Crystal structure of 5,11,17,23-tetrabromo-25,27-dihydroxy-26,28-dimethoxycalix[4]arene, $C_{30}H_{24}Br_4O_4$

Y.-H. Luo[I,II], X.-J. Hu[I], J.-K. Liu[III], H. Zhang[I], Y. Li*[,I], H.-J. Yang[I] and R.-J. Wang[I]

[I] Tsinghua University, Department of Chemistry, Key Laboratory of Bioorganic Phosphorus Chemistry and Chemical Biology, Ministry of Education, Beijing 100084, P. R. China
[II] Hezhou University, Department of Chemistry and Biology, Hezhou, Guangxi 542800, P. R. China
[III] East China University of Science and Technology, Department of Chemistry, Shanghai 200237, P. R. China

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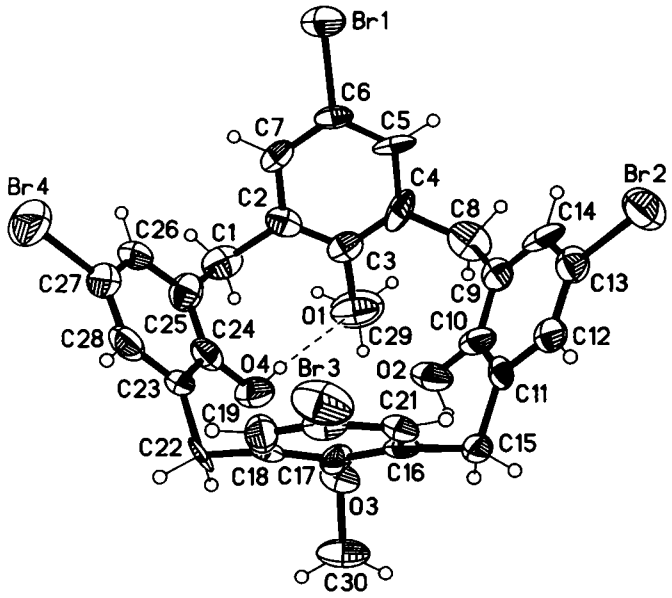

Abstract

$C_{30}H_{24}Br_4O_4$, monoclinic, $P12_1/c1$ (no. 14),
a = 9.810(1) Å, b = 27.121(6) Å, c = 11.410(3) Å,
β = 110.31(1)°, V = 2846.9 Å^3, Z = 4, $R_{gt}(F)$ = 0.068,
$wR_{ref}(F^2)$ = 0.126, T = 295 K.

Source of material

The precursor compound 25,27-dihydroxy-26,28-dimethoxycalix[4]arene was obtained according to [1]. Then the compound was brominated with *N*-bromosuccinimide (NBS) in the molar ratio of 1:9 in butanone at room temperature. After reacting for three days, the title compound was obtained and recrystallized from chloroform/methanol.

Experimental details

The small N_{gt}/N_{param} ratio and the large $R1$ value are caused by the poor quality of the crystals.

Discussion

The brominated calixarenes are important intermediates to synthesize calixarene derivatives. A paramagnetic calix[4]arene has been prepared through selective bromine-lithium exchange of 5,11,17,23-tetrabromocalix[4]arene by *n*-BuLi [2]. It has been reported that bromination of 26,28-dimethoxycalix[4]arene with Br_2 only occurred on the *para* position of the phenoxyl groups to give the corresponding dibromo compound [1], whereas complete bromination of 25,26,27,28-tetramethoxycalix[4]arene with NBS occurred on the upper rim to produce the tetrabromo compound [3]. We recently synthesized a new tetrabromo calix[4]-arene, which has two phenoxyl and two methoxyl groups, with complete bromination on the *para* position.

The molecular structure of the title compound displays approximate twofold symmetry. Two kinds of hydrogen bonds exist in the crystal structure. One is the intermolecular hydrogen bond between O2 and Br3^i, which distance is 3.25 Å. Another one is the intramolecular hydrogen bonding between two hydroxyl and two methoxy groups at the lower rim, where the distances are 2.61 Å for O1···O2, 2.85 Å for O2···O3, 2.68 Å for O3···O4, and 2.95 Å for O4···O1. Therefore the cone conformation of the calix[4]-arene cavity is retained and pinched due to the intramolecular hydrogen bonds. The angles are 76.9° for ∠O4···O1···O2, 103.9° for ∠O1···O2···O3, 77.6° for ∠O2···O3···O4, and 99.8° for ∠O3···O4···O1. The four dihedral angles are 116.6°, 130.7°, 114.9°, and 126.4° for the respective phenyl rings of C2–C7, C9–C14, C16–C21, and C23–28 to the reference plane defined by the bridging C atoms. The distances from C1, C8, C15 and C22 to the reference plane are –0.083 Å, 0.081 Å, –0.079 Å and 0.080 Å, respectively.

Table 1. Data collection and handling.

Crystal:	green prism, size 0.1 × 0.2 × 0.2 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	56.89 cm^{-1}
Diffractometer, scan mode:	Bruker P4, ω
$2\theta_{max}$:	50°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	6240, 5024
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 1519
$N(param)_{refined}$:	345
Program:	SHELXTL [4]

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

Atom	Site	x	y	z	U_{iso}
H(2A)	4*e*	0.0428	0.8695	0.6421	0.091
H(4A)	4*e*	0.2059	0.8440	0.9527	0.084
H(1A)	4*e*	0.2060	0.8749	1.1187	0.090
H(1B)	4*e*	0.3162	0.9010	1.2358	0.090
H(5A)	4*e*	0.2779	1.0511	0.8951	0.075
H(7A)	4*e*	0.4407	0.9757	1.2060	0.066
H(8A)	4*e*	0.0476	1.0249	0.7487	0.099
H(8B)	4*e*	–0.0100	0.9717	0.7573	0.099

* Correspondence author (e-mail: liy@chem.tsinghua.edu.cn)

Table 2. Continued.

Atom	Site	x	y	z	U_{iso}
H(12A)	4e	0.3035	0.9342	0.4307	0.075
H(14A)	4e	0.1924	1.0403	0.6245	0.085
H(15A)	4e	0.2331	0.8519	0.4370	0.063
H(15B)	4e	0.1372	0.8364	0.5160	0.063
H(19A)	4e	0.6995	0.7830	0.8496	0.075
H(21A)	4e	0.4990	0.8576	0.5335	0.070
H(22A)	4e	0.5511	0.7375	0.9489	0.080
H(22B)	4e	0.3832	0.7473	0.9060	0.080

Table 2. Continued.

Atom	Site	x	y	z	U_{iso}
H(26A)	4e	0.5831	0.8872	1.2849	0.094
H(28A)	4e	0.7208	0.7901	1.0950	0.088
H(29A)	4e	−0.1219	0.8887	0.9100	0.161
H(29B)	4e	−0.0972	0.9459	0.9190	0.161
H(29C)	4e	−0.0244	0.9126	1.0364	0.161
H(30A)	4e	0.0672	0.7430	0.6804	0.132
H(30B)	4e	0.2211	0.7204	0.7019	0.132
H(30C)	4e	0.1401	0.7498	0.5790	0.132

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)	4e	0.48849(5)	1.07465(2)	1.13317(4)	0.0679(3)	0.0635(3)	0.1083(3)	−0.0074(3)	0.0237(2)	−0.0243(3)
Br(2)	4e	0.33281(6)	1.04201(2)	0.43339(5)	0.1045(4)	0.0718(3)	0.1129(4)	−0.0156(3)	0.0202(3)	0.0214(3)
Br(3)	4e	0.79851(5)	0.82831(2)	0.66163(5)	0.0726(3)	0.0769(4)	0.1660(4)	−0.0134(3)	0.0563(3)	−0.0136(4)
Br(4)	4e	0.86503(6)	0.84679(2)	1.31766(5)	0.1022(4)	0.1206(5)	0.1339(5)	0.0247(4)	−0.0305(4)	−0.0209(4)
O(1)	4e	0.0738(2)	0.90848(9)	0.9104(2)	0.054(1)	0.074(2)	0.105(2)	−0.018(1)	0.046(1)	−0.047(2)
O(2)	4e	0.0962(2)	0.88850(9)	0.6937(2)	0.059(2)	0.048(2)	0.111(2)	−0.008(2)	0.016(2)	−0.012(2)
O(3)	4e	0.2252(2)	0.79294(8)	0.7272(2)	0.066(2)	0.043(2)	0.086(2)	−0.005(1)	0.034(1)	−0.008(1)
O(4)	4e	0.2544(2)	0.81870(9)	0.9613(2)	0.059(2)	0.065(2)	0.083(2)	−0.007(2)	0.021(1)	−0.018(2)
C(1)	4e	0.2970(4)	0.8930(1)	1.1487(3)	0.085(2)	0.087(3)	0.068(2)	−0.037(3)	0.046(2)	−0.011(3)
C(2)	4e	0.2801(4)	0.9399(1)	1.0758(3)	0.065(2)	0.049(3)	0.071(2)	−0.006(2)	0.046(2)	−0.002(2)
C(3)	4e	0.1783(3)	0.9453(1)	0.9635(3)	0.047(2)	0.067(3)	0.056(2)	0.006(2)	0.022(2)	−0.019(2)
C(4)	4e	0.1809(4)	0.9863(2)	0.8966(3)	0.040(2)	0.116(4)	0.039(2)	0.039(2)	−0.006(2)	−0.007(3)
C(5)	4e	0.2771(3)	1.0237(1)	0.9439(3)	0.051(2)	0.054(3)	0.081(3)	−0.023(2)	0.019(2)	−0.048(2)
C(6)	4e	0.3679(3)	1.0206(1)	1.0583(3)	0.049(2)	0.043(2)	0.063(2)	−0.007(2)	0.027(2)	−0.030(2)
C(7)	4e	0.3731(3)	0.9783(1)	1.1255(3)	0.039(2)	0.074(3)	0.046(2)	0.003(2)	0.007(2)	−0.017(2)
C(8)	4e	0.0765(4)	0.9906(2)	0.7649(3)	0.080(2)	0.072(3)	0.123(3)	0.022(2)	0.072(2)	−0.004(3)
C(9)	4e	0.1364(4)	0.9732(1)	0.6660(3)	0.030(2)	0.064(3)	0.072(3)	−0.013(2)	−0.014(2)	0.014(2)
C(10)	4e	0.1444(4)	0.9241(1)	0.6342(3)	0.056(2)	0.057(3)	0.060(2)	0.003(2)	0.013(2)	−0.024(2)
C(11)	4e	0.2094(3)	0.9082(1)	0.5500(3)	0.035(2)	0.053(3)	0.057(2)	−0.011(2)	−0.017(2)	0.024(2)
C(12)	4e	0.2629(4)	0.9437(1)	0.4897(3)	0.050(2)	0.056(3)	0.059(2)	0.021(2)	−0.008(2)	−0.005(2)
C(13)	4e	0.2559(4)	0.9937(1)	0.5173(3)	0.050(2)	0.067(3)	0.063(3)	−0.006(2)	0.010(2)	0.010(2)
C(14)	4e	0.1947(4)	1.0070(1)	0.6052(3)	0.048(2)	0.073(3)	0.066(3)	0.015(2)	−0.013(2)	−0.046(2)
C(15)	4e	0.2242(4)	0.8541(1)	0.5190(3)	0.071(2)	0.046(3)	0.040(2)	−0.014(2)	0.017(2)	−0.002(2)
C(16)	4e	0.3556(3)	0.8301(1)	0.6147(3)	0.039(2)	0.029(2)	0.064(2)	0.001(2)	0.004(2)	−0.020(2)
C(17)	4e	0.3579(4)	0.8031(1)	0.7150(3)	0.066(2)	0.054(3)	0.032(2)	−0.012(2)	0.022(2)	−0.007(2)
C(18)	4e	0.4811(4)	0.7862(1)	0.8064(3)	0.068(2)	0.021(2)	0.064(2)	0.002(2)	0.017(2)	−0.012(2)
C(19)	4e	0.6140(4)	0.7947(1)	0.7907(3)	0.072(3)	0.057(3)	0.056(2)	0.012(2)	0.018(2)	0.007(2)
C(20)	4e	0.6181(3)	0.8194(1)	0.6919(3)	0.035(2)	0.063(3)	0.079(2)	−0.009(2)	0.034(2)	−0.022(2)
C(21)	4e	0.4926(4)	0.8393(1)	0.6003(3)	0.078(3)	0.030(2)	0.065(3)	−0.010(2)	0.021(2)	−0.004(2)
C(22)	4e	0.4770(4)	0.7629(1)	0.9226(3)	0.081(3)	0.023(2)	0.079(3)	0.018(2)	0.007(2)	0.032(2)
C(23)	4e	0.5017(4)	0.7996(1)	1.0252(3)	0.086(3)	0.029(2)	0.049(2)	−0.008(2)	0.007(2)	0.001(2)
C(24)	4e	0.3901(4)	0.8269(1)	1.0443(3)	0.092(3)	0.040(2)	0.062(2)	0.009(2)	0.039(2)	0.012(2)
C(25)	4e	0.4190(4)	0.8594(2)	1.1401(3)	0.081(3)	0.082(3)	0.056(3)	0.000(3)	0.028(2)	0.005(3)
C(26)	4e	0.5617(4)	0.8645(1)	1.2200(3)	0.116(3)	0.037(3)	0.068(3)	0.005(3)	0.014(3)	−0.009(2)
C(27)	4e	0.6703(4)	0.8373(2)	1.2060(4)	0.079(3)	0.059(3)	0.082(3)	0.006(3)	−0.006(3)	−0.001(3)
C(28)	4e	0.6442(4)	0.8067(1)	1.1080(3)	0.106(3)	0.041(3)	0.075(3)	0.021(3)	0.033(2)	0.006(2)
C(29)	4e	−0.0532(4)	0.9144(2)	0.9471(4)	0.075(2)	0.130(4)	0.147(3)	−0.035(3)	0.075(2)	−0.046(3)
C(30)	4e	0.1577(4)	0.7477(1)	0.6671(3)	0.084(3)	0.062(3)	0.129(3)	−0.037(2)	0.051(2)	−0.037(3)

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References

1. Loon, J.-D. V.; Arduini, A.; Coppi, L.: Selective functionalization of calix[4]arenes at the upper rim. J. Org. Chem. **55** (1990) 5639-5646.
2. Wang, Q.; Li, Y.; Wu, G. S.: Synthesis and reversible thermo-induced conformational transitions of a stable nitroxide biradical based on calix[4]arene. Chem. Commun. **12** (2002) 1268-1269.
3. Gutsche, C. D.; Pagoria, P. F.: Calixarenes 16 functionalized calixarenes: the direct substitution route. J. Org. Chem. **50** (1985) 5639-5646.
4. Sheldrick, G. M.: SHELXTL. Structure Determination Software Suite. Bruker AXS, Madison, Wisconsin, USA 1997.