*Bull. Chem. Soc. Jpn.*, **78**, 718–720 (2005)

# Novel Assembly of Resorcin[4]arene to Form a Self-Dimer Directly Linked via O–H···$\pi$ Interaction in the Solid State

**Katsuyuki Aoki,* Chiharu Shimizu, and Ikuhide Fujisawa**

Department of Materials Science, Toyohashi University of Technology, Tempaku-cho, Toyohashi 441-8580

Received October 8, 2004; E-mail: kaoki@tutms.tut.ac.jp

When tetraethylresorcin[4]arene is crystallized from dioxane, it forms a "head-to-head" arranged self-dimer directly connected by non-conventional O–H···$\pi$ interaction. The resorcinarene molecule adopts the unusual flattened-cone conformation, where two of the four intramolecular hydrogen bonds are broken.

Resorcin[4]arenes have received much attention, mainly because of their interesting structural features when they form a well-defined bowl-shaped cavity constructed by multiple resorcinol rings, providing rich $\pi$-electrons; they also possess multiple hydroxy functional groups on the upper rim. Thus, resorcin[4]arenes form a variety of self-assembled supramolecules in the solid state, a hexamer[1] and dimmers.[2–7] The hexamer[1] forms a shell-like molecular capsule held by water bridges in addition to direct O–H···O hydrogen bonds between substructures; the dimers form spherical molecular capsules held by solvent-bridges (solvent = alcohol,[2] water,[3,4] alcohol and water,[5] or alcohol and halide ion[6]) or a carcerand-like barrel-shaped capsule held by 4,4′-bipyridine bridges[7] through O–H···N hydrogen bonds, where alkylammonium ions,[3–6] *o*-dichlorobenzene and propan-2-ol,[2] or nitrobenzene[7] are incorporated within the cavity. When $HNEt_3^+$ was used as an alkylammonium ion, two additional structures[8,9] other than the capsular structure[4] are formed: a monomeric structure[8] in which a $HNEt_3^+$ ion is located at the upper rim, and a dimeric structure[9] in which $HNEt_3^+$ and $SO_4^{2-}$ molecules are interposed between two "head-to-head" arranged resorcin[4]arenes without any bridges. In addition, resorcin[4]arene forms 1:1 adducts with larger alkylammonium ions, like acetylcholine[10] and 3-phenylpropionic acid choline ester,[11] where the alkylammonium moiety of the ligand is captured in the bowl-shaped cavity through cation–$\pi$ interaction. Resorcin[4]arenes also form a variety of molecular complexes with aromatic amines:[12–18] these include O–H···N hydrogen-bonded 1:2 adducts[12–15] with pyridine,[12] 4-picoline,[13] 1,10-phenanthroline,[13] or 4,4′-bipyridine,[12–15] providing a bowl-shaped enlarged-cavity in which pyridine,[12] $MeNO_2$,[13] MeCN,[12] MeCN and benzene,[13] *p*-chlorotoluene,[14] adamantanone,[14] [2.2]paracyclophane,[14] or acetylated ferrocene[15] are captured. Generally, resorcin[4]arenes form 1:1 adducts with neutral molecules, such as dioxane,[19] acetone,[20] MeOH,[21] EtOH,[18,21] dimethylsulfoxide,[21] or imidazole,[21] which are located within the cavity[18,20,21] or at the upper rim.[19] We report here on the crystal structure of the tetraethylresorcin[4]arene, where two resorcinarene molecules aggregate to form a "head-to-head" arranged self-dimer directly linked through non-conventional O–H···$\pi$ interaction without attracting any other ligand within the cavity, accompanying a conformational change of the resorcinarene moiety to the flattened-cone conformation.

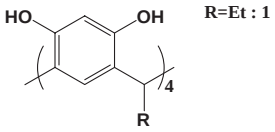


Chart 1.

The crystallization of tetraethylresorcin[4]arene (Chart 1; R = Et, **1**) from dioxane yielded an adduct, $2(\mathbf{1})\cdot 2H_2O$, and its crystal structure was determined by X-ray diffraction. Figure 1 shows the molecular structure of the adduct in which it forms a "head-to-head" arranged self-dimer of resorcin[4]arene across a crystallographic center of symmetry, where ring A (or its inversion center-related ring A*) is situated into a bowl-shaped cavity of the pairing substructure. The two rings, A and A*, are arranged so that they are antiparallel to each other with a ring separation of 3.4 Å, but are scarcely overlapped, and their hydroxy groups are directed toward the phenyl rings of the pairing substructure, forming O(1)–H···$\pi$ (ring B*) and O(2)–H···$\pi$ (ring D*) interactions with perpendicular distances of O(1)···ring B* = 3.12, O(2)···ring D* = 3.09, H(1)···ring B* = 2.5, and H(2)···ring D* = 2.6 Å. This arrangement causes two rings, B and D, to open more than rings A and C, and thus **1** adopts a conformation belonging to a "flattened-cone";[17] dihedral angles of 36° form between rings A and C, while 124° between rings B and D. The conformation of the resorcin[4]arene is also described by the angles between the aromatic rings and the least-squares plane formed by the bridging methylene carbon atoms. Rings A and C are nearly symmetrically bent upward from the least-squares plane by 73 and 71°, respectively, while rings B and D deviate asymmetrically, and only by 21 and 35°, respectively, from the plane. The distances between the opposite hydroxy groups of the resorcinol rings are: O(1)···O(6) = 6.764(5) and O(2)···O(5) = 6.788(5) Å while O(3)···O(8) = 10.186(5) and O(4)···O(7) = 10.022(5) Å. The resorcin[4]arene moiety has been found to take three conformations in the solid state: the usually observed crown conformation stabilized by the formation of four intramolecular hydrogen bonds between the adjacent hydroxy groups, a flattened-cone conformation observed in three crystal structures,[17,18,22] in which none of the four intramolecular hydrogen bonds are formed, and a chair conformation.[23] The former two conformations occur in resorcin[4]arenes that have aliphatic substituents at the lower rim, while the last one occurs in those having aromatic substituents. In the present structure, two intramolecular hydrogen bonds are broken, but the other two are still maintained: O(6)···O(7) = 2.919(3) and O(8)···O(1) = 2.850(4) Å, while O(2)···O(3) = 3.412(4) and O(4)···O(5) = 3.369(5) Å. This

Published on the web April 8, 2005; DOI 10.1246/bcsj.78.718

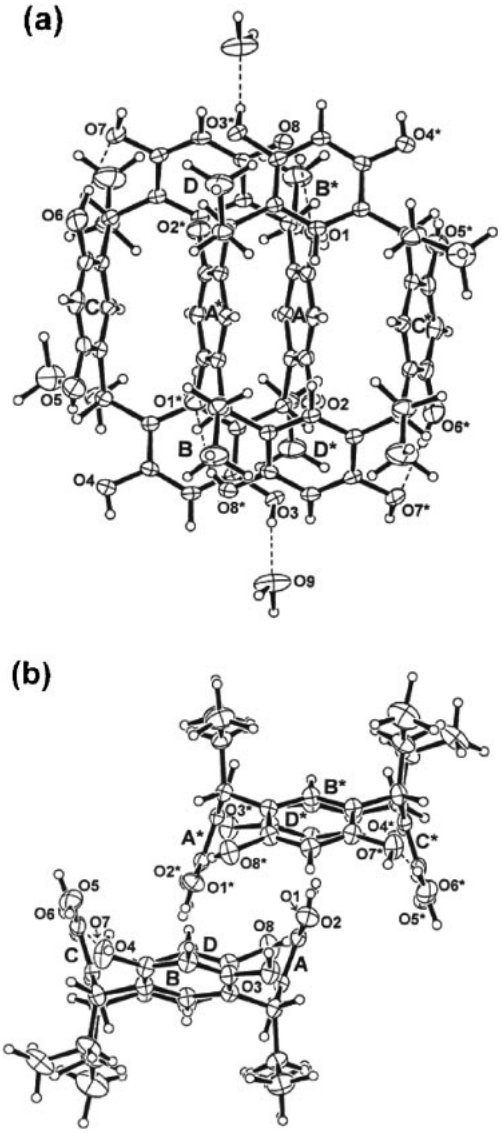


Fig. 1. (a) Top and (b) side view of $2(\mathbf{1})\cdot 2H_2O$, where atoms designated by asterisk (*) are related to their parent atoms by a center of symmetry. Note that tetraethylresorcin[4]arene **1** forms a "head-to-head" arranged self-dimer directly linked through O(1)–H···$\pi$ (ring B*) and O(2)–H···$\pi$ (ring D*) (or O(1*)–H···$\pi$ (ring B) and O(2*)–H···$\pi$ (ring D)) interactions. Broken lines denote hydrogen bonds. In (b), water molecule O(9) is omitted for clarity.

hydrogen-bonding asymmetry is attributed to the asymmetric inclination angles of ring planes B and D. Since the O(1) and O(2) hydroxy groups make nearly the same close contacts with rings B* and D*, respectively, this ring-inclination asymmetry is most probably due to the crystal packing, mainly dominated by intermolecular hydrogen bonds; each of the O(3) and O(4) hydroxy groups of ring B participate in the formation of *two* intermolecular hydrogen bonds, one of which is formed with the O(9) crystallization water molecule, while *one* for each of the O(7) and O(8) hydroxy groups of ring D.

In summary, this study presents two novel features of the structural chemistry of resorcin[4]arene: (i) tetraethylresorcin[4]arene forms a "head-to-head" arranged self-dimer directly linked through O–H···$\pi$ interaction and (ii) the conformation of the resorcinarene is doubly unusual in that it assumes a rare flattened-cone conformation and, in addition, two of the four intramolecular hydrogen bonds are still reserved.

## Experimental

**Crystallization of an Adduct, 2(Tetraethylresorcin[4]-arene)·2H$_2$O.** Tetraethylresorcin[4]arene[24] (R = Et, **1**) was synthesized according to a literature procedure[25] from resorcinol and propionaldehyde. A dark-yellowish adduct, $2(\mathbf{1})\cdot 2H_2O$, was crystallized from slow evaporation of a solution dissolving resorcin-[4]arene (0.1 mmol) in dioxane (10 mL), with a yield of 45%. An elemental microanalysis of the adduct was not possible due to its rapid decomposition out of solution. The molecular formula was determined by X-ray analysis.

**X-ray Crystallography.** For X-ray measurements, a crystal ($0.2 \times 0.3 \times 0.3$ mm$^3$) was sealed in a glass capillary with a drop of mother liquor. All measurements were made on a Rigaku AFC7R diffractometer with graphite-monochromated Mo K$\alpha$ radiation ($\lambda = 0.7107$ Å) using an 18 kW rotating anode generator. The structure was solved by direct methods, and refined by full-matrix least-squares methods, minimizing the function $\Sigma w(|F_o| - |F_c|)^2$. All non-H atoms were refined anisotropically. All hydrogen atoms were located in difference Fourier maps, among which all H-atoms attached to the resorcinol rings and the methylene carbons were refined isotropically; those attached to the ethyl substituents and a water molecule were fixed with their isotropic displacement factors of $B = 6$ Å$^2$. All calculations were carried out using the teXsan crystallographic software package.[26] Crystal data for $\mathbf{1}\cdot H_2O$: $C_{36}H_{42}O_9$, fw = 618.72, triclinic, space group $P\bar{1}$, $a = 13.207(2)$, $b = 13.845(3)$, $c = 9.779(2)$ Å, $\alpha = 104.13(1)$, $\beta = 109.85(1)$, $\gamma = 97.03(2)^\circ$, $V = 1589.2(5)$ Å$^3$, $Z = 2$, $D_{calcd} = 1.293$ g cm$^{-3}$, $\mu$(Mo K$\alpha$) = 0.92 cm$^{-1}$, $R = 0.052$ and $R_w = 0.050$ (4048 unique reflections with $I > 3\sigma(I)$), GOF = 1.63. Crystallographic data have been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. CCDC-259675. Copies of the data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge, CB2 1EZ, UK; Fax: +44 1223 336033; ordeposit @ccdc.cam.ac.uk).

## References

1 L. R. MacGillivray and J. L. Atwood, *Nature*, **389**, 469 (1997).
2 K. N. Rose, L. J. Barbour, G. W. Orr, and J. L. Atwood, *Chem. Commun.*, **1998**, 407.
3 K. Murayama and K. Aoki, *Chem. Commun.*, **1998**, 607.
4 A. Shivanyuk, K. Rissanen, and E. Kolehmainen, *Chem. Commun.*, **2000**, 1107.
5 H. Mansikkamäki, M. Nissinen, and K. Rissanen, *Chem. Commun.*, **2002**, 1902.
6 H. Mansikkamäki, M. Nissinen, C. Schalley, and K. Rissanen, *New J. Chem.*, **2003**, 88.
7 L. R. MacGillivray, P. R. Diamente, J. L. Reid, and J. A. Ripmeester, *Chem. Commun.*, **2000**, 359.
8 P. Thuéry and M. Nierlich, *Supramol. Chem.*, **11**, 185 (2000).
9 T. Lippmann, H. Wilde, M. Pink, A. Schäfer, M. Hesse, and G. Mann, *Angew. Chem., Int. Ed. Engl.*, **32**, 1195 (1993).
10 K. Murayama and K. Aoki, *Chem. Commun.*, **1997**, 119.
11 K. Murayama and K. Aoki, *Chem. Lett.*, **1998**, 301.

12 L. R. MacGillivray and J. L. Atwood, *J. Am. Chem. Soc.*, **119**, 6931 (1997).

13 L. R. MacGillivray and J. L. Atwood, *Chem. Commun.*, **1999**, 181.

14 L. R. Macgillivray, J. L. Reid, and J. A. Ripmeester, *CrystEngComm*, **1999**, 1.

15 L. R. MacGillivray, H. A. Spinney, J. L. Reid, and J. A. Ripmeester, *Chem. Commun.*, **2000**, 517.

16 G. Ferguson, C. Glidewell, A. J. Lough, G. D. MacManus, and P. R. Meehan, *J. Mater. Chem.*, **8**, 2339 (1998).

17 Y. Zhang, C. D. Kim, and P. Coppens, *Chem. Commun.*, **2000**, 2299.

18 M. Nissinen, E. Wegelius, D. Falábu, and K. Rissanen, *CrystEngComm*, **28**, 1 (2000).

19 T. Borowiak, M. Maczynski, M. Pietraszkiewicz, and O. Pietraszkiewcz, *J. Inclusion Phenom. Macrocyclic Chem.*, **35**, 131 (1999).

20 Z. Cao, K. Murayama, and K. Aoki, *Anal. Chim. Acta*, **448**, 47 (2001).

21 K. Aoki, C. Shimizu, T. Nakahara, and R. Matsubara, unpublished results.

22 M. Munakata, L. P. Wu, T. Kuroda-Sowa, M. Maekawa, Y. Suenaga, K. Sugimoto, and I. Ino, *J. Chem. Soc., Dalton Trans.*, **1999**, 373.

23 A. Shivanyuk, V. Böhmer, and E. F. Paulus, *Gazz. Chim. Ital.*, **127**, 741 (1997).

24 2,8,14,20-Tetraethyl-4,6,10,12,16,18,22,24-octahydroxy-calix[4]arene.

25 Y. Aoyama, Y. Tanaka, and S. Sugahara, *J. Am. Chem. Soc.*, **111**, 5397 (1989).

26 "teXsan, Crystal Structure Analysis Package," Molecular Structure Coorporation (1992).