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Solid-State and Solution Structures of Calix[4]arene Tetramethyl Ether Containing Four Diphenylphosphino Moieties at the Upper Rim

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X-ray crystallographic analysis and CPMAS solid-state NMR measurements of tetrakis(diphenylphosphino)calix[4]arene tetramethyl ether (**1**) elucidated that in the solid-state **1** adopts a flattened partial cone conformation having C_1 symmetry. In solution, on the other hand, the ^{1}H, ^{13}C, and ^{31}P NMR spectra measured at −20 °C indicated that **1** has a partial cone conformation with a mirror plane. Two-dimensional ^{31}P EXSY and variable-temperature ^{31}P NMR spectra reveal a fluxional behavior of **1** in solution on the NMR time scale due to annulus rotation from the methoxy side. Concerning the energetics for the four conformers of **1**, an ab initio molecular orbital calculation showed that the partial cone conformation is the most stable form, while the cone and the 1,3-alternate conformers are only slightly less stable.

Calixarenes, which are cyclic products in the phenol–formaldehyde condensation reaction, possess an inner hydrophobic cavity.[1] They are receiving increasing attention in the field of supramolecular chemistry because of simple preparations, easy modifications, and unique properties. Particularly calix[4]arenes have been frequently used as building blocks for the construction of highly sophisticated host molecules.[2] The combination of calix[4]arenes functionality with transition metals may provide novel organometallic materials, which might realize unique supramolecular catalysis[3] by utilizing a spatially confined environment.

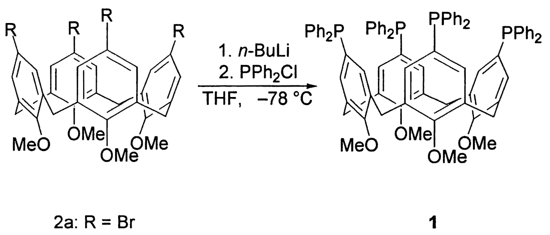
Tertiary phosphines are one of the most useful and widely employed ligands for transition metal complexes, many of which display excellent activity and selectivity in homogeneous catalytic reactions.[4] Therefore, calix[4]arenes having P(III) functionality have attracted considerable attention as the ligands of transition-metal complexes.[5] Among them, many calix[4]arenes in which P(III) functionality is tethered or directly connected to the lower rim via ether linkage have been prepared, since the preparations are rather easy.[6] On the other hand, calix[4]arenes containing P(III) moieties at the upper rim are much more limited.[7] Especially, calix[4]arenes possessing P(III) functionality directly connected to the upper rim are surprisingly unexplored, even though the hydrophobic cavities of calix[4]arenes might be utilized with a P(III) coordination site nearby. Recently, Harvey and co-workers have prepared two calix[4]arenes having *one* P(III) functionality directly on the upper rim.[8] To date, only three calix[4]arenes having *two* P(III) moieties directly connected to the upper rim have been reported,[9,10] whereas there is no precedent for calix[4]arenes having *three* P(III) moieties directly on the upper rim.

We are interested in calix[4]arene having *four* P(III) functionalities directly on the upper rim, since it will work as a unique polydentate ligand for late-transition metals. There is only one precedent for such calix[4]arene derivatives: Hamada and Atwood synthesized tetrakis(diphenylphosphino)calix[4]arene tetramethyl ether (**1**) for liquid-liquid extraction chemistry.[11] However, the molecular structure and full properties of **1** including ^{31}P NMR are still unknown. Here, we reveal the solid-state and solution structures of **1** based on solution and solid-state ^{31}P and ^{13}C NMR, X-ray crystallographic analysis, and ab initio molecular orbital calculations.

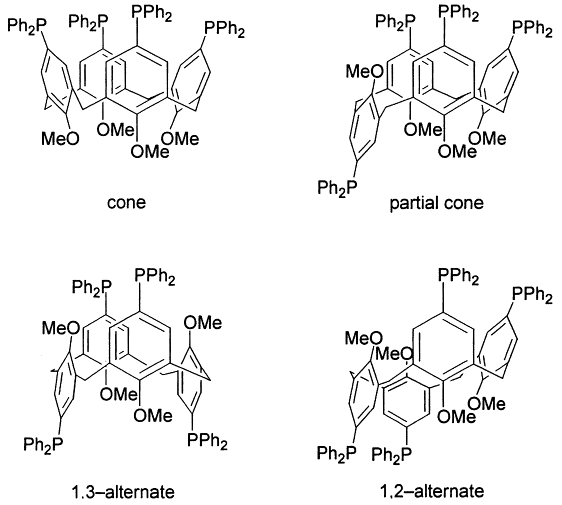
Results and Discussion

Synthesis. Tetrakisphosphinocalix[4]arene **1** was prepared by a modified published procedure,[11] i.e., by lithiation of the corresponding tetrabromocalix[4]arene (**2a**: R = Br)[12] with *n*-BuLi, followed by phosphination with chlorodiphenylphosphine in THF (Scheme 1; see Experimental Section). Analytically pure **1** was isolated from the reaction mixture by medium-pressure column chromatography on silica gel using hexane/acetone (10 : 1) as an eluent in 51% yield. Elemental-analysis data obviously show the high purity of **1**. This purity has also been verified by a melting-point measurement; note that the melting point of **1** (220–222 °C) is much higher than the reported value (113.5–114.6 °C).[11] The FD mass spectrum of **1** shows a molecular ion peak: *m*/*z* 1216 [M]$^{+}$, 608 [M]$^{2+}$.

Solid-State Structure of 1. Four conformers are possible for **1** due to a different orientation of the aryl unit of the calix[4]arene moiety, as shown in Scheme 2. In order to eluci-



Scheme 1.



Scheme 2.

Table 1. Crystallographic Data for Tetrakisphosphinocalix[4]arene **1**

Formula: $C_{80}H_{68}O_4P_4$	fw: 1217.31
Crystal size = 0.40 × 0.14 × 0.10 mm	T = 20 °C
Crystal habit = needle	a = 16.396(1) Å
Crystal color = colorless	b = 18.577(1) Å
Crystal system = triclinic	c = 12.7611(9) Å
Space group = $P\bar{1}$	α = 109.718(3)°
D_{calc} = 1.234 g cm^{-3}	β = 108.787(1)°
$\mu(\mathrm{Mo}K\alpha)$ = 1.67 cm^{-1}	γ = 100.439(2)°
$R^{a)}$ = 0.069	V = 3275.8(8)Å^3
$R_w^{b)}$ = 0.045	Z = 2
GOF = 1.77	

a) $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$.
b) $R_w = \{\Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o^2\}^{1/2}$.

date the conformation of **1** in the solid state, an X-ray structure analysis was carried out. Single crystals of **1** suitable for X-ray analysis were obtained by the slow diffusion of MeOH into a $CHCl_3$ solution of **1** at room temperature. The crystallographic data of **1** are summarized in Table 1. Table 2 lists selected atom distances and bond angles of **1**. Figure 1 clearly shows that **1** possesses the partial cone conformation in which all the methoxy carbons point outward. The structure of **1** is distorted from an ideal partial cone conformer into what is referred to as a flattened partial cone,[13] where three of the aryl groups are almost parallel to one another, while the other is splayed outward. The dihedral angles between the mean plane of the methylene carbons and the aryl rings possessing P1, P2, P3, and P4 (see Fig. 1) on the upper rim are 92.76°, 26.89°, 88.79°, and 96.5°, respectively. Although two aryl rings having P1 and P3 are almost superimposable (the dihedral angle between C2–C5···C19–C16 is 0.3°), the P1–C5 bond and the P3–C19 bond are significantly twisting each other: the dihedral angle between P1–C5···C19–P3 is 10.1°. Accordingly, **1** has no mirror plane in the solid state. Similar C_1 X-ray structures of the corresponding bromo (**2a**)[14a] and cyano (**2b**: R = CN)[14b] analogues were reported previously, while ethylthio (**2c**: R = SEt)[14a] and *t*-butyl (**2d**: R = *t*-Bu)[14c] analogues have C_s symmetry. In addition, the distance between P1 and P3 (5.483(1) Å) might be suitable for chelating with a late transition metal. The P1···P2 and P2···P3 distances (7.423(2) and 7.971(2) Å, respectively) are longer than that of P1···P3 because of the in-

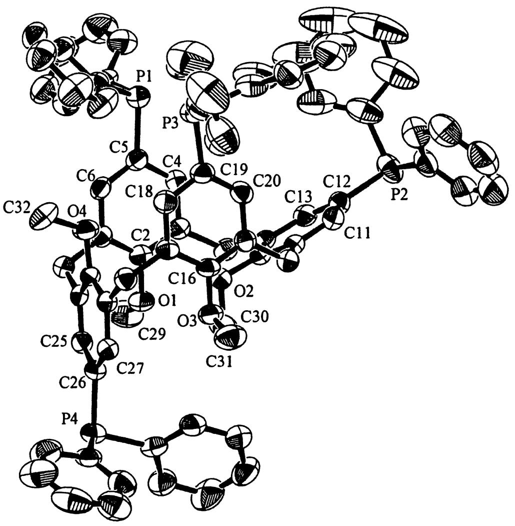


Fig. 1. ORTEP drawing of tetrakisphosphinocalix[4]arene **1** with thermal ellipsoids at 50% probability levels. Hydrogen atoms are omitted for clarity.

Table 2. Selected Bond Distances and Angles for **1**

	Distance (Å)		
P(1)–C(5)	1.826(3)	O(1)–C(29)	1.419(4)
P(2)–C(12)	1.828(3)	O(2)–C(30)	1.420(4)
P(3)–C(19)	1.840(3)	O(3)–C(31)	1.410(4)
P(4)–C(26)	1.836(3)	O(4)–C(32)	1.423(4)
P(1)···P(2)	7.423(2)	P(2)···P(3)	7.971(2)
P(1)···P(3)	5.483(1)	P(2)···P(4)	11.728(2)
P(1)···P(4)	10.187(2)	P(3)···P(4)	10.162(2)
	Angles (deg)		
P(1)–C(5)–C(4)	116.1(2)	P(1)–C(5)–C(6)	126.1(2)
P(2)–C(12)–C(11)	124.2(2)	P(2)–C(12)–C(13)	117.9(2)
P(3)–C(19)–C(18)	116.6(2)	P(3)–C(19)–C(20)	124.9(2)
P(4)–C(26)–C(25)	116.4(2)	P(4)–C(26)–C(27)	125.5(2)

clination of the aromatic ring attached to P2. However, P1···P4 (10.187(2) Å), P2···P4 (11.728(2) Å), and P3···P4 (10.162(1) Å) distances are too long for chelating coordination, assuming that the partial cone conformer is rigid.

Solid-state NMR is a useful technique for investigating the conformation of calix[4]arene derivatives as a complementary method to X-ray analysis.[15] Therefore, CPMAS solid-state ^{31}P and ^{13}C NMR measurements of **1** were carried out (Fig. 2). Since **1** has no symmetry, the ^{31}P resonance (−2.5 ppm, −4.2 ppm, −7.2 ppm, and −11.0 ppm: Fig. 2a) and ^{13}C resonance of the aryl carbons attached to the methoxy groups (159.3 ppm, 159.8 ppm, 161.2 ppm, and 162.0 ppm: Fig. 2b) appear as four peaks with the same intensity. However, other resonances in the ^{13}C NMR spectrum exhibit the partial cone structure of apparent C_s symmetry due to overlapping of the broad peaks: the three resonances of the methoxy carbons at 61.8 ppm, 62.7 ppm, and 63.6 ppm in a 1 : 1 : 2 ratio and the two resonances of the methylene carbons at 31.5 ppm and 37.3 ppm in a 1 : 1 ratio (Fig. 2b). Thus, the CPMAS ^{31}P and ^{13}C NMR spectra indicate that in solid-state **1** has a partial cone conformation without any symmetry.

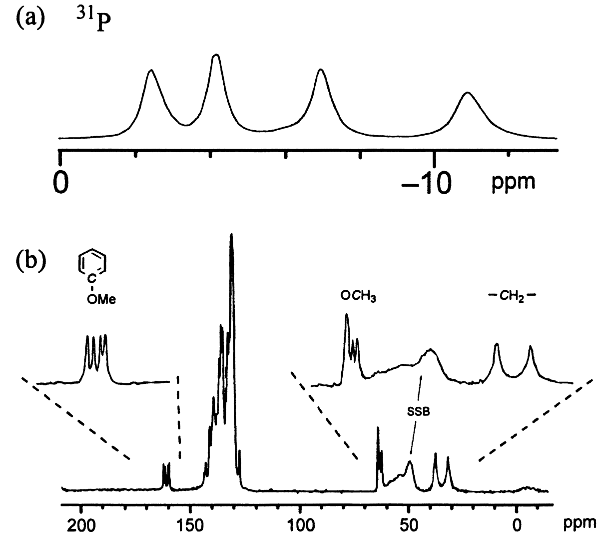


Fig. 2. Solid state CAMAS (a) ^{13}C NMR and (b) ^{31}P NMR spectra of **1**. *SSB: spinning side band.

Structure of 1 in Solution. We next investigated the structure of **1** in solution by high-resolution NMR. The ^{1}H NMR spectrum measured in CD_2Cl_2 at −20 °C (Fig. 3a) shows three signals of methoxy protons (3.23 ppm, 3.32 ppm, and 3.52 ppm) in a 1 : 1 : 2 ratio and four resonances (3.08 ppm, 3.60 ppm, 3.64 ppm, and 4.06 ppm) of the methylene protons having a geminal coupling. Similarly, the ^{13}C NMR spectrum (Fig. 3b) shows three peaks in a 1 : 1 : 2 ratio (57.9 ppm, 59.6 ppm, and 60.0 ppm) and two peaks in a 1 : 1 ratio (29.7 ppm and 35.5 ppm) assignable to the methoxy carbon and the methylene carbon, respectively. These results are most diagnostic of the partial cone structure of **1** in solution, as observed in the solid state. Aryl carbons bonded to the methoxy group of **1** give three resonances at 157.9 ppm, 158.2 ppm, and 158.4 ppm in a 1 : 2 : 1 ratio. This result is distinct from the observation in

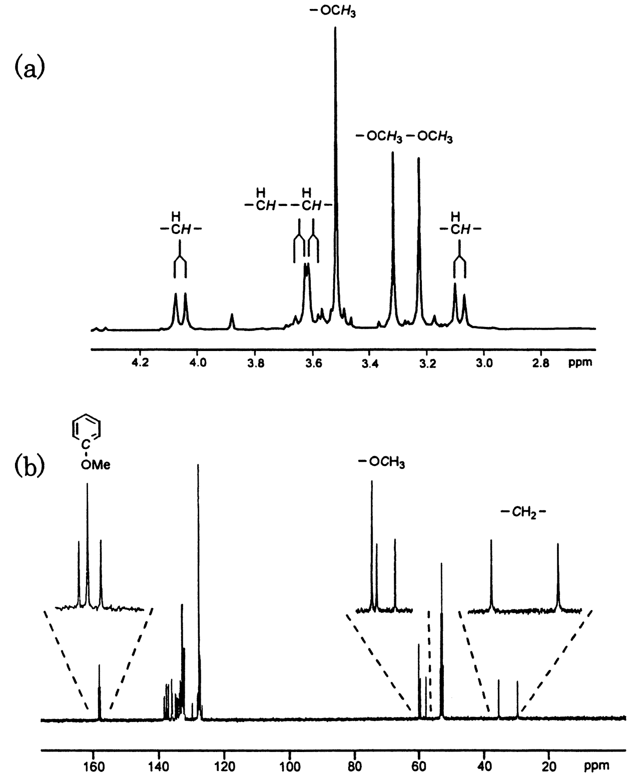


Fig. 3. (a) Partial ^{1}H NMR and (b) ^{13}C NMR spectra of **1** in CD_2Cl_2 at −20 °C.

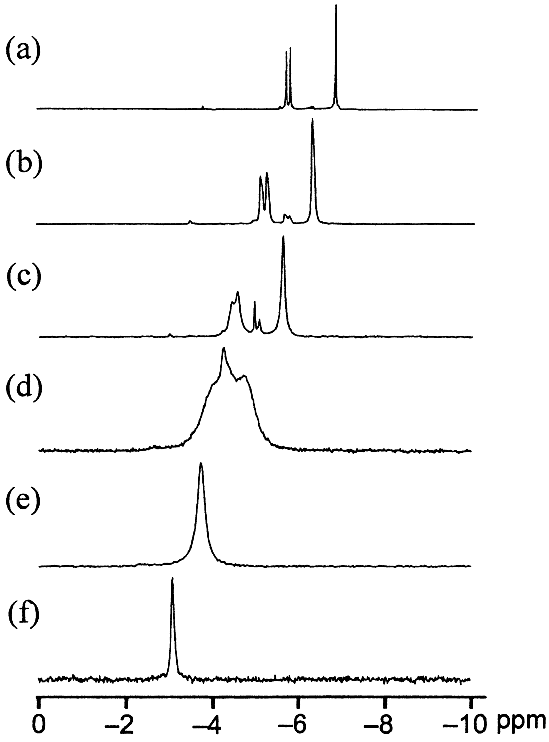


Fig. 4. Variable temperature ^{31}P NMR spectra of **1** in toluene-d_8: (a) −20 °C, (b) 0 °C, (c) 20 °C, (d) 40 °C, (e) 60 °C, and (f) 80 °C.

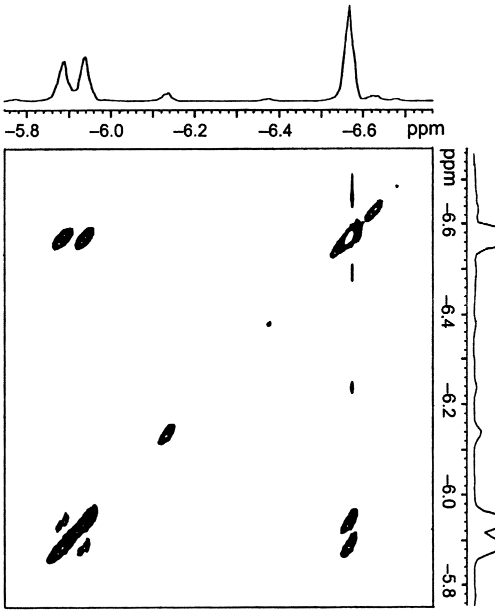


Fig. 5. ^{31}P NMR EXSY NMR spectrum of **1** in CD_2Cl_2 at −20 °C.

the solid-state ^{13}C NMR (Fig. 2b), where four peaks with the same intensity appeared. Similarly, the solution ^{31}P NMR spectrum in toluene-d_8 measured at −20 °C (Fig. 4a) shows three sharp signals in a 1:1:2 ratio (cf. Fig. 2a). These observations suggest that in solution **1** possesses the partial cone conformation with C_s symmetry.

Fluxional Behavior of 1 in Solution. A variable-temperature ^{31}P NMR measurement shows fluxional behavior of **1** (Fig. 4). At −20 °C the resonances are sharp (Fig. 4a). Upon warming, the resonances become broader and coalesce (Figs. 4b–d). Finally, at 80 °C only one signal is observed at −4.70 ppm (Fig. 4f).[16] This behavior is reversible. It is well-known that the methoxy moieties at the lower rim of calix[4]arene derivatives are not bulky enough to hinder the annulus rotation from the methoxy side, and at least a propyl group is necessary to hinder it.[17] Therefore, at 80 °C, all four phosphorus atoms of **1** may be exchanged very rapidly on the NMR time scale through inversion of the aromatic rings from the methoxy side.

Reinhoudt et al.[18] and Detellier et al.[19] independently studied the conformational dynamics of **2d** using two-dimensional ^{1}H EXSY (Exchange Spectroscopy) NMR. Unfortunately, in the present study the ^{1}H NMR spectrum of **1** is too complicated to be fully assigned, even at −20 °C. Therefore, we measured the two-dimensional ^{31}P EXSY NMR. The spectrum measured at −20 °C using 250 ms mixing time is shown in Fig. 5. Since cross peaks were observed between all of the signals assigned to the partial cone conformer, exchanges between all four phosphorus atoms of **1** should take place. Consequently, we postulate that the interconversion among the partial cone conformers would be the main inversion process of **1**. The rates of interconversion at each temperature were estimated by a line-shape analysis of the ^{31}P NMR spectra in Fig. 4. Then, the activation parameters were evaluated by the Eyring plots: $\Delta H^{\ddagger} = 49 \pm 0.6$ kJ mol^{-1}, $\Delta S^{\ddagger} = -42 \pm 2$ J mol^{-1} K^{-1}. These values are similar to those reported by Detellier for **2d**,[19] consistent with the annulus rotation from the methoxy side. Thus, tetrakisphosphinocalix[4]arene **1** is fluxional in solution, and is expected to act as a flexible polydentate phosphine ligand to accommodate late-transition metals.

Molecular Orbital Calculations. Theoretical approaches[20] for calixarenes, particularly the conformational behavior of calix[4]arenes, have recently emerged.[21,22] However, there have been few studies using ab initio molecular-orbital calculations,[21] although a number of molecular-mechanics and semiempirical calculations have been performed so far.[14c,18,22] All of the experimental results in the present study clearly indi-

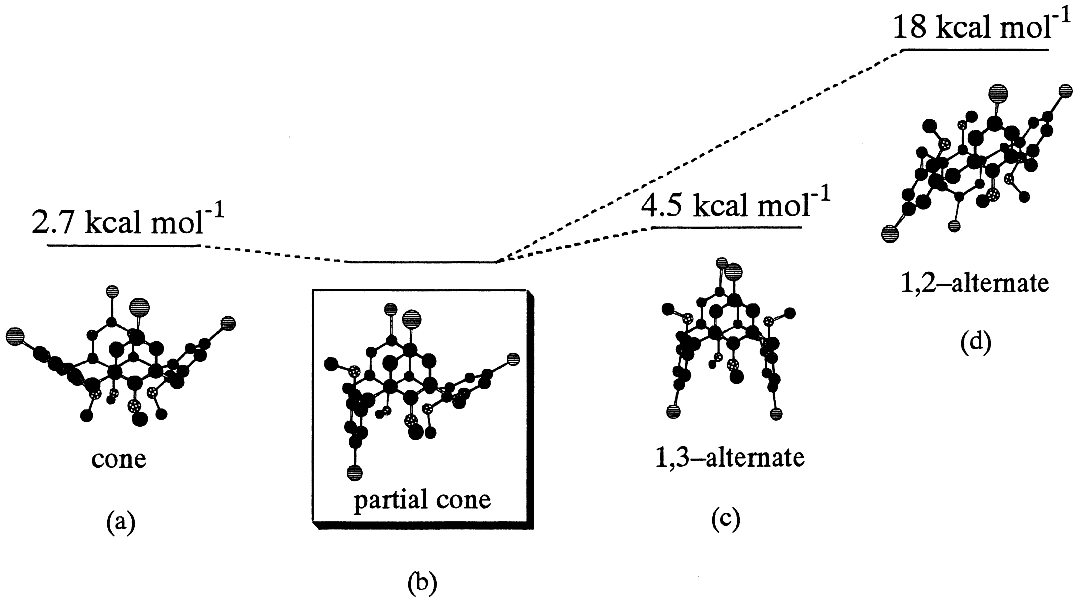


Fig. 6. Energy profiles for optimized conformers of **1** (HF/6-31G*//HF/STO-3G). Phenyl groups on phosphorus atoms and all hydrogen atoms are omitted for clarity.

cate that the partial cone conformation has the lowest energy among the conformations of **1** in both the solid state and solution (vide supra). In order to obtain further information concerning the energetics for the conformers of **1**, ab initio MO calculations were carried out for the four conformers of **1** without using any simplified model compound, namely with retaining all of the eight phenyl groups on the phosphorus atoms. The structures of the four conformers were optimized by the Hartree–Fock method employing the STO-3G basis set, and energy calculations were carried out by the same method with the 6-31G* basis set (Fig. 6). It is noteworthy that the HF/STO-3G optimized structure of the partial cone conformer (Fig. 6b) well-reproduces the two important characteristic of the X-ray structure in Fig. 1: (1) the flattened partial cone structure and (2) the lack of a mirror plane. As for the latter, the optimized structure shows a distortion and the dihedral angle of P1–C5···C19–P3 in Fig. 1 was calculated to be 8.2° (10° in Fig. 1). It is notable that this dihedral angle becomes 0° (no distortion) when the HF/STO-3G optimization is carried out with replacing all of the phenyl groups on the phosphorus with hydrogens (PPh$_2$ → PH$_2$). Thus, the lack of a mirror plane in **1** may be attributed to a distortion caused by an intramolecular steric hindrance between the PPh$_2$ moieties, not by a crystal-packing effect. The energy calculations shown in Fig. 6 indicate that the partial cone conformation is the most stable one, which is consistent with the experimental results. However, the cone (Fig. 6a) and the 1,3-alternate conformer (Fig. 6c) are only slightly less stable by 2.7 kcal mol^{-1} and 4.5 kcal mol^{-1}, while the 1,2-alternate (Fig. 6d) is considerably unstable by 18 kcal mol^{-1}. Actually, small resonances appear in Fig. 3a, Figs. 4a–c, and Fig. 5, even though the sample was very pure. Although a distinct assignment cannot be made, these small resonances may be attributed to the cone and the 1,3-alternate conformer, which would be in equilibrium with the partial cone conformer at 80 °C (Fig. 4).

Experimental

All reactions were performed under an argon atmosphere using standard Schlenk techniques. Solvents were dried and purified before use by the usual method.[23] 5, 11, 17, 23-Tetrabromo-25, 26, 27, 28-tetramethoxycalix[4]arene (**2a**) was prepared according to a literature procedure.[12] ^{1}H NMR (400.13 MHz), ^{13}C NMR (100.61 MHz), and ^{31}P NMR (161.98 MHz) spectra were recorded on a Bruker ARX 400 instrument. The ^{1}H NMR data are referenced relative to the residual protiated solvent (5.32 ppm) in CD$_2$Cl$_2$. ^{13}C NMR chemical shifts are reported relative to CD$_2$Cl$_2$ (53.1 ppm) and the ^{31}P NMR data are given relative to external 85% H$_3$PO$_4$. A ^{31}P NMR simulation was carried out using the program gNMR 4.1.[24] Medium-pressure column chromatography was performed on silica gel (Wakogel® C-400HG; particle size 20–40 μm) with a UV detector (YAMAZEN UV-10V). IR spectra were recorded on a Shimadzu FT-IR 8300. FD mass spectra were recorded on a JEOL JMS-SX102A instrument at the GC-MS & NMR Laboratory of Faculty of Agriculture, Hokkaido University. Elemental analysis was performed at the Center for Instrumental Analysis of Hokkaido University. Molecular-orbital calculations were performed with the Gaussian 98 program[25] on an HP Exemplar V2500 at the Computing Center of Hokkaido University.

5, 11, 17, 23-Tetrakis(diphenylphosphino)-25, 26, 27, 28-tetramethoxycalix[4]arene (1). To a solution of 2.00 g (2.51 mmol) of tetrabromocalix[4]arene tetramethyl ether (**2a**) in 45 mL of dry THF cooled to −78 °C was added 11.6 mL (17.4 mmol) of butyllithium (1.50 M solution in hexane) over 5–10 min. The resulting orange solution was maintained at that temperature for an additional hour. A solution of chlorodiphenylphosphine (2.53 g, 17.3 mmol) in 7.0 mL of dry THF was added dropwise over a period of 30 min at –78 °C. The reaction mixture was allowed to warm to room temperature and stirred for 15 h. After evaporation of the solvent, the mixture was taken up in CHCl$_3$ (50 mL) and washed twice with water. The organic layer was dried over MgSO$_4$ and evaporated to give a yellow residual sludge. The residue was purified by medium-pressure column chromatography on silica gel (300 mm × 50 mm) equipped with a UV detector using hexane/acetone (10:1) as an eluent (10 mL min^{-1}). The product **1** was found in the fraction (ca. 1350–2700 mL) as white microcrystals (1.54 g, 51% yield): mp 220–222 °C; IR (KBr) 3051, 2924, 2822, 2363, 2345, 1468, 1433, 1261, 1213, 1113, 1016, 743, 696 cm^{-1}; ^{1}H NMR (CD$_2$Cl$_2$, −20 °C) δ 7.48−6.85 (m, 48H, ArH), 4.06 (d, 2H, J = 13.2 Hz, ArCH_2Ar), 3.64 (d, 2H, J = 14.0 Hz, ArCH_2Ar), 3.60 (d, 2H, J = 14.0 Hz, ArCH_2Ar), 3.52 (s, 6H, OCH$_3$), 3.31 (s, 3H, OCH$_3$), 3.23 (s, 3H, OCH$_3$), 3.08 (d, 2H, J = 13.2 Hz, ArCH_2Ar); ^{13}C NMR (CD$_2$Cl$_2$, −20 °C) δ 158.4, 158.2, 157.9 (ArC attached to OCH$_3$), 138.5, 138.3, 137.9, 137.8, 137.7, 137.6, 137.2, 137.1, 136.1, 136.0, 135.9, 135.8, 135.0, 134.7, 134.3, 134.1, 133.7, 133.5, 133.4, 133.3, 133.2, 133.1, 132.9, 132.9, 132.7, 132.7, 132.7, 132.5, 132.2, 132.1, 132.0, 129.9, 129.8, 128.2, 128.1, 127.8, 127.7, 127.4, 127.3, 126.8, 126.8 (ArC), 60.0, 59.6, 57.9 (OCH$_3$), 35.5, 31.1 (ArCH$_2$Ar); ^{31}P NMR (Toluene-d_8, −20 °C) δ −6.58, −6.68, −7.74; FD-MS m/z 1216 ([M]$^+$), 608 ([M]$^{2+}$). Found: C, 78.89; H, 5.91%. Calcd for C$_{80}$H$_{68}$O$_4$P$_4$: C, 78.93; H, 5.63%.

X-ray Structure Determination of 1. A comparable amount of single crystals was obtained as a sole conformer under the condition mentioned above. Elemental analysis of the single crystals clearly indicated that the crystals had no any solvents. Crystallographic data are summarized in Table 1. The data were collected with Mo $K\alpha$ radiation (λ = 0.71069 Å) at ambient temperature on a Rigaku RAXIS RAPID imaging-plate area detector to a maximum 2θ value of 55.0°. The structure was solved by direct methods using the program SIR92[26] and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically and hydrogen atoms were included, but not refined. The final cycle of a full-matrix least-squares refinement was based on 8262 observed reflections ($I > 1.50\sigma(I)$) and 793 variable parameters. Neutral atom scattering factors were taken from Cromer and Waber.[27] Anomalous dispersion effects were included in Fcalc.[28] All calculations were performed using the teXsan crystallographic software package of Molecular Structure Corporation. Crystallographic data have been deposited at the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK and copies can be obtained on request, free of charge, by quoting the publication citation and the deposition numbers CCDC 165707. The data are also deposited as Document No. 74046 at the Office of the Editor of Bull. Chem. Soc. Jpn.

CPMAS Solid-State NMR Measurement. CPMAS solid-state NMR spectra were recorded on a Bruker AC 300 instrument using a standard CP pulse sequence. The crystalline powder sample was loaded in a Zirconia rotor and spun at ca. 4 kHz for ^{31}P NMR and ca. 6 kHz for ^{13}C NMR at the magic angle. The ^{31}P NMR chemical shifts are reported relative to 85% H$_3$PO$_4$ in capillary without spinning and the ^{13}C NMR data are referenced relative to a glycine sample.

31P EXSY NMR Measurement. ^{31}P EXSY NMR spectra were recorded on a JEOL α-500 instrument at High-Resolution NMR Laboratory of Faculty of Science in Hokkaido University. A conventional phase-sensitive NOESY pulse sequence was used. The recycle times for the EXSY pulse sequence were 3 s and the number of scans was 16.

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