Crystal structure of 11,23-bis-(*tert*-butyl)-25,27-bis-(ethoxyethoxy)-26,28-bis-(propoxy)calix[4]arene, $C_{50}H_{68}O_6$

I. A. Bagatin[I], F. Balegroune*[,II] and D. Matt[III]

[I] Universidade de São Paulo, Instituto de Química, Caixa Postal 26077, CEP 05513-970, São Paulo, SP, Brazil
[II] USTHB, Faculté de Chimie, Laboratoire de Crystallographie-Thermodynamique, BP 32, El-Alia, Bab-Ezzouar, 16111 Alger, Algérie
[III] Université Louis Pasteur, Laboratoire de Chimie Inorganique Moléculaire, UMR CNRS 7513, 1 Rue Blaise Pascal, F-67008 Strasbourg Cedex, France

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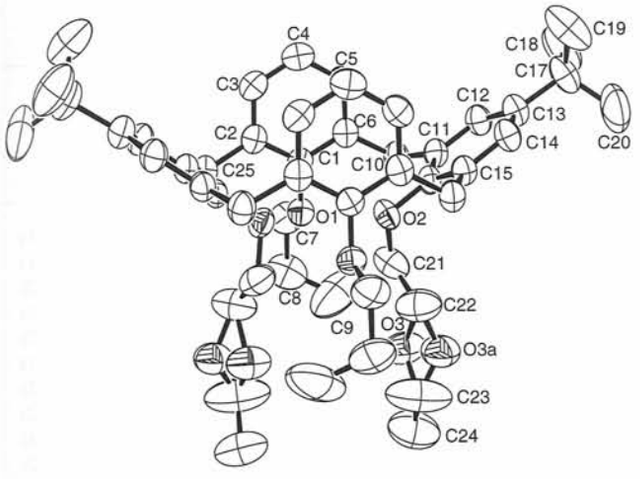

Abstract

$C_{50}H_{68}O_6$, monoclinic, *C*12/*c*1 (No. 15), $a = 25.4702(8)$ Å, $b = 11.013(1)$ Å, $c = 18.5662(8)$ Å, $\beta = 119.078(3)°$, $V = 4551.6$ Å^3, $Z = 4$, $R_{gt}(F) = 0.063$, $wR_{ref}(F^2) = 0.230$, $T = 293$ K.

Source of material

To a solution of 11,23-bis(*tert*-butyl)-25,27-bis(2-ethoxyethoxy)-calix[4]arene[1] (10.000 g, 14.7 mmol) in dimethylformamide (1000 ml) was added NaH (0.888 g, 37.0 mmol), followed by propyl bromide (9.040 g, 73.5 mmol, ca. 6.85 ml). The solution was kept at 80°C under stirring for 3 hours before quenching with methanol (50 ml) and water (50 ml). The compound was extracted with ethyl acetate (300 ml), washed twice with water and the organic layer was dried with $MgSO_4$. The solution was concentrated and methanol was added to precipitate a white microcrystalline powder (yield 9.370 g, 84%). Composition calculated for $C_{50}H_{68}O_6$: C, 78.49%; H, 8.96%; found: C, 78.20%; H, 8.82%. A small single crystal selected from the polycrystalline precipitate was used for X-ray data collection.

Experimental details

The structure was solved by direct methods [2] and the least-squares refinement of the structure was performed by using the program SHELXL-97 [3]. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were placed in corresponding calculated positions (d(C—H) = 0.95 Å for methyl and methylene groups and d(C—H) = 0.93 Å for the phenyl rings), but not refined. The O3 oxygen atom is disordered over two positions.

Discussion

An Ortep [4] drawing of the molecule is shown in the Fig. The molecule is located on a crystallographic two-fold axis. The macrocyclic framework adopts the commonly observed cone conformation with dihedral angles between the mean planes of opposite phenyl rings of 4.7 and 71.8°. The distances between the centroids of these opposite rings are 5.5 and 7.6 Å, respectively. The dihedral angles between neighboring phenol rings are 88°, while the adjacent centroids are 4.7 Å apart. The two long ethoxyethyl chains are oriented in a roughly parallel fashion.

Table 1. Data collection and handling.

Crystal:	colorless prism, size 0.13 × 0.22 × 0.35 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	0.71 cm^{-1}
Diffractometer, scan mode:	Enraf Nonius CAD4, ω-2θ
$2\theta_{max}$:	52.58°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	4408, 4405
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 2431
$N(param)_{refined}$:	263
Programs:	SHELXS-97 [2], SHELXL-97 [3], ORTEP-3 [4]

* Correspondence author (e-mail: fadilabalegroune@yahoo.fr)

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

Atom	Site	x	y	z	U_{iso}
H(3)	8*f*	0.9992	0.0080	0.5741	0.068
H(4)	8*f*	0.9281	–0.0974	0.5913	0.078
H(5)	8*f*	0.8590	0.0051	0.6138	0.069
H(7A)	8*f*	0.8448	0.3709	0.4700	0.085
H(7B)	8*f*	0.9018	0.3703	0.4611	0.085
H(8A)	8*f*	0.9236	0.5672	0.5182	0.110
H(8B)	8*f*	0.8670	0.5626	0.4334	0.110
H(9A)	8*f*	0.8503	0.6802	0.5196	0.260
H(9B)	8*f*	0.8657	0.5722	0.5802	0.262
H(9C)	8*f*	0.8085	0.5676	0.4944	0.262
H(10A)	8*f*	0.7993	0.2128	0.5834	0.065
H(10B)	8*f*	0.8414	0.3234	0.6148	0.065
H(12)	8*f*	0.7775	0.1131	0.6773	0.062
H(14)	8*f*	0.8894	0.1137	0.9192	0.063
H(18A)	8*f*	0.7412	–0.0621	0.7043	0.163
H(18B)	8*f*	0.7055	0.0520	0.7045	0.163
H(18C)	8*f*	0.7022	–0.0662	0.7476	0.163

Table 2. Continued.

Atom	Site	x	y	z	U_{iso}
H(19A)	8*f*	0.8466	–0.0687	0.9147	0.168
H(19B)	8*f*	0.8248	–0.1392	0.8327	0.168
H(19C)	8*f*	0.7854	–0.1358	0.8752	0.168
H(20A)	8*f*	0.7941	0.1251	0.9152	0.197
H(20B)	8*f*	0.7347	0.0516	0.8780	0.197
H(20C)	8*f*	0.7387	0.1690	0.8348	0.197
H(21A)	8*f*	0.8832	0.4485	0.7114	0.090
H(21B)	8*f*	0.9429	0.4774	0.7135	0.090
H(22A)	8*f*	0.9903	0.5131	0.8640	0.050
H(22B)	8*f*	0.9228	0.4992	0.8482	0.050
H(23A)	8*f*	0.9656	0.6651	0.8100	0.050
H(23B)	8*f*	0.9776	0.7467	0.8762	0.050
H(24A)	8*f*	0.9470	0.9036	0.7812	0.201
H(24B)	8*f*	0.8857	0.8742	0.7762	0.201
H(24C)	8*f*	0.8999	0.8257	0.7090	0.201
H(25A)	8*f*	1.0127	0.3278	0.5710	0.061
H(25B)	8*f*	1.0186	0.2217	0.5218	0.061

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(1)	8*f*		0.9236(1)	0.2366(3)	0.5844(2)	0.043(2)	0.048(2)	0.036(1)	0.002(1)	0.017(1)	0.002(1)
C(2)	8*f*		0.9690(1)	0.1762(3)	0.5769(2)	0.044(2)	0.059(2)	0.036(1)	0.003(1)	0.017(1)	–0.001(1)
C(3)	8*f*		0.9699(2)	0.0502(3)	0.5800(2)	0.059(2)	0.059(2)	0.053(2)	0.006(2)	0.028(2)	–0.005(2)
C(4)	8*f*		0.9280(2)	–0.0129(3)	0.5916(2)	0.072(2)	0.052(2)	0.069(2)	–0.000(2)	0.032(2)	–0.005(2)
C(5)	8*f*		0.8861(2)	0.0487(3)	0.6037(2)	0.060(2)	0.058(2)	0.055(2)	–0.008(2)	0.029(2)	0.001(2)
C(6)	8*f*		0.8832(1)	0.1740(3)	0.6013(2)	0.041(2)	0.061(2)	0.037(1)	0.001(1)	0.015(1)	0.002(1)
C(7)	8*f*		0.8846(2)	0.4013(3)	0.4927(2)	0.075(2)	0.073(2)	0.050(2)	0.015(2)	0.020(2)	0.014(2)
C(8)	8*f*		0.8834(2)	0.5380(4)	0.4893(3)	0.090(3)	0.086(3)	0.069(3)	0.011(2)	0.017(2)	0.032(2)
C(9)	8*f*		0.8490(4)	0.5944(6)	0.5239(4)	0.29(1)	0.129(5)	0.126(5)	0.115(6)	0.119(6)	0.059(4)
C(10)	8*f*		0.8390(1)	0.2383(3)	0.6211(2)	0.043(2)	0.070(2)	0.049(2)	0.003(1)	0.022(1)	0.007(2)
C(11)	8*f*		0.8520(1)	0.2113(3)	0.7085(2)	0.041(1)	0.056(2)	0.046(2)	0.004(1)	0.023(1)	0.005(1)
C(12)	8*f*		0.8132(1)	0.1383(3)	0.7224(2)	0.039(1)	0.065(2)	0.048(2)	–0.005(1)	0.019(1)	–0.000(1)
C(13)	8*f*		0.8251(1)	0.1016(3)	0.8000(2)	0.046(2)	0.066(2)	0.049(2)	–0.005(2)	0.024(1)	0.005(2)
C(14)	8*f*		0.8797(1)	0.1390(3)	0.8664(2)	0.048(2)	0.066(2)	0.045(2)	–0.004(1)	0.023(1)	0.008(1)
C(15)	8*f*		0.9197(1)	0.2121(3)	0.8561(2)	0.042(2)	0.056(2)	0.047(2)	–0.002(1)	0.023(1)	0.000(1)
C(16)	8*f*		0.9044(1)	0.2513(3)	0.7771(2)	0.038(1)	0.052(2)	0.049(2)	0.003(1)	0.026(1)	0.005(1)
C(17)	8*f*		0.7809(2)	0.0253(4)	0.8151(2)	0.053(2)	0.093(3)	0.068(2)	–0.022(2)	0.028(2)	0.011(2)
C(18)	8*f*		0.7275(2)	–0.0166(5)	0.7354(3)	0.073(3)	0.146(4)	0.089(3)	–0.055(3)	0.024(2)	0.011(3)
C(19)	8*f*		0.8125(2)	–0.0908(5)	0.8641(3)	0.088(3)	0.125(4)	0.095(3)	–0.035(3)	0.023(3)	0.038(3)
C(20)	8*f*		0.7602(2)	0.0997(6)	0.8655(4)	0.117(4)	0.174(6)	0.154(5)	–0.052(4)	0.107(4)	–0.032(4)
C(21)	8*f*		0.9257(2)	0.4467(3)	0.7451(3)	0.066(2)	0.065(2)	0.084(3)	–0.007(2)	0.029(2)	0.016(2)
C(22)	8*f*		0.9426(2)	0.5251(4)	0.8159(3)	0.088(3)	0.067(3)	0.106(4)	0.009(2)	0.024(3)	–0.002(2)
C(23)	8*f*		0.9410(3)	0.7386(5)	0.8124(4)	0.188(7)	0.073(3)	0.121(5)	–0.017(4)	0.004(4)	0.007(4)
C(24)	8*f*		0.9164(3)	0.8440(5)	0.7660(4)	0.156(5)	0.085(4)	0.133(5)	–0.001(4)	0.049(4)	0.030(3)
C(25)	8*f*		1.0192(1)	0.2428(3)	0.5718(2)	0.045(2)	0.064(2)	0.047(2)	0.006(1)	0.025(1)	0.005(1)
O(1)	8*f*		0.91939(9)	0.3621(2)	0.5768(1)	0.049(1)	0.052(1)	0.045(1)	0.0073(9)	0.0210(9)	0.0094(9)
O(2)	8*f*		0.94436(8)	0.3248(2)	0.7671(1)	0.044(1)	0.058(1)	0.059(1)	–0.0040(9)	0.028(1)	0.008(1)
O(3)	8*f*	0.50	0.9264(4)	0.6439(6)	0.7655(4)	0.125(6)	0.070(4)	0.057(4)	0.001(4)	0.029(4)	–0.002(3)
O(3A)	8*f*	0.50	0.9146(3)	0.6424(6)	0.8089(5)	0.099(5)	0.063(4)	0.119(6)	0.003(3)	0.055(5)	0.003(4)

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