

Calixcrown Binding to Caesium – X-Ray Structural Determination of a 1,3-Alternate Calix[4]arene**biscrown-7** Ligand

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Abstract. The crystal structure of calix[4]*biscrown-7*, **1**, (C₅₂H₆₈O₁₄), (triclinic, space group *P*1, *Z* = 2, *a* = 11.115 (5), *b* = 11.710 (5), *c* = 18.990 (7) Å, α = 85.12 (4), β = 93.11 (5), γ = 91.01 (5)°, *V* = 2458.9 Å³, *R*_w = 0.0737 for 4170 'observed', *I* ≥ 3σ(*I*), reflections) has been determined. It is suggested that the polyether loops with a radius of ca. 2.1 Å are too shallow to efficiently complex the Cs⁺ cation (radius = 1.69 Å).

Key words. Calixarenes, calixcrowns, caesium, complexation.

Supplementary Data relevant to this publication have been deposited with the British Library, Boston Spa, Wetherby, Yorkshire, U.K. as Supplementary Publication SUP 82221 (30 pages).

1. Introduction

Calix[4]arenes fixed in the 1,3-alternate conformation by the linkage of rings 1 and 3 with separate polyether chains, 'doubly-crowned calices' or 'calix-bis-crowns', have recently been shown to be highly selective caesium ion carriers when the polyether chains contain six oxygen donor atoms with the oxygen other than those bound directly to the calixarene moiety, linked by ethylene or 1,2-phenylene groups [1–4]. Although Cs⁺ transport phenomena could be rationalised simply in terms of the formation of 1 : 1 complexes [1–5], more recent conductometric [6], spectroscopic [7, 8] and X-ray structural studies [8, 9] have all shown that dicaesium complexes may also be readily formed by these ligands. In both the 1 : 1 and 2 : 1 complexes that have been characterised structurally, Cs⁺ is bound to the six oxygen atoms of a polyether loop and to one or two atoms of a counteranion (though in the one published study [10] of the 1 : 1 caesium picrate complex of a calix*monocrown-6*, the cation is bound to only five of the ether oxygen atoms).

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There is also evidence of some degree of coordinative interaction of the caesium with π -electrons of the calixarene phenyl rings [9–11], and in this regard it is of interest that our recent structural study of a symmetrical calix**biscrown**-6, in which a single 1,3-phenylene ‘spacer’ group was introduced between one pair of oxygen atoms in each arm, has shown that the tilt of the phenyl rings towards the potential cation binding cavities is opposite to that in other known analogues and unfavourable for cation interaction [12]. This may partly explain why the ligand appears to be a relatively poor caesium binder and forms a complex of 1 : 2 (metal : ligand) stoichiometry.

In the present communication, to further continue our exploration of the factors controlling selectivity in metal cation complexation by calixcrowns, we report the structural characterisation of calix[4]-*bis*-crown-7, **1**.

2. Experimental

2.1. SYNTHESIS

The ligand calix[4]-*bis*-crown-7, **1**, was prepared according to the literature method [4]. Crystals of ligand **1** suitable for an X-ray structure determination were grown from 1 : 1 chloroform/methanol.

2.2. STRUCTURE DETERMINATION

A white crystal of dimensions (0.50 × 0.30 × 0.40) mm³ was mounted on a Philips PW1100 diffractometer with graphite monochromated MoK α radiation. Lattice parameters were determined from least squares analysis of 25 reflections with $15 < \theta < 26^\circ$. The reflection profiles were analysed with the Lehman-Larsen algorithm [13]. Using ω - 2θ step scanning mode, scan speed 0.03°/s, scan width 1.5°, 9139 independent reflections were collected up to $\theta = 25^\circ$ in which 4170 ($I \geq 3\sigma(I)$) were considered as observed and used in the structure analysis and refinement. The intensities of four reference reflections measured every two hours of X-ray exposure time showed no significant variation. Lorentz polarisation corrections were applied but absorption and extinction were ignored.

The structure was solved by direct methods using 499 reflections with $E > 2.0$ in MULTAN80 [14] and refined on F by the full-matrix anisotropic least squares technique [15]. Hydrogen atoms were fixed at their geometric positions. The final R index was 0.073 ($R_w = 0.073$, $w = 1$). Atomic scattering factors in the analytical forms were taken from the *International Tables of X-ray Crystallography*.

3. Results and Discussion

Final atomic co-ordinates of non-H atoms and equivalent isotropic thermal parameters are listed in Table I. Bond lengths and angles are shown in Table II. Figure 1, drawn by the ORTEP [16] program, shows the molecular structure with atom

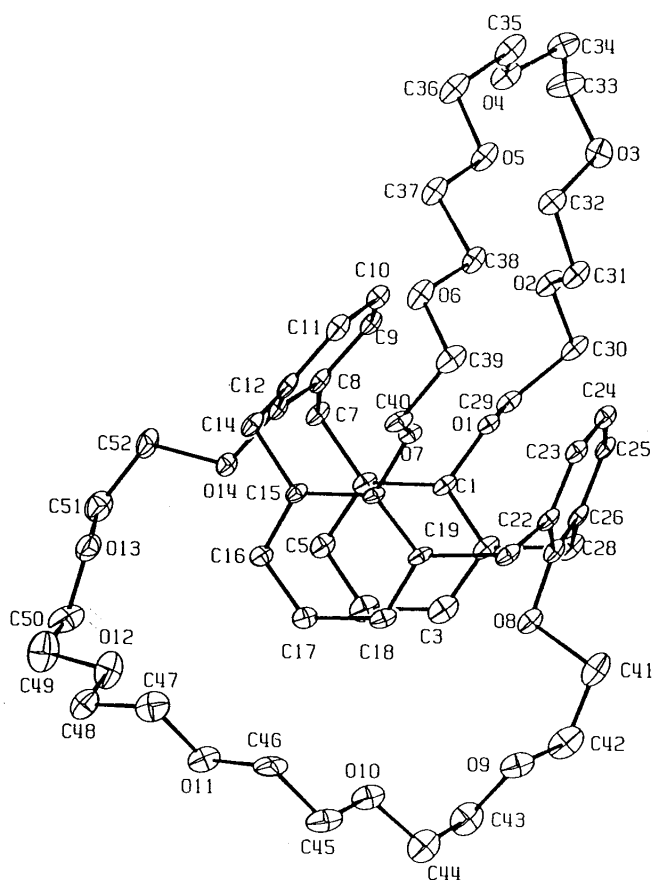


Figure 1. ORTEP [16] perspective view of the title compound with atomic numbering scheme; thermal ellipsoids drawn at 50% probability level. The H atoms have been omitted for clarity.

labelling of the ligand calix[4]-bis-crown-7. Figure 2 shows the stereoscopic view of the compound.

The crystal structure confirms the expected 1,3-alternate conformation of the calixarene moiety and the 1,3 and 2,4 linking by O(7) polyether bridges. As is commonly observed in crown ether structures [17], the conformations of the polyether chains in the free ligand are not such as to direct the lone pairs on all oxygen atoms convergently towards a central point. In the polyether chains, the O—C—C—O torsion angles range from 65.12 to 79.79° except for O(5)—C(37)—C(38)—O(6) where the value is 178.24°. The C—O—C—C angles range from 83.90 to 94.46°. The relative dihedral angles between two opposite aromatic rings are 15.45° and 20.73° whereas they are 91.47°, 87.34°, 90.29° and 91.67° between two adjacent rings. Molecular geometry can be related to the mean molecular plane defined by the bridging methylene groups where the methylene showed out of plane distances

Table I. Fractional atomic co-ordinates ($\times 10^4$) and equivalent isotropic thermal factors ($\text{\AA}^2 \times 10^3$)

$$U_{\text{eq}} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \mathbf{a}_j$$

| | <i>X</i> | <i>Y</i> | <i>Z</i> | U_{eq} |
|-------|-----------|-----------|----------|-----------------|
| C(1) | 7071 (5) | 106 (5) | 3269 (3) | 54 (7) |
| C(2) | 8087 (5) | 614 (5) | 3036 (3) | 63 (8) |
| C(3) | 8014 (7) | 928 (6) | 2348 (4) | 96 (11) |
| C(4) | 7008 (7) | 735 (7) | 1917 (4) | 103 (12) |
| C(5) | 6040 (6) | 156 (6) | 2137 (3) | 77 (10) |
| C(6) | 6093 (5) | -179 (5) | 2833 (3) | 61 (8) |
| C(7) | 5087 (5) | -914 (5) | 3049 (3) | 58 (8) |
| C(8) | 5575 (5) | -2108 (5) | 3135 (3) | 47 (7) |
| C(9) | 5840 (5) | -2451 (5) | 3815 (3) | 52 (8) |
| C(10) | 6376 (6) | -3503 (6) | 3893 (3) | 59 (8) |
| C(11) | 6689 (5) | -4194 (5) | 3320 (3) | 61 (8) |
| C(12) | 6453 (5) | -3875 (5) | 2635 (3) | 48 (8) |
| C(13) | 5852 (5) | -2842 (5) | 2569 (3) | 46 (7) |
| C(14) | 6944 (5) | -4581 (5) | 2013 (3) | 55 (8) |
| C(15) | 8014 (5) | -3986 (5) | 1759 (3) | 55 (8) |
| C(16) | 7884 (6) | -3416 (6) | 1139 (3) | 70 (10) |
| C(17) | 8816 (7) | -2774 (6) | 952 (3) | 77 (10) |
| C(18) | 9845 (6) | -2640 (6) | 1370 (3) | 77 (9) |
| C(19) | 10009 (5) | -3199 (5) | 1992 (3) | 60 (8) |
| C(20) | 9083 (6) | -3897 (5) | 2153 (3) | 56 (8) |
| C(21) | 11073 (5) | -2941 (5) | 2495 (3) | 65 (8) |
| C(22) | 10679 (5) | -2197 (5) | 3126 (3) | 54 (8) |
| C(23) | 10547 (5) | -2646 (5) | 3775 (3) | 60 (8) |
| C(24) | 10053 (5) | -1994 (5) | 4322 (3) | 58 (8) |
| C(25) | 9653 (5) | -903 (5) | 4243 (3) | 48 (8) |
| C(26) | 9781 (5) | -419 (5) | 3604 (3) | 44 (7) |
| C(27) | 10336 (5) | -1067 (5) | 3078 (3) | 53 (8) |
| C(28) | 9223 (5) | 740 (5) | 3498 (3) | 63 (8) |
| O(1) | 7111 (3) | -137 (3) | 3970 (2) | 52 (4) |
| C(29) | 6510 (5) | 708 (5) | 4403 (3) | 59 (8) |
| C(30) | 6866 (6) | 605 (5) | 5166 (3) | 63 (8) |
| O(2) | 6454 (4) | -427 (3) | 5404 (2) | 75 (6) |
| C(31) | 7342 (6) | -1277 (6) | 5467 (4) | 75 (9) |
| C(32) | 6794 (7) | -2255 (5) | 5790 (4) | 80 (10) |
| O(3) | 6577 (5) | -1894 (4) | 6508 (2) | 91 (8) |
| C(33) | 5677 (9) | -2503 (7) | 6803 (4) | 140 (15) |
| C(34) | 6006 (8) | -3673 (7) | 6923 (4) | 104 (13) |
| O(4) | 6021 (5) | -4330 (4) | 6266 (3) | 93 (7) |
| C(35) | 6537 (6) | -5396 (6) | 6327 (4) | 91 (11) |
| C(36) | 6644 (6) | -5996 (6) | 5617 (4) | 79 (10) |

Table I. Continued

| | <i>X</i> | <i>Y</i> | <i>Z</i> | <i>U</i> _{eq} |
|-------|------------|------------|-----------|------------------------|
| O(5) | 7611 (4) | -5536 (4) | 5276 (2) | 71 (6) |
| C(37) | 7783 (6) | -6151 (5) | 4625 (4) | 66 (9) |
| C(38) | 8886 (6) | -5691 (5) | 4326 (3) | 59 (9) |
| O(6) | 8994 (4) | -6306 (4) | 3664 (2) | 71 (6) |
| C(39) | 10067 (6) | -6070 (6) | 3326 (4) | 91 (10) |
| C(40) | 9750 (6) | -5603 (5) | 2620 (3) | 76 (9) |
| O(7) | 9250 (3) | -4476 (3) | 2765 (2) | 60 (5) |
| O(8) | 10512 (3) | -583 (3) | 2447 (2) | 67 (5) |
| C(41) | 11688 (6) | -75 (7) | 2468 (4) | 90 (12) |
| C(42) | 11739 (8) | 522 (8) | 1802 (5) | 120 (15) |
| O(9) | 11899 (5) | -278 (5) | 1229 (3) | 123 (8) |
| C(43) | 11519 (8) | 184 (9) | 587 (5) | 129 (16) |
| C(44) | 11812 (9) | -596 (9) | 5 (5) | 124 (16) |
| O(10) | 11111 (5) | -1593 (5) | -30 (3) | 119 (9) |
| C(45) | 11358 (9) | -2387 (10) | -587 (5) | 146 (16) |
| C(46) | 10645 (10) | -3416 (9) | -574 (4) | 140 (16) |
| O(11) | 9435 (6) | -3188 (5) | -817 (3) | 107 (9) |
| C(47) | 8701 (14) | -4108 (9) | -791 (5) | 129 (18) |
| C(48) | 7518 (16) | -3873 (14) | -1082 (6) | 63 (21) |
| O(12) | 6923 (7) | -3167 (7) | -559 (4) | 112 (14) |
| C(49) | 5739 (15) | -3157 (23) | -741 (8) | 159 (20) |
| C(50) | 5161 (14) | -2455 (25) | -233 (10) | 232 (18) |
| O(13) | 4961 (7) | -2966 (10) | 397 (4) | 95 (15) |
| C(51) | 4227 (10) | -2463 (10) | 883 (6) | 114 (18) |
| C(52) | 4424 (6) | -2868 (7) | 1603 (4) | 81 (12) |
| O(14) | 5577 (4) | -2517 (4) | 1888 (2) | 62 (5) |

of 0.0495, -0.0515, 0.0267 and -0.0247 Å. The conformation of the macrocycle may be defined by the dihedral angles that the aromatic rings make with the mean molecular plane: 100.47, 76.58, 85.04 and 82.70°. The aperture of the crowned calixarene can be measured by the distances between the O atoms (Table III). This geometric feature leads to a radius of each ether loop equal to 2.1 Å.

The present structural data, along with others described in the literature, allows an evaluation of the order of selectivity of complexation of alkali cations by calix[4]-*bis*-crowns-*x* in relation to the number (*x*) of oxygen donor atoms in the glycolic chain (*x* = 5, 6, and 7): (a) *x* = 5 (radius of either polyether loop is ca. 1.51 Å) [17] is complementary to both K⁺ (radius = 1.33 Å) and Rb⁺ (radius = 1.48 Å); (b) *x* = 6 is suitable for Cs⁺ (radius = 1.69 Å); and (c) *x* = 7 (radius of either loop is ca. 2.1 Å) is too shallow for effective complexation, in agreement with the literature data on the alkali cation extractions and transporting properties of calix[4]-*bis*-crowns [4].

Table II. Bond lengths (Å) and angles (°) with e.s.ds.

| Atom(1)—Atom(2) | Distance | Atom(1)—Atom(2) | Distance |
|-----------------|------------|-------------------|------------|
| C(1)—O(2) | 1.346 (8) | O(1)—C(29) | 1.524 (7) |
| C(1)—C(6) | 1.384 (8) | C(29)—C(30) | 1.477 (8) |
| C(1)—O(1) | 1.336 (7) | C(30)—O(2) | 1.336 (7) |
| C(2)—C(3) | 1.325 (9) | O(2)—C(31) | 1.408 (8) |
| C(2)—C(28) | 1.510 (8) | C(31)—C(32) | 1.398 (10) |
| C(3)—C(4) | 1.376 (11) | C(32)—O(3) | 1.494 (8) |
| C(4)—C(5) | 1.343 (8) | O(3)—C(33) | 1.339 (11) |
| C(6)—C(7) | 1.455 (8) | C(33)—C(34) | 1.420 (12) |
| C(7)—C(8) | 1.501 (8) | C(34)—O(4) | 1.522 (9) |
| C(8)—C(9) | 1.338 (8) | O(4)—C(35) | 1.376 (9) |
| C(8)—C(13) | 1.482 (8) | C(35)—C(36) | 1.584 (10) |
| C(9)—C(10) | 1.372 (9) | C(36)—O(5) | 1.363 (8) |
| C(10)—C(11) | 1.471 (9) | O(5)—C(37) | 1.507 (8) |
| C(12)—C(13) | 1.385 (8) | C(37)—C(38) | 1.454 (9) |
| C(12)—C(14) | 1.621 (8) | C(38)—C(39) | 1.398 (8) |
| C(13)—O(14) | 1.337 (7) | C(39)—C(40) | 1.432 (9) |
| C(14)—C(15) | 1.451 (8) | C(40)—C(7) | 1.493 (7) |
| C(15)—C(16) | 1.306 (8) | O(8)—C(41) | 1.427 (8) |
| C(15)—C(20) | 1.376 (8) | C(41)—C(42) | 1.396 (12) |
| C(16)—C(17) | 1.316 (10) | C(42)—O(9) | 1.514 (11) |
| C(17)—C(18) | 1.371 (10) | O(9)—C(43) | 1.340 (11) |
| C(18)—C(19) | 1.306 (8) | C(43)—C(44) | 1.544 (14) |
| C(19)—C(20) | 1.336 (9) | C(44)—O(10) | 1.397 (12) |
| C(19)—C(21) | 1.522 (8) | O(10)—C(45) | 1.505 (12) |
| C(20)—O(7) | 1.301 (7) | C(45)—C(46) | 1.430 (16) |
| C(21)—C(22) | 1.623 (8) | C(46)—O(11) | 1.420 (13) |
| C(22)—C(23) | 1.313 (8) | O(11)—C(47) | 1.338 (14) |
| C(22)—C(27) | 1.379 (8) | C(47)—C(48) | 1.420 (22) |
| C(23)—C(24) | 1.474 (8) | C(48)—O(12) | 1.530 (17) |
| C(24)—C(25) | 1.354 (8) | O(12)—C(49) | 1.342 (18) |
| C(25)—C(26) | 1.309 (8) | C(49)—C(50) | 1.496 (31) |
| C(26)—C(27) | 1.471 (8) | C(50)—O(13) | 1.320 (22) |
| C(26)—C(28) | 1.495 (8) | O(13)—C(51) | 1.434 (14) |
| C(27)—O(8) | 1.306 (7) | C(51)—C(52) | 1.415 (14) |
| | | C(52)—O(14) | 1.431 (8) |
| C(2)—C(1)—C(6) | 124.1 (5) | C(25)—C(26)—C(27) | 119.3 (5) |
| C(2)—C(1)—O(1) | 113.1 (5) | C(25)—C(26)—C(28) | 112.2 (5) |
| C(6)—C(1)—O(1) | 122.7 (5) | C(27)—C(26)—C(28) | 128.3 (5) |
| C(1)—C(2)—C(3) | 113.0 (6) | C(22)—C(27)—C(26) | 129.6 (5) |
| C(1)—C(2)—C(28) | 123.6 (5) | C(22)—C(27)—O(8) | 110.1 (5) |
| C(3)—C(2)—C(28) | 123.3 (6) | C(26)—C(27)—O(8) | 120.1 (5) |
| C(2)—C(3)—C(4) | 123.3 (7) | C(2)—C(28)—C(26) | 106.6 (5) |
| C(3)—C(4)—C(5) | 123.6 (7) | C(1)—O(1)—(29) | 116.7 (4) |

Table II. Continued

| | <i>X</i> | <i>Y</i> | <i>Z</i> | <i>U</i> _{eq} |
|-------------------|-----------|-------------------|------------|------------------------|
| C(4)—C(5)—C(6) | 114.3 (6) | O(1)—C(29)—C(30) | 114.9 (5) | |
| C(1)—C(6)—C(S) | 121.2 (6) | C(29)—C(30)—O(2) | 104.7 (5) | |
| C(1)—C(6)—C(7) | 125.2 (5) | C(30)—O(2)—C(31) | 113.3 (5) | |
| C(5)—C(6)—C(7) | 113.4 (5) | O(2)—C(31)—C(32) | 105.6 (6) | |
| C(6)—C(7)—C(8) | 105.5 (5) | C(31)—C(32)—O(3) | 102.2 (6) | |
| C(7)—C(8)—C(9) | 111.7 (5) | C(32)—O(3)—C(33) | 111.3 (6) | |
| C(7)—C(8)—C(13) | 127.5 (5) | O(3)—C(33)—C(34) | 109.7 (7) | |
| C(9)—C(8)—C(13) | 120.6 (5) | C(33)—C(34)—O(4) | 115.6 (7) | |
| C(8)—C(9)—C(10) | 112.0 (5) | C(34)—O(4)—C(35) | 118.5 (6) | |
| C(9)—C(10)—C(11) | 126.3 (6) | O(4)—C(35)—C(36) | 116.7 (6) | |
| C(10)—C(11)—C(12) | 123.4 (5) | C(35)—C(36)—O(5) | 108.7 (6) | |
| C(11)—C(12)—C(13) | 109.4 (5) | C(36)—O(5)—C(37) | 109.6 (5) | |
| C(11)—C(12)—C(14) | 122.1 (5) | O(5)—C(37)—C(38) | 106.6 (5) | |
| C(13)—C(12)—C(14) | 128.3 (5) | C(37)—C(38)—O(6) | 104.5 (5) | |
| C(8)—C(13)—C(12) | 128.1 (5) | C(38)—O(6)—C(39) | 114.1 (5) | |
| C(8)—C(13)—C(14) | 121.2 (5) | O(6)—C(39)—C(40) | 107.3 (6) | |
| C(1)—C(13)—C(14) | 110.6 (5) | C(39)—C(40)—O(7) | 100.5 (5) | |
| C(12)—C(14)—C(15) | 107.5 (5) | C(20)—O(7)—C(40) | 106.2 (4) | |
| C(14)—C(15)—C(16) | 115.7 (5) | C(27)—O(8)—C(41) | 107.3 (5) | |
| C(14)—C(15)—C(20) | 124.5 (5) | O(8)—C(41)—C(42) | 103.1 (6) | |
| C(16)—C(15)—C(20) | 119.4 (6) | C(41)—C(42)—O(9) | 111.7 (7) | |
| C(15)—C(16)—C(17) | 115.1 (6) | C(42)—O(9)—C(43) | 112.3 (7) | |
| C(16)—C(17)—C(18) | 124.7 (7) | O(9)—C(43)—C(44) | 111.1 (8) | |
| C(17)—C(18)—C(19) | 122.0 (6) | C(43)—C(44)—O(10) | 116.1 (8) | |
| C(18)—C(19)—C(20) | 112.3 (6) | C(44)—O(10)—C(45) | 118.4 (7) | |
| C(18)—C(19)—C(21) | 122.0 (5) | O(10)—C(45)—C(46) | 115.6 (8) | |
| C(20)—C(19)—C(21) | 125.3 (5) | C(45)—C(46)—O(11) | 111.3 (8) | |
| C(15)—C(20)—C(19) | 126.3 (6) | C(46)—O(11)—C(47) | 114.6 (8) | |
| C(15)—C(20)—O(7) | 120.8 (5) | O(11)—C(47)—C(48) | 113.5 (11) | |
| C(19)—C(20)—O(7) | 112.8 (5) | C(47)—C(48)—O(12) | 106.2 (11) | |
| C(19)—C(21)—C(22) | 111.9 (5) | C(48)—O(12)—C(49) | 106.7 (12) | |
| C(21)—C(22)—C(23) | 123.0 (5) | O(12)—C(49)—C(50) | 106.6 (16) | |
| C(21)—C(22)—C(27) | 128.1 (5) | C(49)—C(50)—O(13) | 116.7 (18) | |
| C(23)—C(22)—C(27) | 108.8 (5) | C(50)—O(13)—C(51) | 122.0 (13) | |
| C(22)—C(23)—C(24) | 122.4 (5) | O(13)—C(51)—C(52) | 115.5 (9) | |
| C(23)—C(24)—C(25) | 127.1 (5) | C(51)—C(52)—O(14) | 112.0 (7) | |
| C(24)—C(25)—C(26) | 112.5 (5) | C(13)—O(14)—C(52) | 117.0 (5) | |

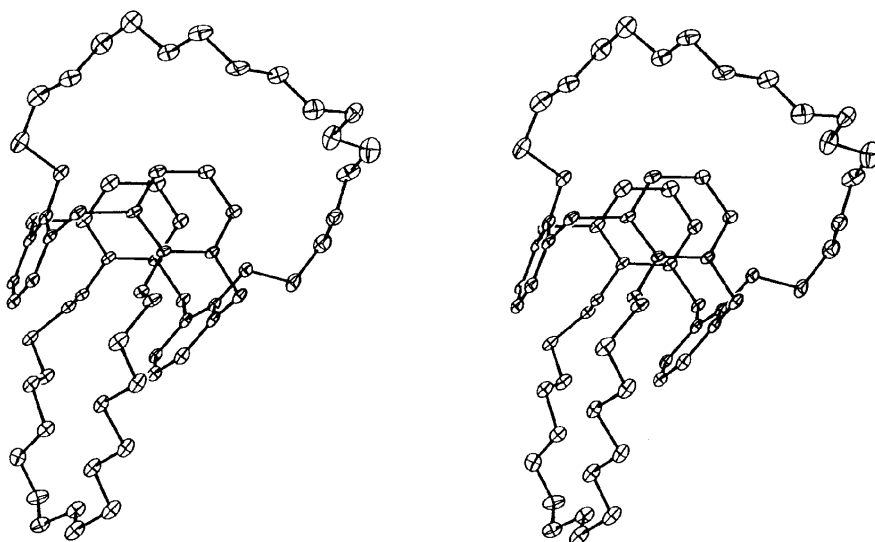


Figure 2. Stereoview of the title compound.

Table III. Distances (Å) between O atoms of the polyether chains characterizing the aperture of the crowned calixarene.

| | |
|---------------------|-----------------------|
| O(1) ··· O(7) 6.301 | O(8) ··· O(14) 5.973 |
| O(2) ··· O(6) 8.476 | O(9) ··· O(13) 8.399 |
| O(3) ··· O(5) 5.210 | O(10) ··· O(12) 5.058 |

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