Crystal structure of 5,17-dibromo-25,27-dimethoxy-26-benzoyloxy-28-hydroxycalix[4]arene dihydrate, $C_{37}H_{34}Br_2O_5 \cdot 2H_2O$

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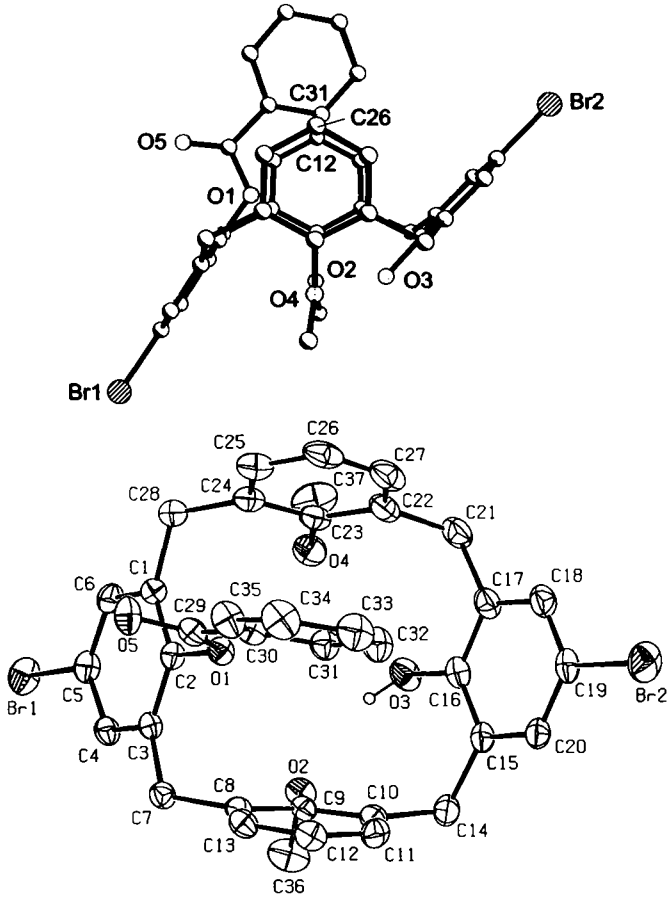

Abstract

$C_{37}H_{34}Br_2O_7$, triclinic, $P\bar{1}$ (no. 2), $a = 9.744(1)$ Å, $b = 10.059(1)$ Å, $c = 18.012(2)$ Å, $\alpha = 91.66(1)°$, $\beta = 99.06(1)°$, $\gamma = 104.536(9)°$, $V = 1683.4$ Å^3, $Z = 2$, $R_{gt}(F) = 0.071$, $wR_{ref}(F^2) = 0.180$, $T = 293$ K.

Source of material

Selective bromination of 25,27-dimethoxy-26,28-dihydroxycalix[4]arene in chloroform afforded 5,17-dibromo-25,27-dimethoxy-26,28-dihydroxycalix[4]arene [1]. Then one phenoxyl group was selectively benzoylated by slowly adding benzoyl chloride (3 mL) to the calix[4]arene (0.6 g) in pyridine (25 mL). The mixture was stirred in ice bath for 24 hours and then filtrated. The excess distilled water was poured into the filtrate to get the pale yellow crude product (0.43 g). After recrystallization from chloroform/methanol, suitable colorless crystals of the title compound were obtained.

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Discussion

Calix[*n*]arenes are macrocyclic molecules made of *n*-phenol units connected by *ortho* methylene groups [2,3]. Calix[4]arenes are the simplest and most common compounds of this family with four phenolic residues in the macrocyclic ring. These molecules and their derivatives have been extensively studied for their interesting properties, e.g. being hosts to cations, anions and neutral molecules, and for the formation of supramolecular assemblies [4]. In the solid state, the cone conformation is exclusively observed for calix[4]arene with free OH-groups [5]. Calix[4]arenes in which one or more of the phenoxyl groups on the lower rim are replaced by other groups can then take different conformations, especially exist in the partial cone conformation [2,5].

The X-ray diffraction analysis of 5,17-dibromo-25,27-dimethoxy-26-benzoyloxy-28-hydroxycalix[4]arene shows that the compound takes a partial cone conformation (figure, top). The phenyl rings with OH and CH_3O groups project upward relative to the average plane defined by bridge methylene groups, but the phenyl ring connected with the benzoyl group projects downward. The dihedral angles between the two phenyl planes with methoxyl groups is 35.6°. An interesting fact is that the benzoyl group inserts in the cavity of the calix[4]arene compound (figure, bottom). Because of steric hindrance, the benzoyl group is strongly twisted with respect to the attached phenyl ring, and appears almost perpendicular to the phenyl rings containing bromine atoms and parallel to those with methoxyl groups. The dihedral angles are 95.6° and 95.4° between the benzoyl plane and the formers, and 18.1° and 18.4° between that and the latters, respectively. In addition, the distances in space of C12···C31 and C31···C26 are 3.453 Å and 3.557 Å, and the angle of C12···C31··· C26 is 164.6° (figure, bottom). It is well known that the distance in space between every two molecular layers in graphite is about 3.4 Å, so it is possible that there are π-π interactions to some extent between the C12 (or C26) and C31 atoms. This may be the key reason why the large benzoyl group can enter the cavity of the compound to form the stable partial cone conformation. The *R* values are somewhat large and the N_{gt}/N_{param} ratio small which is often observed for this kind of macrocyclic compounds.

Table 1. Data collection and handling.

Crystal:	colorless prism, size 0.2 × 0.4 × 0.4 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	24.56 cm^{-1}
Diffractometer, scan mode:	Bruker P4, ω
$2\theta_{max}$:	50°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	7110, 5938
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 2887
$N(param)_{refined}$:	416
Program:	SHELXTL [6]

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

Atom	Site	x	y	z	U_{iso}
H(3A)	2*i*	0.3858	0.3655	0.2975	0.092
H(4A)	2*i*	0.2299	0.5163	0.0242	0.067
H(6A)	2*i*	0.1149	0.1028	0.0066	0.072
H(7A)	2*i*	0.4376	0.6438	0.0946	0.069
H(7B)	2*i*	0.5541	0.5843	0.0654	0.069
H(11A)	2*i*	0.8099	0.6706	0.3680	0.082
H(12A)	2*i*	0.9123	0.6993	0.2613	0.078
H(13A)	2*i*	0.7698	0.6573	0.1451	0.077
H(14A)	2*i*	0.5861	0.6548	0.4253	0.085
H(14B)	2*i*	0.4383	0.5729	0.3774	0.085
H(18A)	2*i*	0.6384	0.1193	0.4808	0.091
H(20A)	2*i*	0.7371	0.5310	0.4958	0.076
H(21A)	2*i*	0.4192	−0.0129	0.4020	0.103
H(21B)	2*i*	0.3111	0.0635	0.3600	0.103
H(25A)	2*i*	0.5827	−0.0426	0.1181	0.102
H(26A)	2*i*	0.7057	−0.0770	0.2324	0.109
H(27A)	2*i*	0.6282	−0.0299	0.3415	0.115

Table 2. Continued.

Atom	Site	x	y	z	U_{iso}
H(28A)	2*i*	0.2507	−0.0255	0.0734	0.085
H(28B)	2*i*	0.3961	0.0251	0.0441	0.085
H(31A)	2*i*	0.6821	0.3236	0.2663	0.079
H(32A)	2*i*	0.8805	0.3353	0.3568	0.097
H(33A)	2*i*	1.0951	0.3282	0.3204	0.116
H(34A)	2*i*	1.1100	0.3028	0.1944	0.119
H(35A)	2*i*	0.9082	0.2887	0.1036	0.105
H(36A)	2*i*	0.1950	0.6064	0.2276	0.134
H(36B)	2*i*	0.3148	0.6949	0.1876	0.134
H(36C)	2*i*	0.3295	0.7102	0.2755	0.134
H(37A)	2*i*	0.0423	0.0183	0.2173	0.170
H(37B)	2*i*	0.1312	−0.0694	0.2649	0.170
H(37C)	2*i*	0.1096	−0.0834	0.1766	0.170
H(1A)	2*i*	1.0199	0.0661	0.4436	0.196
H(1B)	2*i*	0.8844	−0.0447	0.4361	0.196
H(2A)	2*i*	0.1955	0.1896	0.5026	0.251
H(2B)	2*i*	0.2156	0.0633	0.4814	0.251

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}
Br(1)	2*i*	−0.0211(1)	0.3100(1)	−0.05516(5)	0.0526(5)	0.1124(9)	0.0757(6)	0.0264(5)	−0.0108(4)	−0.0046(6)
Br(2)	2*i*	0.8630(1)	0.3307(1)	0.57427(6)	0.1131(9)	0.142(1)	0.0855(8)	0.0584(8)	−0.0343(7)	−0.0003(7)
O(1)	2*i*	0.5354(5)	0.3115(5)	0.1461(3)	0.046(3)	0.063(4)	0.056(3)	0.018(3)	−0.001(3)	0.007(3)
O(2)	2*i*	0.3712(5)	0.5405(6)	0.2382(3)	0.048(3)	0.065(4)	0.074(4)	0.010(3)	0.014(3)	0.011(3)
O(3)	2*i*	0.3613(6)	0.3159(7)	0.3310(3)	0.060(4)	0.083(5)	0.077(4)	0.013(3)	−0.011(3)	0.020(3)
O(4)	2*i*	0.2514(7)	0.0866(6)	0.2217(3)	0.076(4)	0.078(5)	0.088(4)	0.023(4)	0.014(3)	0.013(4)
O(5)	2*i*	0.6432(6)	0.2693(7)	0.0504(3)	0.071(4)	0.120(6)	0.061(4)	0.032(4)	0.015(3)	0.014(4)
C(1)	2*i*	0.3122(8)	0.1828(8)	0.0703(4)	0.059(5)	0.053(5)	0.052(5)	0.016(4)	0.009(4)	0.004(4)
C(2)	2*i*	0.4076(7)	0.3094(8)	0.0967(4)	0.042(4)	0.062(6)	0.047(4)	0.018(4)	0.004(3)	0.003(4)
C(3)	2*i*	0.3797(8)	0.4351(8)	0.0812(4)	0.048(4)	0.059(5)	0.045(4)	0.015(4)	0.011(3)	0.010(4)
C(4)	2*i*	0.2515(8)	0.4338(9)	0.0363(4)	0.053(5)	0.067(6)	0.052(5)	0.025(4)	0.005(4)	0.012(4)
C(5)	2*i*	0.1534(8)	0.308(1)	0.0087(4)	0.042(4)	0.084(7)	0.052(5)	0.021(5)	0.001(4)	0.003(5)
C(6)	2*i*	0.1819(8)	0.1849(9)	0.0252(4)	0.051(5)	0.067(6)	0.053(5)	0.007(4)	−0.004(4)	−0.005(4)
C(7)	2*i*	0.4888(8)	0.5728(8)	0.1016(4)	0.056(5)	0.058(5)	0.055(5)	0.014(4)	0.004(4)	0.008(4)
C(8)	2*i*	0.5794(8)	0.6005(7)	0.1797(4)	0.050(5)	0.042(5)	0.057(5)	0.011(4)	0.003(4)	0.005(4)
C(9)	2*i*	0.5194(8)	0.5865(8)	0.2444(4)	0.051(5)	0.047(5)	0.052(5)	0.016(4)	0.010(4)	0.009(4)
C(10)	2*i*	0.6029(9)	0.6070(8)	0.3160(4)	0.063(5)	0.057(5)	0.059(5)	0.027(4)	0.002(4)	0.005(4)
C(11)	2*i*	0.7515(9)	0.6522(9)	0.3208(5)	0.064(6)	0.071(6)	0.062(6)	0.021(5)	−0.014(5)	−0.004(5)
C(12)	2*i*	0.8129(8)	0.6700(9)	0.2573(5)	0.040(4)	0.070(6)	0.081(6)	0.009(4)	0.001(4)	0.009(5)
C(13)	2*i*	0.7272(9)	0.6445(8)	0.1880(5)	0.060(5)	0.065(6)	0.069(6)	0.015(5)	0.019(5)	0.016(5)
C(14)	2*i*	0.541(1)	0.5794(9)	0.3875(4)	0.086(6)	0.085(7)	0.051(5)	0.040(6)	0.009(5)	0.003(5)
C(15)	2*i*	0.5653(9)	0.4470(9)	0.4165(4)	0.059(5)	0.076(6)	0.043(4)	0.028(5)	0.007(4)	0.006(4)
C(16)	2*i*	0.4777(9)	0.321(1)	0.3846(4)	0.054(5)	0.080(7)	0.049(5)	0.020(5)	0.008(4)	0.015(5)
C(17)	2*i*	0.5037(9)	0.196(1)	0.4072(5)	0.069(6)	0.072(7)	0.059(5)	0.010(5)	0.014(5)	0.019(5)
C(18)	2*i*	0.619(1)	0.201(1)	0.4642(5)	0.091(7)	0.090(8)	0.057(5)	0.042(6)	0.008(5)	0.017(5)
C(19)	2*i*	0.7048(9)	0.326(1)	0.4959(4)	0.064(6)	0.101(8)	0.045(5)	0.032(6)	0.005(4)	0.014(5)
C(20)	2*i*	0.6782(9)	0.448(1)	0.4729(4)	0.070(6)	0.077(6)	0.047(5)	0.026(5)	0.005(4)	0.003(4)
C(21)	2*i*	0.411(1)	0.0600(9)	0.3688(5)	0.099(7)	0.070(7)	0.076(7)	−0.001(6)	0.014(6)	0.027(5)
C(22)	2*i*	0.453(1)	0.0267(9)	0.2946(5)	0.080(7)	0.058(6)	0.077(7)	0.008(5)	−0.007(6)	0.022(5)
C(23)	2*i*	0.376(1)	0.0416(8)	0.2252(5)	0.067(6)	0.046(5)	0.079(6)	0.011(4)	0.003(5)	0.010(5)
C(24)	2*i*	0.423(1)	0.0203(9)	0.1579(5)	0.073(6)	0.048(5)	0.082(7)	0.013(5)	0.010(5)	0.005(5)
C(25)	2*i*	0.549(1)	−0.0255(9)	0.1621(6)	0.084(7)	0.062(6)	0.110(8)	0.023(6)	0.015(6)	0.006(6)
C(26)	2*i*	0.624(1)	−0.045(1)	0.2302(7)	0.074(7)	0.062(7)	0.13(1)	0.022(5)	−0.011(7)	0.021(7)
C(27)	2*i*	0.576(1)	−0.018(1)	0.2955(7)	0.093(8)	0.072(7)	0.103(9)	0.010(6)	−0.023(7)	0.029(7)
C(28)	2*i*	0.342(1)	0.0433(9)	0.0825(5)	0.084(6)	0.057(6)	0.067(6)	0.017(5)	0.007(5)	0.003(4)
C(29)	2*i*	0.6498(9)	0.2930(9)	0.1172(5)	0.057(5)	0.063(6)	0.068(6)	0.019(4)	0.014(5)	0.015(5)
C(30)	2*i*	0.7743(8)	0.3017(8)	0.1771(5)	0.040(4)	0.055(5)	0.075(6)	0.015(4)	0.007(4)	0.015(4)
C(31)	2*i*	0.7681(9)	0.3181(9)	0.2518(5)	0.060(5)	0.075(6)	0.065(6)	0.027(5)	0.006(4)	0.009(5)
C(32)	2*i*	0.887(1)	0.326(1)	0.3059(5)	0.068(6)	0.101(8)	0.074(6)	0.030(6)	−0.002(5)	0.010(5)
C(33)	2*i*	1.014(1)	0.322(1)	0.2840(7)	0.062(7)	0.113(9)	0.112(9)	0.032(6)	−0.015(6)	0.013(7)
C(34)	2*i*	1.023(1)	0.307(1)	0.2087(7)	0.058(6)	0.13(1)	0.12(1)	0.038(6)	0.017(6)	0.025(8)
C(35)	2*i*	0.903(1)	0.298(1)	0.1546(6)	0.065(6)	0.113(9)	0.094(7)	0.038(6)	0.016(5)	0.027(6)
C(36)	2*i*	0.2965(9)	0.647(1)	0.2317(6)	0.047(5)	0.089(7)	0.138(9)	0.030(5)	0.010(5)	0.021(6)
C(37)	2*i*	0.123(1)	−0.021(1)	0.2200(7)	0.063(7)	0.098(9)	0.16(1)	0.005(6)	−0.003(7)	−0.022(8)
O(1W)	2*i*	0.942(1)	0.018(1)	0.4172(5)	0.143(8)	0.23(1)	0.122(7)	0.088(8)	−0.031(6)	−0.006(7)
O(2W)	2*i*	0.158(1)	0.103(1)	0.4972(6)	0.21(1)	0.152(9)	0.26(1)	0.068(8)	0.03(1)	−0.126(9)

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