

| | | | | |
|---------|-------------|-------------|-------------|----------|
| C6 | 0.9434 (4) | 0.5335 (2) | -0.3515 (8) | 5.5 (1) |
| C6a | 0.9386 (3) | 0.5724 (2) | -0.2461 (6) | 4.7 (1) |
| C7 | 0.9489 (4) | 0.5668 (2) | -0.0939 (7) | 6.3 (1) |
| C8 | 0.9445 (4) | 0.6017 (3) | -0.0027 (7) | 7.0 (2) |
| C9 | 0.9282 (4) | 0.6430 (2) | -0.0557 (7) | 6.7 (2) |
| C10 | 0.9171 (4) | 0.6499 (2) | -0.2066 (6) | 5.0 (1) |
| C10a | 0.9236 (3) | 0.6143 (2) | -0.3036 (5) | 3.97 (9) |
| C11 | 0.9132 (3) | 0.6223 (1) | -0.4663 (5) | 3.39 (8) |
| C12 | 0.7244 (4) | 0.6106 (2) | -0.8920 (8) | 6.2 (1) |
| C13 | 0.7091 (6) | 0.6739 (5) | -1.048 (1) | 13.8 (3) |
| C14 | 1.0599 (3) | 0.6693 (2) | -0.5107 (6) | 4.1 (1) |
| C15 | 1.0232 (3) | 0.7071 (1) | -0.5969 (6) | 3.77 (9) |
| C16 | 1.0551 (3) | 0.7656 (2) | -0.4077 (5) | 3.78 (9) |
| C17 | 1.0908 (3) | 0.8111 (2) | -0.3841 (6) | 4.2 (1) |
| C18 | 1.0516 (3) | 0.8457 (1) | -0.4824 (5) | 3.67 (9) |
| C19 | 1.0618 (3) | 0.8308 (2) | -0.6420 (6) | 4.04 (9) |
| C20 | 1.0252 (3) | 0.7855 (1) | -0.6687 (5) | 3.77 (9) |
| C21 | 1.0881 (3) | 0.8926 (2) | -0.4534 (6) | 4.7 (1) |
| C22 | 1.0432 (3) | 0.9292 (1) | -0.5335 (6) | 4.2 (1) |
| C23 | 1.0797 (4) | 0.9530 (2) | -0.6496 (8) | 6.1 (1) |
| C24 | 1.0388 (4) | 0.9866 (2) | -0.7199 (8) | 7.2 (2) |
| C25 | 0.9620 (4) | 0.9968 (2) | -0.6834 (8) | 6.7 (2) |
| C26 | 0.9235 (4) | 0.9737 (2) | -0.5729 (9) | 6.3 (1) |
| C27 | 0.9644 (3) | 0.9403 (2) | -0.4980 (6) | 4.8 (1) |
| P(B) | 0.78687 (6) | 0.76373 (4) | 0.5695 (2) | 3.77 (2) |
| O1(B) | 0.8498 (2) | 0.7291 (1) | 0.5650 (5) | 5.31 (8) |
| O2(B) | 0.7173 (2) | 0.7613 (1) | 0.6739 (4) | 4.58 (7) |
| O3(B) | 0.7423 (2) | 0.7708 (1) | 0.4121 (4) | 3.93 (6) |
| O4(B) | 0.8358 (2) | 0.8101 (1) | 0.5856 (4) | 3.97 (6) |
| C1(B) | 0.7892 (3) | 0.7862 (1) | 0.2945 (6) | 3.72 (9) |
| C2(B) | 0.8105 (3) | 0.7555 (2) | 0.1848 (7) | 5.0 (1) |
| C3(B) | 0.8545 (4) | 0.7693 (2) | 0.0650 (7) | 5.1 (1) |
| C4(B) | 0.8800 (3) | 0.8130 (2) | 0.0550 (6) | 4.6 (1) |
| C5(B) | 0.8594 (3) | 0.8448 (2) | 0.1657 (5) | 3.66 (9) |
| C6(B) | 0.8088 (3) | 0.8302 (1) | 0.2871 (5) | 3.51 (8) |
| C7(B) | 0.9296 (4) | 0.8274 (2) | -0.0654 (6) | 5.7 (1) |
| C8(B) | 0.9588 (4) | 0.8699 (2) | -0.0707 (7) | 6.4 (1) |
| C9(B) | 0.9394 (4) | 0.9003 (2) | 0.0391 (6) | 5.3 (1) |
| C10(B) | 0.8906 (3) | 0.8885 (2) | 0.1553 (6) | 4.2 (1) |
| C11(B) | 0.7816 (2) | 0.8607 (1) | 0.4072 (5) | 3.51 (8) |
| C12(B) | 0.7386 (3) | 0.9010 (2) | 0.3794 (6) | 4.3 (1) |
| C13(B) | 0.7198 (3) | 0.9302 (2) | 0.4988 (7) | 5.3 (1) |
| C14(B) | 0.7395 (3) | 0.9179 (2) | 0.6430 (8) | 5.8 (1) |
| C15(B) | 0.7757 (3) | 0.8779 (2) | 0.6722 (6) | 4.9 (1) |
| C16(B) | 0.7959 (3) | 0.8495 (1) | 0.5509 (5) | 3.57 (8) |
| C17(B) | 0.7120 (3) | 0.9123 (2) | 0.2333 (7) | 5.6 (1) |
| C18(B) | 0.6711 (4) | 0.9521 (2) | 0.2134 (9) | 8.1 (2) |
| C19(B) | 0.6584 (4) | 0.9813 (2) | 0.331 (1) | 8.6 (2) |
| C20(B) | 0.6807 (4) | 0.9703 (2) | 0.4688 (9) | 6.7 (2) |
| O(SOL)* | 0.6256 (6) | 0.7810 (3) | 0.926 (1) | 15.3 (2) |
| C(SOL)* | 0.6355 (8) | 0.8215 (4) | 0.989 (1) | 13.8 (8) |

*Refined isotropically. B and SOL denote (+)-BNPPA and the solvent molecules, respectively.

Table 2. Selected bond lengths (Å) and angles (°)

| | | | |
|--------------|-----------|--------------|-----------|
| S—C11 | 1.865 (4) | C4—C4a | 1.378 (8) |
| O5—C6 | 1.420 (7) | C6a—C10a | 1.387 (7) |
| N—C20 | 1.510 (6) | C14—C15 | 1.508 (6) |
| C1a—C11 | 1.531 (6) | O5—C4a | 1.363 (7) |
| C6a—C7 | 1.400 (8) | N—C16 | 1.510 (6) |
| C10a—C11 | 1.504 (7) | C1a—C4a | 1.398 (6) |
| S—C14 | 1.808 (5) | C6—C6a | 1.516 (8) |
| N—C15 | 1.508 (5) | C10—C10a | 1.392 (7) |
| C1—C1a | 1.381 (7) | | |
| C11—S—C14 | 100.8 (2) | C4a—O5—C6 | 119.9 (4) |
| C15—N—C16 | 112.8 (3) | C15—N—C20 | 108.6 (3) |
| C16—N—C20 | 111.0 (3) | C4a—C1a—C1 | 118.2 (4) |
| C4a—C1a—C11 | 126.5 (4) | C1—C1a—C11 | 115.3 (4) |
| C1a—C4a—C4 | 120.3 (5) | C1a—C4a—O5 | 126.7 (5) |
| C4—C4a—O5 | 113.0 (4) | C6a—C6—O5 | 111.0 (4) |
| C10a—C6a—C6 | 120.1 (5) | C10a—C6a—C6 | 118.6 (5) |
| C7—C6a—C6 | 121.3 (5) | C11—C10a—C10 | 119.1 (4) |
| C11—C10a—C6a | 122.3 (4) | C10—C10a—C6a | 118.6 (5) |
| S—C11—C1a | 105.9 (3) | S—C11—C10a | 111.2 (3) |
| C1a—C11—C10a | 118.5 (4) | S—C14—C15 | 109.3 (3) |
| C14—C15—N | 113.9 (4) | | |

Program used throughout the analysis: CAD-4 SDP-Plus (Frenz, 1983). Program used to solve structure: MULTAN11/82 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1982). Program used to draw the picture: ORTEPII (Johnson, 1976). Refinement was by full-matrix least-squares methods.

Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55535 (28 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: AS1015]

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Tetramethyl *tert*-Butylcalix[4]arene Tetraketone

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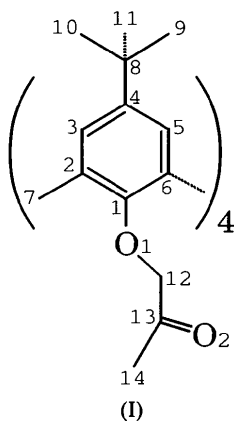
Abstract

The title molecule, 25,26,27,28-tetraacetyloxy-5,11-, 17,23-tetra-*tert*-butylpentacyclo[19.3.1.1^{3,7}.1^{9,13}.1^{15,19}]-octacosane-1(25),3,5,7(28),9,11,13(27),15,17,19,21,23-dodecaene, has twofold crystallographic symmetry and adopts a distorted cone conformation in the solid state.

The orientation of the four aromatic rings is such that two of the rings are almost parallel to each other and the other two almost normal to one another. This conformation precludes a solvent molecule being enclathrated within the cavity.

Comment

The structure determination of the title compound (I) was undertaken to establish the overall molecular conformation in the solid state. The structure of (I)· $y(\text{CH}_3)_2\text{CO}$ has been previously determined in the space group *Pbcn* using crystals grown from acetone (Arnaud-Neu *et al.*, 1989). Crystals for the present structural determination were obtained by the recrystallization of (I) from methanol/acetonitrile.



The calix[4]arene (I) lies about a twofold axis (Fig. 1) and adopts a distorted cone conformation in the solid state. The conformation of the calix moiety of (I) is defined by the interplanar angles between opposite pairs of aromatic rings [$82.3(3)^\circ$ for rings *A* and *A** (related by the operation $y, x, 1-z$) and $7.2(2)^\circ$ for rings *B* and *B**, rings *B* and *B** being tilted so that their *tert*-butyl groups are pitched slightly away from the calix cavity]. The overall calix conformation for molecule (I) is thus very similar to that observed in the previous structural determination of (I)· $y(\text{CH}_3)_2\text{CO}$ which also has twofold crystallographic symmetry and two sets of opposite rings at interplanar angles of 85° and 9° to one another (Arnaud-Neu *et al.*, 1989).

The O···O intramolecular distances for the *cis*-adjacent ethereal O atoms are 3.34(1) (O1A···O1B) and 2.97(1) Å (O1A···O1B*); the distances between symmetry related ethereal O atoms across the twofold axis are 3.57(1) (O1A···O1A*) and 5.17(1) Å (O1B···O1B*). The orientation of the ester groups is presumably determined by crystal packing forces; the shortest intramolecular contacts involving the ester chains are O2A···C7B and O2A···H7BA (3.22 and 2.33 Å, respectively). Inter-molecular contacts correspond to normal van der Waals

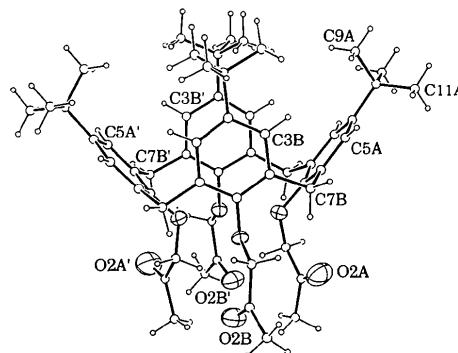


Fig. 1. A view of the molecule showing the general conformation and an indication of the crystallographic numbering (for details of the numbering scheme used see scheme). The molecule has twofold symmetry and the atoms marked with a prime are generated from the unprimed atoms by the operation of the symmetry transformation $y, x, 1-z$ on the coordinates in Table 1. The O atoms are shown with thermal ellipsoids drawn at the 50% probability level; for clarity the C and H atoms are drawn as small spheres of an arbitrary size.

separations. There is no solvent of crystallization present in the lattice and an examination of the structure using *PLATON* (Spek, 1991) reveals no potential solvent volume.

Final fractional coordinates are listed in Table 1. The molecular dimensions (summarized in Table 2) are unexceptional and serve to establish the conformation. The diagram was prepared using *ORTEPII* (Johnson, 1976).

Experimental

Crystal data

$\text{C}_{56}\text{H}_{72}\text{O}_8$
 $M_r = 873.17$
 Trigonal
 $P3_121$
 $a = 12.971(3) \text{ \AA}$
 $c = 25.740(12) \text{ \AA}$
 $V = 3750.3(19) \text{ \AA}^3$
 $Z = 3$
 $D_x = 1.160 \text{ Mg m}^{-3}$

Mo $K\alpha$ radiation
 $\lambda = 0.70930 \text{ \AA}$
 Cell parameters from 25 reflections
 $\theta = 5.00\text{--}12.00^\circ$
 $\mu = 0.07 \text{ mm}^{-1}$
 $T = 293 \text{ K}$
 Block
 $0.20 \times 0.20 \times 0.10 \text{ mm}$
 Colourless

Data collection

Enraf-Nonius CAD-4 diffractometer
 $\omega/2\theta$ scans
 Absorption correction: none
 1400 measured reflections
 1364 independent reflections
 974 observed reflections
 $[I_{\text{net}} > 2.5\sigma(I_{\text{net}})]$

$R_{\text{int}} = 0.016$
 $\theta_{\text{max}} = 19.91^\circ$
 $h = 0 \rightarrow 10$
 $k = 0 \rightarrow 10$
 $l = 0 \rightarrow 24$
 3 standard reflections
 frequency: 120 min
 intensity variation: $< 1\%$

Refinement

Refinement on F
 Final $R = 0.048$

$\Delta\rho_{\text{max}} = 0.29 \text{ e \AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.18 \text{ e \AA}^{-3}$

$wR = 0.062$
 $S = 1.59$
 974 reflections
 289 parameters
 $w = 1/[\sigma^2(F) + 0.0010F^2]$
 $(\Delta/\sigma)_{\max} = 0.001$

Atomic scattering factors
 from *International Tables*
 for *X-ray Crystallography* (1974, Vol. IV, Table
 2.2B)

Data collection: Enraf-Nonius CAD-4 software. Cell refinement: Enraf-Nonius CAD-4 software. Data reduction: *NRCVAX DATRD2* (Gabe, Le Page, Charland, Lee & White, 1989). Program(s) used to solve structure: *NRCVAX SOLVER*. Program(s) used to refine structure: *NRCVAX LSTSQ*. Molecular graphics: *NRCVAX*. Software used to prepare material for publication: *NRCVAX TABLES*.

Table 1. Fractional atomic coordinates and equivalent isotropic thermal parameters (\AA^2)

$$U_{eq} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

| | x | y | z | U_{eq} |
|------|-------------|--------------|--------------|------------|
| O1A | 0.3516 (5) | 0.3111 (5) | 0.56704 (21) | 0.048 (5) |
| O2A | 0.1486 (8) | 0.2170 (8) | 0.6298 (3) | 0.119 (8) |
| C1A | 0.4474 (8) | 0.3636 (8) | 0.6008 (3) | 0.040 (7) |
| C2A | 0.5379 (8) | 0.3388 (7) | 0.6006 (3) | 0.039 (7) |
| C3A | 0.6334 (7) | 0.4004 (8) | 0.6334 (3) | 0.042 (7) |
| C4A | 0.6441 (8) | 0.4898 (8) | 0.6657 (3) | 0.046 (7) |
| C5A | 0.5520 (8) | 0.5168 (8) | 0.6642 (3) | 0.047 (8) |
| C6A | 0.4529 (7) | 0.4546 (8) | 0.6324 (3) | 0.040 (7) |
| C7A | 0.5462 (7) | 0.2613 (7) | 0.5580 (3) | 0.042 (6) |
| C8A | 0.7542 (7) | 0.5658 (8) | 0.6984 (3) | 0.052 (7) |
| C9A | 0.8194 (10) | 0.6917 (9) | 0.6761 (4) | 0.086 (9) |
| C10A | 0.8385 (11) | 0.5171 (11) | 0.6976 (5) | 0.109 (11) |
| C11A | 0.7241 (10) | 0.5721 (12) | 0.7541 (4) | 0.107 (11) |
| C12A | 0.2676 (10) | 0.1877 (10) | 0.5703 (5) | 0.082 (10) |
| C13A | 0.1585 (11) | 0.1516 (11) | 0.5970 (5) | 0.080 (11) |
| C14A | 0.0544 (10) | 0.0353 (9) | 0.5849 (5) | 0.100 (10) |
| O1B | 0.4159 (5) | 0.2024 (5) | 0.46228 (19) | 0.043 (5) |
| O2B | 0.2195 (7) | -0.0167 (6) | 0.4742 (3) | 0.090 (6) |
| C1B | 0.5272 (8) | 0.3052 (7) | 0.4629 (3) | 0.038 (7) |
| C2B | 0.3787 (8) | 0.5660 (8) | 0.5798 (3) | 0.038 (7) |
| C3B | 0.4807 (8) | 0.6793 (8) | 0.5773 (3) | 0.045 (7) |
| C4B | 0.7493 (7) | 0.5088 (7) | 0.4667 (3) | 0.040 (7) |
| C5B | 0.7048 (8) | 0.4342 (8) | 0.5083 (3) | 0.045 (7) |
| C6B | 0.5947 (8) | 0.3338 (8) | 0.5082 (3) | 0.040 (7) |
| C7B | 0.3589 (7) | 0.4908 (7) | 0.6285 (3) | 0.043 (6) |
| C8B | 0.8736 (8) | 0.6228 (8) | 0.4687 (4) | 0.056 (7) |
| C9B | 0.9036 (11) | 0.6988 (11) | 0.4206 (5) | 0.116 (11) |
| C10B | 0.9678 (9) | 0.5875 (10) | 0.4745 (5) | 0.110 (11) |
| C11B | 0.8806 (12) | 0.6974 (11) | 0.5141 (6) | 0.136 (12) |
| C12B | 0.4135 (8) | 0.1056 (9) | 0.4386 (4) | 0.062 (8) |
| C13B | 0.2979 (11) | -0.0073 (10) | 0.4441 (4) | 0.073 (10) |
| C14B | 0.2828 (11) | -0.1102 (9) | 0.4132 (5) | 0.111 (11) |

Table 2. Selected bond lengths (\AA)

| Bond | Range | Mean |
|--------------------------------|-----------------------|------------|
| $C_{ar}-O_{ether}$ | 1.384 (10)–1.392 (10) | 1.388 (10) |
| $C_{sp^3}-O_{ether}$ | 1.382 (12)–1.418 (13) | 1.400 (13) |
| $C_{sp^3}-C_{sp^3}$ | 1.426 (18)–1.489 (15) | 1.466 (16) |
| $C_{sp^2}=O$ | 1.235 (16)–1.247 (17) | 1.241 (17) |
| $C_{ar}-C_{ar}$ | 1.364 (13)–1.407 (13) | 1.384 (13) |
| $C_{ar}-C_{sp^3}$ | 1.512 (11)–1.550 (12) | 1.528 (12) |
| $C_{sp^3}-C(\text{Bu methyl})$ | 1.492 (16)–1.528 (14) | 1.508 (15) |

H atoms, visible in difference maps, were allowed for as riding atoms with C—H 0.95 \AA . U_{ij} were refined for all non-H atoms.

The θ -scan width was $(0.6 + 0.35 \tan \theta)^\circ$ with a θ -scan rate of $2.75^\circ \text{ min}^{-1}$ and background counts for 15 s on each side of every scan.

The systematic absences (00 l only present if $l = 3n$) and the observed $3m$ Laue symmetry allow the space group to be one of the enantimorphous pairs $P3_112$ and $P3_212$ or $P3_121$ and $P3_221$.

The structure was solved and refined in $P3_121$. No attempt was made to determine any absolute configuration in the light of the paucity of observed data and the low values of the anomalous-scattering components for C and O. Very few reflections were observed beyond $\theta = 15^\circ$ and data collection was terminated at $\theta = 20^\circ$.

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Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55687 (12 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: MU1016]

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Structures of Furo[2,3-*b*]indolizine Derivatives

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Abstract

The indolizine and furan rings in the skeleton of 2-benzoyl-9-methylfuro[2,3-*b*]indolizine (**2a**) and 8-benzoyl-5,6-dihydro-4*H*-furo[2',3':4,5]pyrrolo[3,2,1-*ij*]-quinoline (**2b**) are planar [mean deviations 0.023 (4) and 0.006 (4) \AA (**2a**), 0.014 (3) and 0.005 (3) \AA (**2b**), respectively] and inclined at 5.62° (**2a**) and 3.25° (**2b**) to one another. In (**2b**), The nearly planar cyclohexene ring (fused to the indolizine ring at the 1- and 8-positions) is also nearly coplanar with the indolizine ring [mean deviation 0.140 (3) \AA , dihedral angle 5.41°]. The annelation of the cyclohexene ring in (**2b**)