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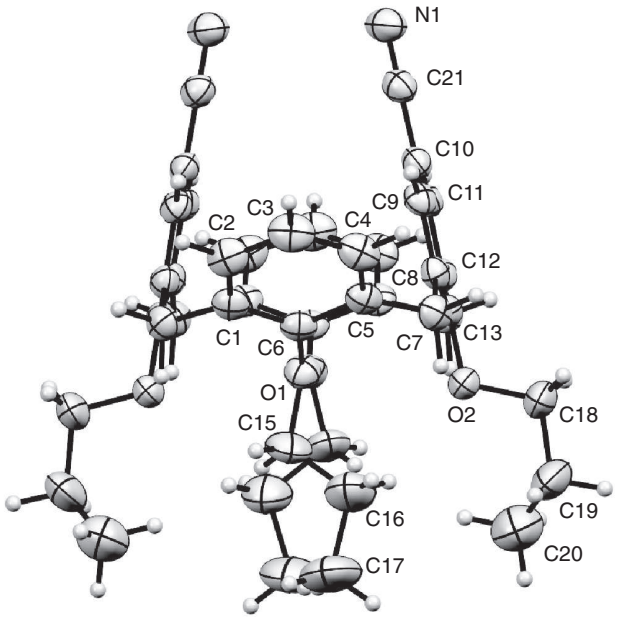
Crystal structure of 5,17-bis-cyano-25,26,27,28-tetrapropyloxy-calix[4]arene, $C_{42}H_{46}N_2O_4$



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Abstract

$C_{42}H_{46}N_2O_4$, orthorhombic, *Pcca* (No. 54), $a = 14.9100(5)$, $b = 17.2508(6)$, $c = 16.0857(6)$ Å, $V = 4137.4(3)$ Å^3, $Z = 4$, $R_{gt}(F) = 0.0710$, $wR_{ref}(F^2) = 0.2308$, $T = 173$ K.

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Tables 1 and 2 contain details of the measurement method and a list of the atoms including atomic coordinates and displacement parameters.

Table 1: Data collection and handling.

Crystal:	Colourless, Prism, size 0.50×0.45×0.40 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	0.66 cm^{-1}
Diffractometer, scan mode:	Bruker Apex II, φ and ω
$2\theta_{max}$, completeness:	58.078°, >99 %
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	35713, 5504, 0.0304
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 3893
$N(param)_{refined}$:	233
Programs:	CrysAlis [6], SIR−97 [7], SHELX [8], PLATON [9]

Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2).

Atom	x	y	z	U_{iso}*/U_{eq}
C1	0.13609(11)	0.81583(11)	0.43074(11)	0.0398(4)
C2	0.19732(13)	0.86541(12)	0.46900(13)	0.0496(5)
H2	0.1864	0.8826	0.5242	0.059*
C3	0.27366(13)	0.88986(13)	0.42795(15)	0.0542(5)
H3	0.3159	0.9220	0.4556	0.065*
C4	0.28852(12)	0.86742(12)	0.34604(14)	0.0488(5)
H4	0.3402	0.8856	0.3175	0.059*
C5	0.22802(11)	0.81817(11)	0.30498(12)	0.0399(4)
C6	0.15468(11)	0.79039(10)	0.35039(11)	0.0371(4)
C7	0.23495(11)	0.80088(12)	0.21339(12)	0.0425(4)
H7A	0.2298	0.7443	0.2041	0.051*
H7B	0.2941	0.8181	0.1923	0.051*
C8	−0.16047(10)	0.84285(10)	0.33337(10)	0.0358(4)
C9	−0.14853(11)	0.92183(10)	0.32185(11)	0.0379(4)
H9	−0.1886	0.9497	0.2871	0.046*
C10	−0.07803(11)	0.96065(10)	0.36095(11)	0.0372(4)
C11	−0.01741(11)	0.91992(10)	0.40990(11)	0.0377(4)
H11	0.0312	0.9466	0.4352	0.045*
C12	−0.02712(11)	0.84092(10)	0.42214(10)	0.0361(4)
C13	−0.10032(11)	0.80318(10)	0.38558(10)	0.0348(4)
C14	0.04579(12)	0.79722(11)	0.46952(11)	0.0418(4)
H14A	0.0455	0.8130	0.5287	0.050*
H14B	0.0344	0.7407	0.4667	0.050*
C15[a]	0.0989(4)	0.6618(3)	0.3350(3)	0.0738(11)
H15A[a]	0.1213	0.6590	0.3928	0.089*

Table 2 (continued)

Atom	x	y	z	U_{iso}*/U_{eq}
H15B[a]	0.0370	0.6411	0.3350	0.089*
C16[a]	0.1531(4)	0.6125(3)	0.2848(4)	0.0957(14)
H16A[a]	0.2171	0.6244	0.2948	0.115*
H16B[a]	0.1402	0.6227	0.2254	0.115*
C17[a]	0.1354(6)	0.5260(3)	0.3039(5)	0.132(3)
H17A[a]	0.1410	0.5170	0.3638	0.198*
H17B[a]	0.1793	0.4940	0.2742	0.198*
H17C[a]	0.0748	0.5121	0.2857	0.198*
C15B[b]	0.1260(10)	0.6666(7)	0.3046(8)	0.0738(11)
H15C[b]	0.1917	0.6661	0.3132	0.089*
H15D[b]	0.1139	0.6472	0.2478	0.089*
C16B[b]	0.0817(9)	0.6118(6)	0.3681(9)	0.0957(14)
H16C[b]	0.1060	0.6242	0.4239	0.115*
H16D[b]	0.0167	0.6232	0.3693	0.115*
C17B[b]	0.0933(15)	0.5275(8)	0.3537(14)	0.132(3)
H17D[b]	0.1568	0.5161	0.3436	0.198*
H17E[b]	0.0579	0.5117	0.3052	0.198*
H17F[b]	0.0728	0.4988	0.4028	0.198*
C18	−0.1640(2)	0.70562(14)	0.46915(18)	0.0706(8)
H18A	−0.2237	0.7306	0.4650	0.085*
H18B	−0.1341	0.7252	0.5199	0.085*
C19	−0.1749(3)	0.62031(18)	0.4749(3)	0.1046(13)
H19A[a]	−0.2081	0.6093	0.5269	0.126*
H19B[a]	−0.2141	0.6041	0.4284	0.126*
H19C[b]	−0.1176	0.6010	0.4980	0.126*
H19D[b]	−0.2204	0.6121	0.5189	0.126*
C20[a]	−0.0958(4)	0.5697(3)	0.4738(4)	0.1092(17)
H20A[a]	−0.0587	0.5821	0.4253	0.164*
H20B[a]	−0.1150	0.5155	0.4707	0.164*
H20C[a]	−0.0608	0.5778	0.5246	0.164*
C20B[b]	−0.1957(11)	0.5718(8)	0.4163(10)	0.1092(17)
H20D[b]	−0.2517	0.5883	0.3896	0.164*
H20E[b]	−0.2037	0.5199	0.4401	0.164*
H20F[b]	−0.1476	0.5705	0.3748	0.164*
C21	−0.06541(12)	1.04223(11)	0.34768(11)	0.0422(4)
O1	0.09512(8)	0.74173(8)	0.31115(9)	0.0442(3)
O2	−0.11140(8)	0.72482(7)	0.39753(8)	0.0419(3)
N1	−0.05521(13)	1.10738(11)	0.33756(12)	0.0550(5)

[a]Occupancy: 0.823(4); [b]Occupancy: 0.177(4).

Source of material

A suspension of 5,17-dibromo-25,26,27,28-tetrapropyloxy calix[4]arene (0.188 g, 0.25 mmol), $[Pd(OAc)_2]$ (0.006 g, 0.0025 mmol), 1,3-bis(diphenylphosphino)propane (0.021 g, 0.005 mmol) and $Zn(CN)_2$ (0.117 g, 1.00 mmol) in DMF (2.5 mL) was heated at 140°C under argon. After 72 h, the reaction mixture was cooled to room temperature and passed through a plot of silica gel. The solvent was evaporated and the solid residue was purified by column chromatography (CH_2Cl_2/petroleum ether, 1:1 v/v) to afford the title compound as a white solid, yield 0.131 g, 82 %. **^{1}H NMR** ($CDCl_3$, 400 MHz): $\delta = 6.83$ (s, 4H, arom. CH), 6.75 (s, 6H, arom. CH), 4.43 and 3.17 (AB spin system, 8H, ArCH_2Ar, $^2J = 13.6$ Hz), 3.87 (t, 4H, OCH_2, $^3J = 8.0$ Hz), 3.85 (t, 4H, OCH_2, $^3J = 7.2$ Hz), 1.95–1.85 (m, 8H, CH_2CH$_3$), 1.03 (t, 6H, CH$_2$CH_3, $^3J = 7.4$ Hz), 0.95 (t, 3H, CH$_2$CH_3, $^3J = 7.4$ Hz); **^{13}C NMR** ($CDCl_3$, 125 MHz): $\delta = 160.01$ (s, arom Cq—O), 156.59 (s, arom Cq—O), 136.27–105.71 (arom. *C*s), 119.06 (s, CN), 77.35 (s, OCH_2), 76.92 (s, OCH_2), 30.79 (s, ArCH$_2$Ar), 23.41 (*C*H$_2$CH$_3$), 23.18 (*C*H$_2$CH$_3$), 10.47 (CH$_2$*C*H$_3$), 10.18 (CH$_2$*C*H$_3$) ppm; **IR**: $\nu = 2223$ cm^{-1} (CN); elemental analysis calcd (%) for $C_{42}H_{46}O_4N_2$ ($Mr = 642.83$): C 78.47, H 7.21, N 4.36; found (%): C 78.52, H 7.18, N 4.41.

Experimental details

The structure was solved by direct methods using the program SIR-97 [7] and refined with SHELXL-2014/6 [8]. The Figure was drawn with CrysAlis software [6]. Carbon-bound H atoms were placed in calculated positions (C—H 0.95 Å for aromatic and C—H 0.99 Å for methylene groups) and were included in the refinement in the riding model approximation, with U_{iso}(H) set to 1.2U_{eq}(C). The H atoms of the methyl groups were allowed to rotate with a fixed angle around the C—C bond to best fit the experimental electron density (HFIX 137 in the SHELX program suite [9]), with U_{iso}(H) set to 1.5U_{eq}(C). The dataset was managed using the program SQUEEZE [9]. The residual electron density was assigned to half a molecule of the dichloromethane solvent [179/8 = 22 e$^-$ per asymmetric unit; half a molecule of CH_2Cl_2 would give 21e$^-$]. The propyl chains are disordered over two positions.

Discussion

Crystals of the title compound suitable for X-ray diffraction formed readily upon diffusion of methanol into a dichloromethane solution of the dicyano calixarene. In the solid state, the calix[4]arene cavity adopts a typical pinched cone conformation [1–3], with interplanar angles between opposite phenoxy rings of 21.2° and 76.2°, respectively. The separations between the aromatic *para*-carbon atoms of opposite phenolic rings are 4.26 and 9.97 Å, respectively. The ^{1}H NMR spectrum of the title compound is in keeping with a C_{2v}-symmetrical molecule. The diastereotopic ArCH_2Ar protons appear as a single AB pattern with a large AB separation (> 1 ppm), this being consistent with a calixarene unit in the cone conformation. The CN bond lengths (N(1)—C(21) 1.146(3) Å) lie in the range found for other cyano-substituted calixarenes [4, 5].

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