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New Syntheses and Physical Properties of *p*-Alkylcalix[*n*]arenes

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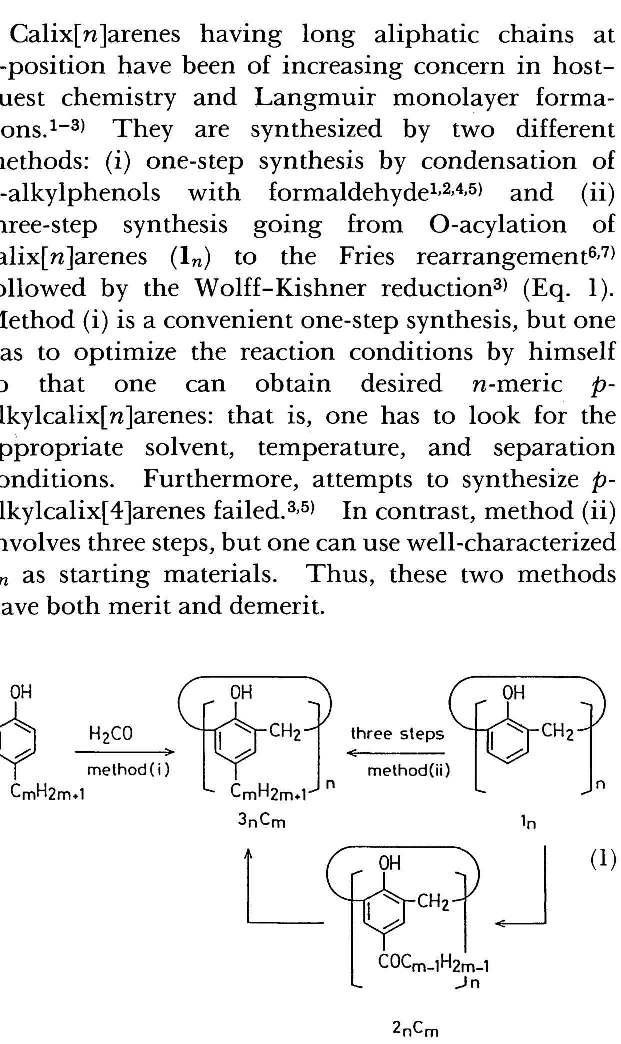
Calix[*n*]arenes (*n*=4, 6, and 8) bearing long *p*-alkyl groups (R=hexyl and dodecyl) have been synthesized by "direct" acylation of the *p*-position followed by silane reduction. The method is convenient and the yields are higher than those reported so far. Among them, *p*-hexanoylcalix[4]arene showed a curious phase transition behavior; with raising the temperature it changed as crystal A→liquid→crystal B→liquid. It was found on the basis of the solid ^{13}C NMR spectra that this behavior is ascribed to a conformational change from "cone" (crystal A) to "partial cone" (crystal B).

Calix[*n*]arenes having long aliphatic chains at *p*-position have been of increasing concern in host-guest chemistry and Langmuir monolayer formations.[1—3] They are synthesized by two different methods: (i) one-step synthesis by condensation of *p*-alkylphenols with formaldehyde[1,2,4,5] and (ii) three-step synthesis going from O-acylation of calix[*n*]arenes (**1**$_n$) to the Fries rearrangement[6,7] followed by the Wolff-Kishner reduction[3] (Eq. 1). Method (i) is a convenient one-step synthesis, but one has to optimize the reaction conditions by himself so that one can obtain desired *n*-meric *p*-alkylcalix[*n*]arenes: that is, one has to look for the appropriate solvent, temperature, and separation conditions. Furthermore, attempts to synthesize *p*-alkylcalix[4]arenes failed.[3,5] In contrast, method (ii) involves three steps, but one can use well-characterized **1**$_n$ as starting materials. Thus, these two methods have both merit and demerit.



(1)

It occurred to us that if the acyl group could be "directly" introduced into the *p*-position of **1**$_n$, one could shorten the reaction route for method (ii). In this paper we report "direct" acylation of **1**$_n$ (*n*=4, 6, and 8) to *p*-acylcalix[*n*]arenes (**2**$_n$C$_m$) followed by reduction with triethylsilane to *p*-alkylcalix[*n*]arenes (**3**$_n$C$_m$). In addition, we found that some of these calix[*n*]arenes show very interesting solid and solution properties.

Experimental

Materials. Preparations of **1**$_n$ were described previously.[8,9] We studied the Friedel-Crafts reaction of **1**$_n$ with $C_{m-1}H_{2m-1}COCl$ (*m*=6 and 12).

***p*-Hexanoylcalix[4]arene (2$_4$C$_6$).** Hexanoyl chloride (1.4 g; 10 mmol) and $AlCl_3$ (1.4 g; 10 mmol) was mixed in 30 ml of nitrobenzene, and after stirring for 30 min at room temperature under a nitrogen stream **1**$_4$ (1.1 g; 2.5 mmol) was added. The reaction mixture was stirred at 50 °C for 10 h and then at 70 °C for 3 h. This operation afforded a homogeneous, brown solution. After cooling, the solution was poured into a 0.1 M# HCl solution (200 ml) and extracted with chloroform (200 ml). The organic layer was separated, washed with 1 M NaCl solution and dried over $MgSO_4$. The solution was concentrated to dryness, the resultant solid being reprecipitated from chloroform to methanol. Finally, the yellow solid product was recrystallized twice from benzene: white powder, mp 94—98 °C, yield 80%; IR (Nujol) ν_{OH} 3600—2500 cm^{-1}, $\nu_{C=O}$ 1680 cm^{-1}; ^{1}H NMR ($CDCl_3$, 30 °C) δ_H=0.6—2.0 (9H, C_4H_9), 2.6—3.0 (2H, CH_2CO), 3.7—4.2 (2H, broad, $ArCH_2Ar$), 7.70 (2H, ArH), 9.5—10.5 (1H, broad, OH).

Other **2**$_n$C$_m$'s were synthesized in a manner similar to that for **2**$_4$C$_6$. The reaction conditions, yields, and mp's are summarized in Table 1. The elemental analysis data are recorded in Table 2.

***p*-Hexylcalix[4]arene (3$_4$C$_6$).** Compound **2**$_4$C$_6$ (0.50 g; 0.60 mmol) was dissolved in 20 ml of trifluoroacetic acid, and triethylsilane (0.70 g; 6.0 mmol) was added dropwise to this solution. The exothermic reaction was initiated immediately after the addition of triethylsilane. After stirring for 10 h at room temperature, the solution was concentrated in vacuo. The residue was dissolved in chloroform and the solution was washed with aqueous $NaHCO_3$. The organic layer was separated and dried over Na_2SO_4. The chloroform solution was concentrated to dryness, the residue being recrystallized from ethanol: white plates, mp 108—109 °C, yield 66%; IR (Nujol) ν_{OH} 3500—2500 cm^{-1}, no $\nu_{C=O}$; ^{1}H NMR ($CDCl_3$, 30 °C) δ_H=0.6—1.9 (11H, C_5H_{11}), 2.2—2.6 (2H, CH_2Ar), 3.2—3.4 (2H, broad, $ArCH_2Ar$), 6.80 (2H, ArH), 10.10 (1H, OH).

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1 M=1 mol dm^{-3}.

Other $\mathbf{3}_n\mathrm{C}_m$'s were synthesized in a manner similar to that for $\mathbf{3}_4\mathrm{C}_6$. Compounds $\mathbf{2}_n\mathrm{C}_{12}$ were less reactive than $\mathbf{2}_n\mathrm{C}_6$ and required the more drastic reaction conditions (e.g., reflux for 100 h). The reaction conditions, yields, and mp's are summarlzed in Table 3. The products were recrystallized either from ethanol or ethanol-$CHCl_3$ (or CCl_4). The elemental analysis data are recorded in Table 4.

25,26,27,28-Tetrapropoxy-*p*-hexanoylcalix[4]arene (with a Partial Cone Conformation: $\mathbf{4}_4\mathrm{C}_6$). Compound $\mathbf{2}_4\mathrm{C}_6$ (200 mg; 0.245 mmol) and propyl bromide (1.21 g; 9.81 mmol) were dissolved in 30 ml of DMF and the solution was stirred at 50 °C for 6 h in the presence of Cs_2CO_3 (3.47 g; 9.81 mmol). The HPLC analysis showed that the product contains 90% of partial-cone-$\mathbf{4}_4\mathrm{C}_6$ and 10% of another isomer (probably, cone-$\mathbf{4}_4\mathrm{C}_6$). The solution was filtered, the filtrate being diluted with water. The aqueous solution was extracted with chloroform. The chloroform solution was concentrated to dryness. The residue was viscous oil. This was subjected to preparative TLC separation (silica gel, chloroform–hexane): caramel-like solid (an attempt to crystallize this solid failed), yield 50%, single peak on HPLC; ^{1}H NMR ($CDCl_3$, 30 °C) δ=0.9—1.2 (56H, m, CH_3CH_2 in *n*-Pr and $CH_3(CH_2)_3$), 3.02, 3.61, 3.81 (4H, 2H, 2N (respectively), q each, OCH_2), 2.26, 2.54, 3.87 (2H, 4H, 2H (respectively), t each, $COCH_2$), 3.19, 3.73, 3.78, 4.07 (2H each, d each, $ArCH_2Ar$), 6.84, 7.60, 7.81, 7.94 (2H each, d, d, s, s (respectively), ArH). Found: C, 77.53; H, 9.01%. Calcd for $(C_{16}H_{22}O_2)_4$: C, 78.00; H, 9.00%.

A partial cone conformation results in three different phenol units. The situation is reflected by OCH_2 and $COCH_2$ which appear as three peaks in an integral intensity ratio of 2 : 1 : 1. The $ArCH_2Ar$ protons in a partial cone conformation feature two pairs of doublets:[10] one pair with the large chemical shift difference (3.19 and 4.07 ppm in $\mathbf{4}_4\mathrm{C}_6$) is ascribed to those flanked by two syn phenol units (H_{exo} and H_{endo}, respectively) and another pair with the small chemical shift difference (3.73 and 3.78 ppm in $\mathbf{4}_4\mathrm{C}_6$) is ascribed to those flanked by two anti phenol units. These results consistently support the partial cone conformation. The peaks for OCH_2 appear as quartets. This is probably due to the rotational restriction of the OCH_2 group.

^{13}C NMR Spectra. The solid-state ^{13}C NMR spectra were measured with a Bruker PC-250. The ^{13}C cross polarization-magic angle spinning NMR spectra were recorded at 30 °C with a CP-MAS method: the crystalline powder sample was contained in a bullet-type rotor and spun at 3.5 kHz. Contact time was 3 ms and repetition time was 5 s. The ^{13}C chemical shifts were calibrated indirectly through external TMS.

Results and Discussion

As mentioned in Introduction, *p*-alkylcalix[4]arenes cannot be synthesized from formaldehyde and *p*-alkylphenols.[3,5] Thus, they have been synthesized through three steps: that is, tetra-O-acylation, Fries rearrangement, and reduction. According to Gutsche and Lin,[10] acetylation and benzoylation of $\mathbf{1}_n$ occur in 23—38% yields. We could enhance the yields for acylation (using hexanoyl chloride and 2-methylbutanoyl chloride) up to 50—51%.[7] On the other hand, Fries rearrangement occurs in 29—64% yields.[6,7] This means that the total yields of these two steps are at most 30%. As shown in Table 1, on the other hand, "direct" acylation of the *p*-position results in $\mathbf{2}_n\mathrm{C}_m$ in 30—88% yields. Thus, the present method is much superior to the previous method.

It is known that O-acylation of $\mathbf{1}_n$ can be effected even at 0 °C whereas Fries rearrangement proceeds at 70—100 °C.[6,7,10] In the present "direct" acylation method, the products were yielded when the solution was heated at 70 °C. When the reaction temperature was not raised, the product gave the $\nu_{C=O}$ band at 1760 cm^{-1} which is assigned to the ester group. This suggests that the present "direct" acylation actually occurs via O-acylation followed by Fries rearrangement. These two steps proceed in one pot.

According to Nakamoto et al.,[3] $\mathbf{2}_4\mathrm{C}_8$ could be reduced to $\mathbf{3}_4\mathrm{C}_8$ by the Wolff–Kishner method in 70% yield. We found, however, that this method is troublesome because in the reducetion of $\mathbf{2}_4\mathrm{C}_m$ the solution foamed over in the flask. As an alternate

Table 2. Elemental Analysis Data for $\mathbf{2}_n\mathrm{C}_m$

$\mathbf{2}_n\mathrm{C}_m$		Found/%		Calcd/%		
n	*m*	C	H	for	C	H
4	6	76.69	7.85[a]	$(C_{13}H_{16}O_2)_4$	76.44	7.89
4	12	79.26	9.26	$(C_{19}H_{28}O_2)_4$	79.12	9.78
6	6	75.61	7.76	$(C_{13}H_{16}O_2)_6 \cdot 0.1\ CCl_4$	75.59	7.80
6	12	79.10	9.68	$(C_{19}H_{28}O_2)_6$	79.12	9.78
8	6	73.87	7.58	$(C_{13}H_{16}O_2)_8 \cdot 0.4\ CCl_4$	73.95	7.61
8	12	77.81	9.39	$(C_{19}H_{28}O_2)_8 \cdot 0.8\ CHCl_3$	78.07	9.65

a) Recrystallized from benzene.

Table 1. Reaction Conditions for the Synthesis of $\mathbf{2}_n\mathrm{C}_m$

$\mathbf{1}_n$		$C_{m-1}H_{2m-1}COCl$		$AlCl_3$	Yield of $\mathbf{2}_n\mathrm{C}_m$	Mp of $\mathbf{2}_n\mathrm{C}_m$
n	Concn/mmol	*m*	Concn/mmol	mmol	%	°C
4	2.5	6	10	10	80	94—98
6	2.5	6	15	15	52	>310
8	2.5	6	20	20	88	310
4	2.5	12	10	10	60	130—133
6	2.5	12	15	15	62	>310
8	2.5	12	20	20	30	>310

Table 3. Reaction Conditions for the Synthesis of $\mathbf{3}_n\mathrm{C}_m$

$\mathbf{2}_n\mathrm{C}_m$			$\mathrm{Et_3SiH}$	$\mathrm{CF_3COOH}$	Yield of $\mathbf{3}_n\mathrm{C}_m$	Mp of $\mathbf{3}_n\mathrm{C}_m$
n	*m*	Concn/mmol	mmol	ml	%	°C
4	6	0.60	6.0	20	66	108—109
4	12	0.50	10	20	55	98—100
6	6	0.25	10	20[a)]	54	249—250
6	12	0.60	20	30[b)]	52	168—169
8	6	0.70	20	30	50	>300
8	12	0.28	10	20[a)]	81	>300

a) $\mathrm{CCl_4}$ (20 ml) was added. b) $\mathrm{CCl_4}$ (30 ml) was added.

Table 4. Elemental Analysis Data for $\mathbf{3}_n\mathrm{C}_m$

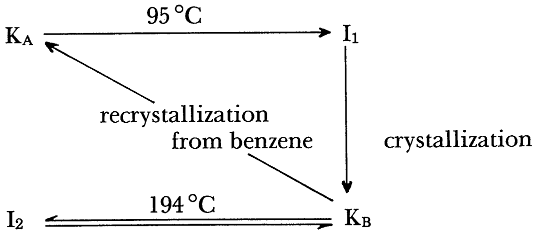
$\mathbf{3}_n\mathrm{C}_m$		Found/%		Calcd/%		
n	*m*	C	H	for	C	H
4	6	81.74	9.57	$\mathrm{(C_{13}H_{18}O)_4 \cdot 0.1\ EtOH}$	81.88	9.56
4	12	82.73	11.14	$\mathrm{(C_{19}H_{30}O)_4}$	83.15	11.02
6	6	80.23	9.31	$\mathrm{(C_{13}H_{18}O)_6 \cdot 0.2\ CCl_4}$	80.10	9.28
6	12	83.05	10.92	$\mathrm{(C_{19}H_{30}O)_6}$	83.15	11.02
8	6	81.06	9.30	$\mathrm{(C_{13}H_{18}O)_8 \cdot 0.6\ CHCl_3}$	80.98	9.39
8	12	81.58	10.57	$\mathrm{(C_{19}H_{30}O)_8 \cdot 0.3\ CCl_4}$	81.60	10.79

method, we employed the silane reduction method. Although the yields (55—81%) are not significantly higher than those for the Wolff-Kisher method, the operation is very simple and convenient.

$\mathbf{2}_n\mathrm{C}_m$ and $\mathbf{3}_n\mathrm{C}_m$ thus synthesized showed several interesting physical properties. First, $\mathbf{2}_8\mathrm{C}_{12}$ gellated when recrystallized from benzene, toluene, hexane, heptane, etc.: that is, the solution was apparently solidified. Thus, this compound was recrystallized from ethanol-chloroform (3 : 1 v/v). Such gelation was not found for other $\mathbf{2}_n\mathrm{C}_m$.

More interesting is a phase transition phenomenon of $\mathbf{2}_4\mathrm{C}_6$. As shown in Scheme 1, crystal A ($\mathrm{K_A}$) obtained by recrystallization from benzene melts at 95 °C. From the isotropic liquid phase ($\mathrm{I_1}$) new crystals ($\mathrm{K_B}$) grow up rapidly, which finally melt at 194 °C. When the final isotropic liquid ($\mathrm{I_2}$) is cooled, crystal B results. Only when crystal B is recrystallized from benzene, crystal A is reproduced.

Figure 1 shows a DSC thermogram of $\mathbf{2}_4\mathrm{C}_6$. It is



Scheme 1.

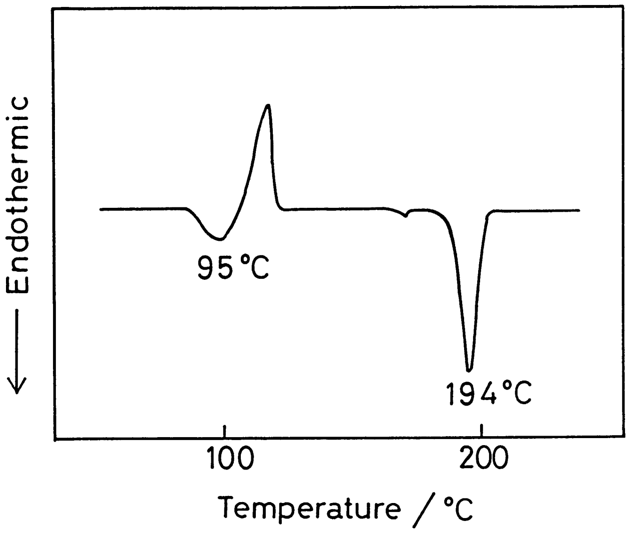
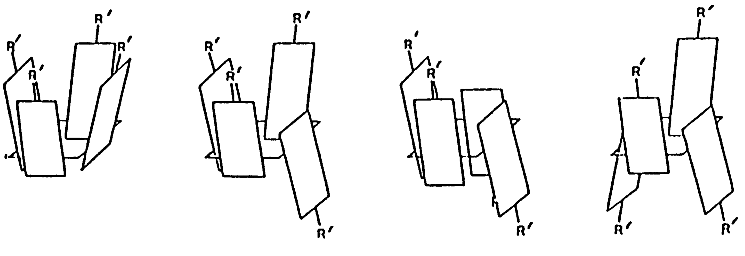


Fig. 1. DSC thermogram of $\mathbf{2}_4\mathrm{C}_6$.



Cone Partial cone 1,2-Alternate 1,3-Alternate

Fig. 2. Four conformational isomers possible for calix[4]-arenes.

seen from Fig. 1 that an endothermic change occurs at 95 °C, which is immediately followed by an exothermic change. These changes correspond to melting of K_A at 95 °C followed by recrystallization to K_B. An endothermic peak at 194 °C corresponds to melting of K_B to I_2. We attempted the preparation of single crystals for X-ray analysis from K_A and K_B but failed. We thus evaluated the structures of these crystals using the solid-state ^{13}C NMR spectroscopy.

Basically, calix[4]arenes can exist in four different conformations; they are cone, partial cone, 1,2-alternate, and 1,3-alternate (Fig. 2). X-ray studies of *p*-*t*-butylcalix[4]arene and some clathrates show the calixarene moiety to be present in a cone conformation with C_{4v} symmetry.[11–13] Since each phenol unit is equivalent around a 4-fold axis, the CP-MAS ^{13}C NMR should result in a single set of ^{13}C peaks for the phenol unit. Other three conformations have never been found for unmodified calix[4]arenes not only in solution but also in the solid state.[14] One can predict on the basis of their symmetry that partial cone, 1,2-alternate, and 1,3-alternate should give three sets, a single set (but two sets for the $ArCH_2Ar$ methylene carbons), and a single set (including the $ArCH_2Ar$ methylene carbons) of ^{13}C peaks for four phenol units, respectively. To test this hypothesis, we prepared tetra-O-propyl derivative (**4**$_4$C$_6$) with a partial cone conformation from **2**$_4$C$_6$ (Eq. 2).[14] It has been established that being different from unmodified calix[4]arenes, the propyl group is bulky enough to suppress the oxygen-through-the-annulus rotation and thus tetra-O-propylated calix[4]arene results in conformationally-immobile isomers.[15] As shown in Fig. 3, the ^{13}C NMR spectrum for partial-cone-**4**$_4$C$_6$ is very complex. It is clearly seen from Fig. 3, however, that there appear three peaks for CO (C-6 in Fig. 3) and O-C (in phenyl: C-10 in Fig. 3). This establishes that as predicted from its symmetry, ^{13}C NMR for the partial

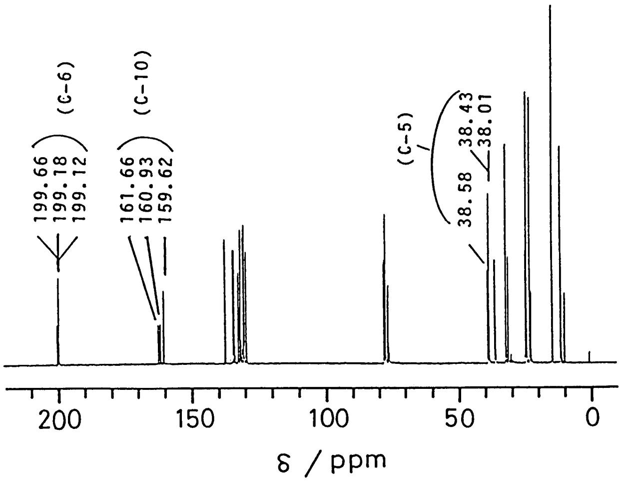
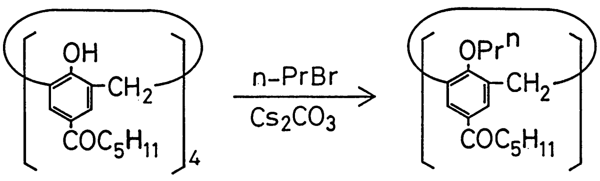


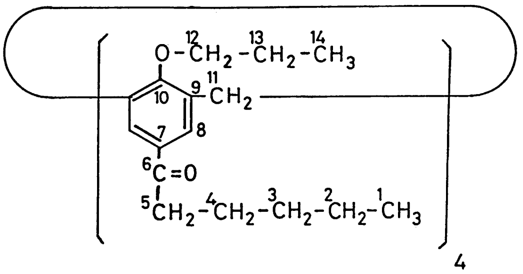
Fig. 3. ^{13}C NMR spectrum of partial-cone-**4**$_4$C$_6$ (CDCl$_3$, 30 °C).



(2)

2$_4$C$_6$

4$_4$C$_6$
cone 10%
partial cone 90%



4$_4$C$_6$

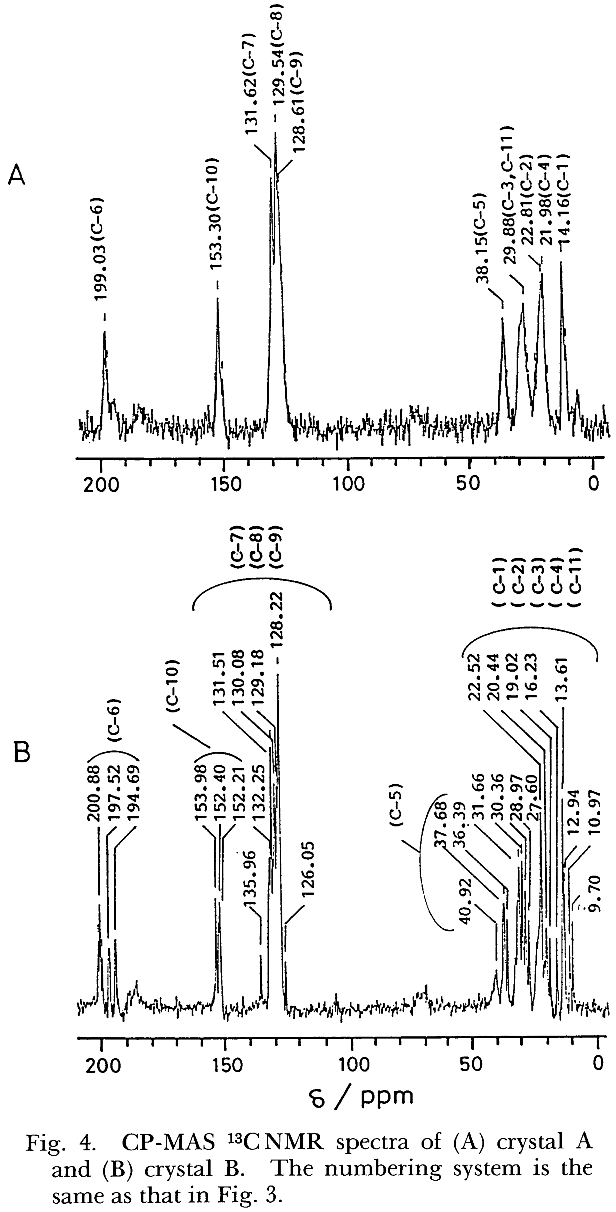


Fig. 4. CP-MAS ^{13}C NMR spectra of (A) crystal A and (B) crystal B. The numbering system is the same as that in Fig. 3.

cone isomer features three sets of ^{13}C peaks.

In Fig. 4, CP-MAS ^{13}C NMR spectra for crystals A and B are illustrated. As expected, crystal A, crystallized from benzene solution, gave a single set of ^{13}C peaks for C-6 and C-10. This provides evidence that crystal A adopts a cone conformation. In contrast, crystal B, which crystallized above 95 °C, gave three sets of ^{13}C peaks for C-6 and C-10. This split pattern is basically commensurate with a partial cone conformation. In the solid state, however, one has to take the presence of noncongruent molecules into consideration: for example, the asymmetry in the solid-state ^{13}C NMR spectra may result from noncongruence in the crystal lattice or from slight distortion of the calix[4]arene ring.16) Thus, we further confirmed the difference between crystals A and B through IR measurements which possibly reflect the intramolecular structural difference rather than the intermolecular one. Unmodified calix[4]arenes (that is, those having four OH groups) adopt a cone conformation not only in solution but also in the solid state.10–13,17–19) The exception against this conclusion has never been found. This is due to a large stabilization effect brought forth by intramolecular hydrogen-bonding interactions among OH groups. Hence, compounds $\mathbf{2_4C}_n$ should adopt a cone conformation in the solid state. The FT-IR spectra (KBr, at room temperature) of these compounds showed only one $\nu_{C=O}$ band at around 1680 cm^{-1}: for instance, the $\nu_{C=O}$ for crystal A appeared at 1675 cm^{-1}. In contrast, crystal B showed three $\nu_{C=O}$ bands at 1670, 1679, and 1684 cm^{-1}. This indicates that compound $\mathbf{2_4C_6}$ in crystal B has three different C=O groups which are commensurate with a partial cone conformation. Partial-cone-$\mathbf{4_4C_6}$, synthesized as a reference compound for crystal B also showed three $\nu_{C=O}$ bands at 1671, 1679, and 1689 cm^{-1}. The results, together with those of the ^{13}C NMR spectra, consistently support the view that $\mathbf{2_4C_6}$ in crystal B is a partial-cone conformer.

As described above, calix[4]arenes favorably adopt a cone conformation because of strong intramolecular hydrogen-bonding interactions.10,17–19) This view is supported not only by X-ray studies11–13) but also by recent computational studies.20) To isomerize to other conformers, one or two hydrogen bonds must be cleaved, which causes destabilization of the calix[4]arene ring.20) Above 95 °C the stabilization effect through hydrogen bonds becomes less important because of a vigorous molecular motion and a cone isomer can isomerize to a partial cone isomer. In the partial cone isomer, one phenol unit is inversed and the hydrogen-bonding interaction with this OH group is disrupted. Instead, the partial cone isomer acquires a flexible seesaw motion around the inversed phenol unit. Probably, this motional freedom is more important than the stabilization by hydrogen bonds above 95 °C. According to the molecular mechanics calculations about *p*-*t*-butylcalix[4]arene, total *E* values for the cone isomer and the partial cone isomer are −2.0 and 5.7 kcal mol^{-1}, respectively.20) This supports the view that the concentration of the partial cone isomer increases with raising the temperature. Anyhow, this is the first example for a partial cone isomer of unmodified calix[4]arenes found in the solid state.

In conclusion, the present paper demonstrated new syntheses of *p*-alkylcalix[4]arenes and their interesting physical properties. In particular, the finding of partial-cone-$\mathbf{2_4C_6}$ in the solid state is noteworthy. Further applications of these calixarenes to T_1 measurements, monolayer formations, etc. are currently investigated in these laboratories.

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