Crystal structure of 5,17-di-*t*-butyl-25,26,27,28-tetrahydroxy-11,23-(3-oxo-pentano)-calix[4]arene hydrate, $C_{41}H_{46}O_5 \cdot 0.29H_2O$

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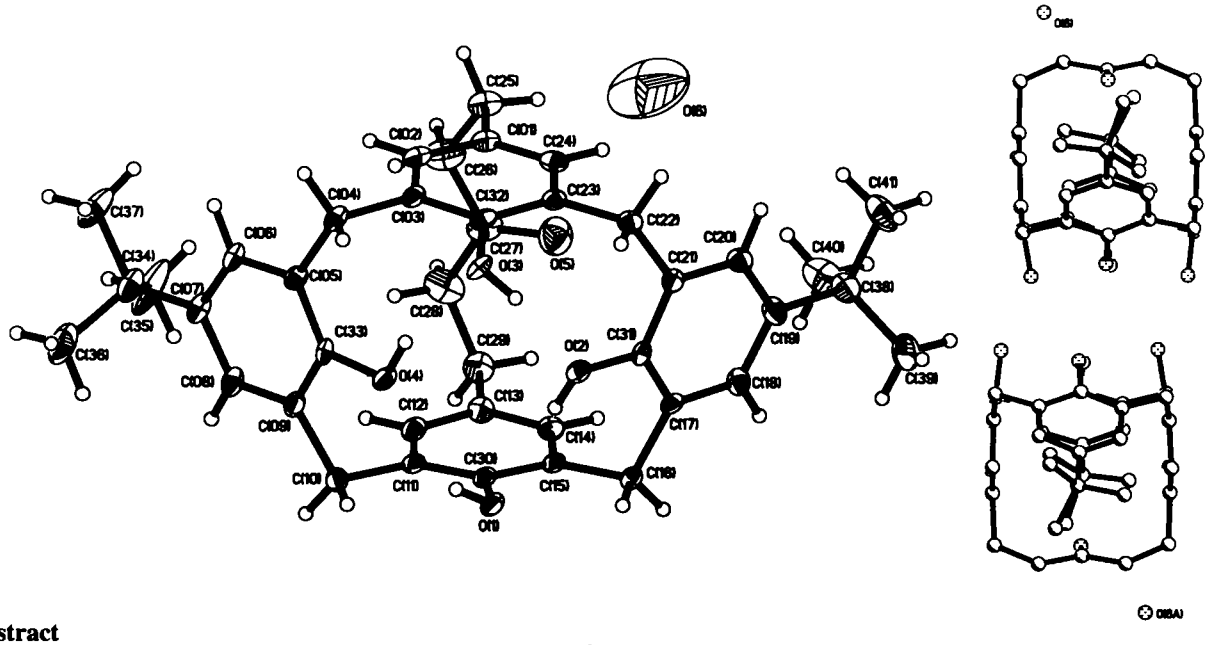

Abstract

$C_{41}H_{46.58}O_{5.29}$, monoclinic, $P12_1/n1$ (No. 14), $a = 13.350(3)$ Å, $b = 18.189(4)$ Å, $c = 14.842(3)$ Å, $\beta = 94.54(3)°$, $V = 3592.7$ Å^3, $Z = 4$, $R_{gt}(F) = 0.059$, $wR_{ref}(F^2) = 0.156$, $T = 293$ K.

Source of material

The compound was synthesized by condensation of 1,5-bis(4-hydroxy-phenyl)pentan-3-one with bisbromomethylated p-*t*-butylphenol in 15% yield [1] in analogy to other bridged calix[4]arenes [2]. Crystals were grown by slow evaporation of a CH_2Cl_2/hexane solution.

Experimental details

The average $I/\sigma(I)$ of the measured X-ray intensities is only 5.3. The C—H and O—H distances were fixed for refinement. The hydrogen atoms of the water molecule were not localized.

Discussion

Calix[4]arenes [3,4] normally assume the cone conformation, which is stabilized by a cyclic array of intramolecular hydrogen bonds. The cone-to-cone ring inversion, which is still possible, can be blocked by covalent connections of two opposite p-positions at the wide rim. The structural formula suggests, that the molecule could have a mirror plane through the two *t*-butyl and the carbonyl group, what is also the impression looking at figure to the left. The dihedral angles of the four phenyl groups C11/C30, C17/C31, C03/C32 and C05/C33 with the plane of the four methylene groups are 91.7°, 146.2°, 92.3° and 141.0°, respectively, while the plane of the carbonyl function (C26, C27, C28, O5) assumes an angle of 15.0° with that plane. These differences to the molecular mirror plane are significant. The four hydroxy groups seem to be connected by intramolecular hydrogen bonds. The O–O distances are 2.851 Å, 2.825 Å, 2.861 Å and 2.983 Å, respectively. The right figure, however, shows, that there could be formulated also intermolecular hydrogen bonds between O1 and O3 and between O3 and O4 with bond lengths of 2.851 Å and 2.849 Å, respectively. Intermolecular OH···OH hydrogen bonding is rare in calix[4]arenes, but was definitely found for an example with substituted methylene bridges [5]. The intramolecular plane of symmetry is again significantly spoiled. The left over maximum in the electron density map was interpreted as a water molecule. Its multiplicity is only 0.29(2). The smallest distance between adjacent water molecules is 2.675 Å and that one to O5 is 3.166 Å.

The average esd for C—C bonds is 0.007 Å, for C—O bonds 0.006 Å and for hydrogen bonds 0.004 Å. For C—H and O—H bonds the distances are fixed. The average esd of bond angles is 0.5° and that of torsion angles is also 0.5°. The average esd for dihedral angles between l.s. planes is 0.1°.

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Table 1. Data collection and handling.

Crystal:	colourless, needle, size 0.25 × 0.25 × 0.6 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	0.78 cm^{-1}
Diffractometer, scan mode:	Siemens R3m/V, ω
$2\theta_{max}$:	45°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	6325, 4702
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 1916
$N(param)_{refined}$:	430
Programs:	SHEXLTL-Plus [6], SHELXS-97 [7], SHELXL-97 [8]

Table 2. Atomic coordinates and displacement parameters (in $Å^2$).

Atom	Site	x	y	z	U_{iso}
H(02)	4e	–0.2808	0.2666	0.4486	0.08
H(041)	4e	–0.2950	0.3969	0.3767	0.08
H(042)	4e	–0.1995	0.4461	0.3934	0.08
H(06)	4e	–0.4138	0.3937	0.4877	0.08
H(08)	4e	–0.3337	0.4536	0.7465	0.08
H(101)	4e	–0.1629	0.4850	0.7951	0.08
H(102)	4e	–0.0941	0.5113	0.7212	0.08
H(12)	4e	–0.1810	0.3377	0.7941	0.08
H(14)	4e	0.0809	0.2277	0.7869	0.08
H(161)	4e	0.2416	0.3162	0.7757	0.08
H(162)	4e	0.2195	0.3828	0.7112	0.08
H(18)	4e	0.2935	0.2058	0.7081	0.08
H(20)	4e	0.2210	0.1610	0.4427	0.08
H(221)	4e	0.1178	0.2422	0.3515	0.08
H(222)	4e	0.1226	0.3254	0.3766	0.08
H(24)	4e	–0.0108	0.1663	0.4429	0.08
H(251)	4e	–0.1484	0.0981	0.4913	0.08
H(252)	4e	–0.2507	0.1188	0.4400	0.08
H(261)	4e	–0.2800	0.1010	0.5918	0.08
H(262)	4e	–0.2829	0.1852	0.5748	0.08
H(281)	4e	–0.2271	0.1340	0.7700	0.08
H(282)	4e	–0.2357	0.2154	0.7397	0.08
H(291)	4e	–0.1328	0.2042	0.8767	0.08
H(292)	4e	–0.0599	0.1621	0.8184	0.08
H(351)	4e	–0.4843	0.3061	0.6793	0.08
H(352)	4e	–0.4547	0.3595	0.7600	0.08
H(353)	4e	–0.5681	0.3417	0.7335	0.08
H(361)	4e	–0.6095	0.4752	0.7067	0.08
H(362)	4e	–0.4975	0.4887	0.7429	0.08
H(363)	4e	–0.5369	0.5181	0.6473	0.08
H(371)	4e	–0.5563	0.3495	0.5363	0.08
H(372)	4e	–0.6430	0.3921	0.5789	0.08
H(373)	4e	–0.5676	0.4346	0.5220	0.08
H(391)	4e	0.4702	0.1403	0.5998	0.08
H(392)	4e	0.4221	0.1352	0.6926	0.08
H(393)	4e	0.4644	0.0643	0.6490	0.08
H(401)	4e	0.2972	0.0016	0.6615	0.08
H(402)	4e	0.2560	0.0724	0.7059	0.08
H(403)	4e	0.1996	0.0397	0.6183	0.08
H(411)	4e	0.3749	0.0850	0.4633	0.08
H(412)	4e	0.3654	0.0095	0.5129	0.08
H(413)	4e	0.2685	0.0512	0.4745	0.08
H(1)	4e	0.0385	0.4833	0.6642	0.065
H(2)	4e	0.1068	0.3922	0.5893	0.065
H(3)	4e	0.0339	0.4090	0.4223	0.064
H(4)	4e	–0.0858	0.4496	0.5094	0.064

Table 3. Atomic coordinates and displacement parameters (in $Å^2$).

Atom	Site	Occ.	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(01)	4e		–0.1532(4)	0.2051(3)	0.4537(3)	0.051(4)	0.046(4)	0.039(3)	–0.013(3)	0.000(3)	–0.003(3)
C(02)	4e		–0.2101(4)	0.2687(3)	0.4410(3)	0.045(4)	0.053(4)	0.034(3)	–0.017(3)	–0.002(3)	–0.002(3)
C(03)	4e		–0.1693(4)	0.3367(3)	0.4192(3)	0.032(3)	0.052(4)	0.030(3)	–0.001(3)	–0.004(2)	0.000(3)
C(04)	4e		–0.2357(3)	0.4054(3)	0.4163(3)	0.030(3)	0.059(4)	0.040(3)	–0.001(3)	–0.006(3)	0.008(3)
C(05)	4e		–0.2664(4)	0.4248(3)	0.5090(3)	0.036(3)	0.049(3)	0.033(3)	–0.001(3)	–0.002(3)	0.007(2)
C(06)	4e		–0.3648(4)	0.4117(3)	0.5332(3)	0.025(3)	0.062(4)	0.046(3)	0.002(3)	–0.002(3)	0.012(3)
C(07)	4e		–0.3936(4)	0.4232(3)	0.6203(3)	0.030(3)	0.059(4)	0.050(3)	0.002(3)	0.000(3)	0.020(3)
C(08)	4e		–0.3178(4)	0.4458(3)	0.6852(3)	0.035(3)	0.072(4)	0.037(3)	0.010(3)	0.003(3)	0.012(3)
C(09)	4e		–0.2197(4)	0.4579(3)	0.6657(3)	0.030(3)	0.052(4)	0.045(3)	0.006(3)	–0.002(3)	0.001(3)
C(10)	4e		–0.1352(3)	0.4715(3)	0.7396(3)	0.041(3)	0.056(4)	0.033(3)	0.012(3)	–0.002(3)	–0.004(3)
C(11)	4e		–0.0693(4)	0.4025(3)	0.7528(3)	0.034(3)	0.054(4)	0.027(3)	0.000(3)	–0.003(2)	–0.008(3)
C(12)	4e		–0.1117(4)	0.3375(3)	0.7811(3)	0.036(3)	0.069(4)	0.032(3)	–0.001(4)	0.002(3)	–0.003(3)
C(13)	4e		–0.0585(4)	0.2715(3)	0.7920(3)	0.050(4)	0.053(4)	0.031(3)	0.000(3)	0.008(3)	0.008(3)
C(14)	4e		0.0426(4)	0.2720(3)	0.7765(3)	0.053(4)	0.055(4)	0.026(3)	0.006(3)	–0.001(3)	0.003(3)
C(15)	4e		0.0892(4)	0.3362(3)	0.7471(3)	0.034(3)	0.056(4)	0.023(3)	0.003(3)	–0.006(2)	–0.006(3)
C(16)	4e		0.1992(3)	0.3337(3)	0.7250(3)	0.037(3)	0.052(3)	0.038(3)	0.009(3)	–0.009(3)	–0.002(3)
C(17)	4e		0.2123(3)	0.2864(3)	0.6424(3)	0.029(3)	0.053(3)	0.023(3)	–0.003(3)	–0.003(2)	0.000(2)
C(18)	4e		0.2637(4)	0.2204(3)	0.6499(3)	0.047(4)	0.052(4)	0.038(3)	0.013(3)	0.002(3)	0.008(3)
C(19)	4e		0.2709(4)	0.1727(3)	0.5770(3)	0.062(4)	0.050(4)	0.038(3)	0.021(3)	0.003(3)	0.006(3)
C(20)	4e		0.2215(4)	0.1932(3)	0.4939(3)	0.053(4)	0.049(3)	0.031(3)	0.004(3)	0.002(3)	0.000(3)
C(21)	4e		0.1690(4)	0.2596(3)	0.4840(3)	0.033(3)	0.048(3)	0.028(3)	0.003(3)	0.005(2)	0.004(3)
C(22)	4e		0.1047(4)	0.2774(3)	0.3973(3)	0.051(4)	0.051(4)	0.025(3)	0.006(3)	0.000(3)	–0.001(2)
C(23)	4e		–0.0071(4)	0.2756(3)	0.4127(3)	0.037(3)	0.051(4)	0.024(3)	–0.004(3)	0.003(2)	–0.005(3)
C(24)	4e		–0.0517(4)	0.2097(3)	0.4369(3)	0.060(4)	0.048(4)	0.031(3)	–0.003(3)	0.000(3)	–0.007(3)
C(25)	4e		–0.1998(4)	0.1351(3)	0.4848(3)	0.074(5)	0.064(4)	0.049(3)	–0.020(4)	0.000(3)	0.000(3)
C(26)	4e		–0.2396(5)	0.1430(3)	0.5797(4)	0.112(6)	0.064(5)	0.073(4)	–0.028(4)	–0.006(5)	0.015(4)
C(27)	4e		–0.1617(5)	0.1514(3)	0.6568(4)	0.071(5)	0.074(5)	0.048(4)	–0.032(4)	0.014(4)	0.007(3)
C(28)	4e		–0.1909(5)	0.1741(4)	0.7458(4)	0.114(6)	0.075(5)	0.081(5)	–0.024(5)	0.033(5)	0.000(4)
C(29)	4e		–0.1096(4)	0.2003(3)	0.8173(3)	0.070(4)	0.075(4)	0.045(3)	0.001(4)	0.012(3)	0.010(3)
C(30)	4e		0.0308(4)	0.3999(3)	0.7329(3)	0.032(3)	0.050(4)	0.027(3)	–0.001(3)	–0.004(2)	–0.003(3)
C(31)	4e		0.1683(3)	0.3070(3)	0.5578(3)	0.022(3)	0.043(3)	0.043(3)	0.000(3)	0.004(2)	0.003(3)

Table 3. Continued.

Atom	Site	Occ.	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(32)	4*e*		–0.0664(4)	0.3389(3)	0.4082(3)	0.038(4)	0.045(4)	0.026(3)	–0.010(3)	–0.005(2)	0.007(2)
C(33)	4*e*		–0.1955(3)	0.4489(3)	0.5759(3)	0.021(3)	0.048(3)	0.046(3)	0.007(3)	0.005(3)	0.006(3)
C(34)	4*e*		–0.5006(4)	0.4089(4)	0.6450(4)	0.036(4)	0.101(5)	0.051(4)	0.002(4)	0.004(3)	0.020(4)
C(35)	4*e*		–0.5036(4)	0.3494(4)	0.7106(5)	0.037(4)	0.208(9)	0.136(6)	–0.016(5)	–0.006(4)	0.116(7)
C(36)	4*e*		–0.5417(4)	0.4788(4)	0.6900(4)	0.040(4)	0.185(9)	0.105(6)	0.010(5)	0.006(4)	–0.002(6)
C(37)	4*e*		–0.5746(4)	0.3949(4)	0.5637(4)	0.035(4)	0.155(7)	0.074(4)	–0.024(4)	–0.006(3)	0.039(4)
C(38)	4*e*		0.3251(5)	0.0982(3)	0.5896(4)	0.087(5)	0.071(4)	0.038(3)	0.026(4)	–0.005(3)	0.002(3)
C(39)	4*e*		0.4307(5)	0.1103(4)	0.6367(5)	0.099(6)	0.083(5)	0.129(6)	0.054(5)	–0.026(5)	–0.018(5)
C(40)	4*e*		0.2642(5)	0.0479(3)	0.6497(4)	0.166(8)	0.075(5)	0.060(4)	0.025(5)	0.001(5)	0.010(4)
C(41)	4*e*		0.3354(5)	0.0570(3)	0.5024(4)	0.131(6)	0.065(4)	0.067(4)	0.045(5)	0.011(4)	0.002(4)
O(1)	4*e*		0.0794(2)	0.4589(2)	0.6956(2)	0.033(2)	0.050(2)	0.045(2)	0.000(2)	–0.009(2)	0.000(2)
O(2)	4*e*		0.1204(3)	0.3739(2)	0.5413(2)	0.041(2)	0.055(2)	0.033(2)	0.005(2)	–0.009(2)	–0.001(2)
O(3)	4*e*		–0.0232(2)	0.4085(2)	0.3975(2)	0.027(2)	0.053(2)	0.044(2)	–0.009(2)	–0.012(2)	0.010(2)
O(4)	4*e*		–0.0972(2)	0.4651(2)	0.5594(2)	0.028(2)	0.063(2)	0.036(2)	–0.006(2)	0.001(2)	–0.003(2)
O(5)	4*e*		–0.0715(4)	0.1331(3)	0.6489(3)	0.083(4)	0.118(4)	0.086(3)	0.008(3)	0.018(3)	0.004(3)
O(6)	4*e*	0.29(2)	–0.063(3)	–0.025(2)	0.559(2)	0.48(7)	0.29(4)	0.30(4)	0.00(4)	–0.20(4)	0.08(3)

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