# Crystal structure of biscalix[4]arene-crown-6, $C_{64}H_{60}O_6$

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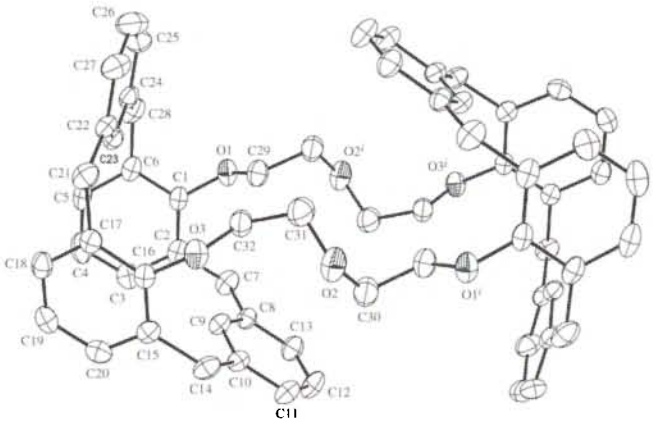

**Abstract**

$C_{64}H_{60}O_6$, triclinic, $P\bar{1}$ (No. 2), $a$ = 8.907(2) Å, $b$ = 12.002(2) Å, $c$ = 12.844(2) Å, α = 92.25(1)°, β = 108.27(1)°, γ = 107.04(1)°, $V$ = 1233.5 Å$^3$, $Z$ = 1, $R_{gt}(F)$ = 0.054, $wR_{ref}(F^2)$ = 0.163, $T$ = 297 K.

**Source of material**

A mixture of dihydrocalix[4]arene (2.00 g, 5.10 mmol), diethyleneglycol ditosylate (2.11 g, 5.10 mmol) and caesium carbonate (3.30 g, 10.2 mmol) was heated in acetonitrile (50 mL). Following solvent evaporation, the residue was partitioned between chloroform and 1 N HCl. The organic phase was washed with saturated NaCl, followed by saturated $NaHCO_3$, then dried over $Na_2SO_4$, and evaporated in vacuo. The title compound was purified by preparative TLC (toluene eluent) and crystallized from hot toluene.

**Discussion**

Recent work has shown that insertion of a calix[4]arene group into a crown ether ring can dramatically increase its extraction efficiency and selectivity towards the caesium ion [1,2]. As part of our continuing research investigating fundamental interactions between crown ether molecules and large cations, we investigated the effect of inserting two calix[4]arene groups into a crown ether ring.

The structure of the title compound clearly demonstrates that it is not preorganized for cation binding, as the oxygen dipoles are oriented exterior to the ring [3]. Extraction studies with the title compound demonstrate that its ability to extract $Cs^+$ from aqueous solution is comparable with some of the best of the simple crown ether extractants (such as dibenzo-21-crown-7), yet it is roughly two orders of magnitude weaker than the more recently studied calix[4]arene-crown-6 extractants. A separation factor of $5 \times 10^{-2}$ is obtained for 10 mM (1) in 1,2-dichloroethane, while a factor of 1 is obtained for calix[4]arene-bis(octylbenzo)-crown-6 [2]. This effect could be partly due to poor preorganization of the oxygen donor atoms.

No π-stacking of arene rings is observed in the title structure. However, close C—H···π contacts, some of which may represent H-bonds [4, and references therein] or edge-face arene interactions, are clearly present. For example, the distance from H30A to a symmetry equivalent of the centroid of C8–C13 is 3.30 Å, with a C30—H30A···centroid angle of 150°. Additionally, H4 is 3.21 Å from the centroid of C22–C27 with a C4—H4···centroid angle of 147 °. H-bond parameters are calculated using PLATON [5].

**Table 1.** Data collection and handling.

| | |
|---|---|
| Crystal: | colourless plate, size 0.11 × 0.59 × 0.71 mm |
| Wavelength: | Mo $K_\alpha$ radiation (0.71073 Å) |
| μ: | 0.79 cm$^{-1}$ |
| Diffractometer, scan mode: | Nonius CAD4, ω/θ |
| $2\theta_{max}$: | 50° |
| $N(hkl)_{measured}$, $N(hkl)_{unique}$: | 5689, 4344 |
| Criterion for $I_{obs}$, $N(hkl)_{gt}$: | $I_{obs} > 2\,\sigma(I_{obs})$, 2730 |
| $N(param)_{refined}$: | 316 |
| Programs: | PLATON [5], SHELXS-86 [5], SHELXL-93 [7], SHELXTL [8] |

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

| Atom | Site | $x$ | $y$ | $z$ | $U_{iso}$ |
|---|---|---|---|---|---|
| H(3) | 2*i* | –0.3512 | 0.3931 | –0.0497 | 0.082 |
| H(4) | 2*i* | –0.4747 | 0.1958 | –0.1152 | 0.092 |
| H(5) | 2*i* | –0.5777 | 0.0695 | –0.0071 | 0.083 |
| H(7A) | 2*i* | –0.3479 | 0.5372 | 0.1963 | 0.079 |
| H(7B) | 2*i* | –0.3433 | 0.5597 | 0.0781 | 0.079 |
| H(9) | 2*i* | –0.0741 | 0.4106 | 0.1647 | 0.060 |
| H(11) | 2*i* | 0.3448 | 0.6830 | 0.2959 | 0.080 |
| H(12) | 2*i* | 0.1883 | 0.8053 | 0.2893 | 0.095 |
| H(13) | 2*i* | –0.0988 | 0.7323 | 0.2213 | 0.081 |
| H(14A) | 2*i* | 0.3373 | 0.4817 | 0.2034 | 0.073 |
| H(14B) | 2*i* | 0.3198 | 0.4551 | 0.3181 | 0.073 |
| H(18) | 2*i* | –0.0954 | 0.0176 | 0.0648 | 0.068 |
| H(19) | 2*i* | –0.0409 | 0.1587 | –0.0462 | 0.077 |
| H(20) | 2*i* | 0.1169 | 0.3490 | 0.0325 | 0.073 |
| H(21A) | 2*i* | 0.0764 | 0.0470 | 0.3521 | 0.072 |
| H(21B) | 2*i* | –0.0245 | –0.0459 | 0.2454 | 0.072 |
| H(23) | 2*i* | –0.2705 | 0.1111 | 0.1924 | 0.058 |
| H(25) | 2*i* | –0.5622 | –0.0192 | 0.3692 | 0.092 |
| H(26) | 2*i* | –0.3740 | –0.1064 | 0.4635 | 0.106 |
| H(28A) | 2*i* | –0.6670 | 0.0393 | 0.1551 | 0.087 |

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**Table 2.** Continued.

| Atom | Site | x | y | z | $U_{iso}$ |
|---|---|---|---|---|---|
| H(28B) | 2*i* | –0.6062 | 0.1439 | 0.2510 | 0.087 |
| H(27) | 2*i* | –0.1316 | –0.0823 | 0.4269 | 0.088 |
| H(29A) | 2*i* | –0.2045 | 0.4198 | 0.3412 | 0.079 |
| H(29B) | 2*i* | –0.2842 | 0.2965 | 0.3732 | 0.079 |
| H(30A) | 2*i* | 0.2233 | 0.5587 | 0.4819 | 0.091 |
| H(30B) | 2*i* | 0.4167 | 0.6199 | 0.5317 | 0.091 |
| H(31A) | 2*i* | 0.1320 | 0.3889 | 0.5761 | 0.096 |
| H(31B) | 2*i* | 0.2344 | 0.3022 | 0.5802 | 0.096 |
| H(32A) | 2*i* | 0.0002 | 0.2550 | 0.4189 | 0.075 |
| H(32B) | 2*i* | 0.0739 | 0.3774 | 0.3838 | 0.075 |

**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) | 2*i* | –0.4476(2) | 0.3521(2) | 0.2641(2) | 0.047(1) | 0.074(1) | 0.063(1) | 0.024(1) | 0.0081(9) | –0.014(1) |
| O(2) | 2*i* | 0.3436(3) | 0.4577(2) | 0.5594(2) | 0.074(2) | 0.078(2) | 0.083(2) | 0.021(1) | 0.007(1) | –0.015(1) |
| O(3) | 2*i* | 0.1950(2) | 0.2659(2) | 0.3726(2) | 0.055(1) | 0.066(1) | 0.050(1) | 0.027(1) | 0.0020(9) | 0.0022(9) |
| C(1) | 2*i* | –0.4448(3) | 0.3092(2) | 0.1638(2) | 0.033(1) | 0.053(2) | 0.057(2) | 0.018(1) | 0.004(1) | –0.009(1) |
| C(2) | 2*i* | –0.3834(3) | 0.3876(2) | 0.0988(2) | 0.041(2) | 0.051(2) | 0.062(2) | 0.024(1) | 0.001(1) | –0.001(1) |
| C(3) | 2*i* | –0.3942(4) | 0.3423(3) | –0.0056(3) | 0.068(2) | 0.079(2) | 0.060(2) | 0.038(2) | 0.010(2) | 0.012(2) |
| C(4) | 2*i* | –0.4668(4) | 0.2244(3) | –0.0447(3) | 0.075(2) | 0.089(3) | 0.056(2) | 0.041(2) | –0.001(2) | –0.013(2) |
| C(5) | 2*i* | –0.5275(4) | 0.1493(3) | 0.0204(3) | 0.049(2) | 0.060(2) | 0.082(2) | 0.020(2) | 0.000(2) | –0.024(2) |
| C(6) | 2*i* | –0.5165(3) | 0.1887(2) | 0.1265(2) | 0.031(1) | 0.051(2) | 0.073(2) | 0.016(1) | 0.005(1) | –0.007(2) |
| C(7) | 2*i* | –0.3060(4) | 0.5180(2) | 0.1391(3) | 0.057(2) | 0.052(2) | 0.087(2) | 0.027(2) | 0.014(2) | 0.011(2) |
| C(8) | 2*i* | –0.1172(3) | 0.5635(2) | 0.1850(2) | 0.055(2) | 0.040(2) | 0.055(2) | 0.017(1) | 0.014(1) | 0.010(1) |
| C(9) | 2*i* | –0.0208(3) | 0.4906(2) | 0.1902(2) | 0.048(2) | 0.038(1) | 0.060(2) | 0.011(1) | 0.015(1) | 0.007(1) |
| C(10) | 2*i* | 0.1524(3) | 0.5325(2) | 0.2320(2) | 0.048(2) | 0.044(2) | 0.055(2) | 0.010(1) | 0.014(1) | 0.011(1) |
| C(11) | 2*i* | 0.2289(4) | 0.6521(3) | 0.2684(3) | 0.054(2) | 0.050(2) | 0.079(2) | 0.002(1) | 0.014(2) | 0.006(2) |
| C(12) | 2*i* | 0.1352(4) | 0.7252(3) | 0.2642(3) | 0.081(2) | 0.038(2) | 0.102(3) | 0.006(2) | 0.022(2) | –0.001(2) |
| C(13) | 2*i* | –0.0369(4) | 0.6817(2) | 0.2232(3) | 0.077(2) | 0.043(2) | 0.081(2) | 0.022(2) | 0.023(2) | 0.007(2) |
| C(14) | 2*i* | 0.2573(3) | 0.4520(2) | 0.2406(3) | 0.040(2) | 0.054(2) | 0.081(2) | 0.009(1) | 0.015(1) | 0.013(2) |
| C(15) | 2*i* | 0.1593(3) | 0.3251(2) | 0.1917(2) | 0.036(1) | 0.051(2) | 0.061(2) | 0.017(1) | 0.014(1) | 0.009(1) |
| C(16) | 2*i* | 0.1252(3) | 0.2387(2) | 0.2576(2) | 0.036(1) | 0.051(2) | 0.050(2) | 0.020(1) | 0.008(1) | 0.001(1) |
| C(17) | 2*i* | 0.0285(3) | 0.1226(2) | 0.2115(2) | 0.038(1) | 0.048(2) | 0.056(2) | 0.021(1) | 0.014(1) | 0.004(1) |
| C(18) | 2*i* | –0.0317(3) | 0.0947(3) | 0.0970(2) | 0.047(2) | 0.056(2) | 0.066(2) | 0.019(1) | 0.015(1) | –0.009(2) |
| C(19) | 2*i* | 0.0008(4) | 0.1787(3) | 0.0304(2) | 0.069(2) | 0.079(2) | 0.049(2) | 0.029(2) | 0.020(2) | 0.000(2) |
| C(20) | 2*i* | 0.0953(4) | 0.2924(3) | 0.0779(3) | 0.058(2) | 0.070(2) | 0.064(2) | 0.025(2) | 0.029(2) | 0.018(2) |
| C(21) | 2*i* | –0.0149(4) | 0.0293(2) | 0.2820(3) | 0.056(2) | 0.048(2) | 0.079(2) | 0.024(1) | 0.020(2) | 0.014(1) |
| C(22) | 2*i* | –0.1749(3) | 0.0173(2) | 0.3058(2) | 0.051(2) | 0.034(1) | 0.057(2) | 0.008(1) | 0.014(1) | 0.004(1) |
| C(23) | 2*i* | –0.2918(3) | 0.0673(2) | 0.2474(2) | 0.047(2) | 0.037(1) | 0.059(2) | 0.008(1) | 0.019(1) | 0.002(1) |
| C(24) | 2*i* | –0.4395(3) | 0.0543(2) | 0.2679(2) | 0.044(2) | 0.041(2) | 0.070(2) | 0.001(1) | 0.019(1) | –0.008(1) |
| C(25) | 2*i* | –0.4659(4) | –0.0106(3) | 0.3518(3) | 0.060(2) | 0.075(2) | 0.086(2) | –0.004(2) | 0.039(2) | 0.004(2) |
| C(26) | 2*i* | –0.3527(5) | –0.0617(3) | 0.4091(3) | 0.082(3) | 0.087(3) | 0.082(3) | 0.003(2) | 0.029(2) | 0.028(2) |
| C(27) | 2*i* | –0.2082(4) | –0.0477(3) | 0.3869(3) | 0.068(2) | 0.063(2) | 0.077(2) | 0.011(2) | 0.015(2) | 0.021(2) |
| C(28) | 2*i* | –0.5707(4) | 0.1042(3) | 0.2005(3) | 0.042(2) | 0.060(2) | 0.113(3) | 0.009(1) | 0.028(2) | –0.002(2) |
| C(29) | 2*i* | –0.3009(4) | 0.3711(3) | 0.3568(2) | 0.060(2) | 0.063(2) | 0.063(2) | 0.021(2) | 0.007(2) | –0.002(2) |
| C(30) | 2*i* | 0.3212(5) | 0.5686(3) | 0.5465(3) | 0.089(2) | 0.063(2) | 0.065(2) | 0.019(2) | 0.017(2) | 0.001(2) |
| C(31) | 2*i* | 0.2028(5) | 0.3645(3) | 0.5424(3) | 0.087(3) | 0.073(2) | 0.064(2) | 0.014(2) | 0.014(2) | 0.008(2) |
| C(32) | 2*i* | 0.1029(4) | 0.3153(3) | 0.4234(2) | 0.060(2) | 0.061(2) | 0.060(2) | 0.015(2) | 0.017(2) | –0.005(1) |

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