26,28-Diallyloxy-5,11,17,23-tetra-*tert*-butyl-25,27-bis(cyanomethoxy)calix[4]arene in the partial cone conformation

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The title compound, $C_{54}H_{66}N_2O_4$, crystallizes with two molecules in the asymmetric unit. Both adopt the typical partial cone conformation which was also found for 26,28-diallyloxy-5,17-di-*tert*-butyl-25,27-bis(cyanomethoxy)-11,23-dinitrocalix[4]arene [Danila, Böhmer & Bolte (2005). *Org. Biomol. Chem.* **3**, 3508–3513]. The crystal structure of the title compound in the 1,2-alternate conformation has been determined recently [Danila, Böhmer & Bolte (2005). *Org. Biomol. Chem.* **3**, 3508–3513].

Comment

Tetraethers of (*p*-substituted)calix[4]arenes may be fixed in one of the four possible conformations (cone, partial cone, 1,2- and 1,3-alternate) by alkylether residues larger than ethyl (Böhmer, 1995). Tetramethylethers, on the other hand, exist as a rapidly interconverting mixture of all four isomers, in which the partial cone conformation is usually preferred (Harada *et al.*, 1992; Blixt & Detellier, 1994). Residues like ethyl (Groenen *et al.*, 1991), cyanomethyl (Kang & Nam, 2000; Nam *et al.*, 2002) or propargyl (Xu *et al.*, 1996) are somewhat on the borderline and can (slowly) pass the annulus. 1,3-Dicyanomethyl ethers of calix[4]arenes exist in the cone conformation, due to their stabilization by intramolecular hydrogen bonds (Wolf *et al.*, 1999). Their exhaustive *O*-alkylation, here by allyl bromide, can lead to isomers in which the cyanomethoxy groups are situated on different sides of the mean plane defined by the four C atoms of the methylene bridges (Danila *et al.*, 2005).
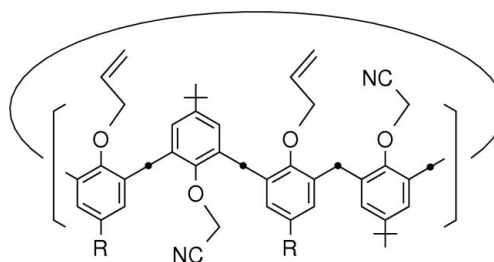
(I*a*) R = NO$_2$

(I*b*) R = C(CH$_3$)$_3$

We recently described the crystal structure of (I*a*), which assumes an unusually deformed partial cone conformation (Danila *et al.*, 2005). We now are able to present the structure of the partial cone conformation for the similar title compound, (I*b*), in which all four *p*-substituents are *tert*-butyl. The present isomer of (I*b*), assuming the partial cone
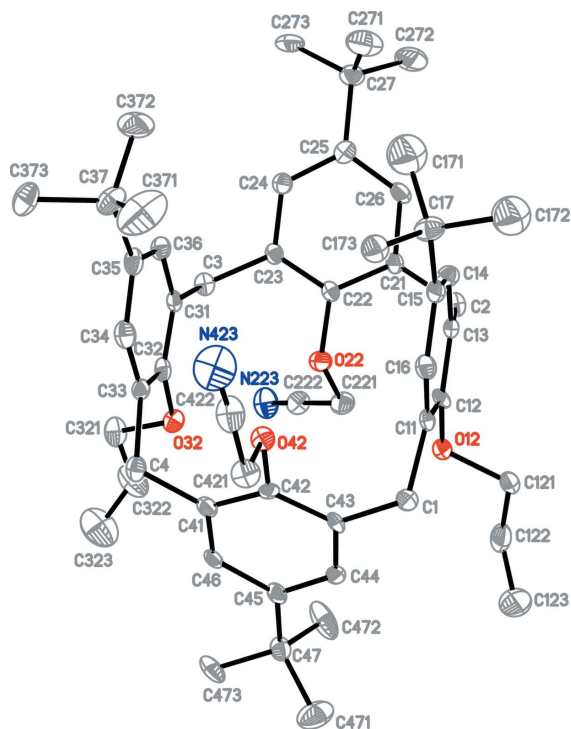
Figure 1
A perspective view of one of the independent molecules of (I*b*), with the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. H atoms have been omitted for clarity and the second molecule in the asymmetric unit compares well with the first one. There are only minor differences in the side chains. Atom numbers in molecule 2 are generated by adding 4, 40, or 400 to those of molecule 1.
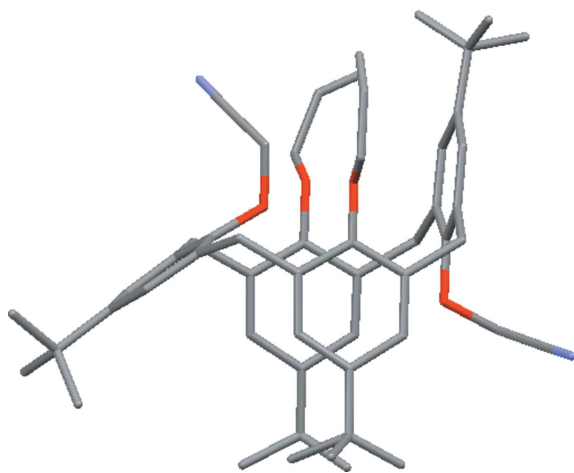
Figure 2
A view molecule 2 of (I*b*), showing the partial cone conformation.

conformation, differs by the *syn*-orientation of the allylether residues from the anti-isomer of (I*b*) (assuming the 1,2-alternate conformation), which has been described recently (Danila *et al.*, 2005).

As shown in Figs. 1 and 2 for one of the two crystallographically independent molecules of (I*b*), they assume a 'typical' partial cone conformation, in which three aromatic rings (*e.g.* 1, 2, 3) correspond to 3/4 of a pinched cone and three (*e.g.* 3, 4, 1) to 3/4 of a 1,3-alternate conformer. Typical geometric parameters are shown in Table 1 and compared with the similar compound, (I*a*), in which the allylether units are substituted in the *p*-position by nitro- instead of *tert*-butyl groups. The main difference is that the cyanomethoxy phenol unit opposite to the inverted one is much more deeply embedded in the cavity in (I*a*) than in (I*b*). The angle with the reference plane (defined by the methylene C atoms) is only 10.9 (7)° for (I*a*), while it is 40.71 (10) and 36.55 (9)° for the two molecules of (I*b*), a value also sometimes found for a pinched cone conformation. The distances within the plane of the reference atoms C1···C4 are larger in (I*b*) [average 5.10 (1) and 5.11 (1) Å] than in (I*a*) [average 5.06 (2) Å], and the two diagonals, C1···C3 and C2···C4, are shorter in (I*a*) [7.15 (2) Å] than in (I*b*) [7.2 (1) and 7.23 (5) Å]. In general, however, all bond lengths, angles and torsion angles are in the expected ranges (Cambridge Structural Database, Version 5.27, updated May 2006; Allen, 2002).

The packing of the molecules of (I*b*) reveals double layers with slightly 'interlocking' *tert*-butyl groups of the inverted unit, and van der Waals contacts to the next double layer *via* the remaining three *tert*-butyl groups.

Experimental

Compound (I*b*) was obtained as described by Danila *et al.* (2005), by alkylation of 1,3-dicyanomethoxy-*tert*-butylcalix[4]arene (Wolf *et al.*, 1999) with allyl bromide, in 68% yield as a mixture of the cone and the partial cone isomers. Slow evaporation of a solution in chloroform–methanol (1:2) led to single crystals of suitable quality for X-ray analysis.

Crystal data

$C_{54}H_{66}N_2O_4$	$V = 4923.3$ (10) Å^3
$M_r = 807.09$	$Z = 4$
Triclinic, $P\bar{1}$	$D_x = 1.089$ Mg m^{-3}
$a = 11.1136$ (14) Å	Mo $K\alpha$ radiation
$b = 18.706$ (2) Å	$\mu = 0.07$ mm^{-1}
$c = 26.013$ (3) Å	$T = 173$ (2) K
$\alpha = 68.951$ (9)°	Block, colourless
$\beta = 79.257$ (9)°	$0.27 \times 0.25 \times 0.23$ mm
$\gamma = 79.858$ (9)°	

Data collection

Stoe IPDS II two-circle diffractometer	17396 independent reflections
ω scans	8660 reflections with $I > 2\sigma(I)$
Absorption correction: none	$R_{int} = 0.097$
26182 measured reflections	$\theta_{max} = 25.0°$

Refinement

Refinement on F^2	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.092$	$w = 1/[\sigma^2(F_o^2) + (0.071P)^2]$
$wR(F^2) = 0.193$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.26$	$(\Delta/\sigma)_{max} = 0.001$
17396 reflections	$\Delta\rho_{max} = 0.81$ e Å^{-3}
1085 parameters	$\Delta\rho_{min} = -0.58$ e Å^{-3}

Table 1
Comparison of geometric parameters of (I*a*) and (I*b*).

Atom numbers in molecule 2 of (I*b*) are generated by adding 4 or 40 to those of molecule 1 of (I*b*).

	Compound (I*a*)	Molecule 1 of (I*b*)	Molecule 2 of (I*b*)
Torsion angles (°)			
C12—C11—C1—C43	−70.8 (3)	−64.9 (3)	−63.4 (4)
C11—C1—C43—C42	−65.6 (3)	−62.0 (5)	−57.6 (5)
C22—C21—C2—C13	−46.1 (3)	−68.3 (3)	−67.5 (3)
C21—C2—C13—C12	114.9 (2)	111.3 (2)	110.3 (3)
C32—C31—C3—C23	−118.3 (3)	−113.1 (2)	−116.3 (3)
C31—C3—C23—C22	47.4 (3)	74.2 (3)	66.6 (3)
C42—C41—C4—C33	68.9 (3)	66.0 (5)	59.9 (4)
C41—C4—C33—C32	70.0 (3)	57.8 (3)	66.3 (3)
Distances in the reference plane C1–C4 (Å)			
C1···C2	5.060 (3)	5.102 (6)	5.111 (5)
C2···C3	5.079 (4)	5.104 (3)	5.110 (4)
C3···C4	5.060 (4)	5.085 (6)	5.095 (5)
C1···C4	5.028 (4)	5.116 (2)	5.124 (4)
C1···C3	7.162 (4)	7.115 (4)	7.191 (2)
C2···C4	7.133 (3)	7.312 (5)	7.262 (6)
Inclination of the aromatic units to the reference plane (°)			
C11–C16	81.5 (6)	89.64 (4)	83.15 (8)
C21–C26	169.1 (7)	139.29 (10)	143.45 (9)
C31–C36	100.1 (7)	95.36 (5)	90.80 (9)
C41–C46	95.1 (6)	93.58 (10)	95.43 (9)

H atoms were located in a difference electron-density map and subsequently refined with fixed individual displacement parameters [$U_{iso}(H) = 1.2U_{eq}(C)$ or $1.5U_{eq}(C_{methyl})$] using a riding model, with C—H distances ranging from 0.95 to 0.99 Å. Two C atoms of one pentoxy chain are disordered over two sites, with occupancy factors of 0.520 (6) and 0.480 (6). The bonds involving the disordered atoms were refined with a distance restraint of 1.54 (1) Å.

Data collection: *X-AREA* (Stoe & Cie, 2001); cell refinement: *X-AREA*; data reduction: *X-AREA*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *XP* in *SHELXTL-Plus* (Sheldrick, 1991) and *MERCURY* (Macrae *et al.*, 2006); software used to prepare material for publication: *SHELXL97* and *PLATON* (Spek, 2003).

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