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Crystal structure of 5,17-diformyl-25,26,27,28-tetrahydroxycalix[4]arene- dichloromethane, $C_{31}H_{26}Cl_2O_6$

Table 1: Data collection and handling.

Crystal:	Yellow block
Size:	0.30 × 0.20 × 0.20 mm
Wavelength:	Mo K α radiation (0.71073 Å)
μ :	0.29 mm ⁻¹
Diffractometer, scan mode:	Bruker APEX-II, φ and ω
$\theta_{\max}$, completeness:	25.0°, >99%
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$, R_{int} :	16403, 2318, 0.107
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 1801
$N(\text{param})_{\text{refined}}$:	179
Programs:	Olex2 [1], Bruker [2], SHELX [3], Diamond [4]

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Abstract

$C_{30}H_{24}O_6 \cdot CH_2Cl_2$, orthorhombic, *Pbcn* (no. 60), $a = 11.6965(10)$ Å, $b = 13.8078(11)$ Å, $c = 16.3257(14)$ Å, $V = 2636.6(4)$ Å³, $Z = 4$, $R_{\text{gt}}(F) = 0.0765$, $wR_{\text{ref}}(F^2) = 0.1487$, $T = 296(2)$ K.

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The molecular structure of the title compound (systematic name: 1²,3²,5²,7²-tetrahydroxy-1,3,5,7(1,3)-tetrabenzencyclooctaphane-1⁵,5⁵-dicarbaldehyde) is shown in the figure. Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

Source of material

To a solution of calix[4]arene (1.0 g, 2.3 mmol) in chloroform (35 mL) cooled at −10 °C were added

Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²).

Atom	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
C1	0.6929(3)	0.7721(2)	0.1667(2)	0.0173(8)
C2	0.6715(3)	0.7394(2)	0.0874(2)	0.0162(8)
C3	0.7406(3)	0.6677(2)	0.0564(2)	0.0160(8)
H3	0.7275	0.6446	0.0037	0.019*
C4	0.8297(3)	0.6291(2)	0.1022(2)	0.0162(8)
C5	0.8487(3)	0.6632(2)	0.1805(2)	0.0178(8)
H5	0.9081	0.6370	0.2112	0.021*
C6	0.7821(3)	0.7348(2)	0.2142(2)	0.0176(8)
C7	0.8026(3)	0.7664(3)	0.3019(2)	0.0202(8)
H7A	0.8798	0.7489	0.3178	0.024*
H7B	0.7959	0.8363	0.3053	0.024*
C8	0.7189(3)	0.7205(2)	0.3608(2)	0.0182(8)
C9	0.6213(3)	0.7701(2)	0.38536(19)	0.0152(8)
C10	0.5400(3)	0.7284(2)	0.4363(2)	0.0181(8)
C11	0.4293(3)	0.7773(2)	0.4606(2)	0.0186(8)
H11A	0.4158	0.7669	0.5186	0.022*
H11B	0.4362	0.8465	0.4516	0.022*
C12	0.5619(3)	0.6350(3)	0.4641(2)	0.0262(9)
H12	0.5096	0.6054	0.4989	0.031*
C13	0.6585(4)	0.5856(3)	0.4416(3)	0.0317(10)
H13	0.6716	0.5235	0.4617	0.038*
C14	0.7358(3)	0.6276(3)	0.3895(2)	0.0246(9)
H14	0.8002	0.5931	0.3732	0.030*
C15	0.8994(3)	0.5522(2)	0.0691(2)	0.0201(8)
H15	0.8795	0.5276	0.0181	0.024*
C16	1.0000	0.0514(4)	0.2500	0.0442(18)

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Table 2 (continued)

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso} ^a / <i>U</i> _{eq}
H16B ^a	1.0460	0.0928	0.2151	0.053*
H16A ^a	0.9540	0.0928	0.2849	0.053*
Cl1	0.91029(13)	−0.01909(11)	0.18934(9)	0.0732(5)
O1	0.6219(2)	0.84201(18)	0.19386(15)	0.0245(6)
H1	0.6321	0.8504	0.2430	0.037*
O2	0.6147(2)	0.86413(15)	0.35835(15)	0.0190(6)
H2	0.5525	0.8870	0.3711	0.029*
O3	0.9820(2)	0.51743(17)	0.10308(16)	0.0269(6)

^aOccupancy: 0.5.

1,1-dichlorodimethylether (2.7 g, 23.4 mmol) and TiCl₄ (4.4 g, 23.4 mmol). The reaction mixture was stirred at −10 °C for 30 min and then treated with water (100 mL). The organic layer was separated, washed three times with water, and dried over Na₂SO₄, and the solvent was removed under reduced pressure. The desired product was purified by silica gel column chromatography (hexane/CHCl₂ 1:1). Single crystals were obtained from acetone by slow evaporation at room temperature.

Experimental details

Using Olex2 [1], the structure was solved using Charge Flipping and refined with the ShelXL [3] refinement. All hydrogen atoms were positioned geometrically, with the *d*(C–H) = 0.97–0.99 Å, *U*_{iso}(H) = 1.2 times *U*_{eq}(C) and *U*_{iso}(H) = 1.5 times *U*_{eq}(O).

Comment

Within the macrocyclic compounds family, calixarenes are certainly amongst the most popular members, due to their fascinating chemical and physical properties [5, 6]. Calixarenes can be readily modified at the phenolic hydroxyl groups (lower rim) as well as at the positions *para* to the HO-groups (upper rim). Calix[4]arene, the smaller member of the family, have proven to be superb molecular scaffolds for the assembly of receptors for neutral and charged guests [7],

as well as of molecular capsules. The selective introduction of formyl groups used to attach various further can be functional groups. The formylation of calix[4]arene by TiCl₄/Cl₂CHOCH₃ could afford the 1,3-diformyl derivative.

The bond length and bond angle of the target compound are within the normal range. The crystal structure shows that aldehyde groups are generated at the 1 and 3 positions of the calix[4]arene, and the crystal structure of 1,3-diformyl derivative exhibited as *cone* conformation. There is intramolecular hydrogen bond formation between the hydroxy groups (O1–H1···O2). In addition, the crystal structure expanded into a two-dimensional structure through non-classical C15–H15···O3, O2–H2···O1 and O2–H2···O3 intermolecular hydrogen bonds.

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