Crystal Structure of 25-(2-*tert*-Butoxyethoxy)-27-hydroxycalix[4]arene-crown-6 in the Cone Conformation

Jean GUILLON,^{*,†} Jean-Michel LEGER,^{*} Pascal SONNET,^{**} and Christian JARRY^{*}

^{*}EA 2962-Pharmacochimie, Université Victor Segalen Bordeaux 2, 146, rue Léo Saignat, 33076 Bordeaux, France

^{**}GRBPD, EA 2629, Université de Picardie Jules Verne, 1, rue des Louvels, 80037 Amiens, France

Alkylation of calix[4]arene-crown-6 by 2-*tert*-butoxyethyl bromide with sodium hydride as a base led to 25-(2-*tert*-butoxyethoxy)-27-hydroxycalix[4]arene-crown-6 in the cone conformation. The conformation of the latter monoalkylated calix[4]arene-crown-6 was established by X-ray crystallography. It crystallizes in the triclinic space group $P\bar{1}$. This monoalkylated calixarene-crown-6 can be used as a synthon useful for the preparation of bisalkylated mixed calix[4]arene-crown-6 atropisomers.

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The chemistry of calix[4]arenes, cyclic tetramers comprising phenolic and methylene moieties, has received considerable attention in recent years. The available sites on these macrocyclic compounds, that can be easily modified to tailor them for application as ionophores in catalysis, and in heavy metal absorption, alkali metal complexation and chemical sensors have been examined.¹ Calix[4]arene-crown-6 compounds show high affinity for the complexation of alkali and alkaline-earth metal ions. During the course of our work on the synthesis of calixarene crown ethers, proposed as potential extractants for the removal of ¹³⁷Cs from nuclear waste solutions by solvent extraction,² we focused our interest on the synthesis of new 1,3-bis(alkyloxy)calix[4]arenes-crown-6 in their three possible conformations, *i.e.* 1,3-alternate, cone, and partial-cone.³ During preparation of the cone conformers, we also isolated the 25-alkyloxy-27-hydroxycalix[4]arene-crown-6 in the cone conformation. These monoalkylated calixcrown ethers are found to be useful synthons for the preparation of bisalkylated mixed calix[4]arene-crown-6 atropisomers.⁴ We herein report on the structural characterization of one of them, *i.e.* the cone 25-(2-*tert*-butoxyethoxy)-27-hydroxycalix[4]arene-crown-6 (Fig. 1), which was synthesized according to a method described by the authors.⁴ Single crystals were obtained from a chloroform-methanol solution.

Fig. 1 Chemical structure.

The structure of 25-(2-*tert*-butoxyethoxy)-27-hydroxycalix[4]arene-crown-6 is illustrated in Fig. 2. X-ray data confirmed the cone conformation in the solid state. Thus, the two rings, C22-C27 and C8-C13, linked by a polyether chain, are almost parallel to one another. This parallelism was corroborated by the O37-O52, C13-C27 and C10-C24 distances, which are 5.33, 5.33 and 5.34 Å, respectively. The

Fig. 2 Views of the crystal structure of the molecule with our numbering scheme. Displacement ellipsoids are drawn at the 30% probability level; H atoms are omitted for clarity.

[†] To whom correspondence should be addressed.
E-mail: Jean.Guillon@chimphys.u-bordeaux2.fr

Table 1 Crystal and experimental data

Formula: C ₄₄ H ₅₄ O ₉
Formula weight: 726.87
Crystal system: triclinic
Space group: $P\bar{1}$
$a = 10.214(1)\text{\AA}$
$b = 12.734(5)\text{\AA}$
$c = 16.062(2)\text{\AA}$
$\alpha = 84.74(2)^\circ$
$\beta = 87.84(1)^\circ$
$\gamma = 75.77(2)^\circ$
Colorless, fragment
Crystal size = $0.75 \times 0.50 \times 0.12\text{ mm}^3$
$D_x = 1.197\text{ mg/m}^3$
$F(0\ 0\ 0) = 780$
$\mu = 0.667\text{ mm}^{-1}$
Temperature = 296(2)K
$\theta_{\text{max}} = 64.88^\circ$
Radiation: CuK α ($\lambda = 1.54178\text{ \AA}$)
No. of reflection used = 6795
$R = 0.088$
$wR = 0.2599$
Goodness-of-fit = 1.069
$(\Delta/\sigma)_{\text{max}} = 0.178$
$(\Delta\rho)_{\text{max}} = 0.325\text{ \AA}^{-3}$
$(\Delta\rho)_{\text{min}} = -0.347\text{ \AA}^{-3}$
Measurement: Enraf-Nonius CAD ⁵
Structure determination: SHELXS-97 ⁶
Refinement: SHELXL-97 ⁷

two oxygen atoms, the one of the hydroxy function and one bearing the alkyloxy chain are pointed to the cavity in a very closed proximity (3.23 Å), leading to a large lengthening of the corresponding para C-atoms (9.92 Å). Crystal and experimental data are given in Table 1.

The interplanar angle of the two aromatic rings linked by the polyether ring (C22–C27, C8–C13) is $0.8(1)^\circ$, while the angle between the two other opposite phenol groups (C1–C6, C15–C20) is $70.4(1)^\circ$. The dihedral angles between the aromatic units of the calix[4]arene skeleton through the methylene carbons are $111.0(3)$, $111.7(3)$, $111.6(2)$ and $111.7(2)^\circ$, respectively. The polyether chain in this cone isomer does not adopt a regular conformation, described by the torsion angles O–C–C–O, which are $74.7(4)$, $-85.6(9)$, $81.5(12)$, $74.9(11)$ and $-71.1(4)^\circ$. Moreover, the C–O–C–C torsion angles ($-169.7(3)$, $-163.0(6)$, $-173.8(9)$, $76.2(11)$ and $-179.6(4)^\circ$) are also markedly different.

Final atomic coordinates and equivalent isotropic thermal parameters are listed in Table 2.

The inter-calixarene contacts are of the van der Waals variety, and there are no solvent accessible voids in the crystal lattice.

Additionally, there is one C–H...O hydrogen bond observed ($\text{H4}\cdots\text{O46}' = 2.58\text{ \AA}$, $\text{C4-H4} = 179^\circ$, with symmetry code $x - 1, 1 + y, z$ for O46').

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Table 2 Final atomic coordinates and equivalent isotropic thermal parameters (U_{eq})

Atom	x	y	z	U_{eq}
C(1)	0.8106(3)	0.5230(2)	0.1952(2)	0.059(1)
C(2)	0.7413(3)	0.5498(2)	0.1197(2)	0.064(1)
C(3)	0.6419(3)	0.6466(3)	0.1121(2)	0.076(1)
C(4)	0.6103(3)	0.7127(3)	0.1765(2)	0.082(1)
C(5)	0.6733(3)	0.6807(2)	0.2513(2)	0.074(1)
C(6)	0.7733(3)	0.5855(2)	0.2623(2)	0.062(1)
C(7)	0.8369(3)	0.5447(3)	0.3474(2)	0.070(1)
C(8)	0.7849(3)	0.4502(3)	0.3876(2)	0.066(1)
C(9)	0.6491(3)	0.4632(3)	0.4073(2)	0.078(1)
C(10)	0.5999(4)	0.3772(3)	0.4401(2)	0.087(1)
C(11)	0.6852(4)	0.2747(3)	0.4526(2)	0.090(1)
C(12)	0.8218(3)	0.2572(3)	0.4339(2)	0.076(1)
C(13)	0.8701(3)	0.3464(3)	0.4036(2)	0.066(1)
C(14)	0.9134(4)	0.1426(3)	0.4416(3)	0.092(1)
C(15)	0.8740(3)	0.0715(3)	0.3810(2)	0.079(1)
C(16)	0.8186(4)	-0.0148(3)	0.4076(3)	0.090(1)
C(17)	0.7772(5)	-0.0758(3)	0.3526(3)	0.100(1)
C(18)	0.7881(4)	-0.0503(3)	0.2676(3)	0.095(1)
C(19)	0.8442(4)	0.0358(3)	0.2370(2)	0.082(1)
C(20)	0.8897(3)	0.0936(2)	0.2942(2)	0.075(1)
C(21)	0.8503(5)	0.0691(3)	0.1449(2)	0.095(1)
C(22)	0.7520(4)	0.1783(3)	0.1234(2)	0.078(1)
C(23)	0.6158(4)	0.1936(3)	0.1407(2)	0.092(1)
C(24)	0.5275(4)	0.2948(4)	0.1272(3)	0.094(1)
C(25)	0.5756(4)	0.3833(3)	0.0979(2)	0.081(1)
C(26)	0.7113(3)	0.3727(3)	0.0789(2)	0.068(1)
C(27)	0.7974(3)	0.2686(3)	0.0897(2)	0.070(1)
C(28)	0.7644(3)	0.4712(3)	0.0522(2)	0.073(1)
O(29)	0.9113(2)	0.4292(2)	0.2067(1)	0.074(1)
C(30)	1.0378(3)	0.4280(4)	0.1658(3)	0.113(2)
C(31)	1.1213(5)	0.4870(5)	0.1939(3)	0.131(2)
O(32)	1.1343(4)	0.5155(4)	0.2654(3)	0.068(1)
C(33)	1.1886(4)	0.6202(4)	0.2685(3)	0.098(1)
C(34)	1.3016(7)	0.6306(7)	0.2103(5)	0.179(3)
C(35)	1.2275(7)	0.5826(6)	0.3554(4)	0.157(2)
C(36)	1.0881(7)	0.7290(6)	0.2712(5)	0.181(3)
O(37)	1.0072(2)	0.3300(2)	0.3842(1)	0.071(1)
C(38)	1.0871(3)	0.3340(3)	0.4547(2)	0.081(1)
C(39)	1.2313(4)	0.2963(4)	0.4338(3)	0.094(1)
O(40)	1.2613(3)	0.1841(3)	0.4282(2)	0.107(1)
C(41)	1.3965(6)	0.1350(7)	0.4055(6)	0.188(3)
C(42)	1.3944(11)	0.0213(10)	0.3758(7)	0.263(6)
O(43)	1.3619(11)	0.0527(18)	0.2910(7)	0.500(15)
C(44)	1.2819(12)	-0.0162(16)	0.2879(11)	0.343(12)
C(45)	1.2610(11)	-0.0120(9)	0.1940(6)	0.215(4)
O(46)	1.3727(6)	-0.0346(5)	0.1501(4)	0.198(2)
C(47)	1.3521(11)	-0.0427(7)	0.0601(6)	0.212(4)
C(48)	1.3049(8)	0.0666(7)	0.0122(5)	0.172(3)
O(49)	1.1706(4)	0.0997(3)	0.0165(2)	0.117(1)
C(50)	1.1157(5)	0.2032(3)	-0.0257(3)	0.101(1)
C(51)	0.9665(4)	0.2273(3)	-0.0140(2)	0.090(1)
O(52)	0.9338(2)	0.2547(2)	0.0705(1)	0.076(1)
O(53)	0.9516(2)	0.1732(2)	0.2635(2)	0.083(1)