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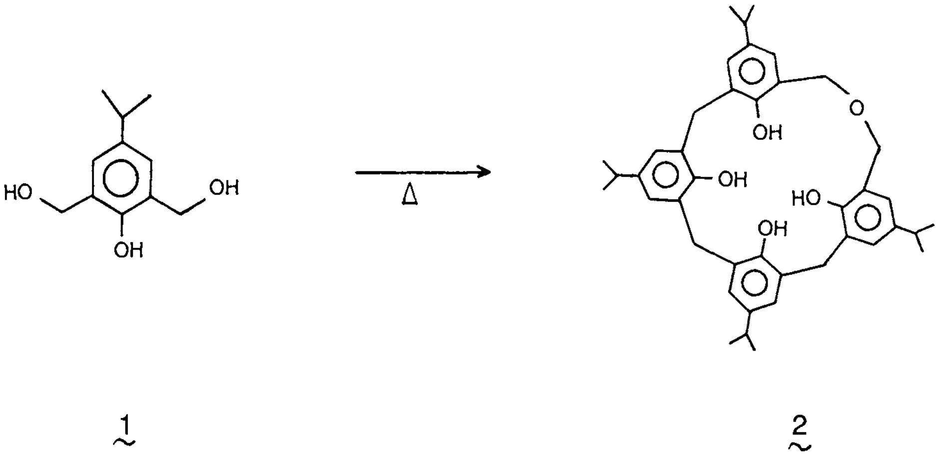
X-Ray Crystal Structure of *p*-Isopropyldihomooxacalix[4]arene – *o*-Xylene (1:1) Complex

Kenji SUZUKI, Anthony E. ARMAH, Satoshi FUJII, Ken-ichi TOMITA,*
Zouhair ASFARI,† and Jacques VICENS†
Faculty of Pharmaceutical Sciences, Osaka University, 1-6 Yamadaoka, Suita, Osaka 565
†Laboratoire de Chimie Analytique et Minérale, URA 405 du CNRS, Ecole Européenne des Hautes Etude des Industries Chimiques de Strasbourg, 1, rue Blaise Pascal, F-67008 Strasbourg, France

The crystal structure of p-isopropyldihomooxacalix[4]arene – *o*-xylene complex was determined by X-ray diffraction method. This oxacalixarene adopts a cone conformation involving *o*-xylene as a guest molecule.

Calixarenes are cyclic phenol-methylene oligomers which are able to include molecules.[1] Various type of calixarenes have so far been synthesized and their functions studied.[2,3] Oxacalixarenes are also a family of inclusion compounds having one or several additional methyleneoxy groups in the structure of calixarenes. *p*-Isopropyldihomooxacalix[4]arene (2) is synthesized from base catalyzed condensation of 2, 6-bis-hydroxymethyl-4-iso-propylphenol (1),[4] and includes *o*-xylene selectively in compared with *m*- or *p*-xylene.[5] X-Ray structure analysis is undertaken to determine the specific interactions between host and guest molecules.



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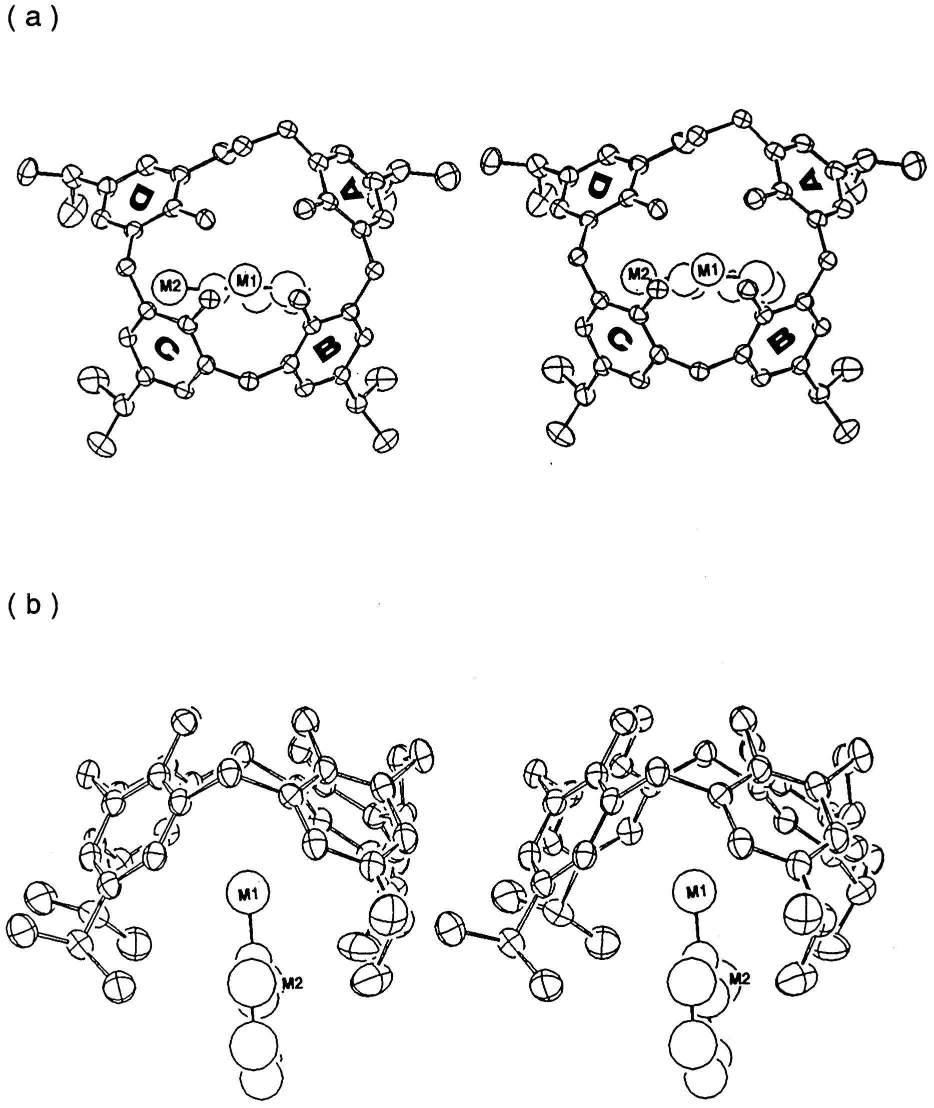

Fig. 1. Stereoscopic views of inclusion complex. Viewed ; (a) down from the hydroxy groups of the host molecule, and (b) from the right side of (a).

Colorless pillar-shape crystals of complex were obtained from *o*-xylene solution by slow evaporation at room temperature. The X-ray diffraction experiment was carried out on a Rigaku AFC-5 diffractometer using Cu-Kα (λ = 1.54178 Å) radiation. Unit cell constants were obtained by the least-squares refinement on 25 reflections with 48° < 2θ < 55°. Crystal data are $C_{41}O_5H_{50} \cdot C_8H_{10}$, Fw = 729.0, F (0 0 0) = 1344, monoclinic, $P2_1/n$, Z = 4, a = 18.808 (3) Å, b = 24.714 (4) Å, c = 9.203 (1) Å, β = 100.31 (1)°, V = 4208.7 (1) Å^3, D_x = 1.151 Mgm^{-3}. Intensity data were collected up to 2θ = 120° by ω–2θ scan technique, scan speed of ω = 6°/min. Independent 6348 reflections were obtained, in which 3782 with $F_o > 5\sigma(F_o)$ were used for structure analysis. Structure was solved by direct method with *SHELX 86*.⁶⁾ Positional and thermal parameters were refined by block-diagonal least-squares method with *HBLS*.⁷⁾ All H atoms were found on difference Fourier maps. Non-H atoms and H-atoms were refined with anisotropic and isotropic temperature factors, respectively. The final R-value is 0.099. All computations were carried out on an ACOS 930 computer at the Crystallographic Research Center, Institute for Protein Research, Osaka University.

The host molecule adopts a cone conformation and *o*-xylene molecule is included in the hydrophobic cavity, as shown in Fig. 1. Four phenol methylene units are designated as A, B, C, and D. The bond lengths and angles were in good agreement with standard values. The dihedral angles between benzene rings and a horizontal plane formed by four centroids of each benzene ring were 49.3 (A), 58.4 (B), 52.0 (C), and 40.8 (D)°, and the distances between centroids of adjacent benzene rings were 4.954 (A–B), 4.936 (B–C), 4.838 (C–D), and 6.208 (D–A) Å as listed in Table 1. The average distance between the best plane containing four oxygen atoms of hydroxy group and the plane containing four root carbon atoms of isopropyl group, which corresponded to the depth of cone cavity, was 4.29 Å. These values indicate that this cone cavity has enough space to include *o*-xylene. Owing to having one CH_2–O–CH_2 unit in the linkage between phenol groups, the molecule lacks a four-fold symmetry. The dihedral angles between adjacent benzene rings, as shown in Table 1, were 116.7, 116.5, 108.0, and 118.2°, for A–B, B–C, C–D, and D–A, respectively.

Table 1. Dihedral angles (°) between benzene rings (upper right) and distances (Å) between centroids of benzene ring (lower left)

	A	B	C	D
A		116.7	99.9	118.2
B	4.954		116.6	89.9
C	7.280	4.936		108.0
D	6.208	5.576	4.838	

The observed cone conformation should be stabilized by the four intramolecular hydrogen bonds [2.769 (7), 2.711 (6), 2.677 (6), and 3.075 (7) Å for A–B (A: hydrogen donor, B: acceptor), B–C, C–D, and D–A, respectively]. There existed several interactions between two methyl groups of *o*–xylene and host molecule. With regard to M1, one of the methyl group of *o*–xylene, there were weak π - CH_3 interactions between B, C benzene rings and M1 [the average distances between B, C and M1 were 3.799 (15), and 3.952 (15) Å, respectively] and van der Waals contact between hydroxy oxygen atom of D ring and M1 [3.664 (16) Å]. A weak CH_3–CH_3 interaction was also found between isopropyl group of D ring and the other methyl group, M2 [3.843 (22) Å]. These observations consist with the specific inclusion of *o*–xylene.

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