

Andreas Decken,^{a*} Pierre D. Harvey^b and Jasmin Douville^b^aDepartment of Chemistry, University of New Brunswick, Fredericton, NB, PO Box 45222, Canada E3B 6E2, and ^bDépartement de Chimie, Université de Sherbrooke, 2500 Blvd. Université, Sherbrooke, Québec, Canada J1K 2R1

Correspondence e-mail: adecken@unb.ca

Key indicators

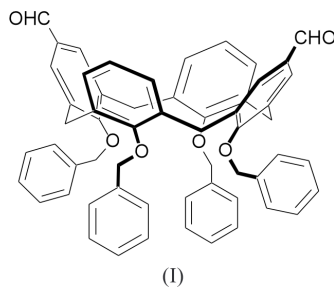
Single-crystal X-ray study
 $T = 198\text{ K}$
Mean $\sigma(\text{C}-\text{C}) = 0.004\text{ \AA}$
 R factor = 0.053
 wR factor = 0.160
Data-to-parameter ratio = 17.9For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

5,17-Diformyl-25,26,27,28-tetrabenzoyloxy-calix[4]arene: functionalization of the upper rim of a calix[4]arene

The structure of the title compound, $\text{C}_{58}\text{H}_{48}\text{O}_6$, is an important example for the functionalization of the upper rim of calix[4]arene molecules. The molecule adopts a pinched cone conformation, placing the formyl groups away from each other.

Comment

Calix[4]arene macrocycles in their cone conformation are versatile molecules that can be used for their host-guest properties because of the bowl-shaped geometry, and the possibility of building architectures in the lower (narrow) and upper rims (wide rim) (Harvey, 2002). The functionalization of the upper rim of this platform molecule is only a recent achievement, compared to the lower rim (Asfari *et al.*, 2001; Gutsche, 1998; Harvey, 2002). Various examples allowing the functionalization of the upper rim exist, but only a few of them are very versatile, notably with respect to the formation of C—C bonds. One functionalization is an aldehyde, which can be converted to alcohols, acids, esters, amides and ethers, *etc.* The shape of the calix[4]arene macrocycle and the steric hindrance between the substituents control the geometry and the final interatomic distances.



We report here the crystal structure of the title compound, (I), which was synthesized in two steps from the known compound 5,17-dibromo-25,26,27,28-tetrahydroxycalix[4]arene, (II). The first step consists of a benzylation of the lower rim using an excess of benzyl chloride, leading to the target compound 5,17-dibromo-25,26,27,28-tetrabenzoyloxy-calix[4]arene, (III). The reaction of (III) with DMF and *n*-butyl lithium leads to the title compound in good yield. The molecule, shown in Fig. 1, adopts a pinched cone conformation, placing the formyl groups away from each other. The cofacial aryl rings of the calix[4]arene macrocycle are tilted towards each other, where the $\text{H}12 \cdots \text{H}26$, $\text{C}12 \cdots \text{C}26$ and $\text{O}38 \cdots \text{O}52$ separations are 4.550 (3), 4.705 (3) and 5.503 (3) Å, respectively. The two other rings are substantially tilted away from each other. The $\text{C}29 \cdots \text{C}30$, $\text{C}5 \cdots \text{C}19$ and $\text{O}31 \cdots \text{O}45$

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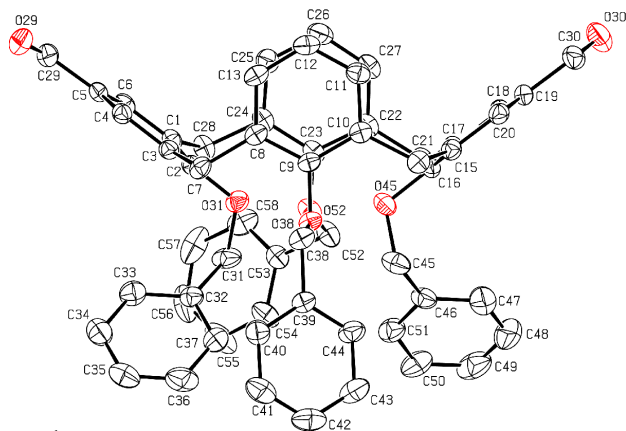


Figure 1
A view of the title compound, with displacement ellipsoids drawn at the 30% probability level. H atoms have been omitted for clarity.

distances are 12.309 (3), 9.948 (3) and 3.456 (3) Å, respectively. Ignoring the benzyl groups, the macrocycle exhibits approximate C_{2v} symmetry. Approximate twofold symmetry for the benzyl and formyl residues belonging to the non-cofacial aryl groups is observed. On the other hand, the benzyl groups linked to the cofacial aryls are not related by symmetry because of the different rotation angles around the O—CH₂ bonds. This structure shows analogies with the recently reported structure of 5,11-diformyl-25,26,27,28-tetrabutoxycalix[4]arene, which also exhibits a pinched cone geometry (Evans *et al.*, 2002). The cofacial C···C distance is 3.90 Å (no standard uncertainty available), which is shorter than that of 4.705 (3) Å for (I). However, the latter turns out to be in the normal range for most calix[4]arene derivatives (4–5 Å; Evans *et al.*, 2002). In conclusion, the dimensions of the pinched cone calix[4]arene do not appear to be a function of the lower rim substituents.

Experimental

All solvents were freshly distilled before use. All reactions were conducted under argon. Compound (II) was synthesized according to a literature procedure (Gagnon *et al.*, 2001). For the preparation of (III), compound (II) (521 mg, 0.9 mmol) and NaH (158 mg, 6.6 mmol) were dissolved in DMF (70 ml). The solution was stirred for 2 h at room temperature. Benzyl chloride (4.5 g, 35.5 mmol) was added and the mixture was further stirred for 4 d. The solvent was evaporated *in vacuo* and the residue was dissolved in CH₂Cl₂ (100 ml). The organic layer was washed twice with HCl (1 M, 100 ml) and once with water (100 ml). The organic layer was dried with MgSO₄ and filtered, and the solvent was evaporated *in vacuo*. The product was recrystallized from CHCl₃/MeOH to afford (III) as a yellow solid in quantitative yield (0.836 g). ¹H NMR (CDCl₃, p.p.m.): 7.28 (*m*, 20H, OCH₂Ph), 6.74 (*s*, 4H, BrPh), 6.52 (*m*, 6H, Ph), 4.91 (*d*, 8H, *J* = 4.8 Hz, OCH₂Ph), 4.09 (*d*, 4H, *J* = 13.6 Hz, PhCH₂Ph), 2.83 (*d*, 4H, *J* = 13.5 Hz, PhCH₂Ph); MS (EI) 942 (M⁺). For the preparation of (I), compound (III) (836 mg, 0.9 mmol) was dissolved in dry THF (100 ml) at 195 K. *n*-Butyl lithium (1.6 M, 1.70 ml, 2.7 mmol) was added and the solution was stirred for 20 min. DMF (1.37 ml, 17.8 mmol) was added and the solution was further stirred for 10 min. The reaction mixture was then poured onto ice (300 g) and HCl (2 M, 200 ml). The aqueous layer was extracted twice with toluene (100 ml).

The organic layer was washed once with water (100 ml), dried over MgSO₄ and filtered, and the solvent was evaporated *in vacuo*. No further purification was required. Compound (I) was obtained as a white solid in 70% yield (0.525 g). ¹H NMR (CDCl₃, p.p.m.): 9.77 (*s*, 2H, CHO), 7.55 (*m*, 20H, OCH₂Ph), 6.95 (*m*, 10H, Ph), 5.26 (*d*, 8H, *J* = 4.6 Hz, OCH₂Ph), 4.48 (*d*, 4H, *J* = 13.8 Hz, PhCH₂Ph), 3.27 (*d*, 4H, *J* = 13.9 Hz, PhCH₂Ph); IR (KBr): ν_{CO} 1687 cm⁻¹; MS (EI) 840 (M⁺).

Crystal data

C₅₈H₄₈O₆
M_r = 840.96
Orthorhombic, *Pbca*
a = 18.1209 (13) Å
b = 19.8137 (14) Å
c = 25.2396 (17) Å
V = 9062.1 (11) Å³
Z = 8
D_x = 1.233 Mg m⁻³

Mo K α radiation
Cell parameters from 14 515 reflections
 θ = 2.1–25.0°
 μ = 0.08 mm⁻¹
T = 198 (2) K
Irregular, colourless
0.4 × 0.4 × 0.3 mm

Data collection

Bruker SMART 1000/P4 diffractometer
 ω and φ scans
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)
*T*_{min} = 0.88, *T*_{max} = 0.98
60 976 measured reflections

10 340 independent reflections
5000 reflections with *I* > 2 σ (*I*)
*R*_{int} = 0.067
 θ _{max} = 27.5°
h = -23 → 21
k = -24 → 25
l = -32 → 32

Refinement

Refinement on *F*²
R [*F*² > 2 σ (*F*²)] = 0.053
wR (*F*²) = 0.160
S = 1.09
10 340 reflections
577 parameters

H-atom parameters constrained
w = 1/[$\sigma^2(F_o^2) + (0.0729P)^2$]
where *P* = (*F*_o² + 2*F*_c²)/3
(Δ / σ)_{max} < 0.001
 $\Delta\rho$ _{max} = 0.36 e Å⁻³
 $\Delta\rho$ _{min} = -0.23 e Å⁻³

All H atoms were placed in calculated positions, with C—H distances fixed at 0.99 (methylene) and 0.95 Å (phenyl), and were subsequently refined as riding atoms, with *U*_{iso} values of 1.2*U*_{eq} of the carrier C atom.

Data collection: *SMART* (Bruker, 1997–1999); cell refinement: *SAINT* (Bruker, 1997–1999); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997*a*); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997*a*); molecular graphics: *PLATON* (Spek, 2004); software used to prepare material for publication: *SHELXTL* (Sheldrick, 1997*b*).

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