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25-Allyloxy-5,11,17,23-tetra-*tert*-butyl-26,27,28-trihydroxycalix[4]-arene chloroform disolvate

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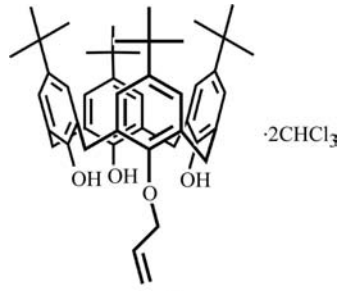
In the title solvated calixarene, $C_{47}H_{60}O_4{\cdot}2CHCl_3$, the host chalice displays an almost undistorted cone conformation, stabilized by three strong O—H···O hydrogen bonds at the calixarene's lower rim. One chloroform solvent molecule is fixed in the calixarene cavity by C—H···π interactions, while the second is accommodated in a clathrate-like mode in elliptical packing voids. These voids are spanned by six host molecules connected *via* C—H···π contacts and van der Waals interactions. Within the crystal structure, one *tert*-butyl group of the calixarene host is disordered over two orientations, with occupancies of 0.884 (4) and 0.116 (4). Furthermore, both solvent molecules show disorder, with occupancies of 0.857 (2) and 0.143 (2) for the cavitate-type, and 0.9359 (17) and 0.0641 (17) for the clathrate-type chloroform solvent molecules.

Comment

Aside from crown compounds and cyclodextrins, calixarenes are the macrocyclic substance class being paid most attention in supramolecular chemistry (Steed *et al.*, 2007; Steed & Atwood, 2009), with calix[4]arene as the archetypal molecule (Gutsche, 2004). Modification of the upper and lower rim sites of the cone structure has been performed using a vast number of different substituents and functional groups, which has given rise to an enormously wide range of individual calix[4]arene derivatives (Gutsche, 2008). In particular, the substitution serves to freeze the calix framework conformationally, to improve the inclusion selectivity or to act as an effective linkage group for the generation of complex calix[4]arene constructions (Mandolini & Ungaro, 2000; Vicens & Harrowfield, 2007). In this respect, lower rim-site substituents featuring an olefinic group have proven very useful (Gutsche *et al.*, 1985; Akine *et al.*, 2001; Vocanson *et al.*, 2003; Shiao *et al.*, 2006; Mocerino *et al.*, 2006).

An example of this type of compound is the monoallyl substituted *p-tert*-butylcalix[4]arene obtained from the reaction of *p-tert*-butylcalix[4]arene with allyl bromide according to Groenen *et al.* (1991). The title compound, (I), which is the 1:2 inclusion compound of this calix[4]arene with the solvent chloroform, is discussed in this study.



(I)

Compound (I) crystallizes from chloroform–methanol (1:1 *v*/*v*) as colourless crystals in the monoclinic space group *C*2/*c*, with one calixarene and two disordered chloroform molecules in the asymmetric unit (Fig. 1). The host chalice displays an almost undistorted cone conformation [interplanar angles: *A*/*C* = 68.19 (7)° and *B*/*D* = 67.19 (7)°; *A*, *B*, *C* and *D* correspond to the aromatic rings C1–C6, C8–C13, C15–C20 and C22–C27, respectively], which is stabilized by three strong hydrogen bonds at the lower rim involving the unsubstituted phenolic hydroxy groups, as well as the ether O atom [O···O = 2.633 (2)–2.671 (2) Å]. One of the disordered chloroform guests is situated in the cavity of the host [site-occupancy factors (SOF) = 0.857 (2) and 0.143 (2)] and the other in a clathrate-like mode in its lattice voids [SOF = 0.9359 (17) and 0.0641 (17)]. In the former case, only the major-occupancy component of the guest displays a C—H···π contact (Nishio *et al.*, 2009) towards aromatic ring *B* of the calixarene [C—H···π = 3.483 (4) Å]. In contrast, only the minor-occupancy component of the clathrate-like chloroform is involved in such interactions, with ring *A* of a neighbouring calixarene molecule [C—H···π = 3.39 (5) Å]. It is worth mentioning the disorder of one of the C41 *tert*-butyl groups [SOF = 0.884 (4) and 0.116 (4)] and the fact that two of them are engaged in weak C—H···Cl interactions with both guest species [C—H···Cl = 3.316 (4)–3.869 (3) Å, involving methyl groups C30–C32 and C36].

The crystal packing of (I) is dominated by weak C—H···π contacts involving two of the methylene bridges and aromatic rings of a neighbouring calixarene [C—H···π = 3.535 (2) and 3.379 (2) Å, respectively], as well as van der Waals interactions. This results in a layered arrangement of calixarene molecules parallel to the crystallographic *bc* plane (Fig. 2). Remarkably, it is always six host molecules that span an elliptical lattice cavity, each containing two clathrate-type chloroform molecules, as shown in Fig. 3.

In conclusion, the presence of one allyl substituent has no significant influence on the conformation of the calix[4]arene cavity, in contrast with the rather distorted cone conformation

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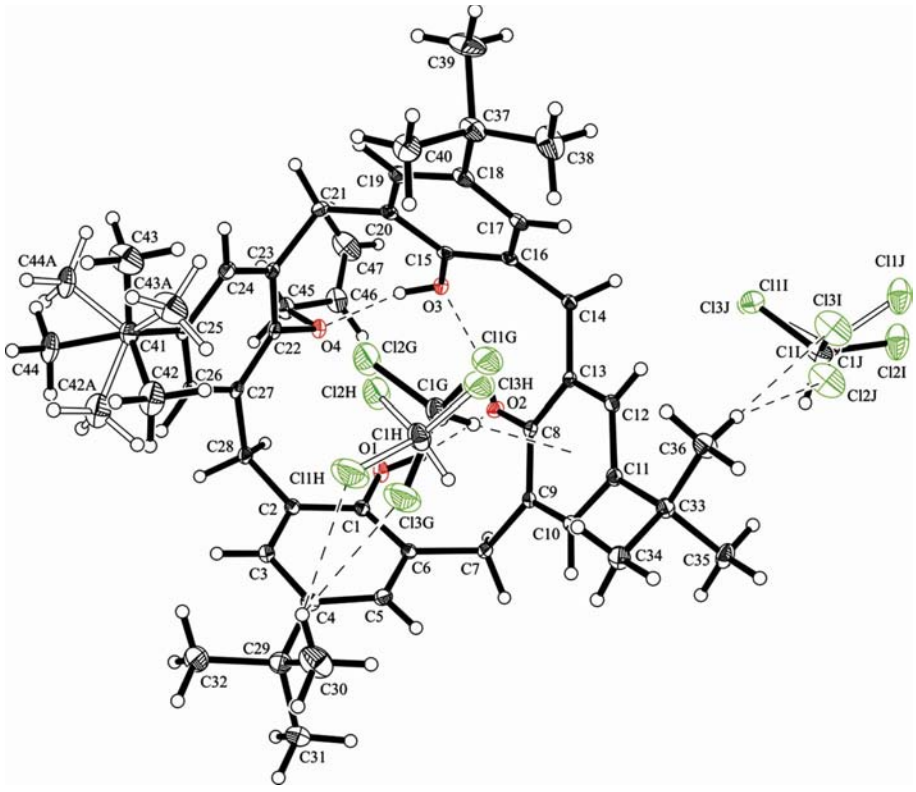

Figure 1
The molecular structure of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii. Dashed lines indicate hydrogen bonds. The minor-occupancy disorder components are drawn with open bonds.

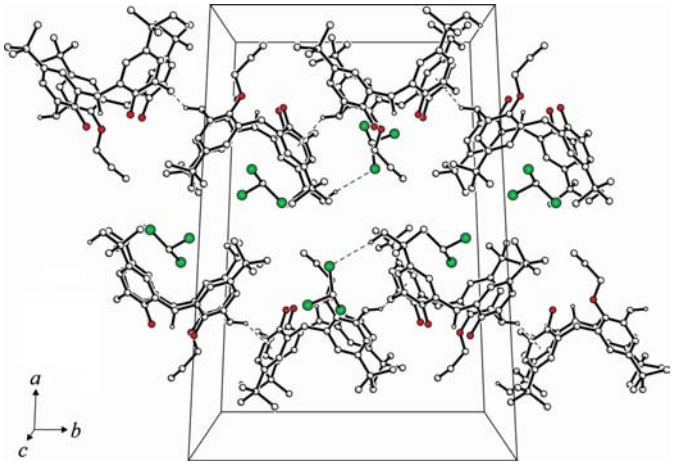

Figure 2
A packing diagram for (I), viewed down the *c* axis, showing the layer arrangement of calixarene molecules. H atoms not involved in hydrogen bonding have been omitted.

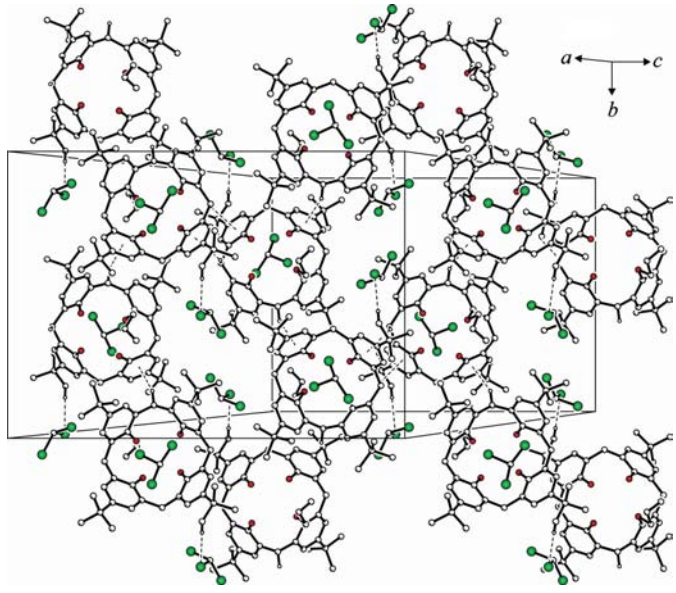

Figure 3
The crystal packing of (I), showing the elliptical lattice voids which consist of six calixarene molecules each.

of the 1:2 chloroform complex of the respective diallyl calixarene showing two clathrate-type guest molecules in the asymmetric unit (Stumpf *et al.*, 2003). For comparison, in the 1:1 complex of unsubstituted *p-tert*-butylcalix[4]arene with chloroform described by Benevelli *et al.* (2000), the single guest molecule is located directly in the host cavity. Hence, the attachment of allyl groups to the lower rim gives rise to lattice voids for the interstitial accommodation of a second guest molecule.

Experimental

The title calixarene was synthesized by stirring commercially available *p-tert*-butylcalix[4]arene (11.20 g, 15 mmol), allyl bromide (3.06 ml, 35.4 mmol) and potassium carbonate (2.07 g, 15 mmol) in acetonitrile (300 ml) under reflux for 4 h. After cooling, the solvent

was removed under reduced pressure. The remaining residue was treated with dilute hydrochloric acid and subsequently recrystallized from a mixture of chloroform and methanol (1:1 *v*/*v*) to give colourless crystals of (I) suitable for X-ray diffraction [yield 2.97 g, 29%; m.p. 573–574 K, literature value 546–548 K (Groenen *et al.*, 1991)].

Crystal data

$C_{47}H_{60}O_4\cdot 2CHCl_3$
M_r = 927.69
Monoclinic, $C2/c$
a = 28.8774 (7) Å
b = 16.8275 (7) Å
c = 23.3186 (8) Å
β = 120.068 (2)°
V = 9806.5 (6) Å^3
Z = 8
Mo $K\alpha$ radiation
μ = 0.39 mm^{-1}
T = 113 K
0.60 × 0.37 × 0.35 mm

Data collection

Bruker Kappa APEXII CCD diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2007)
T_{min} = 0.791, T_{max} = 0.875
102072 measured reflections
8635 independent reflections
7171 reflections with $I > 2\sigma(I)$
R_{int} = 0.045

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.055
$wR(F^2)$ = 0.168
S = 1.10
8635 reflections
586 parameters
11 restraints
H-atom parameters constrained
$\Delta\rho_{max}$ = 1.10 e Å^{-3}
$\Delta\rho_{min}$ = −0.97 e Å^{-3}

Table 1
Geometry of hydrogen bonds and short intermolecular contacts (Å, °).

CgA, *CgB* and *CgC* are the centroids of the aromatic rings *A* (C1–C6), *B* (C8–C13) and *C* (C15–C20), respectively.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H1···O2	0.84	1.86	2.671 (2)	162
O2—H2···O3	0.84	1.83	2.650 (2)	164
O3—H3···O4	0.84	1.81	2.633 (2)	166
C7—H7*B*···*CgB*^{i}	0.99	2.78	3.535 (2)	133
C28—H28*B*···*CgC*^{ii}	0.99	2.59	3.379 (2)	137
C30—H30*A*···Cl3*G*	0.98	2.70	3.316 (4)	121
C30—H30*A*···Cl1*H*	0.98	2.68	3.529 (9)	145
C31—H31*B*···Cl1*J*^{iii}	0.98	2.64	3.480 (15)	144
C32—H32*B*···Cl1*J*^{iii}	0.98	2.84	3.654 (17)	142
C36—H36*A*···Cl3*I*	0.98	2.89	3.869 (3)	175
C36—H36*A*···Cl2*J*	0.98	2.88	3.822 (14)	162
C1*G*—H1*G*···*CgB*	1.00	2.49	3.483 (4)	173
C1*J*—H1*J*···*CgA*^{i}	1.00	2.42	3.39 (5)	163

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

H atoms were positioned geometrically and allowed to ride on their respective parent atoms, with C—H = 0.98 Å and U_{iso}(H) = 1.5U_{eq}(C) for methyl, C—H = 0.99 Å and U_{iso}(H) = 1.2U_{eq}(C) for methylene, C—H = 1.00 Å and U_{iso}(H) = 1.2U_{eq}(C) for methine, C—H = 0.95 Å and U_{iso}(H) = 1.2U_{eq}(C) for aryl/alkenyl, and O—H = 0.84 Å and U_{iso}(H) = 1.5U_{eq}(O) for hydroxy H atoms. The atomic displacement parameters of the corresponding atoms in each orientation of the disordered chloroform molecules and the *tert*-butyl group were constrained to be equal. The C—Cl and Cl···Cl distances within each orientation of the chloroform molecules were restrained to 1.73 (2) and 2.88 (4) Å, respectively.

Data collection: *APEX2* (Bruker, 2007); cell refinement: *SAINT* (Bruker, 2007); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008) and *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *SHELXTL* and *PLATON* (Spek, 2009).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: GD3348). Services for accessing these data are described at the back of the journal.

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