

1,3-Alternate and partial cone conformers of tetramethyl (5,11,17,23-tetra-*tert*-butyl-2,8,14,20-tetrathiacalix[4]arene-25,26,27,28-tetrayltetraoxy)tetraacetate and tetramethyl (5,11,17,23-tetrabromo-2,8,14,20-tetrathiacalix[4]arene-25,26,27,28-tetrayltetraoxy)tetraacetate

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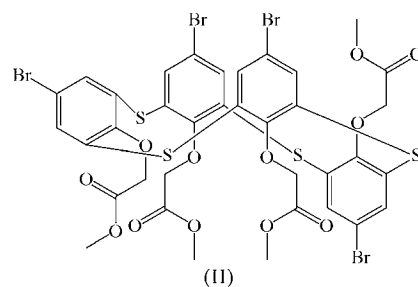
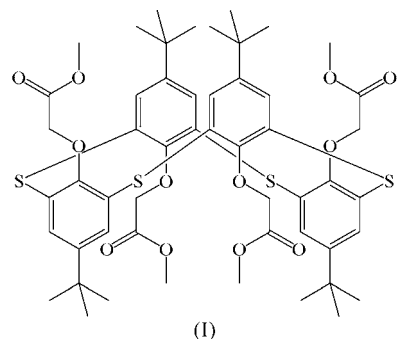
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The crystal structures of the two title thiacalix[4]arene derivatives, $C_{52}H_{64}O_{12}S_4$, (I), and $C_{36}H_{28}Br_4O_{12}S_4$, (II), are reported. Compound (I) has crystallographic C_2 symmetry and adopts a 1,3-alternate conformation where the four $-\text{OCH}_2\text{CO}_2\text{Me}$ groups are located alternately above and below the virtual plane (R) defined by the four bridging S atoms. The dihedral angles between the plane (R) and the aromatic rings are $87.17(7)$ and $87.60(8)^\circ$. Compound (II) has a partial cone conformation in which the pendant $-\text{OCH}_2\text{CO}_2\text{Me}$ group of the rotated aryl ring is oriented away from the thiacalixarene cavity formed by the other three aryl rings. The dihedral angles between the plane (R) and the aryl rings range from $17.47(10)$ to $85.98(6)^\circ$. In the supramolecular structure of (II), the molecular components are linked into a two-dimensional framework by a combination of $\text{C}-\text{H}\cdots\text{O}$ hydrogen bonds and $\text{C}-\text{Br}\cdots\text{C}$ interactions. This study demonstrates the usefulness of these motif-generating interactions and thiacalix[4]arene derivatives in crystal engineering.

Comment

Thiacalix[4]arenes have attracted much interest in recent years as useful building blocks for highly organized receptors (Kumagai *et al.*, 1997; Shokova & Kovalev, 2003; Lhoták, 2004; Morohashi *et al.*, 2006; Guo *et al.*, 2007). Compared with classical calix[4]arenes, the presence of four bridging S atoms results in differing complexation ability, diverse cavity and

conformational behaviour. Among both calix[4]arenes and thiacalix[4]arenes, their ethyl ester derivatives are some of the most versatile intermediates because the acetate group is easily converted into a carboxylic acid, an amide and another ester group. It has been found that the conformational distribution in the exhaustive *O*-alkylation of calix[4]arenes (Pappalardo *et al.*, 1992; Ferguson *et al.*, 1993, 1994) and thiacalix[4]arenes (Akdas *et al.*, 1999) depends largely upon the reaction conditions, the *para* substituent of the starting calix[4]arene or thiacalix[4]arene, and the steric requirement of the derivatizing agent. Several crystal structures of the ethyl ester derivatives of both calix[4]arenes (McKerverey *et al.*, 1985; Genorio *et al.*, 2003) and thiacalix[4]arenes (Iki *et al.*, 1998; Akdas *et al.*, 1999) have been described. We now report the crystal structures of the thiacalix[4]arene methyl ester derivatives 5,11,17,23-tetra-*tert*-butyl- and 5,11,17,23-tetrabromo-25,26,27,28-tetrakis[(methoxycarbonyl)methoxy]-2,8,14,20-tetrathiacalix[4]arene, *viz.* (I) and (II), respectively.



The two title thiacalix[4]arene compounds, (I) and (II), are shown in Figs. 1 and 2. Structural analysis reveals that (I) adopts a 1,3-alternate conformation in which four $\text{OCH}_2\text{CO}_2\text{Me}$ groups are located alternately above and below the virtual plane (R) defined by four bridging S atoms. Compound (II), where four Br atoms replace the four *tert*-butyl groups, has a partial cone conformation in which the pendant $\text{OCH}_2\text{CO}_2\text{Me}$ group of the rotated aryl ring is oriented away from the thiacalixarene cavity made by the other three aryl rings. The geometric parameters of both molecules are comparable to those reported for similar structures (Akdas *et al.*, 1999) and most bond lengths and angles in (I) and (II) are in agreement with the values reported for the 1,3-alternate and partial cone conformers of 5,11,17,23-tetra-*tert*-butyl-25,26,27,28-tetrakis(ethoxycarbonylmethoxy)-2,8,14,20-tetrathiacalix[4]arene, except for some $\text{C}=\text{O}$ and $\text{C}-\text{O}$ (methyl) bond lengths (Akdas *et al.*, 1999). In the packing of (I), 1,3-

alternate molecules are packed along the *b* axis, forming a type of nanotubular array extending in the *b* direction (Fig. 3).

The conformations of both molecules are defined by the angles which the aromatic rings make with the plane (*R*). The molecule of (I) has crystallographic C_2 symmetry. The dihedral angles between the plane (*R*) and the C5–C10 and C18–C23 aryl rings are 87.17 (7) and 87.60 (8)°, respectively. Two pairs of opposite aromatic rings are almost parallel to each other, with interplanar angles of 4.95 (13) and 5.35 (41)°. In (II), the dihedral angles between the plane (*R*) and the C1–C6, C10–C15, C19–C24 and C28–C33 aromatic rings are 75.73 (7), 82.40 (7), 85.98 (6) and 17.47 (10)°, respectively. The C10–C15 and C28–C33 aryl rings are nearly perpendicular to one another, with an interplanar angle of 80.65 (9)°, but with their ester side chains oriented in opposite directions. Moreover, the latter ring is tilted away from the cavity and is almost coplanar with the plane (*R*), at 17.47 (10)° (Fig. 2). A similar molecular conformation with one aryl ring tilted almost into the plane (*R*) was observed in the structure of the related compound 25,26,27,28-tetrakis(2-pyridylmethoxy)calix[4]-arene (Ferguson *et al.*, 1993). The C1–C6 and C19–C24 aromatic rings are almost parallel to one another, with a Br3···Br4 distance of 4.207 (7) Å. The O···O separations of the ethereal O atoms are: O1···O4 = 3.087 (3) Å, O1···O10 = 3.844 (3) Å, O7···O4 = 4.718 (3) Å and O7···O10 = 4.829 (5) Å.

No classical hydrogen bonds are present in either structure, but a number of intra- and intermolecular short contacts exist in the crystal structure of (II), involving weak C–H···O, C–H···S and C–H··· π interactions (Table 1). These stabilize

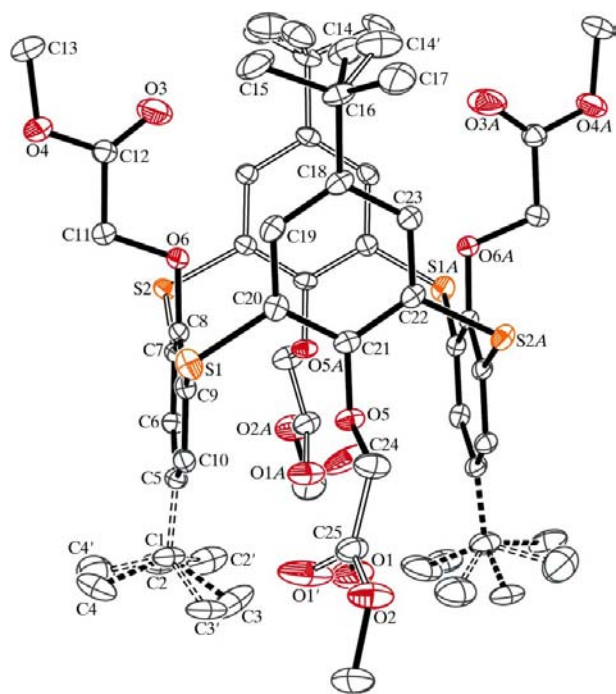


Figure 1

A view of (I), showing the atomic numbering scheme. Displacement ellipsoids are drawn at the 30% probability level for non-H atoms and disordered atoms are shown. [Symmetry code: (A) $-x + 2, y, -z + \frac{1}{2}$.]

the partial cone conformation and packing. The intramolecular C11–H11···O12 and C13–H13···O5 hydrogen bonds, as well as C34–H34A··· π interactions, result in a dihedral angle of 82.40 (7)°, smaller than the reported value of 93.5 (4)° (Ferguson *et al.*, 1993) between the plane (*R*) and the C10–C15 ring. The H34A···Cg1 distance (Cg1 is the centroid of the C10–C15 ring) is consistent with the calculations for such interactions conducted by Tsuzuki *et al.* (2000). In the supramolecular structure of (II), hydrogen-bonded one-dimensional chains parallel to [100] are formed by a combi-

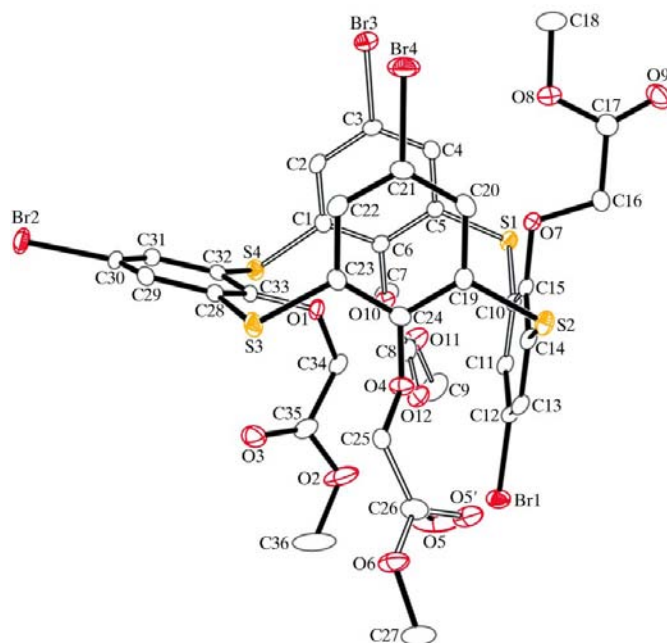


Figure 2

A view of (II), showing the atomic numbering scheme. Displacement ellipsoids are drawn at the 30% probability level for non-H atoms. The disordered carbonyl group is also shown.

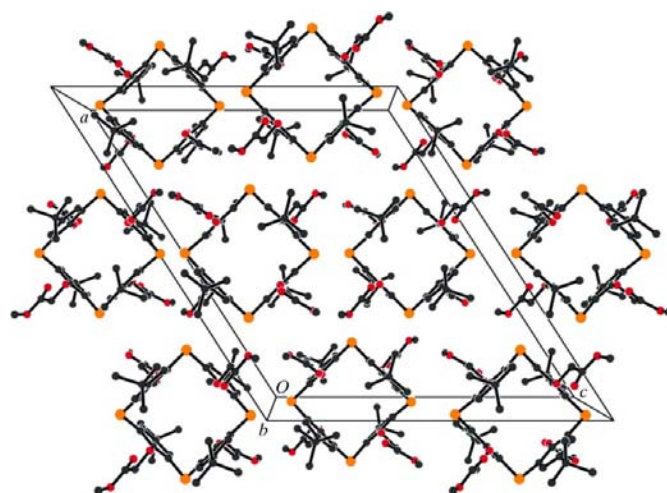


Figure 3

A view of the packing of (I), showing the pattern of channels along the *b* axis.

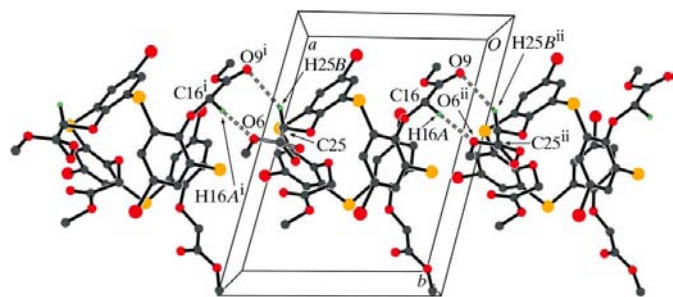


Figure 4

The hydrogen-bonded one-dimensional chains of (II), viewed along the c axis with $R_2^2(8)$ motifs along $[100]$. Some H atoms and the disordered carbonyl group have been omitted for clarity. [Symmetry codes: (i) $x + 1, y, z$; (ii) $x - 1, y, z$.]

nation of two intermolecular C—H···O hydrogen bonds, which locally form an $R_2^2(8)$ ring motif (Bernstein *et al.*, 1995) at each link in the chain (Fig. 4). The motif arises from atoms C25—H25B and C16—H16A in the molecules at (x, y, z) and $(x + 1, y, z)$, respectively, acting as hydrogen-bond donors to atoms O9 at $(x + 1, y, z)$ and O6 at (x, y, z) , respectively. These chains are weakly augmented into a two-dimensional network by the uncommon C—Br···C interactions (Santos-Contreras *et al.*, 2007) between Br4, and C29ⁱⁱⁱ and C30ⁱⁱⁱ [symmetry code: (iii) $-x + 2, -y + 1, -z + 1$]. The Br4···C29ⁱⁱⁱ and Br4···C30ⁱⁱⁱ distances are 3.480 (3) and 3.423 (3) Å, respectively, which are less than the sum of the van der Waals radii for Br and C (C = 1.70 Å and Br = 1.90 Å; Bondi, 1964). C—Br···E interactions (E = electrophile) have been discussed by Lommerse *et al.* (1996) and Bosch & Barnes (2002).

Experimental

For the synthesis of (I), methyl bromoacetate (0.21 ml, 2.22 mmol) was added to a suspension of *p*-tetra-*tert*-butylthiacalix[4]arene (0.200 g, 0.28 mmol) and anhydrous Cs_2CO_3 (0.543 g, 1.66 mmol) in dry acetone (15 ml). The resulting mixture was stirred for 70 h at 343 K and cooled to room temperature. The solvent was removed under reduced pressure. The residue was neutralized with 5% aqueous HCl and extracted with CH_2Cl_2 . The organic layer was separated and washed with saturated sodium hydrogen carbonate and brine, and dried over anhydrous MgSO_4 . Removal of the solvent under reduced pressure gave (I) as a white solid (yield 81%) by recrystallization from $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{OH}$ solution. $^1\text{H NMR}$ (300 MHz, CDCl_3): δ 1.25 (*s*, 36H, *t*-Bu), 3.76 (*s*, 12H, CH_3), 4.56 (*s*, 8H, CH_2), 7.49 (*s*, 8H, ArH). IR (KBr pellets, cm^{-1}): 1770 (C=O). Single crystals of (I) suitable for X-ray diffraction analysis were obtained by slow diffusion of methanol into a CHCl_3 solution at 273 K.

For the synthesis of (II), the same procedure was followed as for (I), but *p*-tetrabromothiocalix[4]arene was used instead of *p*-tetra-*tert*-butylthiacalix[4]arene to afford (II) as a white solid (yield 43%, isolated by flash column chromatography, silica gel, EtOAc/petroleum ether = 1:5, R_f = 0.4). $^1\text{H NMR}$ (300 MHz, CDCl_3): δ 8.09 (*s*, 2H, Ar—H), 7.78 (*s*, 2H, Ar—H), 7.63 (*s*, 2H, Ar—H), 7.10 (*s*, 2H, Ar—H), 4.78 (*s*, 2H, ArOCH_2), 4.68 (*s*, 2H, ArOCH_2), 4.66 (*s*, 2H, ArOCH_2), 4.19 (*s*, 2H, ArOCH_2), 4.09 (*s*, 3H, OCH_3), 3.86 (*s*, 6H, OCH_3), 3.62 (*s*, 3H, OCH_3). Single crystals of (II) suitable for X-ray diffraction analysis were obtained by slow evaporation of a solution in CH_3OH and CH_2Cl_2 at 273 K.

Compound (I)

Crystal data

$\text{C}_{52}\text{H}_{64}\text{O}_{12}\text{S}_4$
 $M_r = 1009.27$
 Monoclinic, $C2/c$
 $a = 23.060$ (4) Å
 $b = 13.547$ (2) Å
 $c = 20.083$ (4) Å
 $\beta = 122.890$ (2)°
 $V = 5268.3$ (16) Å³
 $Z = 4$
 Mo $K\alpha$ radiation
 $\mu = 0.24$ mm⁻¹
 $T = 173$ (2) K
 $0.34 \times 0.23 \times 0.16$ mm

Data collection

Bruker SMART CCD area-detector diffractometer
 Absorption correction: multi-scan (*SADABS*; Bruker, 1999)
 $T_{\min} = 0.923, T_{\max} = 0.963$
 13453 measured reflections
 4893 independent reflections
 3834 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.035$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.061$
 $wR(F^2) = 0.164$
 $S = 1.05$
 4893 reflections
 360 parameters
 51 restraints
 H-atom parameters constrained
 $\Delta\rho_{\text{max}} = 0.47$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.30$ e Å⁻³

Compound (II)

Crystal data

$\text{C}_{36}\text{H}_{28}\text{Br}_4\text{O}_{12}\text{S}_4$
 $M_r = 1100.46$
 Triclinic, $P\bar{1}$
 $a = 10.4298$ (15) Å
 $b = 13.960$ (2) Å
 $c = 14.701$ (2) Å
 $\alpha = 82.296$ (2)°
 $\beta = 84.921$ (2)°
 $\gamma = 74.872$ (2)°
 $V = 2044.5$ (5) Å³
 $Z = 2$
 Mo $K\alpha$ radiation
 $\mu = 4.20$ mm⁻¹
 $T = 173$ (2) K
 $0.58 \times 0.38 \times 0.21$ mm

Data collection

Bruker SMART CCD area-detector diffractometer
 Absorption correction: multi-scan (*SADABS*; Bruker, 1999)
 $T_{\min} = 0.194, T_{\max} = 0.472$
 (expected range = 0.170–0.414)
 10757 measured reflections
 7443 independent reflections
 5974 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.021$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.035$
 $wR(F^2) = 0.091$
 $S = 1.07$
 7443 reflections
 518 parameters
 H-atom parameters constrained
 $\Delta\rho_{\text{max}} = 0.53$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.67$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °) for (II).

$Cg1$ is the centroid of the C10–C15 ring.

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
C25—H25B···O9 ⁱ	0.97	2.59	3.399 (4)	141
C16—H16A···O6 ⁱⁱ	0.97	2.44	3.409 (4)	176
C34—H34B···O10	0.97	2.49	3.242 (4)	135
C34—H34B···S4	0.97	2.60	3.288 (3)	128
C25—H25A···S3	0.97	2.65	3.223 (3)	118
C13—H13···O5	0.93	2.52	3.26 (3)	137
C11—H11···O12	0.93	2.58	3.405 (4)	148
C34—H34A···Cg1	0.97	2.73	3.674 (3)	164

Symmetry codes: (i) $x + 1, y, z$; (ii) $x - 1, y, z$.

H atoms were placed in geometrically idealized positions and refined using a riding model [$C-H = 0.93$ Å and $U_{\text{iso}}(H) = 1.2U_{\text{eq}}(C)$ for aromatic, and $C-H = 0.97$ Å and $U_{\text{iso}}(H) = 1.5U_{\text{eq}}(C)$ for methyl H atoms]. In (I), one of the symmetry-independent *tert*-butyl groups

(C1–C4) is disordered over two orientations, with refined site-occupation factors of 0.742 (10):0.258 (10). One methyl group of the other independent *tert*-butyl group (C14) and carbonyl atom O1 are also disordered over two orientations, with refined site-occupation factors of 0.53 (3):0.47 (3). Some of the C–CH₃ bond lengths involving the disordered C atoms were restrained from 1.50 to 1.55 Å and the atomic displacement parameters of the disordered methyl C atoms were also restrained. In (II), atom O5 of one carbonyl group is disordered over two positions, with refined occupancies of 0.57 (8):0.43 (8) for O5/O5'.

For both compounds, data collection: *SMART* (Bruker, 1999); cell refinement: *SMART*; data reduction: *SAINTE* (Bruker, 1999); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); 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: GG3153). Services for accessing these data are described at the back of the journal.

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