

5,17-Dibenzoyl-25,26,27,28-tetrahydroxy-calix[4]arene

Yong Yang,^{a*} En-Chao Li,^a
Feng-Xiang Chen,^b Cheng Peng^a
and Xian-Fa Shi^a^aDepartment of Chemistry, Tongji University, Shanghai 20092, People's Republic of China, and ^bDepartment of Chemistry, East China Normal University, Shanghai 200062, People's Republic of ChinaCorrespondence e-mail:
yangyong@mail.tongji.edu.cn

Key indicators

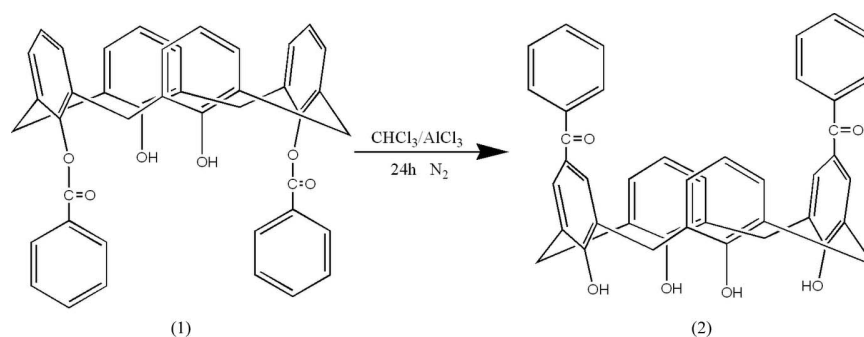
Single-crystal X-ray study
 $T = 293\text{ K}$
Mean $\sigma(\text{C}-\text{C}) = 0.006\text{ \AA}$
 R factor = 0.065
 wR factor = 0.174
Data-to-parameter ratio = 12.5For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

The structure of the title compound, $\text{C}_{42}\text{H}_{32}\text{O}_6$, is an important example of the functionalization of the upper rim of calix[4]arene molecules. It possesses crystallographic twofold rotation symmetry and displays the calixarene cone conformation. The hydroxyl groups form intramolecular hydrogen bonds.

Received 24 October 2006
Accepted 6 November 2006

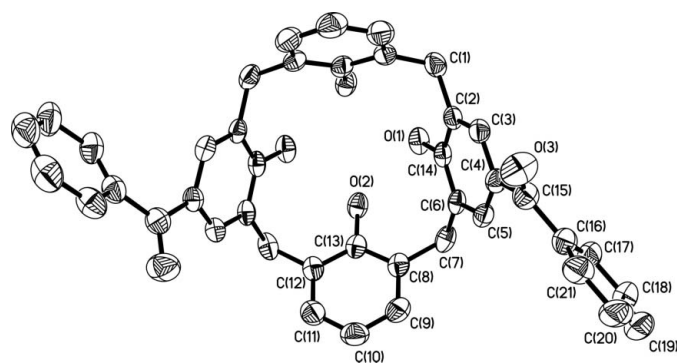
Comment

Calixarenes currently attract considerable interest in the field of supramolecular chemistry because their derivatives can form inclusion complexes with cations or with neutral molecules (Gutsche, 1989; Vicens & Böhmer, 1991). The functionalization of the upper rim of this platform molecule is only a recent achievement compared with the lower rim (Asfari *et al.*, 2001; Harvey, 2002). Various examples allowing the functionalization of the upper rim exist, but only a few of them are very versatile with respect to the formation of C—C bonds. The shape of the calix[4]arene macrocycle and the steric hindrance between the substituents control the geometry and the final interatomic distances. In this investigation, we exploit the possibility of adapting the Fries rearrangement for the preparation of the title partially upper-rim substituted calix[4]arene, (2).



The molecular structure of compound (2) is shown in Fig. 1. The calix[4]arene assumes a conformation with crystallographic C_2 symmetry. The cone conformation of the calixarene core is retained from the precursor, (1).

A benzoyloxy substituent has been introduced on the calix[4]arene *via* the Fries rearrangement. The angles $\text{C4}-\text{C15}-\text{O3}$, $\text{C4}-\text{C15}-\text{C16}$ and $\text{O3}-\text{C15}-\text{C16}$ are $118.9(4)$, $121.8(4)$ and $119.3(4)^\circ$, respectively. The $\text{C15}-\text{O3}$ distance is $1.238(4)\text{ \AA}$. Bond lengths and angles may be considered normal. The shape of the calix cavity is defined by the interplanar angles which the various aromatic rings make with the planes of the four methylene groups. The molecular conformation is stabilized by two symmetry-equivalent pairs of

**Figure 1**

The molecular structure of (2), with 30% probability displacement ellipsoids. For clarity, H atoms have been omitted. Unlabelled atoms are related to labelled atoms by the symmetry operator $(-x + 1, y, -z + \frac{1}{2})$.

intramolecular hydrogen bonds between the hydroxyl groups (Table 1).

Experimental

A mixture of compound (1) (0.5 g) and aluminium chloride in dry chloroform (50 ml) was stirred at 333 K for 24 h. The reaction mixture was poured into ice–water (50 ml). The dichloromethane layer was successively washed with 0.1 M hydrochloric acid and 10% sodium bicarbonate solution. On concentration, the dichloromethane layer provided compound (2). Colourless crystals of (2) were grown from a methanol–dichloromethane (1:15) solution of the material.

Crystal data

$C_{42}H_{32}O_6$	$Z = 4$
$M_r = 632.68$	$D_x = 1.319 \text{ Mg m}^{-3}$
Monoclinic, $C2/c$	Mo $K\alpha$ radiation
$a = 18.615 (4) \text{ \AA}$	$\mu = 0.09 \text{ mm}^{-1}$
$b = 15.609 (4) \text{ \AA}$	$T = 293 (2) \text{ K}$
$c = 12.220 (3) \text{ \AA}$	Pillar, colourless
$\beta = 116.187 (4)^\circ$	$0.20 \times 0.15 \times 0.10 \text{ mm}$
$V = 3186.1 (13) \text{ \AA}^3$	

Data collection

Bruker SMART CCD area-detector diffractometer	6625 measured reflections
φ and ω scans	2819 independent reflections
Absorption correction: multi-scan (SADABS; Bruker, 1997)	1253 reflections with $I > 2\sigma(I)$
$T_{\min} = 0.983, T_{\max} = 0.991$	$R_{\text{int}} = 0.080$
	$\theta_{\text{max}} = 25.0^\circ$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.065$
 $wR(F^2) = 0.174$
 $S = 0.90$
 2819 reflections
 225 parameters

H atoms treated by a mixture of independent and constrained refinement

$$w = 1/[\sigma^2(F_o^2) + (0.0737P)^2]$$

where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} < 0.001$
 $\Delta\rho_{\text{max}} = 0.18 \text{ e \AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.18 \text{ e \AA}^{-3}$

Table 1

Hydrogen-bond geometry ($\text{\AA}, ^\circ$).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
$C17-H17A \cdots O1^i$	0.93	2.58	3.478 (5)	163
$O2-H2 \cdots O1^{ii}$	0.817 (19)	1.86 (2)	2.672 (4)	171 (4)
$O1-H1 \cdots O2$	0.863 (19)	1.81 (2)	2.662 (4)	169 (6)

Symmetry codes: (i) $-x + \frac{3}{2}, -y + \frac{1}{2}, -z + 1$; (ii) $-x + 1, y, -z + \frac{1}{2}$.

H atoms were located in a difference map, but were refined with fixed individual isotropic displacement parameters [$U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$] using a riding model, with $C-H = 0.93$ and 0.97 \AA for C_{aromatic} and $C_{\text{methylene}}$, respectively. The hydroxyl H atoms were refined isotropically (distances are in Table 1).

Data collection: SMART (Bruker, 1997); cell refinement: SMART; data reduction: SHELXTL (Bruker, 1997); program(s) used to solve structure: SHELXS97 (Sheldrick, 1997); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: SHELXTL; software used to prepare material for publication: SHELXTL.

References

- Asfari, Z., Börner, V., Harrowfield, J. & Vicens, J. (2001). *Calixarenes*, pp. 234–246. Dordrecht: Kluwer Academic Publishers.
- Bruker (1997). SMART (Version 5.611), SADABS (Version 2.03) and SHELXTL (Version 5.10). Bruker AXS Inc., Madison, Wisconsin, USA.
- Gutsche, C. D. (1989). In *Calixarenes. Monographs in Supramolecular Chemistry*, Vol. 1, edited by J. F. Stoddart. London: Royal Society of Chemistry.
- Harvey, P. D. (2002). *Coord. Chem. Rev.* **233–234**, 289–309.
- Sheldrick, G. M. (1997). SHELXS97 and SHELXL97. University of Göttingen, Germany.
- Vicens, J. & Böhmer, V. (1991). *Calixarenes: A Versatile Class of Macrocyclic Compounds*, pp. 246–261. Dordrecht: Kluwer Academic Publishers.