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2,4-Dihydroxy-1,3-bis(methoxycarbonylmethoxy)calix[4]arene and 1,3-bis(ethoxycarbonylmethoxy)-2,4-dihydroxycalix[4]arene chloroform solvate

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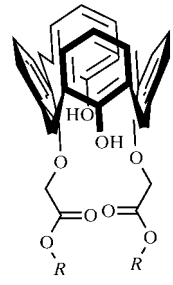
The two title calix[4]arene compounds, $C_{34}H_{32}O_8$, (I), and $C_{36}H_{36}O_8{\cdot}CH_3Cl$, (II), respectively, which differ only in the size of the alkyl function on the pendant ester group, are compared. Compound (I) forms a novel supramolecular array, whilst (II) fails to do so due to accommodating a chloroform guest molecule in the lower-rim cavity.

Comment

There is much current interest in the design of supramolecular structures where the guest–host assembly is formed by non-covalent interactions (Lehn, 1995; Gutsche, 1998). Calixarenes are a promising platform as good candidates for self-assembly (Mandolini & Ungaro, 2000), owing to their high symmetry and ease of chemical modification. The title calix[4]arenes, *i.e.* 2,4-dihydroxy-1,3-bis(methoxycarbonylmethoxy)calix[4]-arene, (I), and 1,3-bis(ethoxycarbonylmethoxy)-2,4-dihydroxycalix[4]arene chloroform solvate, (II), are well established in the literature as building blocks for more elaborate calixarenes (Beer *et al.*, 1998). In addition, compound (I) has been shown to extract Cs^+ and Sr^{2+} (Arena *et al.*, 1998; Grunder *et al.*, 1999); however, their crystal structures have not been reported in the literature.



(I) R = Me
(II) R = Et, CH_3Cl solvate

The molecular structures of (I) and (II) are shown in Figs. 1 and 2, respectively, whilst the supramolecular structure of (I) is shown in Fig. 3. The crystal structure of (I) is unusual in that it forms a honeycomb structure of columnar hexagonal tubes. These tubes have an internal diameter of 4.83 (9) Å and are constructed by the stacking of three calixarenes alternatively offset by 60°, giving overall C_3 symmetry. The driving force to the formation of this structure is π–π-stacking/interlocking between the calixarene rings and dipole–dipole interactions between the lower-rim methyl ester groups. This is demonstrated by the head-to-tail arrangement of the carbonyl groups on the lower rim. To our knowledge, this is the first example of

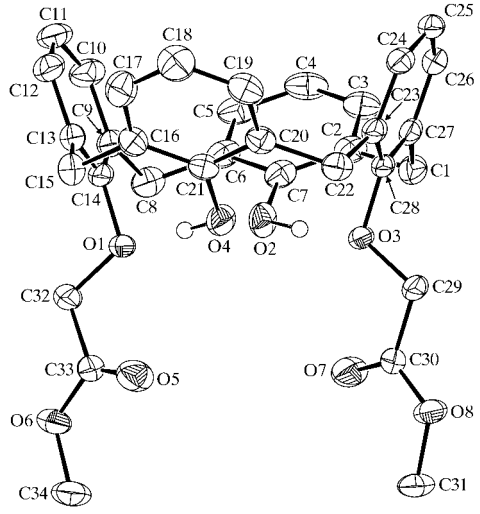


Figure 1
View of (I) shown with 50% probability displacement ellipsoids.

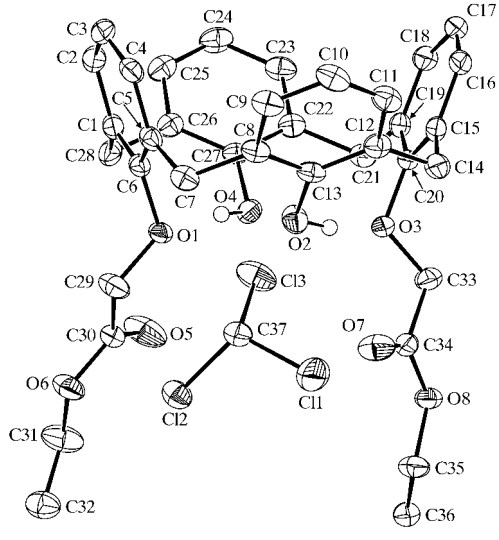


Figure 2
View of (II) shown with 50% probability displacement ellipsoids.

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a honeycomb structure for a purely organic calixarene. Calixarene (II) failed to form a nanotubular array, a result of the carbonyl groups on the ethyl ester pendant arms being directed away from each other due to their conformational rearrangement in order to accommodate the chloroform guest molecule.

The structures of (I) and (II) are best described comparatively, and hence the values in square brackets refer to the equivalent parameter in (II) to that stated for (I). The angles about the *meso*-C atoms [C1, C8, C17 and C24 for (I), and C7, C14, C21 and C28 for (II)] are reasonably close to ideal tetrahedral geometry, indicating a strain-free macrocycle. The upper rim of calixarene (I) forms a cavity, with separations between *meso*-C atoms of 5.067 (2), 5.075 (2), 5.079 (2) and 5.070 (2) Å [5.066 (3), 5.090 (3), 5.067 (3) and 5.099 (3) Å], and cross-ring distances between *meso*-C atoms of 7.312 (2) and 7.031 (2) Å [7.352 (3) and 7.008 (3) Å]. The asymmetry of the macrocycle is caused by the lower-rim substituents, which form a number of intramolecular hydrogen bonds with each other. In addition, the angles of the aromatic rings in the calixarene with respect to the mean plane of the macrocyle (defined by the *meso*-C atoms) are 71.70 (4) and 68.46 (3)° [73.68 (7) and 68.42 (6)°] for the alkyl ester functionalized rings, whilst those for the hydroxy-substituted rings are 42.35 (4) and 37.86 (5)° [45.52 (7) and 49.17 (6)°]. Thus, the hydroxy-substituted rings are allowed to lie more in the plane of the macrocycle due to their relatively small functional groups on the lower rim and the intramolecular interactions in which they are involved. The separation of the terminal methyl groups of the ester functions is 6.475 (2) Å [7.141 (3) Å], reflecting the dilation of the lower-rim substituents in calixarene (II) in order to accommodate the chloroform moiety.

Pertinent hydrogen-bonding parameters are given in Tables 1 and 2. The pendant ester groups are locked in position by strong hydrogen bonding between the hydroxy substituent and the oxy linkage between the calixarene and the ester; these are of comparable strength in (I) and (II). There is a further interaction between the carbonyl group of the ester and the hydroxy substituent, making it a bifurcated donor. This interaction is weaker in (I) compared with (II) as the arms are allowed to adopt the most favourable conformation, as opposed to those of (II) which interact with the chloroform guest molecule. Non-classical interactions, presumably electrostatic, occur in (II) between the guest and host molecules [$D\cdots A$ = Cl2$\cdots$O5 = 3.316 (2) Å, Cl1$\cdots$O8 = 3.349 (2) Å, C37$\cdots$O4 = 3.221 (3) Å and C37$\cdots$O5 = 3.075 (3) Å].

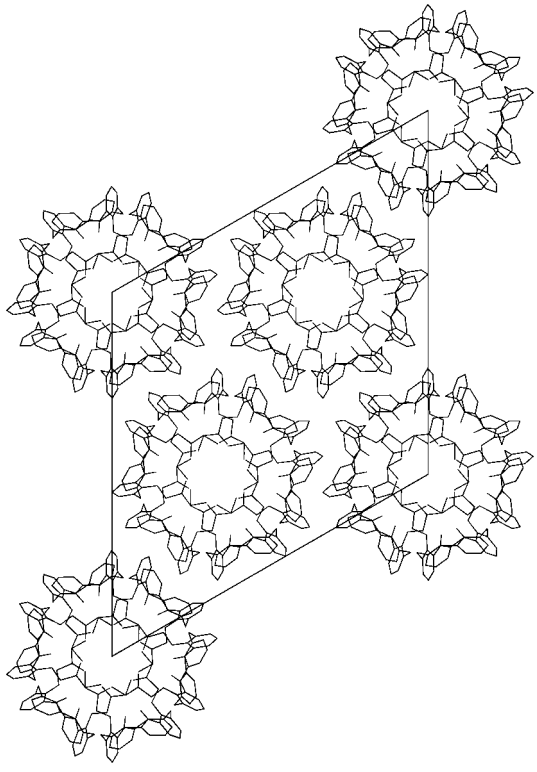

Figure 3
The supramolecular structure exhibited by (I).

Experimental

Calixarenes (I) and (II) were synthesized by reaction of calix[4]arene with the appropriate bromoalkyl acetate according to previously described procedures (Aoki *et al.*, 1992). Calixarene (I) was recrystallized from a methanol/chloroform mixture. Crystals of (II) suitable for diffraction analysis were obtained by recrystallization from an ethyl acetate/chloroform mixture and immediately transferred to the diffractometer, as the crystals degraded, losing solvent, after standing for a short time in air.

Compound (I)

Crystal data

$C_{34}H_{32}O_8$
M_r = 568.6
Rhombohedral, $R\overline{3}$
a = 32.840 (5) Å
c = 13.918 (3) Å
V = 13000 (4) Å^3
Z = 18
D_x = 1.307 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 13 396 reflections
θ = 1.0–30.5°
μ = 0.09 mm^{-1}
T = 150 (2) K
Block, colourless
0.3 × 0.2 × 0.2 mm

Data collection

Nonius KappaCCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SORTAV*; Blessing, 1997)
T_{min} = 0.973, T_{max} = 0.982
25 617 measured reflections
6609 independent reflections
4617 reflections with $I > 2\sigma(I)$
R_{int} = 0.044
θ_{max} = 27.5°
$h = -42 \rightarrow 33$
$k = -30 \rightarrow 42$
$l = -17 \rightarrow 18$

Refinement

Refinement on F^2
$R(F)$ = 0.044
$wR(F^2)$ = 0.114
S = 1.04
6609 reflections
384 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0542P)^2 + 5.4230P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.002
$\Delta\rho_{max}$ = 0.24 e Å^{-3}
$\Delta\rho_{min}$ = −0.20 e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.00040 (7)

Table 1
Hydrogen-bonding geometry (Å, °) for (I).

D—H···A	D—H	H···A	D···A	D—H···A
O2—H2···O3	0.84	1.92	2.7273 (14)	160
O4—H4A···O1	0.84	1.99	2.7987 (15)	161
O2—H2···O7	0.84	2.88	3.4142 (16)	124
O4—H4A···O5	0.84	2.90	3.4434 (16)	124

Compound (II)

Crystal data

$C_{36}H_{36}O_8{\cdot}CH_3Cl$
M_r = 716.02
Monoclinic, $P2_1$
a = 10.027 (2) Å
b = 10.243 (2) Å
c = 16.852 (3) Å
β = 100.39 (3)°
V = 1702.6 (6) Å^3
Z = 2
D_x = 1.397 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 14 325 reflections
θ = 1–27.5°
μ = 0.32 mm^{-1}
T = 100 (2) K
Block, colourless
0.10 × 0.08 × 0.06 mm

Data collection

Nonius KappaCCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SORTAV*; Blessing, 1997)
T_{min} = 0.969, T_{max} = 0.981
24 715 measured reflections
7629 independent reflections
6130 reflections with $I > 2\sigma(I)$
R_{int} = 0.052
θ_{max} = 27.5°
$h = -13 \rightarrow 13$
$k = -13 \rightarrow 13$
$l = -21 \rightarrow 21$

Refinement

Refinement on F^2
$R(F)$ = 0.041
$wR(F^2)$ = 0.100
S = 0.95
7629 reflections
438 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0566P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.03
$\Delta\rho_{max}$ = 0.29 e Å^{-3}
$\Delta\rho_{min}$ = −0.25 e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.0153 (14)
Absolute structure: Flack (1983)
Flack parameter = −0.10 (4)

Table 2
Hydrogen-bonding geometry (Å, °) for (II).

D—H···A	D—H	H···A	D···A	D—H···A
O2—H2A···O3	0.84	1.92	2.706 (2)	154
O2—H2A···O7	0.84	2.53	3.071 (2)	123
O4—H4A···O1	0.84	1.96	2.790 (2)	172
O4—H4A···O5	0.84	2.71	3.119 (3)	112

All H atoms were included in idealized positions with X—H distances of 0.84, 0.95, 0.99 and 0.98 Å for hydroxy, methine, methylene and methyl H atoms, respectively. The coordinates of these fixed atoms were allowed to ride on those of the parent atoms. The displacement parameters of the H atoms were constrained to be a factor of 1.2 greater than those of the parent atoms for those associated with aromatic moieties and 1.5 greater than the parent values for the others. A Flack (1983) parameter of −0.10 (4), determined by refinement using 3510 Friedel pairs, indicated that the correct absolute structure of (II) has been identified.

For both compounds, cell refinement: *DENZO* (Otwinowski & Minor, 1997) and *COLLECT* (Hooft, 1998); data reduction: *DENZO* and *COLLECT*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 1990).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FR1354). Services for accessing these data are described at the back of the journal.

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