Crystal structure of 5,17-di-*t*-butyl-25,26,27,28-tetrahydroxy-11,23-(2-hydroxy-5-nitro-1, 3-xyleno)-calix[4]arene methylenechloride, $C_{44}H_{45}NO_7 \cdot CH_2Cl_2$

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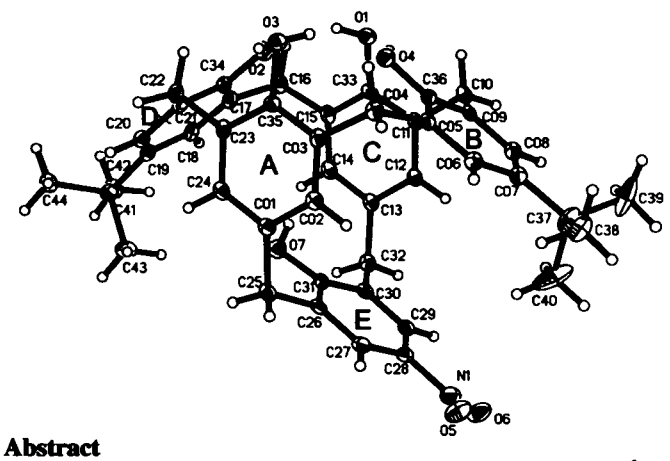
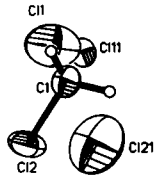
Received December 18, 2001, accepted February 13, 2002; CCDC-No. 1267/780





Abstract

$C_{45}H_{47}Cl_2NO_7$, monoclinic, $P12_1/n1$ (No. 14), $a = 10.581(2)$ Å, $b = 26.185(5)$ Å, $c = 14.195(3)$ Å, $\beta = 91.75(3)°$, $V = 3931.1$ Å^3, $Z = 4$, $R_{gt}(F) = 0.059$, $wR_{ref}(F^2) = 0.177$, $T = 192$ K.

Source of material

The compound was synthesized by di-*O*-alkylation of the *p*-bridged phenolic units of the chemical precursor 5,17-di-*t*-butyl-25,26,27,28-tetrahydroxy-11,23-(3-oxo-pentano)-calix[4]arene [1] with benzylbromide (95%), double aldol condensation with nitromalondialdehyde(50%) and cleavage of the benzylether groups with BBr_3/CH_2Cl_2 (74%). 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 8.7. The C—H and O—H distances were fixed for refinement. The methylene chloride molecule was refined as disordered with extremely large displacement parameters.

Discussion

Bicyclo-calix[4]arenes [2] are macrobicyclic compounds consisting of five phenolic units connected via six methylene bridges. Two phenol rings (A, C), correspond to the bridge heads and three phenol rings (B, D, E) to the bridges of a bicyclic system. The nitrophenol ring E replaces the carbonyl σ-plane in the precursor [1]. The *endo*-calix [4]arene part (A, B, C, D) has a pinched cone conformation [3,4] almost identical to its precursor [3], which is as usual stabilized by a cyclic array of intramolecular hydrogen bonds. The two *endo-exo*-calix [4]arene systems are found in the partial cone (A, D, C, E) and 1,3-alternate (A, B, C, E) conformation. The dihedral angles and distances show significant deviations from the potential mirror plane through the *t*-butyl groups, the nitro and the hydroxy groups of the ring E, as it was in the precursor [1]. The space problem with the bulky p-nitrophenol group is apparently solved by an inclination of 33.6° relative to the plane F compared to 15.0° in the precursor. The *endo*-calix is quite well closed by this inclined lid [O5···H40A: 3.00 Å]; an appropriate distance in the precursor is 3.75 Å (H282···H351). The effective length of the bridge between A and C is almost the same in both compounds. The main difference between the two bridges is its planarity in the present case, whereas in the precursor the carbon atoms attached to the *p*-positions of ring A and C are 0.338 Å and 0.371 Å out of the carbonyl σ plane. In contrast to the precursor there are only intramolecular hydrogen bonds, what seems to shorten the average intramolecular hydrogen bond length from 2.880 Å to 2.848 Å. O7–H does not participate in hydrogen bonding, it points into the cavity. The distance of O7 to the centre of ring D is 3.98 Å. The average esd for a C—C and C—N bond is 0.006 Å, for a C—O and N—O bond 0.006 Å, for a C—Cl bond 0.008 Å and for a hydrogen bond 0.004 Å. For the C—H and O—H bonds the distances are fixed. The average esd of bond angles is 0.4° and that of torsion angles is also 0.4°. The average esd for dihedral angles between l.s. planes is 0.1°.

Table 1. Data collection and handling.

Crystal:	colourless plate, size 0.15 × 0.35 × 0.38 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	2.19 cm^{-1}
Diffractometer, scan mode:	Siemens R3m/V, $2\theta/\theta$
$2\theta_{max}$:	46.52°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	7921, 5637
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 3001
$N(param)_{refined}$:	521
Programs:	SHEXLTL-Plus [5], SHELXS-97 [6], SHELXL-97 [7]

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

Atom	Site	x	y	z	U_{iso}
H(02A)	4e	0.0369	0.2987	0.9514	0.08
H(04A)	4e	0.1816	0.2914	0.8060	0.08
H(04B)	4e	0.2446	0.2379	0.7966	0.08
H(06A)	4e	0.2897	0.3500	0.9083	0.08
H(08A)	4e	0.5192	0.3022	1.1236	0.08
H(10A)	4e	0.5545	0.2132	1.1534	0.08
H(10B)	4e	0.5393	0.1768	1.0675	0.08
H(12A)	4e	0.3472	0.2360	1.2380	0.08
H(14A)	4e	0.1211	0.1130	1.2828	0.08
H(16A)	4e	0.2041	0.0277	1.2166	0.08
H(16B)	4e	0.2662	0.0294	1.1193	0.08
H(18A)	4e	-0.0175	0.0228	1.2241	0.08
H(20A)	4e	-0.2456	0.0676	1.0018	0.08
H(22A)	4e	-0.1584	0.1010	0.8606	0.08
H(22B)	4e	-0.0150	0.0896	0.8467	0.08
H(24A)	4e	-0.1904	0.1751	0.9876	0.08
H(25A)	4e	-0.2252	0.2498	1.0814	0.08
H(25B)	4e	-0.1922	0.3007	1.0317	0.08
H(27A)	4e	-0.0850	0.3610	1.1332	0.08
H(29A)	4e	0.1455	0.3139	1.3512	0.08
H(32A)	4e	0.1871	0.2268	1.3812	0.08
H(32B)	4e	0.0714	0.1918	1.3576	0.08
H(38A)	4e	0.4577	0.4224	0.9169	0.08
H(38B)	4e	0.3196	0.4228	0.9539	0.08

Table 2. Continued.

Atom	Site	x	y	z	U_{iso}
H(38C)	4e	0.4179	0.4636	0.9906	0.08
H(39A)	4e	0.6359	0.3936	1.0247	0.08
H(39B)	4e	0.5910	0.4309	1.1033	0.08
H(39C)	4e	0.5959	0.3720	1.1224	0.08
H(40A)	4e	0.2719	0.3996	1.1177	0.08
H(40B)	4e	0.3833	0.3763	1.1790	0.08
H(40C)	4e	0.3784	0.4352	1.1598	0.08
H(42A)	4e	-0.2236	-0.0391	1.2373	0.08
H(42B)	4e	-0.1728	0.0086	1.2935	0.08
H(42C)	4e	-0.3133	-0.0090	1.3035	0.08
H(43A)	4e	-0.2518	0.0939	1.2586	0.08
H(43B)	4e	-0.3265	0.1056	1.1640	0.08
H(43C)	4e	-0.3958	0.0802	1.2480	0.08
H(44A)	4e	-0.3553	-0.0268	1.0950	0.08
H(44B)	4e	-0.4573	0.0040	1.1492	0.08
H(44C)	4e	-0.3880	0.0294	1.0652	0.08
H(1)	4e	0.3503	0.0863	1.0263	0.071
H(2)	4e	0.1453	0.0978	0.9255	0.071
H(3)	4e	0.2165	0.1557	0.8375	0.069
H(4)	4e	0.3807	0.1640	0.9728	0.062
H(7)	4e	0.0100	0.1763	1.1897	0.066
H(1A)	4e	0.9012	0.4430	0.8306	0.08
H(1B)	4e	0.9635	0.4861	0.8946	0.08

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		-0.0857(4)	0.2409(2)	0.9844(3)	0.028(2)	0.046(3)	0.023(2)	0.004(2)	-0.006(2)	-0.000(2)
C(02)	4e		0.0170(4)	0.2633(2)	0.9404(3)	0.033(3)	0.043(3)	0.025(2)	0.003(2)	-0.005(2)	0.005(2)
C(03)	4e		0.0917(4)	0.2353(2)	0.8797(2)	0.035(3)	0.044(3)	0.020(2)	-0.007(2)	-0.006(2)	0.003(2)
C(04)	4e		0.2072(4)	0.2612(2)	0.8398(3)	0.042(3)	0.051(3)	0.024(2)	-0.002(2)	-0.004(2)	0.001(2)
C(05)	4e		0.3070(4)	0.2726(2)	0.9159(2)	0.030(2)	0.049(3)	0.020(2)	-0.010(2)	0.004(2)	-0.003(2)
C(06)	4e		0.3312(4)	0.3231(2)	0.9433(3)	0.044(3)	0.044(3)	0.026(2)	-0.005(2)	0.003(2)	0.003(2)
C(07)	4e		0.4138(4)	0.3358(2)	1.0188(3)	0.040(3)	0.047(3)	0.023(2)	-0.006(2)	0.003(2)	0.000(2)
C(08)	4e		0.4669(4)	0.2946(2)	1.0689(3)	0.036(3)	0.046(3)	0.024(2)	-0.005(2)	0.001(2)	0.001(2)
C(09)	4e		0.4450(4)	0.2436(2)	1.0445(3)	0.024(2)	0.042(3)	0.027(2)	-0.005(2)	0.007(2)	0.001(2)
C(10)	4e		0.4954(4)	0.2006(2)	1.1064(3)	0.027(2)	0.047(3)	0.041(2)	-0.001(2)	-0.002(2)	0.003(2)
C(11)	4e		0.3884(4)	0.1742(2)	1.1570(3)	0.025(2)	0.043(3)	0.035(2)	0.004(2)	-0.007(2)	0.007(2)
C(12)	4e		0.3224(4)	0.2015(2)	1.2244(3)	0.028(2)	0.044(3)	0.034(2)	-0.001(2)	-0.005(2)	0.005(2)
C(13)	4e		0.2191(4)	0.1798(2)	1.2690(3)	0.029(3)	0.046(3)	0.029(2)	0.001(2)	-0.006(2)	0.006(2)
C(14)	4e		0.1882(4)	0.1288(2)	1.2492(3)	0.032(3)	0.046(3)	0.037(2)	0.002(2)	-0.006(2)	0.011(2)
C(15)	4e		0.2535(4)	0.1004(2)	1.1815(3)	0.027(2)	0.040(3)	0.041(2)	0.001(2)	-0.009(2)	0.011(2)
C(16)	4e		0.2070(4)	0.0464(2)	1.1585(3)	0.041(3)	0.038(3)	0.055(3)	0.003(2)	-0.009(2)	0.009(2)
C(17)	4e		0.0762(4)	0.0482(2)	1.1119(3)	0.039(3)	0.028(2)	0.048(3)	0.000(2)	-0.010(2)	0.002(2)
C(18)	4e		-0.0313(4)	0.0337(2)	1.1600(3)	0.047(3)	0.033(2)	0.039(2)	-0.004(2)	-0.010(2)	0.001(2)
C(19)	4e		-0.1530(4)	0.0404(1)	1.1224(3)	0.040(3)	0.029(2)	0.038(2)	-0.002(2)	-0.004(2)	-0.003(2)
C(20)	4e		-0.1642(4)	0.0620(2)	1.0317(3)	0.038(3)	0.038(3)	0.037(2)	0.002(2)	-0.003(2)	0.000(2)
C(21)	4e		-0.0591(4)	0.0764(2)	0.9810(3)	0.034(3)	0.036(2)	0.035(2)	-0.004(2)	-0.001(2)	-0.007(2)
C(22)	4e		-0.0749(4)	0.1045(2)	0.8882(3)	0.038(3)	0.047(3)	0.034(2)	-0.008(2)	-0.006(2)	-0.004(2)
C(23)	4e		-0.0428(4)	0.1610(2)	0.9020(3)	0.030(2)	0.045(3)	0.024(2)	-0.006(2)	-0.007(2)	0.002(2)
C(24)	4e		-0.1168(4)	0.1906(2)	0.9619(3)	0.029(3)	0.052(3)	0.026(2)	0.002(2)	-0.005(2)	0.005(2)
C(25)	4e		-0.1568(4)	0.2702(2)	1.0593(3)	0.028(2)	0.056(3)	0.033(2)	0.000(2)	-0.001(2)	-0.001(2)
C(26)	4e		-0.0707(4)	0.2836(2)	1.1441(3)	0.023(2)	0.050(3)	0.027(2)	0.004(2)	0.004(2)	-0.003(2)
C(27)	4e		-0.0448(4)	0.3337(2)	1.1677(3)	0.035(3)	0.044(3)	0.042(3)	0.009(2)	0.005(2)	-0.002(2)
C(28)	4e		0.0356(4)	0.3445(2)	1.2441(3)	0.032(3)	0.047(3)	0.040(2)	0.002(2)	0.005(2)	-0.013(2)
C(29)	4e		0.0935(4)	0.3061(2)	1.2965(3)	0.030(3)	0.058(3)	0.028(2)	0.000(2)	0.003(2)	-0.012(2)
C(30)	4e		0.0707(4)	0.2552(2)	1.2748(3)	0.027(2)	0.049(3)	0.024(2)	0.000(2)	0.003(2)	-0.003(2)
C(31)	4e		-0.0135(4)	0.2448(2)	1.1988(3)	0.026(2)	0.041(3)	0.029(2)	-0.004(2)	0.003(2)	-0.004(2)
C(32)	4e		0.1357(4)	0.2127(2)	1.3307(3)	0.036(3)	0.052(3)	0.030(2)	-0.004(2)	-0.001(2)	0.003(2)
C(33)	4e		0.3482(4)	0.1248(2)	1.1343(3)	0.028(2)	0.036(3)	0.039(2)	0.006(2)	-0.003(2)	0.003(2)
C(34)	4e		0.0600(4)	0.0688(2)	1.0215(3)	0.035(3)	0.030(2)	0.043(3)	-0.004(2)	0.003(2)	-0.004(2)
C(35)	4e		0.0628(4)	0.1839(2)	0.8647(2)	0.031(3)	0.047(3)	0.022(2)	-0.001(2)	0.002(2)	-0.004(2)
C(36)	4e		0.3678(4)	0.2338(2)	0.9655(3)	0.031(2)	0.037(3)	0.028(2)	-0.006(2)	0.008(2)	-0.000(2)
C(37)	4e		0.4393(5)	0.3908(2)	1.0490(3)	0.086(4)	0.042(3)	0.037(3)	-0.008(3)	-0.018(3)	0.000(2)
C(38)	4e		0.4070(5)	0.4288(2)	0.9706(3)	0.088(4)	0.046(3)	0.051(3)	-0.014(3)	-0.007(3)	-0.001(2)
C(39)	4e		0.5791(7)	0.3978(2)	1.0756(5)	0.139(7)	0.053(4)	0.140(6)	-0.038(4)	-0.088(5)	0.013(4)

Table 3. Continued.

Atom	Site	Occ.	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(40)	4*e*		0.3605(8)	0.4021(2)	1.1336(4)	0.26(1)	0.061(4)	0.047(3)	0.026(5)	0.022(5)	–0.014(3)
C(41)	4*e*		–0.2723(4)	0.0300(2)	1.1784(3)	0.045(3)	0.043(3)	0.035(2)	0.001(2)	–0.001(2)	0.001(2)
C(42)	4*e*		–0.2450(5)	–0.0059(2)	1.2609(3)	0.057(3)	0.061(3)	0.046(3)	–0.002(3)	–0.001(3)	0.011(2)
C(43)	4*e*		–0.3175(5)	0.0822(2)	1.2158(3)	0.062(4)	0.058(3)	0.058(3)	0.009(3)	0.013(3)	–0.003(3)
C(44)	4*e*		–0.3787(4)	0.0063(2)	1.1175(3)	0.041(3)	0.062(3)	0.053(3)	–0.005(3)	0.005(2)	0.000(2)
N(1)	4*e*		0.0605(4)	0.3978(2)	1.2690(3)	0.045(3)	0.056(3)	0.066(3)	0.011(2)	–0.006(2)	–0.019(2)
O(1)	4*e*		0.4047(3)	0.1007(1)	1.0591(2)	0.036(2)	0.052(2)	0.054(2)	0.007(2)	0.001(2)	–0.011(2)
O(2)	4*e*		0.1664(3)	0.0827(1)	0.9741(2)	0.042(2)	0.048(2)	0.053(2)	–0.003(2)	0.004(2)	0.002(2)
O(3)	4*e*		0.1446(3)	0.1531(1)	0.8148(2)	0.040(2)	0.060(2)	0.040(2)	–0.001(2)	0.005(2)	–0.015(2)
O(4)	4*e*		0.3470(3)	0.1839(1)	0.9351(2)	0.043(2)	0.041(2)	0.041(2)	–0.001(2)	0.001(2)	–0.001(1)
O(5)	4*e*		0.0336(4)	0.4313(1)	1.2111(3)	0.097(3)	0.046(2)	0.084(3)	0.010(2)	0.003(2)	–0.007(2)
O(6)	4*e*		0.1078(4)	0.4070(1)	1.3480(3)	0.071(3)	0.073(3)	0.096(3)	0.020(2)	–0.035(2)	–0.044(2)
O(7)	4*e*		–0.0487(3)	0.1957(1)	1.1768(2)	0.042(2)	0.047(2)	0.044(2)	0.001(2)	–0.007(2)	0.000(2)
C(1)	4*e*		0.9164(7)	0.4547(3)	0.8940(5)	0.108(6)	0.103(5)	0.084(5)	–0.009(5)	–0.016(4)	0.002(4)
Cl(1)	4*e*	0.725(6)	0.988(1)	0.4053(3)	0.9385(6)	0.39(1)	0.178(6)	0.264(8)	0.088(7)	0.121(7)	0.105(6)
Cl(2)	4*e*	0.725	0.7841(4)	0.4670(2)	0.9387(3)	0.116(3)	0.206(4)	0.158(3)	0.015(3)	0.043(2)	–0.069(3)
Cl(11)	4*e*	0.275	1.0386(8)	0.4211(4)	0.9618(5)	0.077(5)	0.102(6)	0.049(3)	–0.007(4)	–0.021(3)	0.014(3)
Cl(21)	4*e*	0.275	0.920(2)	0.4916(9)	0.990(1)	0.38(3)	0.40(3)	0.22(2)	–0.04(3)	–0.10(2)	–0.05(2)

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