

(5,11,17,23-Tetra-*tert*-butyl-26,28-dihydroxycalix[4]arene-25,27-dioxy)diacetic acid *N,N*-dimethylformamide trisolvate

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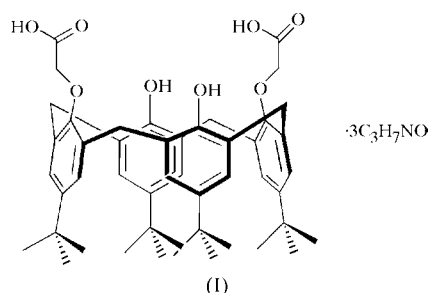
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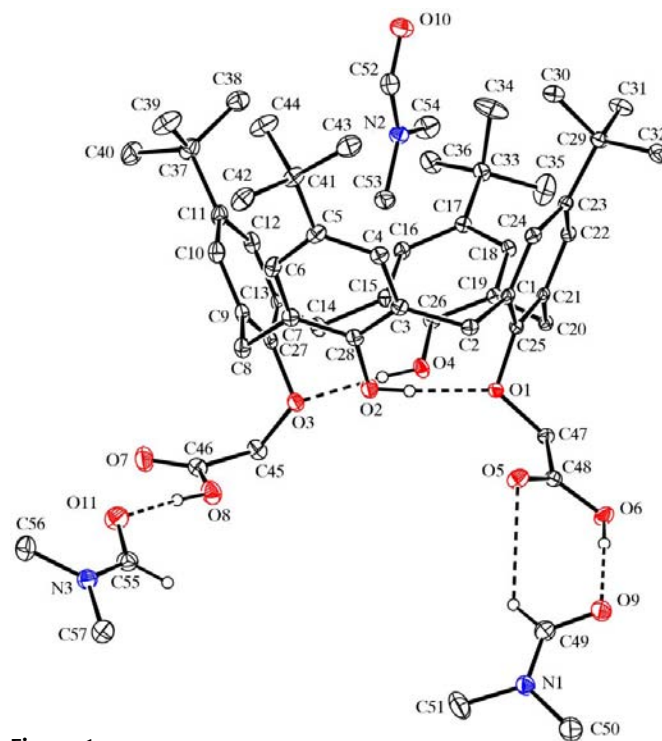
The title compound, $C_{48}H_{60}O_8 \cdot 3C_3H_7NO$, is a derivative of calix[4]arene in the cone conformation, modified with distal carboxylic acid functional groups at the lower rim. A clathrate dimethylformamide (DMF) molecule is located within the calix[4]arene cone, and two DMF solvate molecules participate in hydrogen bonding with the carboxylic acid groups. Intramolecular hydrogen bonds are also formed between the OH groups and the adjacent ether groups in the partially substituted calix[4]arene.

Comment

Calixarenes have macrocyclic structural frameworks that are known to exist in a variety of conformations, and well developed synthetic procedures are available for functionalization at the upper or lower rim. Modification of the basic framework has led to applications in catalysis, ionic and molecular separations, sensors, scaffolds for supramolecular arrays, ligands for metal binding, and in host–guest interactions (Gutsche, 1998). Calixarenes functionalized with carboxylic acid groups have been shown to be active towards extraction of heavy metals (Dung & Ludwig, 1999), as well as to display complexation properties toward alkali and alkali earth metal cations (McKervey *et al.*, 1996) and lanthanide cations (Arnaud-Neu *et al.*, 1997).



This report describes the crystal structure of the title compound, (I), initially prepared by Ungaro & Pochini (1984)

**Figure 1**

A view of the asymmetric unit of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level and intra- and intermolecular hydrogen bonds are shown as dashed lines. H atoms have been omitted for clarity, except for those involved in hydrogen bonding.

and subsequently by Collins *et al.* (1991), but of which the structure has not been reported previously.

Compound (I) is a calix[4]arene in the cone conformation which has been functionalized at the lower rim with distal carboxylic acid groups. Intramolecular hydrogen bonds on the lower rim stabilize the cone conformation.

Carboxylic acids tend to crystallize as like–like acid pairs that make up a common synthon in crystal engineering (Frankenbach & Etter, 1992). It is rare to obtain unlike acid pairs, although they can occur when the balance of shapes and intermolecular van der Waals forces is suitable, such as with the facial amphiphile Kemp's triacid (Childs & Hagen, 2002).

A number of crystallizations from different solvent systems, including ones with potential carboxylic acid co-crystals, resulted in the formation of very fine needles. It was only from DMF/H₂O (2:1; DMF is dimethylformamide) that we were able to grow sufficiently large needles of (I) for this study, which have a DMF clathrate molecule inside the cone of the calix[4]arene. It is common for calixarenes to host solvent molecules inside the cone, although only one other example of a DMF clathrate has been reported (Froidevaux *et al.*, 2000). In both cases, the DMF molecule adopts a 'methyl-in, carbonyl-out' orientation.

The conformation of the calixarene in (I) (Fig. 1) is partially controlled by intramolecular O–H...O hydrogen bonds (Table 1) between the phenolic O2 and O4 groups with adjacent phenolate atoms O1 and O3, respectively. One DMF

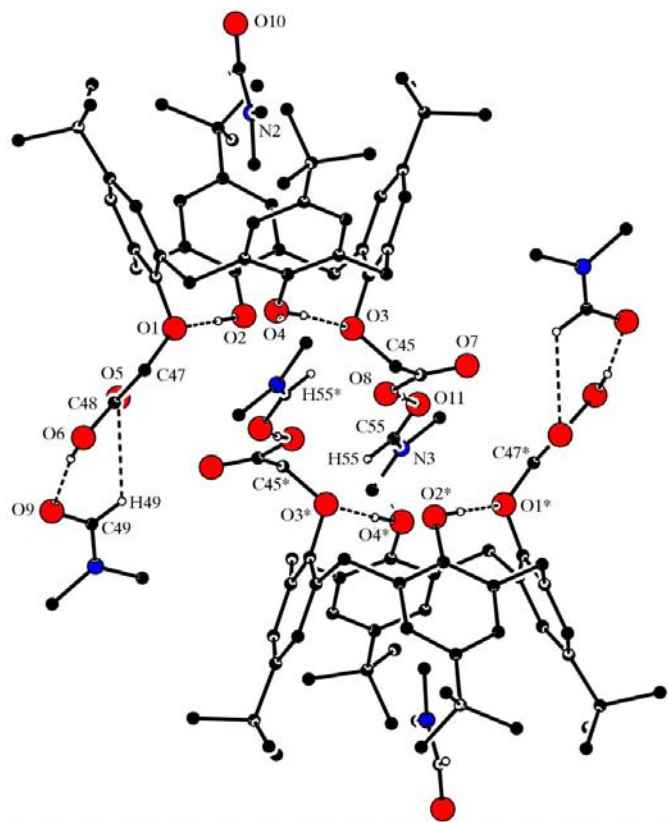


Figure 2

A view of an inversion-related pair of calixarene molecules, showing O—H...O and C—H...O interactions. Atom labels with an asterisk (*) are at the equivalent position ($1 - x, -y, 1 - z$).

molecule lies within the calixarene cone with a 'methyl-in' orientation. The calixarenes in (I) crystallize in a face-to-face pattern (Fig. 2), with the acid groups of the molecule at (x, y, z) directed towards, but not interacting directly with inversion-related pairs (at $1 - x, -y, 2 - z$) (Fig. 1). Instead, the other two DMF solvate molecules participate in intermolecular hydrogen bonding with the carboxylic acid groups on the lower rim of the calix[4]arene. Each of the carboxylic acid groups of the diacid interacts differently with an adjacent DMF molecule. In one carboxylic acid group (C48/O5/O6), the O6—H6 hydroxy group forms an O—H...O hydrogen bond with carbonyl atom O9 of a DMF molecule (Table 1), while carbonyl atom O5 of the same carboxylic acid group forms a hydrogen bond with the carbonyl C—H group (C49—H49) of the same DMF molecule (Table 1).

There are only a few cases of DMF—carboxylic acid inclusion compounds in which the formyl group of the DMF is involved in C—H...O-type weak hydrogen-bonding interactions in addition to traditional O—H...O-type hydrogen bonding, resulting in cyclic hydrogen-bonded pairs (Desiraju & Steiner, 1999). This cyclic group is decidedly non-planar in (I), with an angle of 128° between the planes of the carboxylic acid and amide groups.

The other carboxylic acid group (C46/O7/O8) forms one hydrogen bond between the carboxylic acid O8—H8 hydroxy group and carbonyl atom O11 of another DMF molecule

(Table 1). Instead of being positioned toward the carbonyl O atom of the carboxylic acid, the DMF carbonyl C—H group (C55—H55) is, in this case, oriented towards phenolic atom O4 of a neighboring calixarene at ($1 - x, -y, 2 - z$) (Table 1 and Fig. 2) in the lattice. The net effect of all intermolecular forces results in weak interactions between acid atoms O7 and O8 with C45, C47 and C48 of the same inversion-related calixarene [$O7 \cdots C47^* = 3.072$ (2) Å, $O7 \cdots C48^* = 2.930$ (2) Å and $O8 \cdots C45^* = 3.399$ (2) Å; see Fig. 2 for symmetry code].

Experimental

Compound (I) was prepared as described by Collins *et al.* (1991) and was recrystallized by adding water to a DMF solution until a precipitate formed (DMF—H₂O ratio 2:1), warming the solution to dissolve the precipitate and allowing the solution to stand at room temperature.

Crystal data

C₄₈H₆₀O₈·3C₃H₇NO
M_r = 984.25
 Monoclinic, *P*2₁/*c*
a = 11.3624 (3) Å
b = 35.224 (1) Å
c = 13.7180 (4) Å
 β = 96.991 (2)°
V = 5449.6 (3) Å³
Z = 4

D_x = 1.200 Mg m⁻³
 Cu *K*α radiation
 Cell parameters from 7352 reflections
 θ = 5.0–131.9°
 μ = 0.66 mm⁻¹
T = 100 (2) K
 Needle, colorless
 0.30 × 0.11 × 0.07 mm

Data collection

Bruker SMART 1000 CCD area-detector diffractometer
 ω scans
 Absorption correction: by integration [face-indexing of crystal; *SHELXTL* (Bruker, 2000)]
T_{min} = 0.862, *T_{max}* = 0.961
 25 773 measured reflections

9142 independent reflections
 6845 reflections with $I > 2\sigma(I)$
R_{int} = 0.056
 θ_{max} = 66.2°
h = -12 → 13
k = -41 → 41
l = -15 → 16

Refinement

Refinement on *F*²
R [*F*² > 2σ(*F*²)] = 0.044
wR (*F*²) = 0.127
S = 1.07
 9142 reflections
 662 parameters

H-atom parameters constrained
 $w = 1/[\sigma^2(F_o^2) + (0.0712P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{max} = 0.012$
 $\Delta\rho_{max} = 0.25 \text{ e } \text{Å}^{-3}$
 $\Delta\rho_{min} = -0.28 \text{ e } \text{Å}^{-3}$

Table 1

Hydrogen-bonding and short-contact geometry (Å, °).

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
O2—H2...O1	0.84	1.95	2.762 (2)	163
O4—H4...O3	0.84	1.96	2.780 (2)	165
O6—H6...O9	0.84	1.75	2.584 (2)	170
O8—H8...O11	0.84	1.75	2.581 (2)	168
C49—H49...O5	0.95	2.63	3.271 (3)	125
C55—H55...O4 ⁱ	0.95	2.65	3.193 (2)	117

Symmetry code: (i) $1 - x, -y, 2 - z$.

H atoms were placed in geometric positions, with O—H distances of 0.84 Å and C—H distances in the range 0.95–0.99 Å, and refined using a riding model, with $U_{iso}(\text{H}) = 1.5U_{eq}(\text{C}, \text{O})$.

Data collection: *SMART* (Bruker, 2000); cell refinement: *SMART*; data reduction: *SAINT* (Bruker, 2000); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics:

SHELXTL (Bruker, 2000); software used to prepare material for publication: *SHELXTL*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: HJ1009). Services for accessing these data are described at the back of the journal.

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