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Crystal structure of 25,27-bis[(2-cyanophenyl)methoxy] calix[4]arene

**Chuan-Ming Jin,(1) Guo-Yuan Lu,(1)* Yan Xu,(1) Qian Li,(1) Fang Liu,(1)
and Xiao-Zeng You(1)**

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The crystal structure of 25,27-bis[(2-cyanophenyl)methoxy] calix[4]arene ($C_{44}H_{34}N_2O_4$) was determined by X-ray crystallographic analysis. It possesses space group $R\bar{3}$, with $a = b = 35.993(8)$ Å, $c = 13.842(3)$ Å, $\alpha = \beta = 90^\circ$, $\gamma = 120^\circ$, and $D_{\text{calc}} = 1.260$ mg/cm^3 for $Z = 18$. Crystal data indicate that Compound **1** exists in a pinched-cone conformation with intramolecular hydrogen bonds.

KEY WORDS: Functionalized calix[4]arene; tweezers; crystal structure.

Introduction

Calixarenes are a class of macrocyclic host compounds that is attracting increasing interest owing to their potential for forming host–guest complexes and acting as enzyme mimics, especially if appropriately functionalized.[1−6] Our interest lies in the syntheses and possible applications of functionalized calixarenes that have the ability to catch ions or neutral molecules.[7−9] Recently, a series of functionalized calixarenes have been prepared in our laboratory (Scheme 1). In these calix[4]arenes, two functional groups such as cyano, amino, carboxylic, or guanidinium groups have been introduced to each calix[4]arene molecule under suitable conditions to form the so-called tweezer molecules,[10−12] which can bind some metal cations or organic molecules. Among these tweezer molecules, Compound **1** is a crucial one because it is not only the synthetic intermediate for the preparation of Compounds **2**, **3**, and **4** but also a possibly good host compound for some metal cations.[13,14] Recently, single crystals of Compound **1** were obtained from its acetone solution and subjected to X-ray crystallographic structure analysis. The result indicates that the Tweezer molecule **1** exists as a pinched-cone conformation. In this paper, we report the synthesis and crystal structure of Compound **1**. The details on the syntheses of other compounds will be published elsewhere.

Experimental

*Preparation of Compound **1***

The calix[4]arene was prepared according to the literature.[15] The calix[4]arene (0.57 g, 1.35 mmol) and 2-cyanobenzyl bromide (0.53 g, 2.7 mmol) were dissolved in 10 mL of anhydrous acetonitrile, and the solution refluxed for 42 h in

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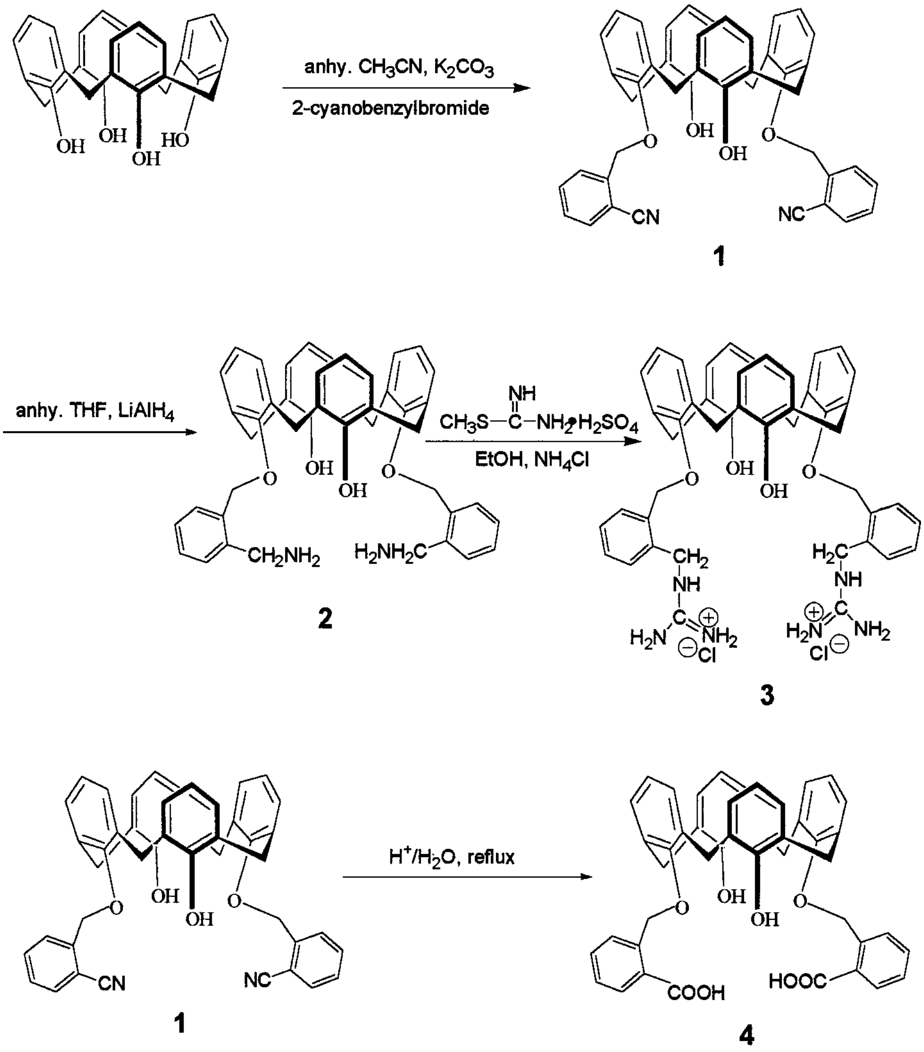
(1) Department of Chemistry, State Key Laboratory of Coordination Chemistry, Nanjing University, 210093 Nanjing, People's Republic of China.

*To whom correspondence should be addressed; e-mail: nnj.lugy@jonline.com.



Scheme 1

the presence of anhydrous potassium carbonate (0.21 g, 1.5 mmol). The solvent was evaporated in vacuo and the residue was dissolved in 20 mL of dichloromethane, washed with 1.0 mol/L HCl solution (20 mL) and water (20 mL), respectively, dried over anhydrous magnesium sulfate. The solvent was evaporated in vacuo to dryness and the residue was recrystallized from chloroform and methyl alcohol to give **1** (610 mg, 69%), white needle crystal, m.p. > 300°C; IR ($\nu_{\max}$, cm^{-1}); 3415.5 (OH), 2227.9 (CN), 1593.8, 1531.6, 1475.7 (Ar); ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 8.32$ (d, $J = 7.5$ Hz, 2H, $2 \times {}^{3}H$ArCN), 7.72 (d, $J = 7.3$ Hz, 2H, $2 \times {}^{6}H$ArCN), 7.47 (m, 4H, $2 \times {}^{4,5}H$ArCN), 7.38 (s, 2H, $2 \times$ArOH), 7.06 (d, $J = 7.4$ Hz, 4H, $2 \times {}^{3,5}H$ArOH), 6.86 (d, $J = 7.5$ Hz, 4H, $2 \times {}^{3,5}H$Ar), 6.75 (t, $J = 7.5$ Hz, 2H, $2 \times {}^{4}H$Ar), 6.68 (t, $J = 7.4$ Hz, 2H, $2 \times {}^{4}H$ArOH), 5.28 (s, 4H, $2 \times$ ArCH_2O), 4.23 (d, $J = 12.5$ Hz, 4H, $4 \times$ endo-ArCHAr), 3.30 (d, $J = 12.5$ Hz, 4H, $4 \times$ exo-ArCHAr); Anal. for $C_{44}H_{34}N_2O_4$. Calcd: C, 80.71; H, 5.23; N, 4.28. Found: C, 80.66; H, 5.44; N, 4.26.

Crystal structure determination

Colorless single crystals were obtained by slow evaporation of the acetone solution of Compound **1**, and a single crystal with dimensions of $0.30 \times 0.26 \times 0.26$ mm was mounted on a Siemens P4 four-circle diffractometer with graphite monochromated Mo Kα ($\lambda = 0.71073$ Å) radiation, using θ–2θ scan mode (range $4 < 2\theta < 50^\circ$), variable from 5.0 to 50.0° min^{-1} in ω. The data were corrected for Lorentz and Polarization effects during data reduction using XSCANS.[16] The structure was solved by direct methods and all non-hydrogen atoms were refined anisotropically on F^2 by full-matrix least squares using SHELXTL.[17] All the H atoms were placed in the calculated positions (C—H=0.96 Å, O—H=0.85 Å), assigned fixed isotropic displacement parameters 1.2 times the equivalent isotropic U value (1.5 times for OH) of the attached atom, and allowed to ride on their respective parent atoms. Crystallographic data and non-hydrogen atomic coordinates are summarized in Tables 1 and 2, respectively.

Table 1. Crystal Data and Summary of Intensity Data Collection and Structure Refinement

Color/shape	Colorless/needle
CCDC deposit no.	CCDC-1003/6021
Chemical formula	$C_{44}H_{34}N_2O_4$
Formula weight	654.73
Temperature, K	293(2)
Crystal system	Rhombohedral
Space group	$R\bar{3}$
Unit cell dimensions (7038 reflections in full θ range)	$a = 35.993(8)$ Å $b = 35.993(8)$ Å $c = 13.842(3)$ Å
Volume, $Å^3$	15530(6)
Z	18
Density (calculated), Mg/cm^3	1.260
Diffractometer	Siemens P4
θ range for data collection, deg	1.96–25.00
Independent reflections	5836 ($R_{\text{int}} = 0.1064$)
Data/restraints/parameters	5836/24/452
Goodness of fit on F^2	0.988
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0821$, $wR2 = 0.1500$
R indices (all data)	$R1 = 0.2404$, $wR2 = 0.2139$
Computer programs	XSCANS
Structure solution	SHELXTL

Table 2. Non-Hydrogen Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameter ($Å^2 \times 10^3$) for Compound **1**

Atom	x	y	z	U_{eq}[a]
O(1)	8400(1)	705(1)	−1208(2)	72(1)
O(2)	9325(1)	1420(1)	−1971(2)	69(1)
O(3)	8730(1)	727(1)	−3075(2)	64(1)
O(4)	9106(1)	1229(1)	68(2)	62(1)
C(1)	9524(2)	1824(2)	−2332(4)	58(2)
C(2)	9530(2)	1897(2)	−3334(4)	64(2)
C(3)	9744(2)	2307(2)	−3661(5)	82(2)
C(4)	9954(2)	2646(2)	−3036(6)	92(2)
C(5)	9950(2)	2572(2)	−2066(5)	84(2)
C(6)	9741(2)	2163(2)	−1693(4)	62(2)
C(7)	9725(2)	2075(2)	−613(4)	69(2)
C(8)	9299(2)	1965(2)	−188(4)	62(2)
C(9)	9180(2)	2275(2)	−112(4)	75(2)
C(10)	8782(2)	2181(2)	203(4)	78(2)
C(11)	8487(2)	1763(2)	437(4)	64(2)
C(12)	8584(2)	1437(2)	384(3)	54(1)
C(13)	8998(2)	1555(2)	108(3)	51(1)
C(14)	9389(2)	1239(2)	829(4)	67(2)
C(15)	9158(2)	1081(2)	1778(4)	60(2)
C(16)	9181(2)	1373(2)	2457(5)	87(2)
C(17)	8970(3)	1231(3)	3333(5)	116(3)
C(18)	8738(3)	803(4)	3506(6)	124(3)
C(19)	8705(2)	496(3)	2869(5)	100(2)
C(20)	8915(2)	643(2)	1979(5)	72(2)
C(21)	8890(2)	340(3)	1288(6)	90(2)
C(22)	8233(2)	976(2)	587(4)	63(2)
C(23)	7912(2)	791(2)	−208(4)	53(2)
C(24)	7501(2)	727(2)	−85(4)	70(2)
C(25)	7192(2)	539(2)	−808(5)	82(2)
C(26)	7305(2)	428(2)	−1668(4)	75(2)
C(27)	7708(2)	489(2)	−1825(4)	58(2)
C(28)	8007(2)	669(2)	−1079(4)	55(1)
C(29)	7825(2)	375(2)	−2796(4)	78(2)
C(30)	8099(2)	772(2)	−3419(4)	58(2)
C(31)	7924(2)	990(2)	−3885(4)	73(2)
C(32)	8177(3)	1361(2)	−4380(4)	74(2)
C(33)	8611(2)	1530(2)	−4429(4)	73(2)
C(34)	8808(2)	1326(2)	−4000(4)	64(2)
C(35)	8541(2)	937(2)	−3524(4)	56(2)
C(36)	9290(2)	1515(2)	−4013(4)	74(2)
C(37)	8751(2)	407(2)	−3652(4)	67(2)
C(38)	8959(2)	207(2)	−3087(4)	56(2)
C(39)	9064(2)	300(2)	−2121(4)	65(2)
C(40)	9255(2)	106(2)	−1618(5)	76(2)
C(41)	9343(2)	−179(2)	−2069(5)	79(2)
C(42)	9242(2)	−278(2)	−3043(5)	80(2)
C(43)	9047(2)	−84(2)	−3543(4)	59(2)
C(44)	8951(2)	−172(2)	−4544(5)	65(2)
N(1)	8861(3)	94(2)	737(5)	134(3)
N(2)	8874(2)	−237(2)	−5350(4)	94(2)

[a] U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

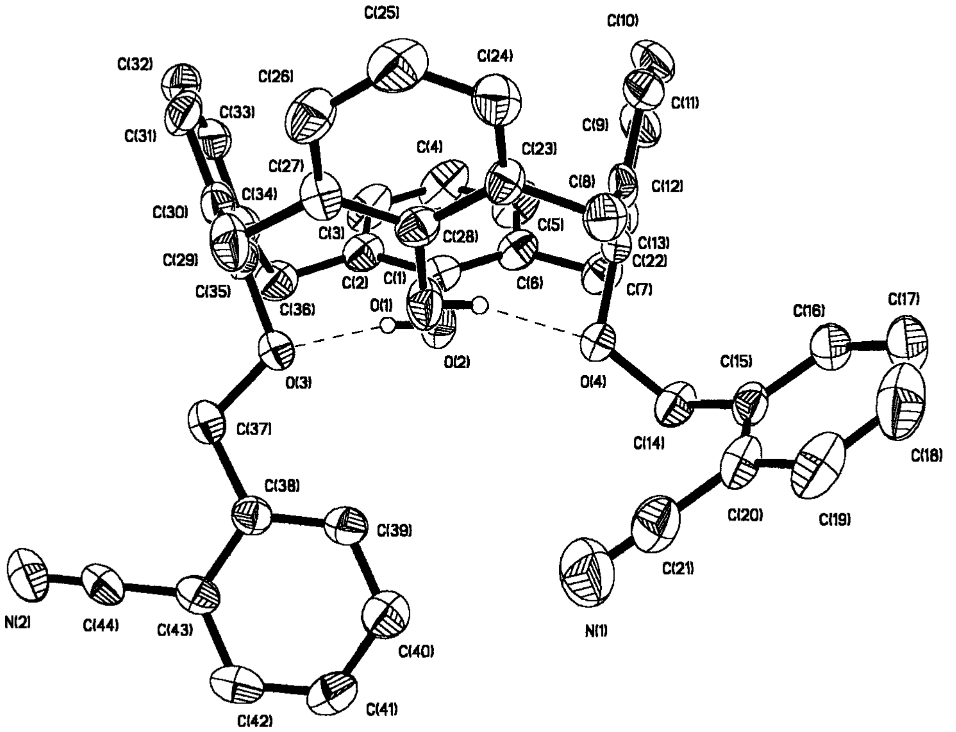


Fig. 1. ORTEP drawing of Compound **1** (dashed lines indicate the H-bonding interaction).

Result and discussion

As shown in Fig. 1, Compound **1** exists in a cone conformation in the crystal, which is stabilized by intramolecular hydrogen bonds between the phenol hydroxy groups and ether oxygen atoms (—O—H· · ·O—), and the geometric data of the hydrogen bonds are given as follows: O(1)—O(4), 2.889(3) Å, O(1)—H· · ·O(4), 164°; O(2)—O(3), 2.793(3) Å, O(2)—H· · ·O(3), 163°. There is a pseudo C_2 symmetrical axis in the calix[4]arene moiety of **1**. Two phenolic ring planes of the calix[4]arene make an angle of 15.9° with the respective pseudo C_2 axis, and so they are nearly parallel to each other, whereas the other two phenyl planes with (2-cyanophenyl)methoxy make an angle of 50.9° with the pseudo C_2 axis. Therefore, the calix[4]arene moiety of Compound **1** adopts a pinched-cone conformation in the crystal though the two 2-cyanophenyl planes attached at the lower rim of calix[4]arene make a dihedral angle of 61.2° to each other.

In the ^{1}H NMR spectra of Compound **1** in $CDCl_3$, the peaks of the $ArCH_2Ar$ protons appeared as doublets at 4.23 (H_{endo}) and 3.30 (H_{exo}) ppm, and the chemical shift difference of H_{endo} and H_{exo} is about 1.0. This fact also indicates that Compound **1** exists in the cone conformation in solution.[7,18,19]

In conclusion, the calix[4]arene moiety of Compound **1** adopts a cone conformation both in the crystal and in the solution. The two functional units attached at the lower rim may be able to form face-to-face tweezer structures and bind metal cations.

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References

1. Vicens, J.; Böhmer, V. *Calixarenes—A Versatile Class of Macrocyclic Compounds*; Kluwer: Dordrecht, 1991.
2. Ireda, A.; Shinkai, S. *Chem. Rev.* **1997**, *97*, 1713.
3. Pochini, A.; Ungaro, R. In *Comprehensive Supramolecular Chemistry, Vol 2: Calix[4]arenes and Related Hosts*; Lehn, J.M.; Vögtle, F., Eds.; Pergamon: New York, 1996; pp. 103–142.
4. Arduini, A.; McGregor, W.M.; Paganuzzi, D.; Pochini, A.; Secchi, A.; Ugozzoli, F.; Ungaro, R. *J. Chem. Soc., Perkin Trans. 2* **1996**, 839.
5. Beer, P.D.; Drew, M.G.B.; Kan, M.; Lesson, P.B.; Ogden, M.I.; Williams, G. *Inorg. Chem.* **1996**, *35*, 2202.
6. Arnaud-Neu, F.; Ferguson, G.; Fuangswasdi, S.; Notti, A.; Pappalardo, S.; Parisi, M. F.; Petringa, A. *J. Org. Chem.* **1998**, *63*, 7770.
7. Lu, G.Y.; Chen, Z.J.; Zhao, R.Z.; Huang, X.H.; Hu, H.W. *Chem. J. Chin. Univ.* **1996**, *17*, 1244.
8. Lu, G.Y.; Li, Q.; Liu, F.; Wan, X.B. *Chin. J. Chem.* **2000**, *18*, 207.
9. Lu, G.Y.; Liu, F.; Liu, Y.J.; He, W.J.; Li, Q.; Zhu, L.G. *J. Chem. Crystallogr.* **1999**, *29*, 1121.
10. Zimmerman, S.C. In *Bio-Organic Chemistry Frontiers, Vol. 2*: *Molecular Tweezers*; Dugas, H., Ed.; Springer: Berlin, 1991; pp. 35–70.
11. Lu, G.Y.; Hu, H.W. *Sci. China B* **1996**, *39*, 398.
12. Löwik, D.W.P.M.; Weingarten, M.D.; Broekema, M.; Brouwer, A.J.; Still, W.C.; Liskamp, R.M.J. *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 1846.
13. Choe, W.Y.; Kiang, Y.H.; Xu, Z.T.; Lee, S. *Chem. Mater.* **1999**, 1776.
14. Kuroda-Sowa, T.; Horino, T.; Yamamoto, M.; Ohno, Y.; Maekawa, M.; Munakata, M. *Inorg. Chem.* **1997**, 6382.
15. Van Loon, J.D.; Arduini, A.; Coppi, L.; Verboom, W.; Pochini, A.; Ungaro, R.; Harkema, S.; Reinhoudt, D.N. *J. Org. Chem.* **1990**, *55*, 5639.
16. *XSCANS (Version 2.1)*; Siemens Analytical X-ray Instruments: Madison, WI, 1994.
17. *SHELXTL (Version 5.0), Reference Manual*; Siemens Industrial Automation, Analytical Instrumentation: Madison, WI, 1995.
18. Jaime, C.; Mendoza, J.D.; Prados, P.; Nieto, P.M.; Sanchez, C. *J. Org. Chem.* **1991**, *56*, 3372.
19. Gutsch, C.D.; Dhawan, B.; Levine, J.A.; No, K.H.; Bauer, L.J. *Tetrahedron* **1983**, *39*, 409.