Crystal structure of 5-(imidazol-1-yl)-25,26,27,28-tetrabenzyloxy-calix[4]arene (cone), $C_{59}H_{50}N_2O_4$

Eric Brenner[I], Dominique Matt*,[I] and Loïc Toupet[II]

[I] Université de Strasbourg, Laboratoire de Chimie Inorganique Moléculaire et Catalyse, UMR 7177, 1 rue Blaise Pascal, 67008 Strasbourg cedex, France
[II] Institut de Physique de Rennes, UMR CNRS 6251, Université de Rennes 1, Campus de Beaulieu, 35042 Rennes cedex, France

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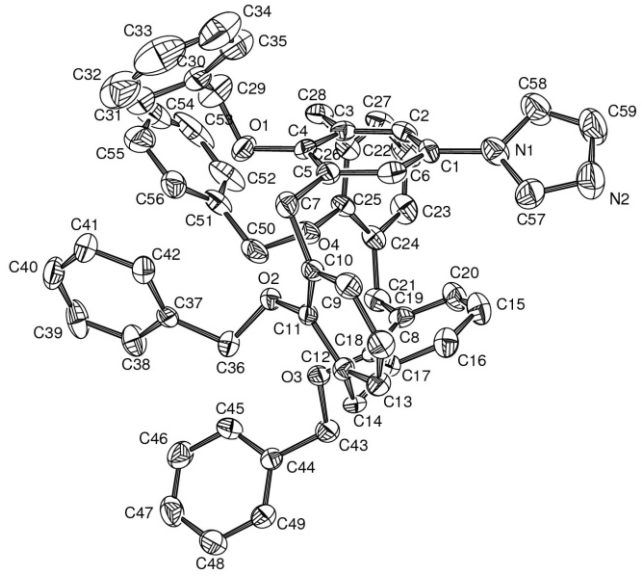

Abstract

$C_{59}H_{50}N_2O_4$, monoclinic, $P2_1/n$ (no. 14), a = 19.028(3) Å, b = 12.605(1) Å, c = 20.943(3) Å, β = 114.91(2)°, V = 4555.9 Å^3, Z = 4, $R(F)$ = 0.043, $wR_{ref}(F^2)$ = 0.085, T = 140 K.

Source of material

The title compound was prepared in 88 % yield by Ullmann-type coupling between imidazole and 5-iodo-25,26,27,28-tetrabenzyloxy-calix[4]arene in the presence of CuI, *N*,*N*′-dimethylethane-1,2-diamine, and K_2CO_3 in dimethylformamide (120 °C, 5 days).

Experimental details

Due to the size ($1.9 \cdot 10^{-3}$ mm^{-3}) of the sample and its poor diffraction, the ratio of the number of observed reflections to the number of refined parameters is very low.

Discussion

The unit cell contains four molecules of the title compound. The calixarene skeleton adopts a typical pinched cone conformation [1,2], with dihedral angles between opposing phenoxy rings of 109.8° and 25.3°. The two distal rings with the smaller interplanar angle have their upper part (i. e. the C atoms in *para* to the oxygen atoms) pushed towards the calixarene axis (d(C1—C15 = 4.08 Å). The separation between the centroids of the distal phenoxy ring pairs are 4.65 Å and 7.79 Å, respectively. The dihedral angle between the imidazole plane and the phenyl ring to which it is linked is 35.6°, a value which reflects a high degree of conjugation between these two fragments. The particular orientation of the imidazole plane having the C57—H57 bond oriented sideways may explain why the three protons of the C15 ring (facing the phenoxy that bears the imidazolyl group) appear as an ABM pattern in the ^{1}H NMR spectrum.

* Correspondence author (e-mail: dmatt@unistra.fr)

Table 1. Data collection and handling.

Crystal:	colourless prism, size 0.06 × 0.11 × 0.29 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	0.77 cm^{-1}
Diffractometer, scan mode:	CCD Saphire 3 Xcalibur, ω
$2\theta_{max}$:	54°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	31028, 9778
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 2223
$N(param)_{refined}$:	586
Programs:	SIR-97 [3], SHELXL-97 [4], PLATON [5]

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

Atom	Site	x	y	z	U_{iso}
H(2)	4*e*	–0.0075	–0.0402	0.3895	0.035
H(6)	4*e*	–0.0665	0.1624	0.2256	0.037
H(7A)	4*e*	–0.0236	0.3691	0.2655	0.036
H(7B)	4*e*	0.0662	0.3680	0.3199	0.036
H(8)	4*e*	–0.0268	0.2667	0.0545	0.039
H(9)	4*e*	–0.0554	0.3343	0.1445	0.037
H(13)	4*e*	0.0877	0.1716	0.0843	0.038
H(14A)	4*e*	0.2482	0.1491	0.2388	0.033
H(14B)	4*e*	0.2025	0.0933	0.1638	0.033
H(15)	4*e*	0.0504	–0.1629	0.2177	0.054
H(16)	4*e*	0.0774	–0.0136	0.1660	0.043
H(20)	4*e*	0.1370	–0.2132	0.3298	0.050
H(21A)	4*e*	0.3161	–0.0809	0.4369	0.044
H(21B)	4*e*	0.2908	–0.2028	0.4202	0.044
H(22)	4*e*	0.1612	–0.2682	0.5569	0.057
H(23)	4*e*	0.2396	–0.2770	0.4972	0.054
H(27)	4*e*	0.0913	–0.1145	0.5516	0.050
H(28A)	4*e*	0.1299	0.1364	0.5166	0.042
H(28B)	4*e*	0.0598	0.0680	0.5183	0.042
H(29A)	4*e*	0.1043	0.3706	0.5149	0.057
H(29B)	4*e*	0.0302	0.2942	0.4855	0.057
H(31)	4*e*	0.1014	0.5400	0.4536	0.066
H(32)	4*e*	0.0259	0.6813	0.3853	0.084
H(33)	4*e*	–0.1063	0.6603	0.3207	0.093
H(34)	4*e*	–0.1664	0.4997	0.3253	0.081
H(35)	4*e*	–0.0915	0.3574	0.3886	0.064
H(36A)	4*e*	0.2495	0.3181	0.2827	0.034
H(36B)	4*e*	0.2841	0.2235	0.3383	0.034
H(38)	4*e*	0.3910	0.3205	0.4207	0.049
H(39)	4*e*	0.4412	0.4484	0.5101	0.058

Table 2. Continued.

Atom	Site	x	y	z	U_{iso}
H(40)	4*e*	0.3580	0.5662	0.5294	0.060
H(41)	4*e*	0.2262	0.5594	0.4586	0.064
H(42)	4*e*	0.1762	0.4346	0.3683	0.047
H(43A)	4*e*	0.3403	–0.0113	0.2699	0.041
H(43B)	4*e*	0.3766	–0.0782	0.3416	0.041
H(45)	4*e*	0.4426	0.0833	0.4470	0.047
H(46)	4*e*	0.5552	0.1858	0.4867	0.057
H(47)	4*e*	0.6138	0.2254	0.4119	0.058
H(48)	4*e*	0.5619	0.1593	0.2985	0.055
H(49)	4*e*	0.4478	0.0610	0.2570	0.044

Table 2. Continued.

Atom	Site	x	y	z	U_{iso}
H(50A)	4*e*	0.2938	0.1689	0.4607	0.051
H(50B)	4*e*	0.3229	0.0571	0.4990	0.051
H(52)	4*e*	0.3110	0.0198	0.6106	0.076
H(53)	4*e*	0.3067	0.0924	0.7137	0.108
H(54)	4*e*	0.2794	0.2714	0.7162	0.114
H(55)	4*e*	0.2581	0.3796	0.6216	0.086
H(56)	4*e*	0.2585	0.3078	0.5190	0.055
H(57)	4*e*	–0.0863	–0.0045	0.1618	0.056
H(58)	4*e*	–0.1477	–0.1090	0.3109	0.066
H(59)	4*e*	–0.2202	–0.2068	0.2018	0.072

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

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
O(1)	4*e*	0.0970(1)	0.2816(2)	0.4337(1)	0.037(2)	0.039(2)	0.031(2)	–0.000(1)	0.014(2)	–0.011(1)
O(2)	4*e*	0.1715(1)	0.2512(2)	0.3110(1)	0.025(2)	0.028(1)	0.024(2)	–0.004(1)	0.010(1)	–0.003(1)
O(3)	4*e*	0.3057(1)	0.0381(2)	0.3430(1)	0.024(2)	0.026(2)	0.038(2)	0.002(1)	0.018(2)	–0.003(1)
O(4)	4*e*	0.2077(1)	0.0647(2)	0.4426(1)	0.037(2)	0.027(2)	0.040(2)	0.002(1)	0.022(2)	0.009(1)
N(1)	4*e*	–0.0968(2)	–0.0277(2)	0.2544(2)	0.036(2)	0.042(2)	0.037(2)	–0.006(2)	0.015(2)	0.006(2)
N(2)	4*e*	–0.1639(2)	–0.1179(2)	0.1550(2)	0.061(3)	0.046(2)	0.066(3)	–0.015(2)	0.023(3)	–0.012(2)
C(1)	4*e*	–0.0455(2)	0.0512(3)	0.3014(2)	0.025(3)	0.033(3)	0.029(3)	–0.009(2)	0.011(2)	–0.005(2)
C(2)	4*e*	–0.0036(2)	0.0279(3)	0.3718(2)	0.028(3)	0.031(2)	0.033(3)	–0.002(2)	0.018(2)	0.007(2)
C(3)	4*e*	0.0446(2)	0.1052(3)	0.4169(2)	0.026(3)	0.035(3)	0.021(3)	0.003(2)	0.012(2)	0.003(2)
C(4)	4*e*	0.0488(2)	0.2048(3)	0.3893(2)	0.026(3)	0.031(3)	0.034(3)	–0.001(2)	0.017(2)	–0.010(2)
C(5)	4*e*	0.0108(2)	0.2257(3)	0.3179(2)	0.026(3)	0.025(3)	0.036(3)	0.002(2)	0.016(2)	–0.002(2)
C(6)	4*e*	–0.0380(2)	0.1484(3)	0.2744(2)	0.032(3)	0.034(2)	0.030(3)	0.008(2)	0.017(2)	0.004(2)
C(7)	4*e*	0.0242(2)	0.3256(2)	0.2843(2)	0.027(2)	0.020(2)	0.043(3)	0.002(2)	0.015(2)	–0.003(2)
C(8)	4*e*	0.0087(2)	0.2586(2)	0.1024(2)	0.033(3)	0.036(2)	0.025(3)	–0.002(2)	0.009(2)	0.003(2)
C(9)	4*e*	–0.0069(2)	0.3006(2)	0.1558(2)	0.026(3)	0.032(2)	0.033(3)	0.001(2)	0.012(2)	0.003(2)
C(10)	4*e*	0.0461(2)	0.2948(2)	0.2254(2)	0.025(3)	0.022(2)	0.028(3)	–0.001(2)	0.014(2)	0.002(2)
C(11)	4*e*	0.1181(2)	0.2484(2)	0.2413(2)	0.030(3)	0.022(2)	0.018(2)	–0.008(2)	0.012(2)	–0.001(2)
C(12)	4*e*	0.1332(2)	0.1956(2)	0.1896(2)	0.029(3)	0.019(2)	0.024(2)	–0.000(2)	0.012(2)	0.001(2)
C(13)	4*e*	0.0778(2)	0.2043(2)	0.1206(2)	0.040(3)	0.027(2)	0.034(3)	–0.005(2)	0.022(2)	–0.005(2)
C(14)	4*e*	0.1985(2)	0.1158(2)	0.2074(2)	0.033(3)	0.030(2)	0.029(2)	–0.004(2)	0.022(2)	–0.005(2)
C(15)	4*e*	0.0970(2)	–0.1242(3)	0.2418(2)	0.043(3)	0.033(3)	0.054(3)	–0.009(2)	0.016(3)	–0.002(2)
C(16)	4*e*	0.1141(2)	–0.0363(3)	0.2109(2)	0.033(3)	0.031(3)	0.039(3)	0.002(2)	0.009(2)	–0.002(2)
C(17)	4*e*	0.1830(2)	0.0193(2)	0.2437(2)	0.027(3)	0.024(2)	0.030(3)	–0.005(2)	0.015(2)	–0.008(2)
C(18)	4*e*	0.2352(2)	–0.0163(3)	0.3092(2)	0.021(3)	0.026(2)	0.041(3)	–0.001(2)	0.020(2)	–0.015(2)
C(19)	4*e*	0.2182(2)	–0.1005(3)	0.3440(2)	0.034(3)	0.030(3)	0.035(3)	0.007(2)	0.020(2)	0.002(2)
C(20)	4*e*	0.1489(2)	–0.1541(3)	0.3080(2)	0.039(3)	0.028(3)	0.058(3)	–0.006(2)	0.021(3)	0.002(2)
C(21)	4*e*	0.2711(2)	–0.1297(2)	0.4188(2)	0.038(3)	0.024(2)	0.055(3)	0.008(2)	0.027(3)	0.007(2)
C(22)	4*e*	0.1669(2)	–0.2077(3)	0.5324(2)	0.045(3)	0.046(3)	0.056(3)	–0.007(2)	0.025(3)	0.020(2)
C(23)	4*e*	0.2148(2)	–0.2120(3)	0.4982(2)	0.046(3)	0.026(3)	0.058(3)	0.007(2)	0.018(3)	0.013(2)
C(24)	4*e*	0.2278(2)	–0.1227(3)	0.4647(2)	0.022(3)	0.030(2)	0.038(3)	0.003(2)	0.009(2)	0.008(2)
C(25)	4*e*	0.1926(2)	–0.0285(3)	0.4704(2)	0.025(3)	0.032(3)	0.025(2)	0.000(2)	0.010(2)	0.010(2)
C(26)	4*e*	0.1398(2)	–0.0240(3)	0.5000(2)	0.024(3)	0.036(3)	0.028(2)	0.002(2)	0.006(2)	0.008(2)
C(27)	4*e*	0.1273(2)	–0.1156(3)	0.5311(2)	0.036(3)	0.054(3)	0.042(3)	–0.002(2)	0.023(2)	0.010(2)
C(28)	4*e*	0.0938(2)	0.0774(2)	0.4937(2)	0.029(3)	0.046(3)	0.036(3)	0.003(2)	0.019(2)	0.001(2)
C(29)	4*e*	0.0626(2)	0.3419(3)	0.4715(2)	0.060(3)	0.045(3)	0.034(3)	0.019(2)	0.015(3)	0.005(2)
C(30)	4*e*	0.0136(3)	0.4320(3)	0.4289(2)	0.044(3)	0.051(3)	0.033(3)	–0.009(3)	0.023(3)	–0.014(2)
C(31)	4*e*	0.0473(2)	0.5304(3)	0.4270(2)	0.058(3)	0.056(3)	0.066(3)	–0.013(3)	0.040(3)	–0.024(3)
C(32)	4*e*	0.0020(3)	0.6156(3)	0.3863(3)	0.101(5)	0.041(3)	0.086(5)	0.017(3)	0.057(4)	0.006(3)
C(33)	4*e*	–0.0761(3)	0.6032(4)	0.3484(2)	0.097(5)	0.081(4)	0.059(4)	0.044(4)	0.038(4)	0.015(3)
C(34)	4*e*	–0.1119(3)	0.5074(4)	0.3503(2)	0.065(4)	0.080(4)	0.049(3)	0.029(3)	0.016(3)	–0.012(3)
C(35)	4*e*	–0.0670(3)	0.4232(3)	0.3890(2)	0.063(4)	0.052(3)	0.054(3)	0.001(3)	0.034(3)	–0.010(3)
C(36)	4*e*	0.2491(2)	0.2857(2)	0.3255(2)	0.029(3)	0.024(2)	0.029(2)	0.000(2)	0.009(2)	–0.003(2)
C(37)	4*e*	0.2782(2)	0.3653(2)	0.3849(2)	0.035(3)	0.019(2)	0.030(3)	–0.003(2)	0.020(2)	0.005(2)
C(38)	4*e*	0.3570(2)	0.3694(3)	0.4278(2)	0.039(3)	0.030(3)	0.047(3)	–0.003(2)	0.012(3)	0.005(2)
C(39)	4*e*	0.3870(2)	0.4453(3)	0.4815(2)	0.045(3)	0.041(3)	0.034(3)	–0.018(2)	–0.007(3)	0.004(2)
C(40)	4*e*	0.3380(3)	0.5152(3)	0.4928(2)	0.078(4)	0.036(3)	0.038(3)	–0.022(3)	0.027(3)	–0.015(2)
C(41)	4*e*	0.2601(3)	0.5111(3)	0.4509(2)	0.068(4)	0.039(3)	0.068(4)	–0.018(3)	0.043(3)	–0.025(2)
C(42)	4*e*	0.2303(2)	0.4364(3)	0.3971(2)	0.038(3)	0.034(3)	0.048(3)	–0.009(2)	0.020(3)	–0.012(2)
C(43)	4*e*	0.3625(2)	–0.0059(2)	0.3219(2)	0.037(3)	0.028(2)	0.044(3)	0.002(2)	0.023(2)	–0.003(2)
C(44)	4*e*	0.4339(2)	0.0631(2)	0.3476(2)	0.025(3)	0.023(2)	0.037(3)	0.006(2)	0.015(2)	–0.002(2)
C(45)	4*e*	0.4661(2)	0.0996(3)	0.4162(2)	0.035(3)	0.044(3)	0.048(3)	–0.004(2)	0.026(3)	–0.003(2)
C(46)	4*e*	0.5331(2)	0.1600(3)	0.4397(2)	0.037(3)	0.061(3)	0.040(3)	–0.005(2)	0.012(3)	–0.017(2)

Table 3. Continued.

Atom	Site	*x*	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(47)	4*e*	0.5682(2)	0.1832(3)	0.3956(2)	0.033(3)	0.043(3)	0.068(4)	–0.008(2)	0.019(3)	–0.012(3)
C(48)	4*e*	0.5371(2)	0.1452(3)	0.3286(2)	0.049(3)	0.042(3)	0.058(3)	–0.005(2)	0.033(3)	–0.001(2)
C(49)	4*e*	0.4696(2)	0.0860(2)	0.3042(2)	0.041(3)	0.034(3)	0.042(3)	0.001(2)	0.023(3)	–0.005(2)
C(50)	4*e*	0.2819(2)	0.1118(2)	0.4871(2)	0.046(3)	0.028(2)	0.066(3)	–0.003(2)	0.036(3)	0.009(2)
C(51)	4*e*	0.2831(2)	0.1569(3)	0.5538(2)	0.029(3)	0.047(3)	0.040(3)	–0.007(2)	0.013(2)	0.015(2)
C(52)	4*e*	0.2989(2)	0.0927(3)	0.6121(2)	0.037(3)	0.088(4)	0.062(4)	–0.012(3)	0.018(3)	0.026(3)
C(53)	4*e*	0.2971(3)	0.1360(5)	0.6739(3)	0.051(4)	0.155(6)	0.049(4)	–0.054(4)	0.008(3)	0.029(4)
C(54)	4*e*	0.2811(3)	0.2422(5)	0.6751(3)	0.063(4)	0.184(7)	0.044(4)	–0.066(5)	0.028(4)	–0.026(5)
C(55)	4*e*	0.2678(2)	0.3061(4)	0.6192(3)	0.051(4)	0.100(4)	0.076(4)	–0.026(3)	0.038(4)	–0.039(4)
C(56)	4*e*	0.2684(2)	0.2631(3)	0.5584(2)	0.041(3)	0.058(3)	0.038(3)	–0.017(2)	0.015(2)	–0.011(2)
C(57)	4*e*	–0.1112(2)	–0.0431(3)	0.1854(2)	0.057(3)	0.054(3)	0.031(3)	–0.010(2)	0.020(3)	–0.004(2)
C(58)	4*e*	–0.1439(2)	–0.0992(3)	0.2675(2)	0.052(3)	0.068(4)	0.047(3)	–0.020(3)	0.022(3)	0.002(3)
C(59)	4*e*	–0.1835(2)	–0.1524(3)	0.2073(2)	0.068(4)	0.054(3)	0.059(4)	–0.030(3)	0.028(3)	–0.004(3)

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