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25-Decyloxy-26,27,28-trihydroxy-5,11,17-tris(4-nitrophenyldiazenyl)-2,8,14,20-thiacalix[4]arene toluene hemisolvate

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Key indicators

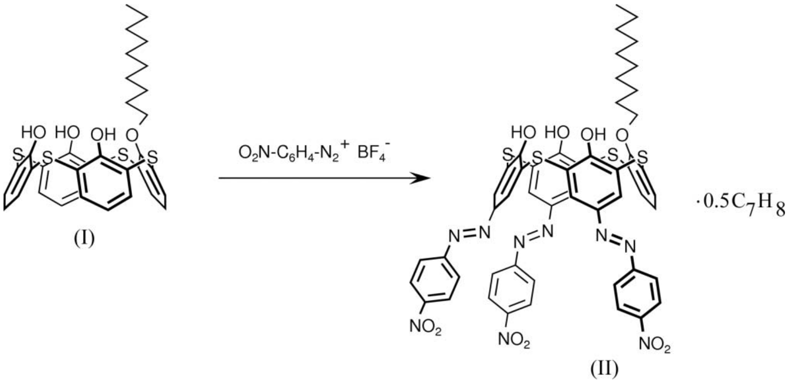
Single-crystal X-ray study
T = 173 K
Mean σ(C–C) = 0.009 Å
Disorder in main residue
R factor = 0.077
wR factor = 0.212
Data-to-parameter ratio = 15.0

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Molecules of the title compound, $C_{52}H_{45}N_9O_{10}S_4 \cdot 0.5C_7H_8$, are found in the typical cone conformation in the crystal structure. Intramolecular hydrogen bonds stabilize the molecular conformation, which is similar to that of 25-decyloxy-26,27,28-trihydroxy-2,8,14,20-thiacalix[4]arene.

Comment

Calix[4]arenes and thiacalix[4]arenes (Lhotak, 2004) are versatile building blocks for the synthesis of larger molecular structures or assemblies. They are easily available in large quantities and they can be easily modified by selective reactions involving the wide or narrow rim of the molecule. Usually, selective substitutions on the wide rim start with selective *O*-alkylation at the narrow rim of the calix[4]arene, utilizing the different reactivity of phenol and phenylether units in electrophilic substitutions. Thus, the unsubstituted thiacalix[4]arene was easily monoalkylated with decyl bromide to furnish compound (I) (Kasyan *et al.*, 2007), from which the title compound, (II) (Fig. 1), was obtained by coupling with *p*-nitrophenyldiazonium tetrafluoridoborate in pyridine at room temperature in 84% yield. It crystallizes as the toluene hemisolvate.



The bond lengths and angles in (II) can be regarded as normal [Cambridge Structural Database, Version 5.28, November 2006, updated January 2007 (Allen, 2002); *Mogul*, Version 1.1 (Bruno *et al.*, 2004)] and the molecule adopts the typical cone conformation. The bridging S atoms are almost coplanar (r.m.s. deviation 0.0812 Å), defining a reference plane for the calixarene. The rings C11–C16, C21–C26, C31–C36 and C41–C46 subtend angles of 68.34 (10), 36.36 (15), 87.13 (7) and 31.26 (14)°, respectively, with this plane. All three azo groups adopt a *trans* configuration. Two pairs of aromatic rings attached to the azo groups are almost coplanar [C31–C36/C301–C306 = 4.1 (2)° and C41–C46/C401–C406 =

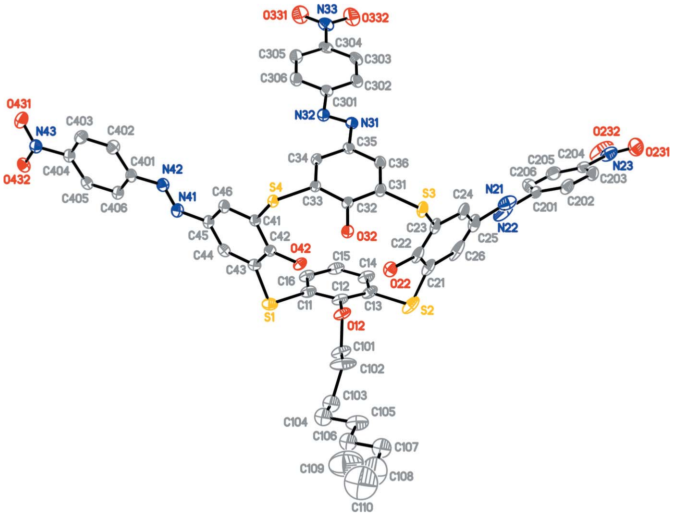


Figure 1
The molecular structure of (II), with the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level. The minor occupied sites of the disordered atoms and all H atoms have been omitted for clarity. The toluene molecule is not shown.

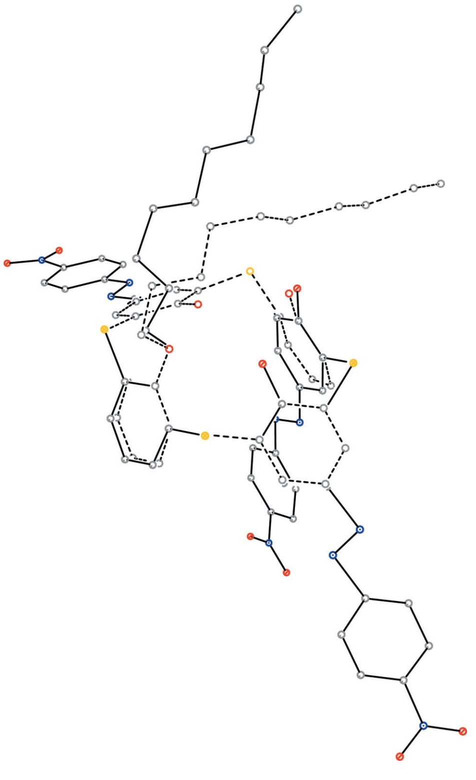


Figure 2
Least-squares fit of the S atoms of (I) (full lines) and (II) (dashed lines). Disordered atoms, solvent molecule and H atoms have been omitted for clarity.

7.2 (3)°], whereas the dihedral angle between the rings formed by C21–C26 and C201–C206 is 49.25 (19)°. A packing diagram (Fig. 3) reveals that the unsubstituted aromatic ring is directed into the cavity of a symmetry-equivalent molecule.

A comparable structure, *viz.* 25-decyloxy-26,27,28-trihydroxy-2,8,14,20-thiacalix[4]arene, (I) (Kasyan *et al.*, 2007), shows a similar conformation. In (I), the dihedral angles between the planes of the S atoms and of the aromatic rings are 73.7, 33.6, 75.3 and 33.0°. A least-squares fit of the S atoms of (I) and (II) (r.m.s. deviation 0.044 Å) is shown in Fig. 2. On the other hand, the hydrogen-bond patterns in (I) and (II) (Table 1) are different. Whereas the ether O atom in (I) accepts just one hydrogen bond from a hydroxy group, it accepts two such bonds in (II).

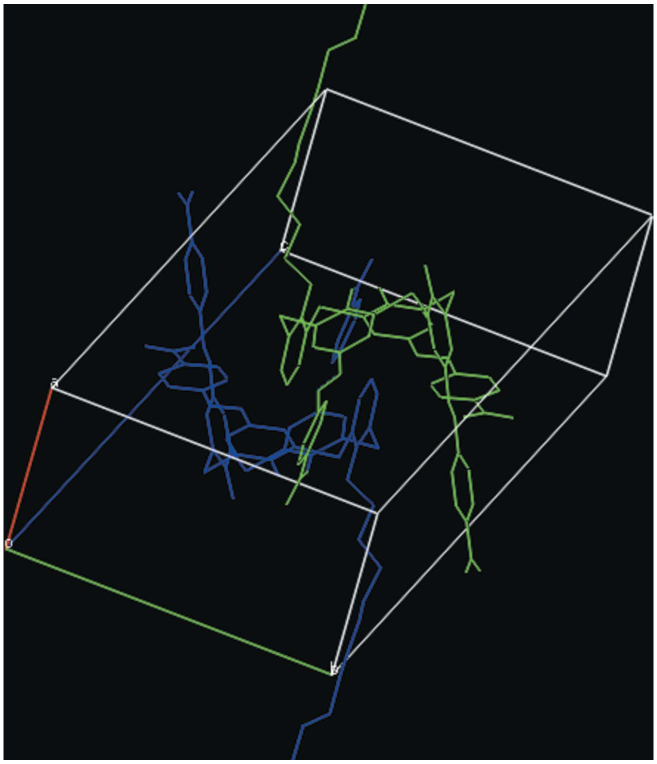


Figure 3
A packing diagram for (II). H atoms and solvent have been omitted. Only one disorder component is shown.

Experimental

Pyridine (1.0 ml) was added to a suspension of (I) (0.50 g, 0.79 mmol) and *p*-nitrophenyldiazonium tetrafluoridoborate (0.58 g, 2.45 mmol) in dry tetrahydrofuran (20 ml). The reaction mixture was stirred for 20 h at 293 K. MeOH (100 ml) was added and the crystalline residue was filtered off, washed with MeOH (1 × 5 ml), concentrated HCl (1 × 5 ml), H_2O (2 × 5 ml) and MeOH (2 × 5 ml), and dried for 1 h under vacuum (10 mm H g) at 373 K. The title compound was obtained as a red powder (0.71 g, 84%). Single crystals of (II) were grown by slow evaporation of a toluene solution.

Crystal data

$C_{52}H_{45}N_9O_{10}S_4 \cdot 0.5C_7H_8$
M_r = 1130.28
Triclinic, $P\overline{1}$
a = 14.0437 (10) Å
b = 14.6038 (11) Å
c = 16.0762 (12) Å
α = 69.893 (6)°
β = 65.769 (5)°
γ = 76.226 (6)°
V = 2805.2 (4) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 0.24 mm^{-1}
T = 173 (2) K
0.26 × 0.24 × 0.11 mm

Acta Cryst. (2007). E**63**, o2346–o2348 Kasyan *et al.* • $C_{52}H_{45}N_9O_{10}S_4 \cdot 0.5C_7H_8$ **o2347**

Data collection

Stoe IPDSII two-circle diffractometer
Absorption correction: multi-scan (*MULABS*; Spek, 2003; Blessing, 1995)
$T_{\min} = 0.931$, $T_{\max} = 0.965$
46855 measured reflections
10524 independent reflections
6244 reflections with $I > 2\sigma(I)$
$R_{\text{int}} = 0.073$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.077$
$wR(F^2) = 0.212$
$S = 1.00$
10524 reflections
701 parameters
27 restraints
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{\max} = 0.67$ e Å^{-3}
$\Delta\rho_{\min} = -0.65$ e Å^{-3}

Table 1

Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
O22—H22···O12	0.79 (5)	2.11 (5)	2.786 (6)	144 (5)
O32—H32···O42	0.87 (6)	2.64 (6)	3.061 (5)	111 (5)
O42—H42···O12	0.79 (5)	2.15 (5)	2.868 (4)	151 (5)
O32—H32···O432^{i}	0.87 (6)	2.46 (7)	3.252 (5)	151 (5)

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

The C-bound H atoms were located in a difference electron-density map, relocated in idealized positions with C—H = 0.95–0.99 Å, and refined as riding, with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$, or $1.5U_{\text{eq}}$(methyl C). H atoms bonded to O were located in difference maps and their positions and U_{iso} values were refined freely. The disordered atoms of the methylene chain were refined with distance restraints of 1.54 (5) Å. The disordered atoms and their site-occupation factors are C103 [0.742 (9)], C104 [0.742 (9)], C106 [0.742 (9)], C107 [0.742 (9)], C110 [0.56 (3)], C113 [0.258 (9)], C114 [0.258 (9)], C116 [0.258 (9)], C117 [0.258 (9)], and C111 [0.44 (3)]. The toluene molecule is disordered over a centre of inversion. It was refined with distance restraints of 1.39 (5) and 2.4 (1) Å for intraring 1–2 and 1–3 distances, respectively, and half occupancy of the methyl group. For the $\text{C}_{\text{aromatic}}$—$\text{C}_{\text{methyl}}$ distance, a restraint of 1.50 (5) Å was employed. The disordered atoms were only isotropically refined.

Data collection: *X-AREA* (Stoe & Cie, 2001); cell refinement: *X-AREA*; data reduction: *X-AREA*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *XP* in *SHELXTL-Plus* (Sheldrick, 1991); software used to prepare material for publication: *SHELXL97*.

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o2348 Kasyan *et al.* • $C_{52}H_{45}N_9O_{10}S_4\cdot0.5C_7H_8$ *Acta Cryst.* (2007). E**63**, o2346–o2348