

Received 5 April 2024

Accepted 24 April 2024

Edited by M. Weil, Vienna University of Technology, Austria

Keywords: crystal structure; macrocycles; calix[4]arene; synthesis; NMR study.**CCDC references:** 2350927; 2350926; 2350925**Supporting information:** this article has supporting information at journals.iucr.org/e

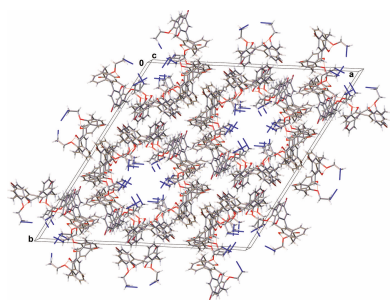
Synthesis and crystal structures of 5,17-dibromo-26,28-dihydroxy-25,27-dipropynyloxy-calix[4]-arene, 5,17-dibromo-26,28-dipropoxy-25,27-dipropynyloxy-calix[4]arene and 25,27-bis(2-azidoethoxy)-5,17-dibromo-26,28-dihydroxy-calix[4]arene

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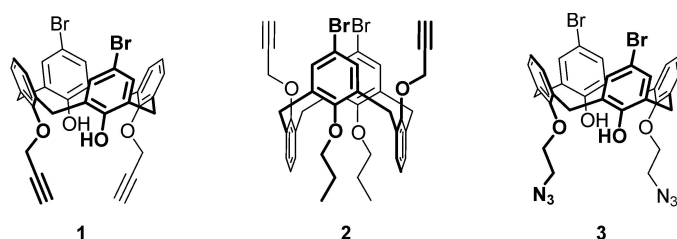
The calixarenes, 5,17-dibromo-26,28-dihydroxy-25,27-dipropynyloxy-calix[4]-arene (C₃₄H₂₆Br₂O₄, **1**), 5,17-dibromo-26,28-dipropoxy-25,27-dipropynyloxy-calix[4]arene (C₄₀H₃₈Br₂O₄, **2**) and 25,27-bis(2-azidoethoxy)-5,17-dibromo-26,28-dihydroxy-calix[4]arene (C₃₂H₂₈Br₂N₆O₄, **3**) possess a pinched cone molecular shape for **1** and **3**, and a 1,3-alternate shape for compound **2**. In calixarenes **1** and **3**, the cone conformations are additionally stabilized by intramolecular O—H···O hydrogen bonds, while in calixarene **2** intramolecular Br···Br interactions consolidate the 1,3-alternate molecular conformation. The dense crystal packing of the cone dialkyne **1** is a consequence of π – π , C—H··· π and C—H···O interactions. In the crystal of the diazide **3**, there are large channels extending parallel to the *c* axis, which are filled by highly disordered CH₂Cl₂ solvent molecules. Their contribution to the intensity data was removed by the SQUEEZE procedure that showed an accessible void volume of 585 Å³ where there is room for 4.5 CH₂Cl₂ solvent molecules per unit cell. Rigid molecules of the 1,3-alternate calixarene **2** form a columnar head-to-tail packing parallel to [010] *via* van der Waals interactions, and the resulting columns are held together by weak C—H··· π contacts.

1. Chemical context

Calixarene macrocycles offer the possibility to combine several functional groups of a different nature and to preorganize them spatially. The polyfunctional nature of calixarenes allows their use in the development of new materials, drugs, substances for medical applications and in other areas of organic chemistry, biochemistry or materials science where supramolecular organizations are of importance. The versatility of calixarenes as molecular platforms is due to the availability of the polyphenolic macrocycles themselves, and to well-developed approaches for the exhaustive and partial modification of phenolic hydroxyl groups and/or aromatic *para*-positions (Asfari *et al.*, 2001; Vicens *et al.*, 2007; Bohmer, 2003; Neri *et al.*, 2016). The modification of calixarene macrocycles by azide or alkyne functional groups makes them suitable for copper(I)-catalyzed azide-alkyne cycloaddition (CuAAC) (Song *et al.*, 2014). Under the usual CuAAC conditions, biscalixarene (Gorbunov *et al.*, 2021) or triscalixarene (Malakhova *et al.*, 2022a) molecular semitubes were synthesized, and the processes of intramolecular oscillations



of Ag⁺ inside them were studied (Malakhova *et al.*, 2022b). It is expected that grafting of additional substituents into the *para*-positions of phenolic fragments of the azide/alkyne-containing calix[4]arenes, on the one hand, should improve shielding of the internal cavity of the calixarene semitube and, on the other hand, may provide possibilities for further modifications of the multicalixarene assemblies. In this context, we synthesized the *para*-dibromo-substituted calix[4]arenes **1–3** bearing 2-azidoethyl and propargyl functionalities. The compositions and structures of the synthesized compounds were analyzed by ¹H, ¹³C NMR (Scheme S1, Figs. S1–S6 in the supporting information), and single-crystal X-ray diffraction.



2. Structural commentary

The calix[4]arenes **1** and **3** occupy general positions, while the macrocycle **2** possesses molecular *C*₂ symmetry with the twofold rotation axis passing through the center of the calixarene cavity (Figs. 1–3). The cone conformation of **1** is stabilized by moderate intramolecular O–H···O hydrogen bonds (Table 1, Fig. 1). The *para*-bromo-substituted rings (the second Br atom (Br²) is generated by the symmetry operation 1 – *x*, *y*, $\frac{1}{2} - z$) are located further apart [$d(\text{C1} - \text{C5}/\text{C25}_{\text{centroid}} - \text{C13} - \text{C17}/\text{C27}_{\text{centroid}}) = 7.4083(11) \text{ \AA}$, interplanar angle 71.29(6)°] than the unsubstituted ones [$d(\text{C7} - \text{C11}/\text{C26}_{\text{centroid}} - \text{C19} - \text{C23}/\text{C28}_{\text{centroid}}) = 6.1827(11) \text{ \AA}$, interplanar angle 34.54(6)°].

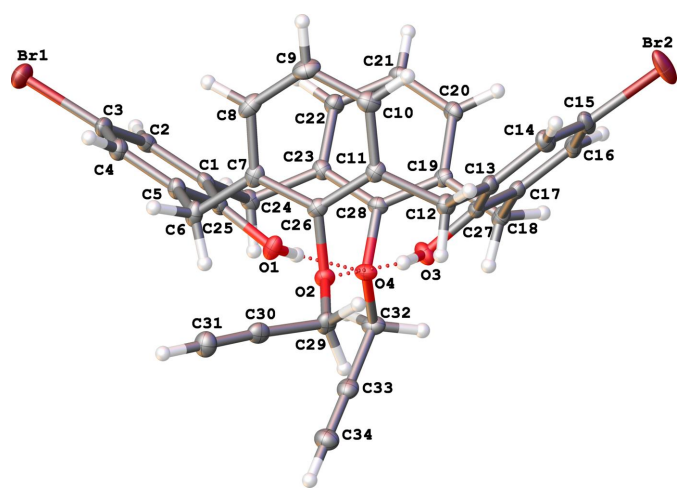


Figure 1

Molecular structure of 5,17-dibromo-26,28-dihydroxy-25,27-dipropynyloxycalix[4]arene (**1**), with displacement ellipsoids drawn at the 50% probability level. The minor part of the disordered bromine atom is omitted for clarity. O–H···O hydrogen bonds are shown by dotted lines.

Table 1
Hydrogen-bond geometry (Å, °) for **1**.

<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>
O1–H1···O4	0.84	1.81	2.6270 (18)	165
O3–H3···O2	0.84	2.02	2.8207 (18)	160

Table 2
Hydrogen-bond geometry (Å, °) for **3**.

<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>
O3–H3···O4	0.84	1.87	2.691 (3)	164
O1–H1···O2	0.84	1.95	2.764 (3)	162

Compound **3** also has a cone conformation supported by intramolecular O–H···O hydrogen bonds (Table 2, Fig. 3) with the analogous mutual arrangement of the substituted

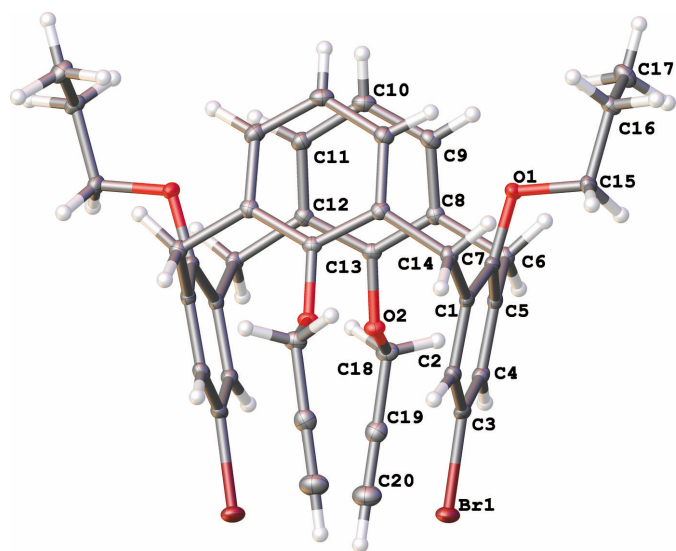


Figure 2

Molecular structure of 5,17-dibromo-26,28-dipropoxy-25,27-dipropynyloxycalix[4]arene (**2**), with displacement ellipsoids drawn at the 50% probability level.

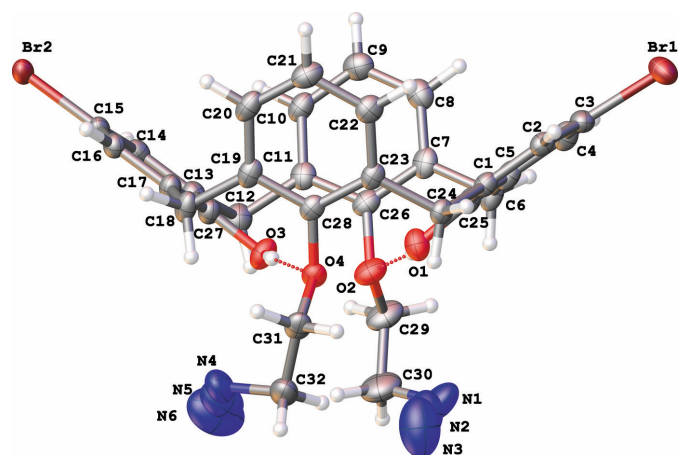


Figure 3

Molecular structure of 25,27-bis(2-azidoethoxy)-5,17-dibromo-26,28-dihydroxy-calix[4]arene (**3**), with displacement ellipsoids drawn at the 50% probability level. O–H···O hydrogen bonds are shown by dotted lines.

$[d(\text{C1}-\text{C5}/\text{C25}_{\text{centroid}}-\text{C13}-\text{C17}/\text{C27}_{\text{centroid}}) = 7.4401 (16) \text{ \AA}$, interplanar angle $70.96 (9)^\circ$] and unsubstituted rings [$d(\text{C7}-\text{C11}/\text{C26}_{\text{centroid}}-\text{C19}-\text{C23}/\text{C28}_{\text{centroid}}) = 6.0604 (15) \text{ \AA}$, interplanar angle $31.57 (9)^\circ$]. Compound **2** possesses a 1,3-alternate conformation with an intramolecular halogen...halogen interaction [$d(\text{Br}\cdots\text{Br}') = 3.9765 (4) \text{ \AA}$]. The closer contacts of the bromine atoms leads to a significant increase in the angle between the planes of the corresponding rings [C1–C6, $22.48 (6)^\circ$] and, as a result, an almost equal increase of the interplanar angle between the pair of unsubstituted rings [C8–C13, $21.63 (6)^\circ$].

^1H NMR spectra of compounds **1** and **3** are quite similar and simple due to the highly symmetrical structure of the calixarenes. Indeed, in each spectrum, a singlet corresponding to phenolic hydroxyl groups and two multiplets and a singlet from the aromatic calixarene H atoms are located in the low-field part of the spectrum, while the doublet and triplet from the propargyl groups (for calixarene **1**) and two multiplets from the azidoethyl fragments (for calixarene **3**) as well as two doublets from the calixarene methylene bridges appear in the middle part of the spectrum. In the ^{13}C NMR spectra of both compounds **1** and **3**, the characteristic signal from the methylene bridges at ~ 31 ppm reflects a cone shape of the macrocycle. In the case of calixarene **2**, the doublets from the methylene bridges in the ^1H NMR spectrum appear to be located closer to each other and have an increased spin-spin coupling constant value. In the ^{13}C NMR spectrum of **2** the signal of the methylene groups appears downfield shifted with respect to the above cone calixarenes (~ 37 ppm), which confirms a 1,3-alternate shape of the macrocycle.

3. Supramolecular features

In the crystal structure of **1** (Fig. 4), there are π - π -bonded centrosymmetric dimers [$d(\text{C21}\cdots\text{C19}-\text{C23}/\text{C28}_{\text{centroid}}) = 3.361 (2) \text{ \AA}$, centroid-to-centroid shift of $1.862 (3) \text{ \AA}$], which are additionally stabilized by C–H... π interactions between the H20 atom and the centroid of the C1–C5/C25 ring [$3.1375 (8) \text{ \AA}$, $147.00 (12)^\circ$], between the H21 atom and the centroid of the C7–C11/C26 ring [$3.0179 (8) \text{ \AA}$, $127.00 (12)^\circ$]

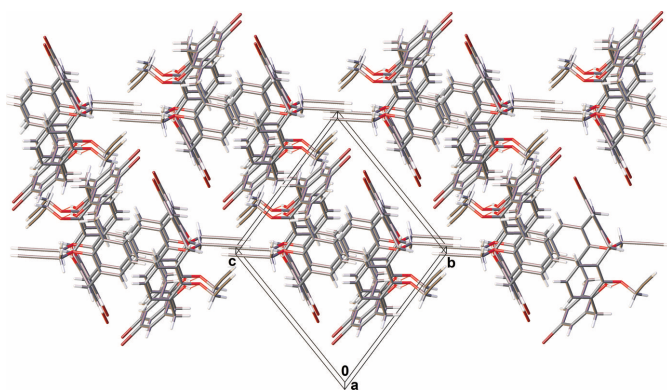


Figure 4
Fragment of the crystal packing of 5,17-dibromo-26,28-dihydroxy-25,27-dipropynyloxy-calix[4]arene (**1**). The minor part of the disordered bromine atom is omitted for clarity.

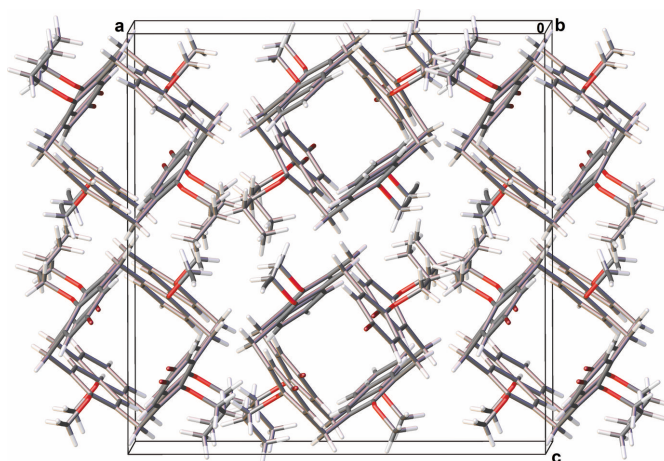


Figure 5
Fragment of the crystal packing of 5,17-dibromo-26,28-dipropoxy-25,27-dipropynyloxy-calix[4]arene (**2**).

and between the H22 atom and the centroid of the C13–C17/C27 ring [$2.7990 (8) \text{ \AA}$, $157.54 (12)^\circ$]. These dimers are linked into chains extending parallel to $[011]$ via C–H...O contacts involving the H34 and the O1 atoms [$d(\text{H}\cdots\text{O}) = 2.3436 (13) \text{ \AA}$, C–H...O angle = $164.45 (13)^\circ$]. The resulting chains are assembled by further C–H... π interactions between the H31 atom and the mid-point of the triple C33–C34 bond [$2.7043 (6) \text{ \AA}$, $146.08 (13)^\circ$], forming thick layers parallel to (110). These layers are related to each other by inversion centers and are joint by π - π interactions [$d(\text{C27}\cdots\text{C13}-\text{C17}/\text{C27}_{\text{centroid}}) = 3.623 (2) \text{ \AA}$, centroid-to-centroid shift of $2.276 (3) \text{ \AA}$].

In the crystal structure of **2** (Fig. 5), molecules form a columnar head-to-tail packing parallel to $[010]$ via van der Waals interactions, with the columns held together by weak C–H... π contacts between the H16B atom and the centroid of the C1–C6 ring [$2.862 (19) \text{ \AA}$, $125.4 (10)^\circ$] and between the

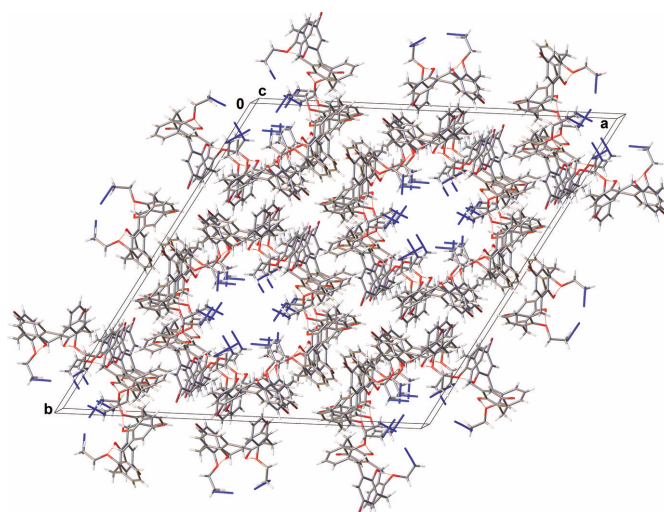


Figure 6
Fragment of the crystal packing of 25,27-bis(2-azidoethoxy)-5,17-dibromo-26,28-dihydroxy-calix[4]arene (**3**).

H17B atom and the centroid of the C8–C13 ring [2.97 (2) Å, 120.1 (12)°].

In the crystal structure of **3** (Fig. 6), C–H··· π contacts between the H31A atom and the centroid of the C1–C5/C25 ring [2.6130 (11) Å, 122.1 (2)°] and between the H29B atom and the centroid of the C13–C17/C27 ring [2.8400 (11) Å, 129.56 (18)°] organize molecules into large channels passing parallel to the *c* axis, which are filled by highly disordered CH₂Cl₂ solvent molecules. According to the applied SQUEEZE procedure (Spek, 2015), the solvent-accessible void volume is as large as 585 Å³ per unit cell and contains fragments with an electron count of 171 e⁻. This correspond to about 4.5 CH₂Cl₂ molecules in the unit cell, or 0.25 CH₂Cl₂ molecules per formula unit. The nitrogen atoms of the azide groups have comparatively large displacement parameters because these groups are directed into the channels and do not participate in any strong intermolecular interactions. Adjacent channels are assembled into the tri-periodic structure by π – π [$d(\text{C21}\cdots\text{C19-C23/C28}_{\text{centroid}}) = 3.446$ (4) Å, centroid-to-centroid shift of 2.533 (4) Å] and C–H··· π interactions between the H20 atom and the centroid of the C1–C5/C25 ring [3.0326 (11) Å, 154.5 (2)°] and between the H22 atom and the centroid of the C13–C17/C27 ring [3.6003 (11) Å, 152.69 (18)°].

4. Database survey

The crystal structures of more than 750 calix[4]arenes have been published so far, as revealed by a search of the Cambridge Structural Database (CSD, version 5.45, updated to November 2023; Groom *et al.*, 2016). The database analysis shows that calix[4]arenes, which are distally disubstituted at the lower rim, prefer a pinched cone conformation in solution and in the solid state, which agrees well with the result of the present study. In addition, there are three thiocalix[4]arenes having OH groups in distal positions of the lower rim: JIPQIJ01 (Dvořáková *et al.*, 2007); KURKAL, KURKEP (Wang *et al.*, 2015), which are isostructural with compound **3**. Several crystal structures of dibromo-substituted calix[4]arene 1,3-alternates have also been reported, in which the Br···Br distance varies from 3.967 (5) Å (BAGYAJ; Krebs *et al.*, 1998) to 4.112 (8) Å (KARNAT; Sykora *et al.*, 2005).

5. Synthesis and crystallization

The title compounds were prepared as follows:

5,17-Dibromo-26,28-dihydroxy-25,27-dipropynyloxycalix[4]arene (**1**) (cone)

To a stirred solution of 26,28-dihydroxy-25,27-dipropynyloxycalix[4]arene (0.50 mg, 1.0 mmol) (Xu *et al.*, 1996) in dichloromethane *N*-bromosuccinimide (0.39 g, 2.2 mmol) was added and the resultant mixture stirred at 298 K for 24 h. The solvent was removed under reduced pressure and the residue was purified by flash chromatography (silica, dichloromethane) followed by crystallization from a dichloromethane/methanol solvent mixture. Single crystals suitable for X-ray analysis were grown by slow evaporation of the solvent from a

solution of the substance in a CH₂Cl₂/MeOH mixture (1:1 *v/v*). Yield 0.55 g (77%). M.p. 515–516 K. ESI-MS: *m/z*: 676.0516 [$M + \text{NH}_4$]⁺ for C₃₄H₃₀Br₂NO₄ (676.0516). ¹H NMR (CDCl₃, 400 MHz): δ = 7.19 (s, 4H; ArH), 7.15 (s, 2H; OH), 6.88–6.83 (*m*, 4H; ArH), 6.80–6.75 (*m*, 2H; ArH), 4.76 (*d*, 4H, ⁴*J*_{HH} = 2.4 Hz; OCH₂), 4.34 (*d*, 4H, ²*J*_{HH} = 13.4 Hz; ArCH₂Ar), 3.35 (*d*, 4H, ²*J*_{HH} = 13.4 Hz; ArCH₂Ar), 2.58 (*t*, 2H, ⁴*J*_{HH} = 2.4 Hz; CH) ppm; ¹³C NMR (100 MHz, CDCl₃): δ = 152.12, 151.26, 132.62 (C_{Ar}), 130.83 (CH_{Ar}), 130.03 (C_{Ar}), 129.29, 125.91 (CH_{Ar}), 110.76 (C_{Ar}), 77.92 (CCH), 76.95 (CCH), 63.50 (OCH₂), 31.51 (ArCH₂Ar) ppm.

5,17-Dibromo-26,28-dipropoxy-25,27-dipropynyloxycalix[4]arene (**2**) (1,3-alternate)

A mixture of calix[4]arene **1** (0.45g, 0.7 mmol) and anhydrous Cs₂CO₃ (0.90 g, 1.8 mmol) in dry DMF (15 ml) was stirred at room temperature for 2 h. 1-Iodopropane (0.40 ml, 4.1 mmol) was added and the mixture stirred for 48 h at 298 K. The solvent was removed under reduced pressure with heating below 333 K, and the residue was parted between dichloromethane and 2M HCl. The organic layer was separated, washed with water, dried with MgSO₄ and concentrated to dryness. The residue was purified by flash chromatography (silica, gradient from hexane to hexane/dichloromethane (1:1)). Single crystals suitable for X-ray analysis were grown by slow evaporation of the solvent from a solution of the substance in a CH₂Cl₂/MeOH mixture (1:1 *v/v*). Yield 0.16 g (31%). M.p. 478–479 K. ESI-MS: *m/z*: 760.1462 [$M + \text{NH}_4$]⁺ for C₄₀H₄₂Br₂NO₄ (760.1455). ¹H NMR (CDCl₃, 400 MHz): δ = 7.28 (s, 4H; ArH), 6.97 (*d*, 4H, ³*J*_{HH} = 7.6 Hz; ArH), 6.72 (*t*, 2H, ³*J*_{HH} = 7.6 Hz; ArH), 4.22 (*d*, 4H, ⁴*J*_{HH} = 2.4 Hz; OCH₂CCH), 3.66 (*d*, 4H, ²*J*_{HH} = 14.5 Hz; ArCH₂Ar), 3.57 (*d*, 4H, ²*J*_{HH} = 14.5 Hz; ArCH₂Ar), 3.49–3.43 (*m*, 4H; OCH₂CH₂), 2.55 (*t*, 2H, ⁴*J*_{HH} = 2.4 Hz; CCH), 1.67–1.57 (*m*, 4H; CH₂CH₃), 0.88 (*t*, 6H, ³*J*_{HH} = 7.5 Hz; CH₃) ppm; ¹³C NMR (100 MHz, CDCl₃): δ = 155.40, 155.07, 135.09, 133.59 (C_{Ar}), 132.88, 130.15, 122.58 (CH_{Ar}), 114.72 (C_{Ar}), 79.48 (CCH), 75.14 (CCH), 73.68 (OCH₂CH₂), 58.77 (OCH₂CCH), 36.25 (ArCH₂Ar), 23.53 (CH₂CH₃), 10.34 (CH₃) ppm.

25,27-Bis(2-azidoethoxy)-5,17-dibromo-26,28-dihydroxycalix[4]arene (**3**) (cone)

To a stirred solution of 25,27-bis(2-azidoethoxy)-26,28-dihydroxycalix[4]arene (0.56 mg, 1.0 mmol) (Gorbunov *et al.*, 2021) in dichloromethane *N*-bromosuccinimide (0.39 g, 2.2 mmol) was added and the resultant mixture stirred at 298 K for 24 h. The solvent was removed under reduced pressure and the residue was purified by flash chromatography (silica, dichloromethane) followed by crystallization from dichloromethane/methanol solvent mixture. Single crystals suitable for X-ray analysis were grown by slow evaporation of the solvent from a solution of the substance in a CH₂Cl₂/MeOH mixture (1:1 *v/v*). Yield 0.63g (88%). M.p. 538–539 K. ESI-MS: *m/z*: 738.0861 [$M + \text{NH}_4$]⁺ for C₃₂H₃₂Br₂N₇O₄ (738.0857). ¹H NMR (CDCl₃, 400 MHz): δ = 7.57 (s, 2H; OH), 7.19 (s, 4H; ArH), 6.91–6.86 (*m*, 4H; ArH), 6.81–6.76 (*m*, 2H; ArH), 4.29 (*d*, 4H, ²*J*_{HH} = 13.2 Hz; ArCH₂Ar), 4.07–4.02 (*m*, 4H; CH₂CH₂), 3.88–3.83 (*m*, 4H; CH₂CH₂), 3.34 (*d*, 4H, ²*J*_{HH} = 13.2 Hz; ArCH₂Ar) ppm; ¹³C NMR (100 MHz, CDCl₃): δ =

Table 3
Experimental details.

	1	2	3
Crystal data			
Chemical formula	C ₃₄ H ₂₆ Br ₂ O ₄	C ₄₀ H ₃₈ Br ₂ O ₄	C ₃₂ H ₂₈ Br ₂ N ₆ O ₄
<i>M_r</i>	658.37	742.52	720.42
Crystal system, space group	Triclinic, <i>P</i> $\bar{1}$	Orthorhombic, <i>Pbcn</i>	Trigonal, <i>R</i> $\bar{3}$
Temperature (K)	100	100	100
<i>a</i> , <i>b</i> , <i>c</i> (Å)	10.1542 (3), 11.9156 (3), 11.9964 (4)	18.1223 (7), 9.9840 (4), 18.2863 (7)	36.3261 (7), 36.3261 (7), 12.1054 (4)
α , β , γ (°)	75.221 (1), 88.341 (1), 81.751 (1)	90, 90, 90	90, 90, 120
<i>V</i> (Å ³)	1388.90 (7)	3308.6 (2)	13834.0 (7)
<i>Z</i>	2	4	18
Radiation type	Mo <i>K</i> α	Mo <i>K</i> α	Mo <i>K</i> α
μ (mm ⁻¹)	2.96	2.49	2.69
Crystal size (mm)	0.32 × 0.16 × 0.12	0.35 × 0.25 × 0.22	0.37 × 0.13 × 0.1
Data collection			
Diffractometer	Bruker D8 Venture	Bruker D8 Venture	Bruker D8 Venture
Absorption correction	Multi-scan (<i>SADABS</i> ; Krause <i>et al.</i> , 2015)	Multi-scan (<i>SADABS</i> ; Krause <i>et al.</i> , 2015)	Multi-scan (<i>SADABS</i> ; Krause <i>et al.</i> , 2015)
<i>T_{min}</i> , <i>T_{max}</i>	0.501, 0.746	0.545, 0.746	0.516, 0.746
No. of measured, independent and observed [<i>I</i> > 2 σ (<i>I</i>)] reflections	31619, 8481, 6661	55960, 5529, 4481	45251, 7804, 6043
<i>R_{int}</i>	0.043	0.060	0.047
(<i>sin</i> θ / λ) _{max} (Å ⁻¹)	0.715	0.736	0.671
Refinement			
<i>R</i> [<i>F</i> ² > 2 σ (<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i>	0.036, 0.087, 1.04	0.030, 0.069, 1.04	0.040, 0.097, 1.03
No. of reflections	8481	5529	7804
No. of parameters	373	283	399
No. of restraints	7	0	24
H-atom treatment	H-atom parameters constrained	Only H-atom coordinates refined	H-atom parameters constrained
$\Delta\rho_{\max}$, $\Delta\rho_{\min}$ (e Å ⁻³)	0.49, -0.80	0.42, -0.51	1.30, -1.12

Computer programs: *APEX3* and *SAINT* (Bruker, 2017), *SHELXT* (Sheldrick, 2015a), *SHELXL* (Sheldrick, 2015b) and *OLEX2* (Dolomanov *et al.*, 2009).

152.40, 151.43, 132.23 (C_{Ar}), 130.84 (CH_{Ar}), 129.79 (C_{Ar}), 129.40, 125.77 (CH_{Ar}), 110.53 (C_{Ar}), 74.41 (OCH₂), 51.07 (CH₂N₃), 30.90 (ArCH₂Ar) ppm.

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 3. All C-bound hydrogen atoms in the structures of **1** and **3** were placed in calculated positions and refined using a riding model [C–H = 0.94–0.97 Å with *U*_{iso}(H) = 1.2–1.5*U*_{eq}(C)]. Hydrogen atoms of hydroxy groups were located from difference electron-density maps and were refined with *U*_{iso}(H) = 1.5*U*_{eq}(O). In the structure of **2**, hydrogen atoms were located from difference electron-density maps and were refined freely. In the structure of **1**, one bromine atom was found to be disordered over two positions with a refined occupancy ratio of 0.928 (5):0.072 (5). In the structure of **3**, highly disordered solvent CH₂Cl₂ molecules are present. Their contributions to the intensity data was removed by the SQUEEZE procedure (Spek, 2015) as implemented in the *OLEX2* package (Dolomanov *et al.*, 2009). The SIMU instruction was used to restrain the *U*^{ij} components of the disordered bromine atoms in the structure of **1** and nitrogen atoms in the structure of **3**. The most disagreeable reflections with an error/s.u. of more than 10 (100 in the data for **1**; $\bar{2}40$, $\bar{3}60$ and 030 in the data for **3**) were omitted using the OMIT instruction in *SHELXL* (Sheldrick, 2015b).

Acknowledgements

X-ray diffraction studies were performed at the Centre of Shared Equipment of IGIC RAS.

Funding information

Funding for this research was provided by: Russian Science Foundation (grant No. 22-73-00052, <https://rscf.ru/en/project/22-73-00052/>).

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supporting information

Acta Cryst. (2024). E80, 555-560 [https://doi.org/10.1107/S2056989024003785]

Synthesis and crystal structures of 5,17-dibromo-26,28-dihydroxy-25,27-dipropyloxylix[4]arene, 5,17-dibromo-26,28-dipropoxy-25,27-dipropyloxylix[4]arene and 25,27-bis(2-azidoethoxy)-5,17-dibromo-26,28-dihydroxylix[4]arene

Alexander Gorbunov, Stanislav Bezzubov, Maria Malakhova, Vladimir Kovalev and Ivan Vatsouro

Computing details

5,17-Dibromo-26,28-dihydroxy-25,27-dipropyloxylix[4]arene (1)

Crystal data

$C_{34}H_{26}Br_2O_4$	$Z = 2$
$M_r = 658.37$	$F(000) = 664$
Triclinic, $P\bar{1}$	$D_x = 1.574 \text{ Mg m}^{-3}$
$a = 10.1542 (3) \text{ \AA}$	Mo $K\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$
$b = 11.9156 (3) \text{ \AA}$	Cell parameters from 9976 reflections
$c = 11.9964 (4) \text{ \AA}$	$\theta = 2.5\text{--}30.5^\circ$
$\alpha = 75.221 (1)^\circ$	$\mu = 2.96 \text{ mm}^{-1}$
$\beta = 88.341 (1)^\circ$	$T = 100 \text{ K}$
$\gamma = 81.751 (1)^\circ$	Block, yellow
$V = 1388.90 (7) \text{ \AA}^3$	$0.32 \times 0.16 \times 0.12 \text{ mm}$

Data collection

Bruker D8 Venture diffractometer	$T_{\min} = 0.501, T_{\max} = 0.746$
Radiation source: microfocus sealed X-ray tube, Incoatec $I\mu S$ microsource	31619 measured reflections
Focusing mirrors monochromator	8481 independent reflections
Detector resolution: $10.4 \text{ pixels mm}^{-1}$	6661 reflections with $I > 2\sigma(I)$
ω -scan	$R_{\text{int}} = 0.043$
Absorption correction: multi-scan (<i>SADABS</i> ; Krause <i>et al.</i> , 2015)	$\theta_{\max} = 30.6^\circ, \theta_{\min} = 1.8^\circ$
	$h = -14 \rightarrow 14$
	$k = -17 \rightarrow 17$
	$l = -16 \rightarrow 17$

Refinement

Refinement on F^2	Hydrogen site location: inferred from neighbouring sites
Least-squares matrix: full	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.036$	$w = 1/[\sigma^2(F_o^2) + (0.0365P)^2 + 0.736P]$
$wR(F^2) = 0.087$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.04$	$(\Delta/\sigma)_{\max} = 0.001$
8481 reflections	$\Delta\rho_{\max} = 0.49 \text{ e \AA}^{-3}$
373 parameters	$\Delta\rho_{\min} = -0.80 \text{ e \AA}^{-3}$
7 restraints	

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$	Occ. (<1)
Br1	0.13667 (2)	0.10801 (2)	0.34716 (2)	0.02325 (6)	
Br3	0.4344 (16)	0.8992 (4)	0.7623 (12)	0.0478 (18)	0.072 (5)
O1	0.37255 (13)	0.20076 (13)	0.76345 (11)	0.0175 (3)	
H1	0.455133	0.201641	0.759281	0.026*	
O4	0.62310 (13)	0.22902 (12)	0.77582 (11)	0.0147 (3)	
O2	0.21281 (13)	0.28716 (12)	0.93959 (11)	0.0149 (3)	
O3	0.45446 (13)	0.37816 (12)	0.88209 (12)	0.0175 (3)	
H3	0.381434	0.360749	0.910983	0.026*	
C1	0.40950 (19)	0.16828 (16)	0.57182 (16)	0.0142 (4)	
C25	0.32705 (19)	0.18609 (16)	0.66343 (16)	0.0140 (4)	
C2	0.3504 (2)	0.14541 (16)	0.47770 (16)	0.0164 (4)	
H2	0.404008	0.131552	0.415021	0.020*	
C23	0.60857 (18)	0.28084 (16)	0.57005 (16)	0.0142 (4)	
C26	0.14200 (18)	0.37135 (17)	0.85034 (16)	0.0144 (4)	
C5	0.18917 (19)	0.18555 (17)	0.65907 (16)	0.0158 (4)	
C28	0.63632 (18)	0.31164 (16)	0.67091 (16)	0.0136 (4)	
C4	0.1333 (2)	0.16353 (17)	0.56418 (17)	0.0177 (4)	
H4	0.040104	0.162716	0.560404	0.021*	
C20	0.68421 (18)	0.49935 (17)	0.56564 (16)	0.0155 (4)	
H20	0.707334	0.574420	0.563143	0.019*	
C7	0.08651 (18)	0.33525 (18)	0.76248 (16)	0.0159 (4)	
C27	0.45330 (19)	0.49577 (16)	0.85977 (16)	0.0144 (4)	
C3	0.2149 (2)	0.14269 (17)	0.47470 (16)	0.0173 (4)	
C33	0.70622 (19)	0.05765 (18)	0.91211 (17)	0.0183 (4)	
C30	0.0378 (2)	0.18942 (18)	1.04971 (17)	0.0183 (4)	
C19	0.66961 (18)	0.42045 (17)	0.67255 (16)	0.0137 (4)	
C16	0.5776 (2)	0.65712 (18)	0.79072 (16)	0.0182 (4)	
H16	0.656387	0.687064	0.759724	0.022*	
C13	0.34441 (19)	0.57215 (17)	0.88396 (16)	0.0153 (4)	
C11	0.13953 (18)	0.48938 (17)	0.84800 (16)	0.0151 (4)	
C32	0.74233 (19)	0.14878 (18)	0.81472 (17)	0.0174 (4)	
H32A	0.810036	0.190259	0.838597	0.021*	
H32B	0.779649	0.113938	0.751985	0.021*	
C22	0.62569 (19)	0.36187 (17)	0.46568 (16)	0.0163 (4)	
H22	0.610029	0.343350	0.395175	0.020*	
C6	0.10297 (19)	0.20789 (18)	0.75864 (17)	0.0182 (4)	
H6A	0.014234	0.185145	0.751264	0.022*	
H6B	0.143676	0.158222	0.831971	0.022*	
C12	0.21709 (19)	0.52806 (18)	0.93450 (17)	0.0163 (4)	

H12A	0.160564	0.591182	0.960687	0.020*	
H12B	0.239323	0.461186	1.002593	0.020*	
C8	0.02054 (19)	0.42259 (19)	0.67312 (17)	0.0196 (4)	
H8	-0.019001	0.400917	0.612324	0.023*	
C24	0.56005 (19)	0.16485 (17)	0.57366 (17)	0.0161 (4)	
H24A	0.596010	0.106554	0.644376	0.019*	
H24B	0.597657	0.136945	0.506871	0.019*	
C29	0.1451 (2)	0.26107 (18)	1.04853 (16)	0.0185 (4)	
H29A	0.106800	0.335589	1.066540	0.022*	
H29B	0.210651	0.218888	1.109793	0.022*	
C34	0.6739 (2)	-0.01519 (19)	0.99099 (19)	0.0218 (4)	
H34	0.647887	-0.073636	1.054290	0.026*	
C21	0.66540 (19)	0.46942 (17)	0.46356 (17)	0.0168 (4)	
H21	0.679652	0.522512	0.391855	0.020*	
C14	0.3541 (2)	0.69105 (18)	0.86054 (17)	0.0186 (4)	
H14	0.280958	0.744225	0.875755	0.022*	
C15	0.4698 (2)	0.73211 (17)	0.81518 (17)	0.0202 (4)	
C17	0.57032 (19)	0.53733 (17)	0.81171 (16)	0.0143 (4)	
C18	0.68642 (18)	0.45380 (18)	0.78479 (16)	0.0159 (4)	
H18A	0.697858	0.381654	0.848659	0.019*	
H18B	0.768496	0.490555	0.780692	0.019*	
C9	0.0116 (2)	0.5402 (2)	0.67141 (18)	0.0219 (4)	
H9	-0.036051	0.598057	0.611156	0.026*	
C31	-0.0464 (2)	0.13008 (19)	1.05713 (18)	0.0224 (4)	
H31	-0.114571	0.082004	1.063136	0.027*	
C10	0.07224 (19)	0.57330 (18)	0.75746 (17)	0.0188 (4)	
H10	0.067891	0.654129	0.754765	0.023*	
Br2	0.48141 (12)	0.89367 (4)	0.79296 (8)	0.03315 (19)	0.928 (5)

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Br1	0.02602 (12)	0.02894 (12)	0.01807 (10)	-0.00387 (9)	-0.00172 (8)	-0.01170 (8)
Br3	0.069 (4)	0.023 (2)	0.058 (3)	-0.023 (2)	0.021 (3)	-0.015 (2)
O1	0.0128 (6)	0.0278 (8)	0.0150 (6)	-0.0074 (6)	0.0039 (5)	-0.0092 (6)
O4	0.0113 (6)	0.0160 (7)	0.0140 (6)	0.0000 (5)	0.0021 (5)	0.0003 (5)
O2	0.0143 (6)	0.0176 (7)	0.0125 (6)	-0.0027 (5)	0.0027 (5)	-0.0032 (5)
O3	0.0125 (6)	0.0134 (6)	0.0264 (7)	-0.0036 (5)	0.0043 (5)	-0.0044 (6)
C1	0.0163 (9)	0.0103 (8)	0.0159 (8)	-0.0030 (7)	0.0038 (7)	-0.0028 (7)
C25	0.0166 (9)	0.0129 (8)	0.0135 (8)	-0.0043 (7)	0.0020 (7)	-0.0044 (7)
C2	0.0223 (10)	0.0132 (9)	0.0138 (8)	-0.0022 (7)	0.0042 (7)	-0.0041 (7)
C23	0.0100 (8)	0.0152 (9)	0.0176 (9)	-0.0016 (7)	0.0032 (7)	-0.0049 (7)
C26	0.0095 (8)	0.0197 (9)	0.0139 (8)	-0.0013 (7)	0.0025 (7)	-0.0044 (7)
C5	0.0157 (9)	0.0169 (9)	0.0164 (9)	-0.0050 (7)	0.0034 (7)	-0.0061 (7)
C28	0.0105 (8)	0.0150 (9)	0.0139 (8)	-0.0013 (7)	0.0028 (6)	-0.0015 (7)
C4	0.0167 (9)	0.0193 (10)	0.0186 (9)	-0.0044 (8)	0.0008 (7)	-0.0065 (8)
C20	0.0111 (8)	0.0163 (9)	0.0189 (9)	-0.0036 (7)	0.0017 (7)	-0.0032 (7)
C7	0.0099 (8)	0.0238 (10)	0.0161 (9)	-0.0045 (7)	0.0052 (7)	-0.0083 (8)

C27	0.0160 (9)	0.0144 (9)	0.0130 (8)	-0.0040 (7)	-0.0017 (7)	-0.0026 (7)
C3	0.0238 (10)	0.0158 (9)	0.0144 (9)	-0.0040 (8)	-0.0009 (7)	-0.0066 (7)
C33	0.0144 (9)	0.0186 (10)	0.0210 (9)	0.0015 (7)	-0.0021 (7)	-0.0052 (8)
C30	0.0202 (10)	0.0202 (10)	0.0144 (9)	-0.0010 (8)	0.0035 (7)	-0.0057 (8)
C19	0.0085 (8)	0.0178 (9)	0.0146 (8)	-0.0031 (7)	0.0014 (6)	-0.0033 (7)
C16	0.0197 (10)	0.0218 (10)	0.0159 (9)	-0.0110 (8)	0.0019 (7)	-0.0056 (8)
C13	0.0170 (9)	0.0166 (9)	0.0137 (8)	-0.0038 (7)	0.0003 (7)	-0.0057 (7)
C11	0.0099 (8)	0.0201 (9)	0.0160 (9)	-0.0017 (7)	0.0035 (7)	-0.0065 (7)
C32	0.0122 (9)	0.0196 (10)	0.0177 (9)	0.0010 (7)	0.0012 (7)	-0.0017 (8)
C22	0.0152 (9)	0.0190 (9)	0.0151 (9)	-0.0033 (7)	0.0022 (7)	-0.0050 (7)
C6	0.0139 (9)	0.0255 (10)	0.0196 (9)	-0.0082 (8)	0.0046 (7)	-0.0113 (8)
C12	0.0146 (9)	0.0183 (9)	0.0177 (9)	-0.0018 (7)	0.0024 (7)	-0.0081 (8)
C8	0.0096 (9)	0.0335 (12)	0.0170 (9)	-0.0007 (8)	0.0011 (7)	-0.0104 (8)
C24	0.0156 (9)	0.0150 (9)	0.0188 (9)	-0.0023 (7)	0.0048 (7)	-0.0065 (7)
C29	0.0200 (10)	0.0231 (10)	0.0145 (9)	-0.0068 (8)	0.0044 (7)	-0.0070 (8)
C34	0.0190 (10)	0.0203 (10)	0.0237 (10)	-0.0008 (8)	0.0005 (8)	-0.0025 (8)
C21	0.0137 (9)	0.0185 (9)	0.0163 (9)	-0.0032 (7)	0.0028 (7)	-0.0006 (7)
C14	0.0225 (10)	0.0169 (9)	0.0183 (9)	-0.0027 (8)	0.0036 (8)	-0.0080 (8)
C15	0.0315 (11)	0.0154 (9)	0.0168 (9)	-0.0090 (8)	0.0040 (8)	-0.0068 (8)
C17	0.0145 (9)	0.0178 (9)	0.0118 (8)	-0.0042 (7)	0.0000 (7)	-0.0046 (7)
C18	0.0112 (9)	0.0222 (10)	0.0154 (9)	-0.0040 (7)	0.0004 (7)	-0.0058 (8)
C9	0.0131 (9)	0.0290 (11)	0.0195 (10)	0.0040 (8)	-0.0006 (7)	-0.0025 (9)
C31	0.0180 (10)	0.0266 (11)	0.0243 (10)	-0.0057 (8)	0.0042 (8)	-0.0087 (9)
C10	0.0155 (9)	0.0194 (10)	0.0203 (9)	0.0015 (8)	0.0048 (7)	-0.0053 (8)
Br2	0.0503 (4)	0.01800 (14)	0.0381 (3)	-0.01664 (17)	0.0244 (2)	-0.01573 (14)

Geometric parameters (Å, °)

Br1—C3	1.9052 (19)	C30—C31	1.173 (3)
Br3—C15	1.913 (5)	C19—C18	1.519 (3)
O1—H1	0.8400	C16—H16	0.9500
O1—C25	1.359 (2)	C16—C15	1.385 (3)
O4—C28	1.403 (2)	C16—C17	1.397 (3)
O4—C32	1.439 (2)	C13—C12	1.517 (3)
O2—C26	1.400 (2)	C13—C14	1.390 (3)
O2—C29	1.442 (2)	C11—C12	1.518 (3)
O3—H3	0.8400	C11—C10	1.393 (3)
O3—C27	1.356 (2)	C32—H32A	0.9900
C1—C25	1.403 (3)	C32—H32B	0.9900
C1—C2	1.397 (3)	C22—H22	0.9500
C1—C24	1.524 (3)	C22—C21	1.392 (3)
C25—C5	1.403 (3)	C6—H6A	0.9900
C2—H2	0.9500	C6—H6B	0.9900
C2—C3	1.383 (3)	C12—H12A	0.9900
C23—C28	1.398 (3)	C12—H12B	0.9900
C23—C22	1.396 (3)	C8—H8	0.9500
C23—C24	1.523 (3)	C8—C9	1.386 (3)
C26—C7	1.396 (3)	C24—H24A	0.9900

C26—C11	1.396 (3)	C24—H24B	0.9900
C5—C4	1.385 (3)	C29—H29A	0.9900
C5—C6	1.516 (3)	C29—H29B	0.9900
C28—C19	1.391 (3)	C34—H34	0.9500
C4—H4	0.9500	C21—H21	0.9500
C4—C3	1.388 (3)	C14—H14	0.9500
C20—H20	0.9500	C14—C15	1.381 (3)
C20—C19	1.402 (3)	C15—Br2	1.895 (2)
C20—C21	1.385 (3)	C17—C18	1.513 (3)
C7—C6	1.515 (3)	C18—H18A	0.9900
C7—C8	1.398 (3)	C18—H18B	0.9900
C27—C13	1.401 (3)	C9—H9	0.9500
C27—C17	1.405 (3)	C9—C10	1.384 (3)
C33—C32	1.456 (3)	C31—H31	0.9500
C33—C34	1.184 (3)	C10—H10	0.9500
C30—C29	1.475 (3)		
C25—O1—H1	109.5	H32A—C32—H32B	108.5
C28—O4—C32	114.33 (14)	C23—C22—H22	119.6
C26—O2—C29	115.53 (14)	C21—C22—C23	120.87 (18)
C27—O3—H3	109.5	C21—C22—H22	119.6
C25—C1—C24	123.34 (17)	C5—C6—H6A	109.2
C2—C1—C25	117.70 (17)	C5—C6—H6B	109.2
C2—C1—C24	118.84 (17)	C7—C6—C5	112.17 (16)
O1—C25—C1	123.84 (17)	C7—C6—H6A	109.2
O1—C25—C5	114.80 (16)	C7—C6—H6B	109.2
C1—C25—C5	121.32 (17)	H6A—C6—H6B	107.9
C1—C2—H2	119.6	C13—C12—C11	112.16 (15)
C3—C2—C1	120.79 (18)	C13—C12—H12A	109.2
C3—C2—H2	119.6	C13—C12—H12B	109.2
C28—C23—C24	121.58 (17)	C11—C12—H12A	109.2
C22—C23—C28	117.03 (17)	C11—C12—H12B	109.2
C22—C23—C24	121.38 (17)	H12A—C12—H12B	107.9
C7—C26—O2	119.17 (17)	C7—C8—H8	119.3
C7—C26—C11	122.50 (17)	C9—C8—C7	121.32 (19)
C11—C26—O2	118.10 (16)	C9—C8—H8	119.3
C25—C5—C6	119.75 (17)	C1—C24—H24A	108.4
C4—C5—C25	119.64 (17)	C1—C24—H24B	108.4
C4—C5—C6	120.61 (17)	C23—C24—C1	115.60 (16)
C23—C28—O4	117.21 (17)	C23—C24—H24A	108.4
C19—C28—O4	119.01 (16)	C23—C24—H24B	108.4
C19—C28—C23	123.71 (17)	H24A—C24—H24B	107.4
C5—C4—H4	120.4	O2—C29—C30	113.22 (16)
C5—C4—C3	119.26 (18)	O2—C29—H29A	108.9
C3—C4—H4	120.4	O2—C29—H29B	108.9
C19—C20—H20	119.5	C30—C29—H29A	108.9
C21—C20—H20	119.5	C30—C29—H29B	108.9
C21—C20—C19	120.95 (18)	H29A—C29—H29B	107.7

C26—C7—C6	122.24 (17)	C33—C34—H34	180.0
C26—C7—C8	117.23 (19)	C20—C21—C22	120.23 (18)
C8—C7—C6	120.43 (18)	C20—C21—H21	119.9
O3—C27—C13	123.07 (17)	C22—C21—H21	119.9
O3—C27—C17	115.61 (17)	C13—C14—H14	119.9
C13—C27—C17	121.31 (18)	C15—C14—C13	120.17 (19)
C2—C3—Br1	120.20 (15)	C15—C14—H14	119.9
C2—C3—C4	121.25 (18)	C16—C15—Br3	128.5 (3)
C4—C3—Br1	118.55 (15)	C16—C15—Br2	120.16 (15)
C34—C33—C32	178.5 (2)	C14—C15—Br3	108.5 (4)
C31—C30—C29	176.3 (2)	C14—C15—C16	121.34 (18)
C28—C19—C20	117.00 (17)	C14—C15—Br2	118.44 (16)
C28—C19—C18	121.74 (16)	C27—C17—C18	120.63 (17)
C20—C19—C18	121.25 (17)	C16—C17—C27	118.52 (18)
C15—C16—H16	120.1	C16—C17—C18	120.85 (17)
C15—C16—C17	119.89 (18)	C19—C18—H18A	108.9
C17—C16—H16	120.1	C19—C18—H18B	108.9
C27—C13—C12	121.59 (17)	C17—C18—C19	113.51 (16)
C14—C13—C27	118.76 (18)	C17—C18—H18A	108.9
C14—C13—C12	119.65 (17)	C17—C18—H18B	108.9
C26—C11—C12	122.03 (17)	H18A—C18—H18B	107.7
C10—C11—C26	118.15 (18)	C8—C9—H9	120.0
C10—C11—C12	119.61 (18)	C10—C9—C8	119.99 (19)
O4—C32—C33	107.29 (15)	C10—C9—H9	120.0
O4—C32—H32A	110.3	C30—C31—H31	180.0
O4—C32—H32B	110.3	C11—C10—H10	119.7
C33—C32—H32A	110.3	C9—C10—C11	120.69 (19)
C33—C32—H32B	110.3	C9—C10—H10	119.7
O1—C25—C5—C4	-175.79 (17)	C27—C13—C12—C11	-70.9 (2)
O1—C25—C5—C6	3.6 (3)	C27—C13—C14—C15	-0.6 (3)
O4—C28—C19—C20	178.82 (16)	C27—C17—C18—C19	80.0 (2)
O4—C28—C19—C18	-2.5 (3)	C19—C20—C21—C22	2.9 (3)
O2—C26—C7—C6	-1.5 (3)	C16—C17—C18—C19	-100.8 (2)
O2—C26—C7—C8	-177.89 (16)	C13—C27—C17—C16	1.5 (3)
O2—C26—C11—C12	3.5 (3)	C13—C27—C17—C18	-179.27 (17)
O2—C26—C11—C10	178.24 (16)	C13—C14—C15—Br3	167.1 (6)
O3—C27—C13—C12	-1.7 (3)	C13—C14—C15—C16	0.8 (3)
O3—C27—C13—C14	178.42 (17)	C13—C14—C15—Br2	-176.50 (15)
O3—C27—C17—C16	-177.58 (16)	C11—C26—C7—C6	172.93 (17)
O3—C27—C17—C18	1.6 (3)	C11—C26—C7—C8	-3.5 (3)
C1—C25—C5—C4	2.0 (3)	C32—O4—C28—C23	89.9 (2)
C1—C25—C5—C6	-178.60 (18)	C32—O4—C28—C19	-93.1 (2)
C1—C2—C3—Br1	-178.64 (14)	C22—C23—C28—O4	-178.14 (16)
C1—C2—C3—C4	0.6 (3)	C22—C23—C28—C19	5.0 (3)
C25—C1—C2—C3	1.2 (3)	C22—C23—C24—C1	-86.3 (2)
C25—C1—C24—C23	-68.5 (2)	C6—C5—C4—C3	-179.61 (18)
C25—C5—C4—C3	-0.2 (3)	C6—C7—C8—C9	-175.93 (18)

C25—C5—C6—C7	72.9 (2)	C12—C13—C14—C15	179.61 (18)
C2—C1—C25—O1	175.13 (17)	C12—C11—C10—C9	173.74 (18)
C2—C1—C25—C5	-2.4 (3)	C8—C7—C6—C5	64.4 (2)
C2—C1—C24—C23	115.69 (19)	C8—C9—C10—C11	-1.7 (3)
C23—C28—C19—C20	-4.4 (3)	C24—C1—C25—O1	-0.8 (3)
C23—C28—C19—C18	174.25 (17)	C24—C1—C25—C5	-178.33 (18)
C23—C22—C21—C20	-2.2 (3)	C24—C1—C2—C3	177.25 (17)
C26—O2—C29—C30	74.3 (2)	C24—C23—C28—O4	2.7 (3)
C26—C7—C6—C5	-111.9 (2)	C24—C23—C28—C19	-174.19 (17)
C26—C7—C8—C9	0.5 (3)	C24—C23—C22—C21	177.62 (17)
C26—C11—C12—C13	101.7 (2)	C29—O2—C26—C7	-105.57 (19)
C26—C11—C10—C9	-1.1 (3)	C29—O2—C26—C11	79.8 (2)
C5—C4—C3—Br1	178.16 (15)	C21—C20—C19—C28	0.3 (3)
C5—C4—C3—C2	-1.1 (3)	C21—C20—C19—C18	-178.34 (17)
C28—O4—C32—C33	-170.24 (16)	C14—C13—C12—C11	108.9 (2)
C28—C23—C22—C21	-1.6 (3)	C15—C16—C17—C27	-1.3 (3)
C28—C23—C24—C1	92.9 (2)	C15—C16—C17—C18	179.50 (18)
C28—C19—C18—C17	-104.1 (2)	C17—C27—C13—C12	179.24 (17)
C4—C5—C6—C7	-107.7 (2)	C17—C27—C13—C14	-0.6 (3)
C20—C19—C18—C17	74.5 (2)	C17—C16—C15—Br3	-163.2 (8)
C7—C26—C11—C12	-170.94 (17)	C17—C16—C15—C14	0.2 (3)
C7—C26—C11—C10	3.8 (3)	C17—C16—C15—Br2	177.39 (15)
C7—C8—C9—C10	2.0 (3)	C10—C11—C12—C13	-72.9 (2)

Hydrogen-bond 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>
O1—H1...O4	0.84	1.81	2.6270 (18)	165
O3—H3...O2	0.84	2.02	2.8207 (18)	160

5,17-Dibromo-26,28-dipropoxy-25,27-dipropyloxyalix[4]arene (2)

Crystal data

C₄₀H₃₈Br₂O₄*M_r* = 742.52Orthorhombic, *Pbcn**a* = 18.1223 (7) Å*b* = 9.9840 (4) Å*c* = 18.2863 (7) Å*V* = 3308.6 (2) Å³*Z* = 4*F*(000) = 1520*D_x* = 1.491 Mg m⁻³Mo *Kα* radiation, λ = 0.71073 Å

Cell parameters from 9929 reflections

θ = 2.3–31.5°

μ = 2.49 mm⁻¹*T* = 100 K

Block, colourless

0.35 × 0.25 × 0.22 mm

Data collection

Bruker D8 Venture
diffractometerRadiation source: microfocus sealed X-ray tube,
Incoatec IμS microsource

Focusing mirrors monochromator

Detector resolution: 10.4 pixels mm⁻¹

ω-scan

Absorption correction: multi-scan
(*SADABS*; Krause *et al.*, 2015)*T_{min}* = 0.545, *T_{max}* = 0.746

55960 measured reflections

5529 independent reflections

4481 reflections with *I* > 2σ(*I*)*R_{int}* = 0.060

$\theta_{\max} = 31.5^\circ$, $\theta_{\min} = 2.2^\circ$
 $h = -26 \rightarrow 26$

$k = -14 \rightarrow 14$
 $l = -26 \rightarrow 26$

Refinement

Refinement on F^2
 Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.030$
 $wR(F^2) = 0.069$
 $S = 1.04$
 5529 reflections
 283 parameters
 0 restraints

Primary atom site location: dual
 Hydrogen site location: difference Fourier map
 Only H-atom coordinates refined
 $w = 1/[\sigma^2(F_o^2) + (0.0275P)^2 + 1.7553P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.001$
 $\Delta\rho_{\max} = 0.42 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -0.51 \text{ e } \text{\AA}^{-3}$

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Br1	0.58375 (2)	0.73040 (2)	0.32024 (2)	0.01950 (5)
O1	0.63861 (5)	0.13925 (9)	0.35764 (5)	0.01210 (18)
O2	0.40187 (5)	0.38259 (9)	0.37445 (5)	0.01229 (19)
C1	0.57053 (7)	0.33574 (14)	0.39089 (7)	0.0121 (2)
C2	0.55903 (7)	0.47314 (14)	0.38265 (8)	0.0132 (2)
H2	0.5264 (10)	0.5205 (18)	0.4150 (10)	0.022 (5)*
C3	0.59636 (7)	0.54202 (14)	0.32816 (8)	0.0139 (3)
C4	0.64115 (7)	0.47686 (13)	0.27830 (7)	0.0130 (2)
H4	0.6605 (9)	0.5244 (16)	0.2376 (9)	0.014 (4)*
C5	0.65355 (7)	0.33956 (13)	0.28585 (7)	0.0113 (2)
C6	0.62149 (7)	0.27266 (13)	0.34495 (7)	0.0113 (2)
C7	0.52365 (8)	0.25329 (14)	0.44288 (8)	0.0131 (2)
H7A	0.5539 (10)	0.1879 (17)	0.4687 (9)	0.011 (4)*
H7B	0.4995 (10)	0.3097 (18)	0.4804 (9)	0.017 (4)*
C8	0.46578 (7)	0.17719 (14)	0.39939 (7)	0.0118 (2)
C9	0.47238 (8)	0.03988 (14)	0.38663 (8)	0.0148 (3)
H9	0.5125 (10)	-0.0059 (17)	0.4081 (9)	0.018 (4)*
C10	0.42317 (8)	-0.02671 (15)	0.34115 (8)	0.0157 (3)
H10	0.4300 (10)	-0.116 (2)	0.3325 (10)	0.019 (5)*
C11	0.36687 (8)	0.04353 (14)	0.30659 (8)	0.0141 (3)
H11	0.3354 (10)	0.0006 (18)	0.2722 (10)	0.020 (4)*
C12	0.35870 (7)	0.18099 (14)	0.31759 (7)	0.0122 (2)
C13	0.40748 (7)	0.24448 (13)	0.36548 (7)	0.0112 (2)
C14	0.69566 (7)	0.26270 (14)	0.22740 (8)	0.0126 (2)
H14A	0.7316 (10)	0.2045 (18)	0.2481 (10)	0.019 (5)*
C15	0.70695 (8)	0.12828 (14)	0.39858 (8)	0.0139 (3)
H15A	0.7029 (9)	0.1811 (17)	0.4442 (9)	0.012 (4)*
H15B	0.7467 (10)	0.1659 (17)	0.3699 (9)	0.014 (4)*

C16	0.72114 (8)	-0.01789 (14)	0.41520 (8)	0.0136 (3)
H16A	0.7153 (9)	-0.0676 (17)	0.3706 (10)	0.015 (4)*
H16B	0.7734 (11)	-0.0273 (18)	0.4308 (10)	0.022 (5)*
C17	0.67134 (9)	-0.07477 (16)	0.47447 (8)	0.0182 (3)
H17A	0.6817 (11)	-0.169 (2)	0.4837 (10)	0.027 (5)*
H17B	0.6797 (12)	-0.027 (2)	0.5232 (12)	0.037 (6)*
H17C	0.6186 (11)	-0.0630 (19)	0.4634 (10)	0.027 (5)*
C18	0.35282 (8)	0.42342 (14)	0.43170 (8)	0.0148 (3)
H18A	0.3726 (10)	0.4016 (17)	0.4800 (10)	0.016 (4)*
H18B	0.3044 (10)	0.3780 (17)	0.4257 (9)	0.016 (4)*
C19	0.34403 (8)	0.56881 (15)	0.42539 (8)	0.0167 (3)
C20	0.33838 (9)	0.68613 (16)	0.41828 (9)	0.0227 (3)
H14B	0.7229 (11)	0.324 (2)	0.1945 (11)	0.034*
H20	0.3365 (13)	0.776 (2)	0.4114 (12)	0.041 (6)*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Br1	0.02093 (8)	0.00958 (7)	0.02800 (9)	0.00170 (5)	-0.00372 (6)	-0.00016 (5)
O1	0.0104 (4)	0.0103 (4)	0.0157 (5)	0.0006 (3)	-0.0024 (4)	0.0012 (4)
O2	0.0125 (4)	0.0102 (4)	0.0142 (4)	0.0004 (3)	0.0032 (4)	-0.0016 (3)
C1	0.0094 (6)	0.0146 (6)	0.0124 (6)	-0.0005 (5)	-0.0023 (4)	-0.0006 (5)
C2	0.0112 (5)	0.0140 (6)	0.0146 (6)	0.0003 (5)	-0.0015 (5)	-0.0035 (5)
C3	0.0133 (6)	0.0098 (6)	0.0185 (7)	-0.0008 (4)	-0.0052 (5)	-0.0012 (5)
C4	0.0128 (6)	0.0124 (6)	0.0136 (6)	-0.0020 (5)	-0.0024 (5)	0.0014 (5)
C5	0.0092 (5)	0.0127 (6)	0.0121 (6)	-0.0005 (4)	-0.0021 (4)	-0.0008 (5)
C6	0.0099 (5)	0.0104 (6)	0.0136 (6)	-0.0005 (5)	-0.0027 (5)	0.0002 (5)
C7	0.0119 (6)	0.0148 (6)	0.0125 (6)	0.0001 (5)	0.0004 (5)	0.0011 (5)
C8	0.0107 (5)	0.0140 (6)	0.0107 (6)	-0.0004 (5)	0.0025 (5)	0.0007 (5)
C9	0.0131 (6)	0.0146 (6)	0.0167 (6)	0.0023 (5)	0.0017 (5)	0.0030 (5)
C10	0.0166 (6)	0.0115 (6)	0.0188 (7)	0.0002 (5)	0.0041 (5)	0.0006 (5)
C11	0.0136 (6)	0.0135 (6)	0.0152 (6)	-0.0015 (5)	0.0007 (5)	-0.0004 (5)
C12	0.0113 (6)	0.0129 (6)	0.0125 (6)	-0.0006 (5)	0.0020 (5)	0.0015 (5)
C13	0.0115 (6)	0.0111 (6)	0.0111 (6)	-0.0005 (4)	0.0033 (4)	0.0007 (4)
C14	0.0098 (6)	0.0143 (6)	0.0138 (6)	0.0007 (5)	-0.0002 (5)	0.0004 (5)
C15	0.0115 (6)	0.0144 (6)	0.0157 (6)	0.0003 (5)	-0.0028 (5)	0.0018 (5)
C16	0.0124 (6)	0.0137 (6)	0.0148 (6)	0.0028 (5)	0.0017 (5)	0.0030 (5)
C17	0.0169 (7)	0.0198 (7)	0.0181 (7)	0.0017 (6)	0.0015 (5)	0.0065 (6)
C18	0.0165 (6)	0.0138 (6)	0.0141 (6)	0.0004 (5)	0.0044 (5)	-0.0019 (5)
C19	0.0151 (6)	0.0194 (7)	0.0156 (6)	0.0006 (5)	0.0029 (5)	-0.0023 (5)
C20	0.0268 (8)	0.0173 (7)	0.0240 (8)	0.0014 (6)	0.0063 (6)	-0.0012 (6)

Geometric parameters (Å, °)

Br1—C3	1.9002 (14)	C10—H10	0.91 (2)
O1—C6	1.3872 (16)	C10—C11	1.390 (2)
O1—C15	1.4513 (16)	C11—H11	0.950 (18)
O2—C13	1.3923 (15)	C11—C12	1.3949 (19)

O2—C18	1.4325 (16)	C12—C13	1.3966 (19)
C1—C2	1.3957 (19)	C12—C14 ⁱ	1.5209 (19)
C1—C6	1.3982 (18)	C14—H14A	0.952 (18)
C1—C7	1.5176 (19)	C14—H14B	0.99 (2)
C2—H2	0.961 (18)	C15—H15A	0.990 (17)
C2—C3	1.387 (2)	C15—H15B	0.967 (17)
C3—C4	1.3833 (19)	C15—C16	1.5126 (19)
C4—H4	0.950 (17)	C16—H16A	0.962 (18)
C4—C5	1.3959 (18)	C16—H16B	0.992 (19)
C5—C6	1.3971 (19)	C16—C17	1.520 (2)
C5—C14	1.5211 (19)	C17—H17A	0.97 (2)
C7—H7A	0.974 (17)	C17—H17B	1.02 (2)
C7—H7B	0.990 (18)	C17—H17C	0.98 (2)
C7—C8	1.5197 (19)	C18—H18A	0.978 (17)
C8—C9	1.3957 (19)	C18—H18B	0.993 (18)
C8—C13	1.3971 (18)	C18—C19	1.465 (2)
C9—H9	0.944 (18)	C19—C20	1.183 (2)
C9—C10	1.389 (2)	C20—H20	0.90 (2)
C6—O1—C15	110.46 (10)	C11—C12—C13	118.02 (12)
C13—O2—C18	114.41 (10)	C11—C12—C14 ⁱ	121.23 (12)
C2—C1—C6	118.46 (12)	C13—C12—C14 ⁱ	120.38 (12)
C2—C1—C7	121.14 (12)	O2—C13—C8	118.64 (12)
C6—C1—C7	120.12 (12)	O2—C13—C12	118.50 (12)
C1—C2—H2	120.6 (11)	C12—C13—C8	122.59 (12)
C3—C2—C1	119.48 (13)	C5—C14—H14A	111.9 (11)
C3—C2—H2	119.9 (11)	C5—C14—H14B	111.3 (13)
C2—C3—Br1	119.14 (10)	C12 ⁱ —C14—C5	109.01 (11)
C4—C3—Br1	119.07 (11)	C12 ⁱ —C14—H14A	109.3 (11)
C4—C3—C2	121.77 (13)	C12 ⁱ —C14—H14B	109.0 (12)
C3—C4—H4	119.9 (10)	H14A—C14—H14B	106.2 (16)
C3—C4—C5	119.42 (13)	O1—C15—H15A	109.4 (10)
C5—C4—H4	120.6 (10)	O1—C15—H15B	109.1 (10)
C4—C5—C6	118.62 (12)	O1—C15—C16	108.76 (11)
C4—C5—C14	120.45 (12)	H15A—C15—H15B	107.8 (14)
C6—C5—C14	120.73 (12)	C16—C15—H15A	110.9 (10)
O1—C6—C1	118.67 (12)	C16—C15—H15B	110.9 (10)
O1—C6—C5	119.70 (12)	C15—C16—H16A	108.0 (10)
C5—C6—C1	121.60 (12)	C15—C16—H16B	108.1 (10)
C1—C7—H7A	110.6 (10)	C15—C16—C17	113.74 (12)
C1—C7—H7B	111.9 (10)	H16A—C16—H16B	107.4 (14)
C1—C7—C8	109.25 (11)	C17—C16—H16A	110.3 (10)
H7A—C7—H7B	107.1 (14)	C17—C16—H16B	109.0 (10)
C8—C7—H7A	107.9 (10)	C16—C17—H17A	111.7 (11)
C8—C7—H7B	110.0 (10)	C16—C17—H17B	111.1 (12)
C9—C8—C7	121.29 (12)	C16—C17—H17C	112.6 (11)
C9—C8—C13	117.57 (12)	H17A—C17—H17B	105.8 (16)
C13—C8—C7	120.91 (12)	H17A—C17—H17C	109.8 (16)

C8—C9—H9	118.1 (11)	H17B—C17—H17C	105.5 (16)
C10—C9—C8	121.02 (13)	O2—C18—H18A	111.7 (10)
C10—C9—H9	120.8 (11)	O2—C18—H18B	109.8 (10)
C9—C10—H10	118.9 (12)	O2—C18—C19	106.97 (11)
C9—C10—C11	120.13 (13)	H18A—C18—H18B	108.7 (14)
C11—C10—H10	120.8 (12)	C19—C18—H18A	109.4 (10)
C10—C11—H11	120.9 (11)	C19—C18—H18B	110.3 (10)
C10—C11—C12	120.58 (13)	C20—C19—C18	177.81 (16)
C12—C11—H11	118.4 (11)	C19—C20—H20	176.8 (15)
Br1—C3—C4—C5	176.93 (10)	C7—C8—C9—C10	-173.85 (13)
O1—C15—C16—C17	-73.91 (15)	C7—C8—C13—O2	-2.26 (18)
C1—C2—C3—Br1	-177.17 (10)	C7—C8—C13—C12	171.66 (12)
C1—C2—C3—C4	4.4 (2)	C8—C9—C10—C11	1.0 (2)
C1—C7—C8—C9	105.00 (14)	C9—C8—C13—O2	-176.87 (12)
C1—C7—C8—C13	-69.41 (16)	C9—C8—C13—C12	-2.95 (19)
C2—C1—C6—O1	173.62 (12)	C9—C10—C11—C12	-0.6 (2)
C2—C1—C6—C5	-8.25 (19)	C10—C11—C12—C13	-1.5 (2)
C2—C1—C7—C8	101.52 (14)	C10—C11—C12—C14 ⁱ	171.60 (13)
C2—C3—C4—C5	-4.7 (2)	C11—C12—C13—O2	177.27 (11)
C3—C4—C5—C6	-1.51 (19)	C11—C12—C13—C8	3.34 (19)
C3—C4—C5—C14	173.39 (12)	C13—O2—C18—C19	-170.66 (11)
C4—C5—C6—O1	-173.87 (11)	C13—C8—C9—C10	0.7 (2)
C4—C5—C6—C1	8.02 (19)	C14—C5—C6—O1	11.25 (19)
C4—C5—C14—C12 ⁱ	-104.49 (14)	C14—C5—C6—C1	-166.87 (12)
C6—O1—C15—C16	176.59 (11)	C14 ⁱ —C12—C13—O2	4.09 (18)
C6—C1—C2—C3	1.98 (19)	C14 ⁱ —C12—C13—C8	-169.84 (12)
C6—C1—C7—C8	-72.24 (15)	C15—O1—C6—C1	-98.40 (14)
C6—C5—C14—C12 ⁱ	70.31 (16)	C15—O1—C6—C5	83.44 (15)
C7—C1—C2—C3	-171.87 (12)	C18—O2—C13—C8	-96.01 (14)
C7—C1—C6—O1	-12.46 (18)	C18—O2—C13—C12	89.82 (14)
C7—C1—C6—C5	165.67 (12)		

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

25,27-Bis(2-azidoethoxy)-5,17-dibromo-26,28-dihydroxycalix[4]arene (3)

Crystal data

$C_{32}H_{28}Br_2N_6O_4$

$M_r = 720.42$

Trigonal, $R\bar{3}$

$a = 36.3261$ (7) Å

$c = 12.1054$ (4) Å

$V = 13834.0$ (7) Å³

$Z = 18$

$F(000) = 6552$

$D_x = 1.557$ Mg m⁻³

Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 9927 reflections

$\theta = 2.2$ – 28.3°

$\mu = 2.69$ mm⁻¹

$T = 100$ K

Block, colourless

$0.37 \times 0.13 \times 0.1$ mm

Data collection

Bruker D8 Venture
diffractometer

Radiation source: microfocus sealed X-ray tube,
Incoatec I μ S microsource

Focusing mirrors monochromator

Detector resolution: 10.4 pixels mm⁻¹

ω -scan

Absorption correction: multi-scan
(SADABS; Krause *et al.*, 2015)

$$T_{\min} = 0.516, T_{\max} = 0.746$$

45251 measured reflections

7804 independent reflections

6043 reflections with $I > 2\sigma(I)$

$$R_{\text{int}} = 0.047$$

$$\theta_{\max} = 28.5^\circ, \theta_{\min} = 1.8^\circ$$

$$h = -47 \rightarrow 48$$

$$k = -48 \rightarrow 48$$

$$l = -16 \rightarrow 16$$

Refinement

Refinement on F^2

Least-squares matrix: full

$$R[F^2 > 2\sigma(F^2)] = 0.040$$

$$wR(F^2) = 0.097$$

$$S = 1.03$$

7804 reflections

399 parameters

24 restraints

Hydrogen site location: inferred from
neighbouring sites

H-atom parameters constrained

$$w = 1/[\sigma^2(F_o^2) + (0.0383P)^2 + 55.0341P]$$

$$\text{where } P = (F_o^2 + 2F_c^2)/3$$

$$(\Delta/\sigma)_{\max} = 0.003$$

$$\Delta\rho_{\max} = 1.30 \text{ e } \text{\AA}^{-3}$$

$$\Delta\rho_{\min} = -1.12 \text{ e } \text{\AA}^{-3}$$

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Br2	0.77808 (2)	0.64422 (2)	0.11845 (2)	0.02592 (8)
Br1	0.94747 (2)	0.64087 (2)	1.04746 (3)	0.03614 (9)
O4	0.73344 (6)	0.53322 (6)	0.69360 (15)	0.0235 (4)
O3	0.76702 (7)	0.53195 (7)	0.49646 (16)	0.0304 (5)
H3	0.754079	0.534255	0.551158	0.046*
O1	0.81215 (6)	0.53626 (7)	0.71561 (16)	0.0296 (4)
H1	0.821251	0.526224	0.667258	0.044*
O2	0.82909 (7)	0.50491 (6)	0.52611 (17)	0.0317 (5)
C16	0.75008 (8)	0.60698 (9)	0.3311 (2)	0.0237 (5)
H16	0.735357	0.622450	0.332302	0.028*
C15	0.77434 (8)	0.60962 (9)	0.2407 (2)	0.0233 (5)
C3	0.90557 (9)	0.61047 (9)	0.9377 (2)	0.0260 (6)
C2	0.86500 (9)	0.60483 (9)	0.9485 (2)	0.0241 (5)
H2	0.858609	0.617607	1.008329	0.029*
C24	0.78870 (8)	0.57243 (9)	0.8817 (2)	0.0231 (5)
H24A	0.784545	0.580534	0.956822	0.028*
H24B	0.768569	0.541658	0.872265	0.028*
C10	0.89056 (9)	0.60072 (9)	0.3603 (2)	0.0274 (6)
H10	0.889258	0.612151	0.290757	0.033*
C20	0.76455 (9)	0.64427 (10)	0.6366 (2)	0.0296 (6)
H20	0.760226	0.660610	0.582331	0.036*

C17	0.74717 (8)	0.58147 (9)	0.4209 (2)	0.0241 (5)
C11	0.85771 (9)	0.56095 (9)	0.3911 (2)	0.0255 (6)
C14	0.79580 (8)	0.58721 (9)	0.2352 (2)	0.0238 (5)
H14	0.812203	0.589504	0.171789	0.029*
C19	0.74568 (9)	0.60024 (9)	0.6231 (2)	0.0257 (6)
C25	0.84464 (9)	0.56262 (9)	0.7832 (2)	0.0248 (6)
C28	0.75217 (8)	0.57733 (9)	0.7062 (2)	0.0226 (5)
C13	0.79333 (8)	0.56136 (9)	0.3226 (2)	0.0241 (5)
C8	0.92731 (9)	0.60764 (10)	0.5302 (2)	0.0308 (6)
H8	0.950790	0.624029	0.577501	0.037*
C1	0.83381 (9)	0.58053 (9)	0.8717 (2)	0.0231 (5)
C5	0.88617 (9)	0.56989 (9)	0.7704 (2)	0.0277 (6)
C23	0.77852 (8)	0.59706 (9)	0.7970 (2)	0.0227 (5)
C22	0.79695 (9)	0.64103 (9)	0.8067 (2)	0.0274 (6)
H22	0.814878	0.655309	0.867784	0.033*
C21	0.78926 (10)	0.66417 (10)	0.7275 (2)	0.0304 (6)
H21	0.801203	0.693985	0.736316	0.037*
C7	0.89577 (9)	0.56776 (10)	0.5635 (2)	0.0277 (6)
C4	0.91627 (9)	0.59369 (10)	0.8493 (2)	0.0296 (6)
H4	0.944407	0.598510	0.842644	0.036*
C26	0.86166 (9)	0.54477 (9)	0.4921 (2)	0.0261 (6)
C27	0.76893 (9)	0.55853 (9)	0.4151 (2)	0.0248 (6)
C18	0.72006 (9)	0.57839 (10)	0.5199 (2)	0.0287 (6)
H18A	0.700519	0.548016	0.536836	0.034*
H18B	0.702496	0.591249	0.500219	0.034*
C31	0.69060 (9)	0.50925 (10)	0.7339 (2)	0.0309 (6)
H31A	0.674011	0.522648	0.709611	0.037*
H31B	0.690578	0.508623	0.815710	0.037*
C9	0.92504 (9)	0.62399 (10)	0.4281 (3)	0.0316 (6)
H9	0.947183	0.651128	0.405307	0.038*
N4	0.66469 (11)	0.46548 (11)	0.5687 (3)	0.0530 (8)
C6	0.89773 (11)	0.55028 (11)	0.6759 (2)	0.0337 (7)
H6A	0.878111	0.519168	0.676259	0.040*
H6B	0.926863	0.555358	0.687975	0.040*
C12	0.81799 (9)	0.53781 (10)	0.3211 (2)	0.0293 (6)
H12A	0.799872	0.508657	0.350041	0.035*
H12B	0.825950	0.535615	0.244215	0.035*
C32	0.67100 (10)	0.46485 (11)	0.6891 (3)	0.0393 (7)
H32A	0.689825	0.453040	0.704496	0.047*
H32B	0.643333	0.446505	0.725666	0.047*
C29	0.83526 (12)	0.47048 (10)	0.4902 (3)	0.0410 (8)
H29A	0.860714	0.472574	0.526160	0.049*
H29B	0.839456	0.471768	0.409152	0.049*
N5	0.68006 (13)	0.44967 (14)	0.5103 (3)	0.0736 (11)
C30	0.79672 (14)	0.42988 (11)	0.5213 (4)	0.0551 (10)
H30A	0.797717	0.405718	0.486638	0.066*
H30B	0.770974	0.429853	0.494378	0.066*
N6	0.69206 (17)	0.43548 (18)	0.4454 (4)	0.1068 (16)

N1	0.79469 (12)	0.42496 (12)	0.6448 (3)	0.0627 (10)
N2	0.76567 (14)	0.42481 (14)	0.6888 (3)	0.0696 (10)
N3	0.74014 (17)	0.42453 (19)	0.7425 (4)	0.0991 (13)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Br2	0.02212 (13)	0.02979 (15)	0.02155 (13)	0.00975 (11)	-0.00145 (10)	0.00350 (11)
Br1	0.02894 (16)	0.03163 (16)	0.04687 (19)	0.01439 (13)	-0.00821 (13)	-0.00860 (13)
O4	0.0183 (9)	0.0272 (10)	0.0253 (9)	0.0116 (8)	0.0057 (7)	0.0035 (8)
O3	0.0372 (12)	0.0398 (12)	0.0249 (10)	0.0273 (10)	0.0095 (9)	0.0086 (9)
O1	0.0292 (10)	0.0423 (12)	0.0267 (10)	0.0249 (10)	-0.0010 (8)	-0.0068 (9)
O2	0.0373 (11)	0.0288 (11)	0.0378 (12)	0.0233 (10)	0.0125 (9)	0.0051 (9)
C16	0.0219 (13)	0.0267 (14)	0.0244 (13)	0.0135 (11)	-0.0011 (10)	0.0006 (11)
C15	0.0197 (12)	0.0256 (13)	0.0197 (12)	0.0077 (11)	-0.0018 (10)	0.0023 (10)
C3	0.0247 (14)	0.0212 (13)	0.0298 (14)	0.0098 (11)	-0.0020 (11)	0.0003 (11)
C2	0.0282 (14)	0.0241 (13)	0.0225 (13)	0.0150 (12)	0.0035 (11)	0.0017 (10)
C24	0.0244 (13)	0.0294 (14)	0.0189 (12)	0.0160 (12)	0.0042 (10)	0.0027 (10)
C10	0.0304 (15)	0.0353 (15)	0.0268 (14)	0.0241 (13)	0.0082 (11)	0.0067 (12)
C20	0.0309 (15)	0.0396 (16)	0.0299 (15)	0.0263 (14)	0.0116 (12)	0.0124 (13)
C17	0.0216 (13)	0.0302 (14)	0.0225 (13)	0.0144 (11)	0.0015 (10)	0.0029 (11)
C11	0.0276 (14)	0.0314 (14)	0.0276 (14)	0.0223 (12)	0.0028 (11)	-0.0030 (11)
C14	0.0196 (12)	0.0277 (14)	0.0208 (12)	0.0093 (11)	0.0007 (10)	-0.0030 (11)
C19	0.0247 (13)	0.0369 (15)	0.0236 (13)	0.0215 (12)	0.0088 (11)	0.0069 (11)
C25	0.0297 (14)	0.0289 (14)	0.0213 (13)	0.0189 (12)	0.0016 (11)	0.0031 (11)
C28	0.0214 (12)	0.0284 (14)	0.0236 (13)	0.0167 (11)	0.0084 (10)	0.0041 (11)
C13	0.0224 (13)	0.0267 (14)	0.0240 (13)	0.0128 (11)	-0.0013 (10)	-0.0031 (11)
C8	0.0274 (15)	0.0386 (17)	0.0346 (16)	0.0227 (14)	-0.0008 (12)	-0.0072 (13)
C1	0.0246 (13)	0.0256 (13)	0.0238 (13)	0.0161 (11)	0.0054 (11)	0.0046 (11)
C5	0.0356 (16)	0.0351 (15)	0.0246 (13)	0.0268 (13)	0.0064 (12)	0.0052 (12)
C23	0.0223 (13)	0.0302 (14)	0.0214 (12)	0.0174 (11)	0.0077 (10)	0.0045 (11)
C22	0.0284 (14)	0.0332 (15)	0.0257 (14)	0.0192 (13)	0.0083 (11)	0.0015 (11)
C21	0.0341 (16)	0.0288 (15)	0.0352 (16)	0.0208 (13)	0.0124 (13)	0.0047 (12)
C7	0.0306 (15)	0.0393 (16)	0.0278 (14)	0.0283 (14)	0.0034 (11)	-0.0011 (12)
C4	0.0257 (14)	0.0385 (16)	0.0307 (15)	0.0205 (13)	0.0059 (12)	0.0066 (13)
C26	0.0299 (14)	0.0278 (14)	0.0292 (14)	0.0209 (12)	0.0084 (11)	0.0024 (11)
C27	0.0229 (13)	0.0281 (14)	0.0244 (13)	0.0134 (11)	0.0006 (10)	0.0033 (11)
C18	0.0239 (14)	0.0434 (17)	0.0262 (14)	0.0224 (13)	0.0051 (11)	0.0097 (12)
C31	0.0204 (13)	0.0369 (16)	0.0323 (15)	0.0118 (12)	0.0079 (11)	0.0106 (13)
C9	0.0260 (14)	0.0332 (16)	0.0408 (17)	0.0188 (13)	0.0081 (13)	0.0022 (13)
N4	0.0470 (18)	0.0516 (19)	0.0449 (18)	0.0130 (15)	-0.0156 (15)	-0.0026 (15)
C6	0.0432 (18)	0.0516 (19)	0.0262 (15)	0.0386 (16)	0.0029 (13)	0.0018 (13)
C12	0.0338 (15)	0.0337 (15)	0.0267 (14)	0.0215 (13)	0.0005 (12)	-0.0049 (12)
C32	0.0264 (15)	0.0382 (18)	0.0444 (19)	0.0094 (14)	-0.0015 (14)	0.0092 (15)
C29	0.055 (2)	0.0330 (17)	0.0484 (19)	0.0324 (17)	0.0147 (16)	0.0051 (14)
N5	0.066 (2)	0.071 (2)	0.059 (2)	0.0148 (19)	-0.0020 (19)	-0.0098 (19)
C30	0.067 (3)	0.0323 (18)	0.072 (3)	0.0296 (19)	0.008 (2)	0.0039 (18)
N6	0.103 (3)	0.106 (3)	0.080 (3)	0.029 (3)	0.016 (3)	-0.020 (3)

N1	0.066 (2)	0.063 (2)	0.074 (2)	0.0436 (19)	0.0163 (19)	0.0304 (19)
N2	0.075 (2)	0.096 (3)	0.063 (2)	0.063 (2)	-0.0062 (19)	-0.004 (2)
N3	0.098 (3)	0.151 (4)	0.074 (3)	0.082 (3)	-0.008 (2)	-0.011 (3)

Geometric parameters (Å, °)

Br2—C15	1.902 (3)	C28—C23	1.397 (4)
Br1—C3	1.903 (3)	C13—C27	1.400 (4)
O4—C28	1.401 (3)	C13—C12	1.517 (4)
O4—C31	1.436 (3)	C8—H8	0.9500
O3—H3	0.8400	C8—C7	1.383 (4)
O3—C27	1.356 (3)	C8—C9	1.391 (4)
O1—H1	0.8400	C5—C4	1.382 (4)
O1—C25	1.360 (3)	C5—C6	1.514 (4)
O2—C26	1.397 (3)	C23—C22	1.394 (4)
O2—C29	1.444 (3)	C22—H22	0.9500
C16—H16	0.9500	C22—C21	1.392 (4)
C16—C15	1.377 (4)	C21—H21	0.9500
C16—C17	1.399 (4)	C7—C26	1.394 (4)
C15—C14	1.382 (4)	C7—C6	1.519 (4)
C3—C2	1.389 (4)	C4—H4	0.9500
C3—C4	1.380 (4)	C18—H18A	0.9900
C2—H2	0.9500	C18—H18B	0.9900
C2—C1	1.388 (4)	C31—H31A	0.9900
C24—H24A	0.9900	C31—H31B	0.9900
C24—H24B	0.9900	C31—C32	1.501 (5)
C24—C1	1.518 (4)	C9—H9	0.9500
C24—C23	1.523 (4)	N4—C32	1.477 (4)
C10—H10	0.9500	N4—N5	1.209 (5)
C10—C11	1.388 (4)	C6—H6A	0.9900
C10—C9	1.378 (4)	C6—H6B	0.9900
C20—H20	0.9500	C12—H12A	0.9900
C20—C19	1.400 (4)	C12—H12B	0.9900
C20—C21	1.374 (4)	C32—H32A	0.9900
C17—C27	1.408 (4)	C32—H32B	0.9900
C17—C18	1.519 (4)	C29—H29A	0.9900
C11—C26	1.394 (4)	C29—H29B	0.9900
C11—C12	1.515 (4)	C29—C30	1.488 (5)
C14—H14	0.9500	N5—N6	1.139 (6)
C14—C13	1.387 (4)	C30—H30A	0.9900
C19—C28	1.399 (4)	C30—H30B	0.9900
C19—C18	1.522 (4)	C30—N1	1.502 (5)
C25—C1	1.408 (4)	N1—N2	1.179 (5)
C25—C5	1.404 (4)	N2—N3	1.128 (6)
C28—O4—C31	114.6 (2)	C20—C21—C22	120.6 (3)
C27—O3—H3	109.5	C20—C21—H21	119.7
C25—O1—H1	109.5	C22—C21—H21	119.7

C26—O2—C29	113.0 (2)	C8—C7—C26	118.0 (3)
C15—C16—H16	120.1	C8—C7—C6	120.8 (3)
C15—C16—C17	119.8 (2)	C26—C7—C6	121.2 (3)
C17—C16—H16	120.1	C3—C4—C5	120.2 (3)
C16—C15—Br2	119.7 (2)	C3—C4—H4	119.9
C16—C15—C14	121.8 (2)	C5—C4—H4	119.9
C14—C15—Br2	118.5 (2)	C11—C26—O2	118.9 (3)
C2—C3—Br1	120.1 (2)	C7—C26—O2	118.5 (3)
C4—C3—Br1	118.5 (2)	C7—C26—C11	122.6 (3)
C4—C3—C2	121.3 (3)	O3—C27—C17	122.8 (2)
C3—C2—H2	120.0	O3—C27—C13	116.0 (2)
C1—C2—C3	120.0 (3)	C13—C27—C17	121.2 (2)
C1—C2—H2	120.0	C17—C18—C19	113.8 (2)
H24A—C24—H24B	107.8	C17—C18—H18A	108.8
C1—C24—H24A	109.0	C17—C18—H18B	108.8
C1—C24—H24B	109.0	C19—C18—H18A	108.8
C1—C24—C23	112.8 (2)	C19—C18—H18B	108.8
C23—C24—H24A	109.0	H18A—C18—H18B	107.7
C23—C24—H24B	109.0	O4—C31—H31A	110.0
C11—C10—H10	119.2	O4—C31—H31B	110.0
C9—C10—H10	119.2	O4—C31—C32	108.4 (2)
C9—C10—C11	121.5 (3)	H31A—C31—H31B	108.4
C19—C20—H20	119.6	C32—C31—H31A	110.0
C21—C20—H20	119.6	C32—C31—H31B	110.0
C21—C20—C19	120.8 (3)	C10—C9—C8	119.8 (3)
C16—C17—C27	118.3 (2)	C10—C9—H9	120.1
C16—C17—C18	119.6 (2)	C8—C9—H9	120.1
C27—C17—C18	122.1 (2)	N5—N4—C32	117.2 (4)
C10—C11—C26	117.3 (3)	C5—C6—C7	113.5 (2)
C10—C11—C12	120.8 (3)	C5—C6—H6A	108.9
C26—C11—C12	121.8 (3)	C5—C6—H6B	108.9
C15—C14—H14	120.1	C7—C6—H6A	108.9
C15—C14—C13	119.9 (2)	C7—C6—H6B	108.9
C13—C14—H14	120.1	H6A—C6—H6B	107.7
C20—C19—C18	120.9 (2)	C11—C12—C13	110.4 (2)
C28—C19—C20	117.6 (3)	C11—C12—H12A	109.6
C28—C19—C18	121.4 (3)	C11—C12—H12B	109.6
O1—C25—C1	116.0 (2)	C13—C12—H12A	109.6
O1—C25—C5	122.6 (2)	C13—C12—H12B	109.6
C5—C25—C1	121.3 (3)	H12A—C12—H12B	108.1
C19—C28—O4	118.2 (2)	C31—C32—H32A	109.8
C23—C28—O4	119.3 (2)	C31—C32—H32B	109.8
C23—C28—C19	122.4 (3)	N4—C32—C31	109.5 (3)
C14—C13—C27	118.9 (2)	N4—C32—H32A	109.8
C14—C13—C12	121.1 (2)	N4—C32—H32B	109.8
C27—C13—C12	119.9 (2)	H32A—C32—H32B	108.2
C7—C8—H8	119.6	O2—C29—H29A	110.1
C7—C8—C9	120.7 (3)	O2—C29—H29B	110.1

C9—C8—H8	119.6	O2—C29—C30	107.8 (3)
C2—C1—C24	121.9 (2)	H29A—C29—H29B	108.5
C2—C1—C25	118.4 (2)	C30—C29—H29A	110.1
C25—C1—C24	119.7 (2)	C30—C29—H29B	110.1
C25—C5—C6	121.3 (3)	N6—N5—N4	172.0 (6)
C4—C5—C25	118.8 (3)	C29—C30—H30A	109.7
C4—C5—C6	119.8 (3)	C29—C30—H30B	109.7
C28—C23—C24	122.3 (2)	C29—C30—N1	109.6 (3)
C22—C23—C24	119.8 (3)	H30A—C30—H30B	108.2
C22—C23—C28	117.9 (2)	N1—C30—H30A	109.7
C23—C22—H22	119.8	N1—C30—H30B	109.7
C21—C22—C23	120.5 (3)	N2—N1—C30	116.2 (4)
C21—C22—H22	119.8	N3—N2—N1	171.8 (5)
Br2—C15—C14—C13	-179.3 (2)	C8—C7—C26—O2	-178.4 (2)
Br1—C3—C2—C1	-176.2 (2)	C8—C7—C26—C11	-2.0 (4)
Br1—C3—C4—C5	177.3 (2)	C8—C7—C6—C5	75.5 (4)
O4—C28—C23—C24	1.7 (4)	C1—C24—C23—C28	106.9 (3)
O4—C28—C23—C22	179.5 (2)	C1—C24—C23—C22	-70.9 (3)
O4—C31—C32—N4	-69.0 (3)	C1—C25—C5—C4	2.7 (4)
O1—C25—C1—C2	174.8 (2)	C1—C25—C5—C6	179.4 (3)
O1—C25—C1—C24	-4.4 (4)	C5—C25—C1—C2	-1.7 (4)
O1—C25—C5—C4	-173.5 (3)	C5—C25—C1—C24	179.1 (2)
O1—C25—C5—C6	3.1 (4)	C23—C24—C1—C2	107.3 (3)
O2—C29—C30—N1	-69.2 (4)	C23—C24—C1—C25	-73.5 (3)
C16—C15—C14—C13	-0.3 (4)	C23—C22—C21—C20	-2.2 (4)
C16—C17—C27—O3	-177.9 (3)	C21—C20—C19—C28	1.3 (4)
C16—C17—C27—C13	0.7 (4)	C21—C20—C19—C18	-177.0 (2)
C16—C17—C18—C19	-109.8 (3)	C7—C8—C9—C10	1.5 (4)
C15—C16—C17—C27	-1.0 (4)	C4—C3—C2—C1	2.5 (4)
C15—C16—C17—C18	-179.5 (3)	C4—C5—C6—C7	-115.9 (3)
C15—C14—C13—C27	0.0 (4)	C26—O2—C29—C30	-174.4 (3)
C15—C14—C13—C12	-177.4 (2)	C26—C11—C12—C13	108.9 (3)
C3—C2—C1—C24	178.3 (2)	C26—C7—C6—C5	-102.6 (3)
C3—C2—C1—C25	-0.9 (4)	C27—C17—C18—C19	71.7 (4)
C2—C3—C4—C5	-1.5 (4)	C27—C13—C12—C11	-76.6 (3)
C24—C23—C22—C21	177.5 (2)	C18—C17—C27—O3	0.6 (4)
C10—C11—C26—O2	179.7 (2)	C18—C17—C27—C13	179.2 (3)
C10—C11—C26—C7	3.3 (4)	C18—C19—C28—O4	-1.6 (4)
C10—C11—C12—C13	-66.7 (3)	C18—C19—C28—C23	174.4 (2)
C20—C19—C28—O4	-180.0 (2)	C31—O4—C28—C19	-86.8 (3)
C20—C19—C28—C23	-4.0 (4)	C31—O4—C28—C23	97.1 (3)
C20—C19—C18—C17	80.6 (3)	C9—C10—C11—C26	-2.2 (4)
C17—C16—C15—Br2	179.8 (2)	C9—C10—C11—C12	173.6 (2)
C17—C16—C15—C14	0.8 (4)	C9—C8—C7—C26	-0.5 (4)
C11—C10—C9—C8	-0.1 (4)	C9—C8—C7—C6	-178.6 (2)
C14—C13—C27—O3	178.5 (2)	C6—C5—C4—C3	-177.8 (3)
C14—C13—C27—C17	-0.2 (4)	C6—C7—C26—O2	-0.2 (4)

C14—C13—C12—C11	100.8 (3)	C6—C7—C26—C11	176.2 (2)
C19—C20—C21—C22	1.7 (4)	C12—C11—C26—O2	3.9 (4)
C19—C28—C23—C24	-174.3 (2)	C12—C11—C26—C7	-172.5 (2)
C19—C28—C23—C22	3.5 (4)	C12—C13—C27—O3	-4.0 (4)
C25—C5—C4—C3	-1.1 (4)	C12—C13—C27—C17	177.2 (3)
C25—C5—C6—C7	67.5 (4)	C29—O2—C26—C11	90.4 (3)
C28—O4—C31—C32	165.3 (2)	C29—O2—C26—C7	-93.0 (3)
C28—C19—C18—C17	-97.7 (3)	C29—C30—N1—N2	115.8 (4)
C28—C23—C22—C21	-0.4 (4)	N5—N4—C32—C31	125.4 (4)

Hydrogen-bond 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>
O3—H3...O4	0.84	1.87	2.691 (3)	164
O1—H1...O2	0.84	1.95	2.764 (3)	162