0.5710 (3)	4.0 (3)
C6B	0.6730 (8)	0.5530 (4)	0.6093 (3)	3.9 (3)
C7B	0.8351 (8)	0.5603 (4)	0.6011 (4)	4.5 (3)
C8B	0.3265 (9)	0.6035 (5)	0.5360 (4)	4.9 (3)
C9B	0.2558 (13)	0.6679 (5)	0.5569 (5)	8.6 (5)
C10B	0.4001 (11)	0.6183 (7)	0.4848 (4)	8.3 (4)
C11B	0.2078 (11)	0.5498 (6)	0.5255 (4)	7.7 (4)
C12B	0.4045 (9)	0.4817 (5)	0.7048 (4)	5.4 (3)
C1X	0.5476 (2)	0.7140 (10)	0.75000*	10.9 (8)
C2X	0.4910 (12)	0.7457 (7)	0.7058 (4)	9.5 (4)
C3X	0.3959 (13)	0.7998 (7)	0.7023 (5)	10.3 (5)
C4X	0.3520 (2)	0.8261 (9)	0.75000*	9.0 (7)
C5X	0.6505 (3)	0.6640 (13)	0.75000*	10.6 (12)
C6X†	0.3694 (2)	0.8216 (11)	0.6488 (7)	11.0 (8)

* These atoms lie on the mirror plane.

† Occupancy 0.5.

4354 reflections were collected ($-11 \leq h \leq 0$, $0 \leq k \leq 22$, $-30 \leq l \leq 0$), of which 3885 were unique. Three standard reflections (120, 022, 412) monitored every 200 reflections showed an intensity decrease of less than 1% during the data collection. No corrections for absorption and extinction were applied.

The structure was solved by direct methods using the program *SHELXS86* (Sheldrick, 1985). The structure was refined by full-matrix least squares with anisotropic temperature factors for all non-H atoms using *SHELX76* (Sheldrick, 1976). All H atoms except for those of a disordered methyl group (C6X of the guest) were located on difference Fourier maps using the programs of *The Universal Crystallographic Computing System-Osaka* (1979). Final refinement including the H atoms with fixed equivalent isotropic temperature factors reduced R to 0.077 ($wR = 0.073$, $S = 1.809$) for 1446 observed reflections [$|F_o| > 3\sigma(F_o)$] and 351 parameters; function minimized $\sum w(|F_o| - k|F_c|)^2$, where $w = 1/\sigma^2(F_o)$. Highest and lowest residuals in the final $\Delta\rho$ map were 0.52 and -0.14 e \AA^{-3} ; maximum Δ/σ value in the final refinement cycle was 0.30. The high R value is a result of the high temperature factors observed in some of the atoms. Atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV). All computations were

Table 2. Selected bond distances (\AA), bond angles ($^\circ$) and torsional angles ($^\circ$) with e.s.d.'s in parentheses

O2—C12B	1.430 (1)	C1B—C6B	1.381 (1)
O1A—C1A	1.387 (1)	C2B—C3B	1.395 (1)
C1A—C2A	1.375 (1)	C2B—C12B	1.501 (1)
C1A—C6A	1.406 (1)	C3B—C4B	1.386 (1)
C2A—C3A	1.389 (1)	C4B—C5B	1.391 (1)
C2A—C7A	1.514 (1)	C4B—C8B	1.539 (1)
C3A—C4A	1.393 (1)	C5B—C6B	1.414 (1)
C4A—C5A	1.385 (1)	C6B—C7B	1.533 (1)
C4A—C8A	1.552 (1)	C1X—C2X	1.403 (2)
C5A—C6A	1.397 (1)	C1X—C5X	1.364 (3)
C6A—C7B	1.518 (1)	C2X—C3X	1.375 (3)
O1B—C1B	1.386 (1)	C3X—C4X	1.399 (2)
C1B—C2B	1.376 (1)	C3X—C6X	1.472 (3)
O2—C12B—C2B	107.5 (8)	C1B—C2B—C3B	119.5 (8)
O1A—C1A—C2A	120.8 (8)	C1B—C6B—C5B	118.6 (8)
O1A—C1A—C6A	118.2 (8)	C1B—C6B—C7B	122.5 (9)
C1A—C2A—C3A	118.0 (8)	C1B—C2B—C12B	121.7 (8)
C1A—C2A—C7A	121.9 (8)	C2B—C1B—C6B	120.9 (8)
C1A—C4A—C5A	118.4 (8)	C2B—C3B—C4B	121.8 (8)
C1A—C6A—C7B	122.7 (8)	C3B—C2B—C12B	118.6 (8)
C2A—C1A—C6A	120.9 (8)	C3B—C4B—C5B	117.5 (8)
C2A—C3A—C4A	123.7 (8)	C3B—C4B—C8B	120.1 (8)
C3A—C2A—C7A	120.0 (8)	C4B—C5B—C6B	121.6 (8)
C3A—C4A—C5A	116.4 (8)	C5B—C4B—C8B	122.4 (8)
C3A—C4A—C8A	122.3 (8)	C5B—C6B—C7B	119.0 (8)
C4A—C5A—C6A	122.3 (9)	C1X—C2X—C3X	128.9 (14)
C5A—C4A—C8A	121.4 (8)	C2X—C1X—C5X	125.1 (19)
C5A—C6A—C7B	119.0 (8)	C2X—C3X—C4X	114.1 (13)
C6A—C7B—C6B	112.2 (7)	C2X—C3X—C6X	112.9 (13)
O1B—C1B—C2B	120.2 (8)	C4X—C3X—C6X	132.9 (14)
O1B—C1B—C6B	119.0 (8)		
C1A—C2A—C7A—C2A'	-90.6 (11)	C6A—C7B—C6B—C1B	-79.9 (11)
C1A—C6A—C7B—C6B	101.6 (10)	C2B—C12B—O2—C12B'	-177.4 (8)

carried out on an ACOS-930 computer at the Research Center for Protein Engineering, Institute for Protein Research, Osaka University, Japan.

Discussion. Final positional and equivalent isotropic thermal parameters of non-H atoms are listed in Table 1.* The bond distances, bond angles and selected torsional angles are shown in Table 2. These bond distances and angles were found to compare well with those of other oxacalixarenes; *tert*-butylhexahomotrioxacalix[3]arene (Suzuki, Minami, Yamagata, Fujii, Tomita, Asfari & Vicens, 1992), *p*-isopropylbishomooxacalix[4]arene-*o*-xylene (1:1) (Suzuki, Armah, Fujii, Asfari, Vicens & Tomita, 1991). The molecular structure (Fig. 1) shows the 'cone' conformation (Gutsche, Dhawan, Levin, No & Bauer, 1983) of the host molecule with the guest molecule occupying the cavity created. In the structure, the mirror symmetry passes through O2 and C7A of the host molecule. This mirror symmetry also passes through C5X, C1X and C4X of the guest indicating two possible positions for the C6X methyl group. The dihedral angles formed between the horizontal plane composed of the four centroids of the aromatic rings and each of the aromatic rings A and

* Lists of structure factors, anisotropic thermal parameters and H-atom coordinates have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55005 (14 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: AS0555]

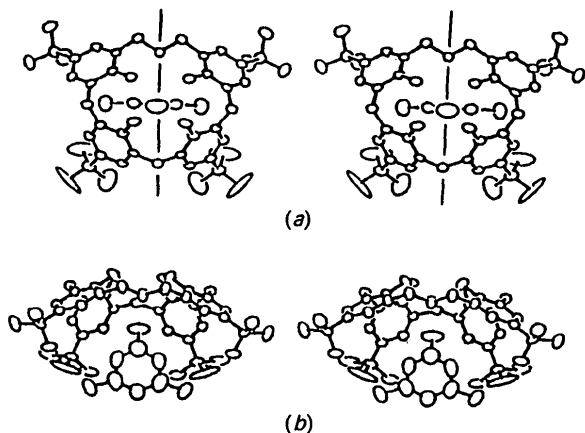


Fig. 1. An ORTEP (Johnson, 1965) plot of the host-guest complex (a) viewed through the mirror plane (the broken line indicates the mirror plane) and (b) viewed parallel to the plane of the guest molecule.

B are 58.5 (2) and 41.0 (2)°, respectively. The methyl group, C5X, of the guest was found to be directed towards the cavity. This methyl group penetrates directly and deeper into the cavity showing CH₃- π interaction between the guest and the host molecule. This interaction could be between the π electrons of the aromatic ring of the host molecule and the methyl group of the guest molecule. Also likely to be a factor in the interaction is the presence of the O2 atom of the host molecule. The introduction of this O atom widens the space of the 'cone' shape to produce the ellipsoidal cavity which nicely fits the molecular dimensions of the guest molecule, and also

indicates the possible interaction with the C5X methyl group of the guest molecule: a C—H...O interaction. This particular C—H...O interaction may be a very important key for the separation of the structural isomers of the guest molecules by the extractive crystallization with calixarenes, which shows about 73% extraction for *m*-xylene (Vicens, Armah, Fujii & Tomita, 1991). In the *m*-xylene molecule, disorder was observed. Several high thermal parameters (Table 1) probably result from the disorder, which may be the reason for the high *R* value.

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Structure of a Highly Substituted Pyrazolidin-3-one

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Abstract. Trimethylsilylethyl *cis*-4,5-dimethyl-1-(*o*-nitrobenzyl)-3-oxopyrazolidine-2-carboxylate, C₁₈H₂₇N₃O₅Si, *M_r* = 393.51, triclinic, *P* $\bar{1}$, *a* = 11.237 (3), *b* = 13.073 (2), *c* = 8.040 (3) Å, α = 106.40 (2), β = 105.48 (2), γ = 85.70 (2)°, *V* = 1092.0 (5) Å³, *Z* = 2, *D_x* = 1.20 Mg m⁻³, λ (Mo *K* α) = 0.71069 Å, μ = 1.32 mm⁻¹, *F*(000) = 420, *T* = 296 K, *R* = 0.063, *wR* = 0.083 for 1970 observed unique reflections. The observed structure establishes

the relative stereochemistry between the C2 and C3 methyl groups as *cis*. The nitro group is twisted out of the plane containing the phenyl ring by 32.7 (7)°, and the N1—N2 bond distance of 1.435 (4) Å is representative of an N—N single bond.

Introduction. The clinical importance of antibiotics containing a β -lactam ring has led to intense study of the reactivity and synthesis of compounds