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Synthesis and Properties of *N*-Substituted Azacalix[*n*]arenes*

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Abstract. Side arm modifications of hexahomotriazacalix[3]arene (**1**) were achieved by simple synthetic methods. Compound **5** has picolyl side arms and liquid–liquid extraction experiments showed that the alkali cation affinity of **5** is much stronger than that of **1**. A chiral group was also introduced into the azacalixarene structure. Calix[4]arene was converted into dihomoazacalix[4]arene (**2**) in 8% yield. Clathrate formation of **2** with various solvents is described. MM3 calculations were carried out on *p*-substituted analogs of **2**. The 'self-filled' structure, in which the benzyl side arm is placed in its cavity, is the most stable structure when the *p*-positions of the aromatic rings carry small substituents. Strong hydrogen bonds between nitrogen and phenolic hydroxyl groups in dihomoazacalix[4]arene (**2**) were observed at low temperatures. The ^{1}H-NMR signals of phenolic hydroxyl groups appeared as six singlets in the range of 9.8 ~ 17.1 ppm at -70°C.

Key words: Azacalixarene, azacyclophane, chiral molecule, MM3 calculation, strong hydrogen bond.

1. Introduction

Azacalixarenes are a recently developed branch of the calixarene family [1, 2]. They have phenolic oxygen and nitrogen as donor atoms. Some of the compounds in this series are fixed in rigid cone conformations by strong hydrogen bonds between OH and N atoms. One-pot reactions between bis(hydroxymethyl)phenol derivatives and benzylamine produced the desired azacalixarenes in satisfactory yields, and the macrocyclic compounds were isolated in a simple manner. By this procedure, the functionalized side arms can be easily introduced into the macrocyclic structures using the appropriate amines as starting materials. In this

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report, we describe the one-step synthesis of hexahomotriazacalix[3]arenes with chiral benzyl arms and picolyl side arms. Previously, we described the synthesis of **2** by a one-pot procedure [2]. Here, a newly developed conversion reaction from calix[4]arene into dihomoazacalix[4]arene (**2**) is reported. Basic studies on compound **2** concerning structural analyses by MM3 calculations, the hydrogen bonds between N and OH groups, and the clathrate formation are described.

2. Experimental

2.1. Apparatus

Melting points were measured with a Yanaco MP-500D apparatus and are uncorrected. NMR spectra were recorded on a JEOL GSX-270 (270 MHz for ^{1}H) spectrometer. UV spectra were recorded on a Shimadzu UV-2200 spectrometer.

2.2. Synthesis of chiral azacalixarene (4)

A mixture of 2,6-bis(hydroxymethyl)-4-methylphenol (4.02 g, 23.9 mmol) and (*S*)-(−)-α-methylbenzylamine (Tokyo Kasei, 2.98 g, 24.6 mmol) in 100 mL of toluene was refluxed for 24 h, and the water generated was removed during the course of the reaction. The toluene was evaporated, and the residual oily material was heated at 120°C for an additional 20 h. After the reaction mixture cooled, the oil was dispersed in 100 mL of methanol by vigorous stirring. The yellow powder thus obtained was collected by filtration, washed with methanol, and then chromatographed on silica gel with CH_2Cl_2/MeOH (98/2) as an eluent. Recrystallization of the resulting yellow powder from a mixture of C_6H_6–CH_3OH–CH_2Cl_2 afforded **4** as pale yellow powder (3.23 g, 53%), m.p. 138–140.9°C; ^{1}H-NMR (270 MHz, $CDCl_3$) δ 11.0 (bs, 3H, OH), 7.32 (s, 15H, aromatic), 6.87–6.68 (m, 6H, aromatic), 3.80 (s, 3H, —(Me)—CH—Ph), 3.75 (s, 12H, CH_2N), 2.16 (s, 9H, CH_3—Ar), 1.48 (s, 9H, —CH_3); FAB-Mass m/z 760 $(M+H)^+$; $[\alpha]_D^{24} = 67.9 \pm 0.5°$ (optical purity unknown). *Anal. Calcd.* for $C_{51}H_{57}N_3O_3 \cdot C_6H_6 \cdot 1/2\ CH_2Cl_2$: C, 78.43; H, 7.33; N, 4.77. *Found*: C, 78.46; H, 7.24; N, 4.62. The contents of the solvents in the analytical sample were confirmed by the ^{1}H-NMR spectrum.

2.3. Synthesis of 5

The preparation of **5** was achieved in a way similar to that of compound **1** [1]. The reaction products obtained from 3.37 g (20.0 mmol) of 2,6-bis(hydroxymethyl)-4-methylphenol and 2.31 g (21.4 mmol) of 2-picolylamine were chromatographed on silica gel with CH_2Cl_2/CH_3OH (98/2) as an eluent. Recrystallization of the resultant powder from cyclohexane gave 1.59 g (29%) of **5**, m.p. 129–135° (decomp.); ^{1}H-NMR (270 MHz, $CDCl_3$) δ 11.8 (bs, 3H, OH), 8.51 (bs, 3H, picolyl-H_6), 7.52 (bs, 3H, picolyl-H_4), 7.28 (s, 3H, picolyl-H_3), 7.09 (bs, 3H, picolyl-H_5), 6.84–6.73 (m, 6H, aromatic), 3.68 (s, 12H, —CH_2—), 3.75 (s, 6H, —CH_2—picolyl), 2.15 (s, 9H,

CH_3—Ar); FAB-Mass m/z 721 $(M+H)^+$. *Anal. Calcd.* for $C_{45}H_{48}N_6O_3 \cdot H_2O$: C, 73.15; H, 6.82; N, 11.37. *Found*: C, 73.35; H, 6.47; N, 10.95.

2.4. CONVERSION OF CALIX[4]ARENE INTO DIHOMOAZACALIX[4]-ARENE (**2**)

A mixture of *p-tert*-butylcalix[4]arene (171 mg, 0.27 mmol), benzylamine (0.55 g, 5.1 mmol), paraformaldehyde (0.30 g, 10 mmol), and aq. KOH (5 N, 0.01 mL) in 30 mL of xylene was heated under reflux for 150 h. The solution was washed with water and evaporated under reduced pressure. Column chromatography on silica gel (C_6H_6, followed by CH_2Cl_2) of the resultant mixture gave 16 mg (8%) of dihomoazacalix[4]arene (**2**) and 74 mg of recovered *p-tert*-butylcalix[4]arene. The product was confirmed by the ^{1}H-NMR spectrum and FAB mass spectrum, which were the same as those previously reported [2].

2.5. LIQUID–LIQUID EXTRACTION

Solvent extraction experiments were carried out as follows. A water-saturated chloroform solution of the ligand (1.00×10^{-4}, 5 mL) and an aqueous alkali metal chloride solution (0.10–0.11 M of Li^+–Cs^+ containing 2.1×10^{-4} M of potassium picrate, 5 mL) were introduced into Teflon-sealed tubes, which were shaken for 5 min for three times 25 ± 0.1°C. Prolonged times of shaking gave identical results. The resulting mixtures were allowed to stand for 30 min at 25 ± 0.1°C and then centrifuged. The aqueous phases were carefully withdrawn and the concentrations of the picrates were determined spectrophotometrically at 353 nm ($\varepsilon = 1.54 \times 10^4$). The extraction ratio, E, was calculated using the following equation:

$$E = ([\mathrm{Pic}^-]_i - [\mathrm{Pic}^-])/[\mathrm{Pic}^-]_i.$$

Here $[\mathrm{Pic}^-]_i$ is the initial concentration of aqueous picrate and $[\mathrm{Pic}^-]$ is the observed concentration after the extraction.

2.6. FORMATION OF CLATHRATE COMPOUNDS

Compound **2** was recrystallized from the solvents listed in Table I. The methanol or ethanol solutions were prepared using CH_2Cl_2 as a cosolvent. Alternatively, compound **2** was dissolved in a mixture of DMF and DMSO (1/2, v/v) by heating, and allowed to stand at room temperature. The crystals thus formed were collected and dried in a vacuum for 12 h at room temperature. The host : solvent ratios were confirmed by NMR spectra.

TABLE I. Clathrate formation of **2** with various solvents.

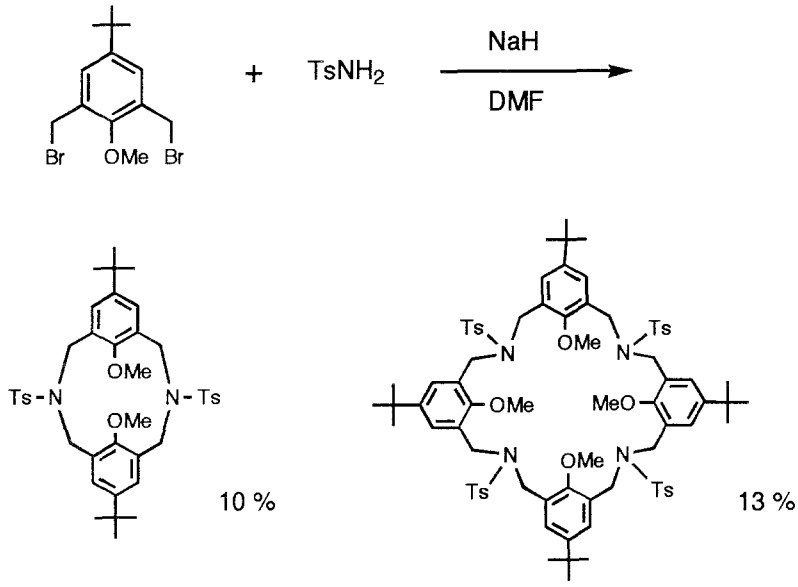
Solvents	Crystal form	Molar ratios (host : solvents)
Ethyl acetate	Colorless granules	– (no clathrate formation)
Dioxane	Colorless granules	1 : 1
Methanol	Colorless needles	–
Ethanol	Colorless needles	–
Acetone	Colorless resin	–
Acetonitrile	Colorless needles	3 : 2
Cyclohexane	Colorless granules	1 : 1
Hexane	Colorless granules	–
Chloroform	Colorless needles	–
Benzene	Colorless needles	2 : 3
Toluene	Colorless granules	1 : 1
p-Xylene	Colorless needles	1 : 1
m-Xylene	Colorless needles	1 : 1
o-Xylene	Colorless granules	2 : 3
Tetrahydrofuran	Colorless granules	1 : 1
Nitromethane	Yellow granules	1 : 1
DMF/DMSO	Yellow plates	1 : 1 (DMF only)

3. Results and Discussion

3.1. SYNTHESIS OF AZACALIX[n]ARENES

In our research on the azacyclophane series, cyclization methods using toluenesulfonamide and trifluoroacetamide were developed [3, 4]. However, to apply these methods to the synthesis of the azacalixarenes, the phenolic group had to be protected.

Starting from 4-*tert*-butyl-2,6-bis(bromomethyl)anisole, 2,11-diaza[3.3]- and 2,11,20,29-tetraaza[3.3.3.3]metacyclophanes were obtained in 10 and 13% yields, respectively [5]. However, the desired triaza[3.3.3]cyclophane was not obtained (Scheme 1). Subsequent deprotections of two functional groups, the methoxy and Ts groups, were not only troublesome but also led to poor results. Thus, the newly developed direct coupling method using 2,6-bis(hydroxymethyl)-4-alkylphenols and amines has many advantages for the construction of azacalixarenes. Compounds **1–3** were synthesized by direct coupling between bis(hydroxymethyl)-phenols and benzylamine (Figure 1) [1, 2]. The cyclization reaction proceeds in nonpolar solvents like toluene or xylene. In a polar solvent, however, only a mixture of oligomeric acyclic compounds was obtained, and generation of cyclic compounds was not observed [1]. The template effects of the OH—OH and OH—N hydrogen bonds play important roles in the formation of cyclic compounds.



Scheme 1. Synthetic scheme for azacyclophanes: cyclization with toluenesulfonamide.

3.2. SIDE ARM FUNCTIONALIZATION

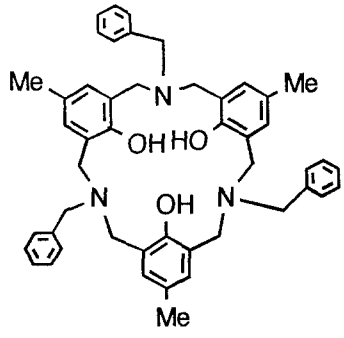
3.2.1. *Introduction of Picolyl Side Arms into Hexahomotriazacalix[3]arene*

Various kinds of functionalization methods of the phenol OH groups of calix[*n*]-arenes have been reported to yield ionophores [6]. Also, armed crown ethers with functional groups on nitrogen have been synthesized and effective recognitions of ions have been reported [7].

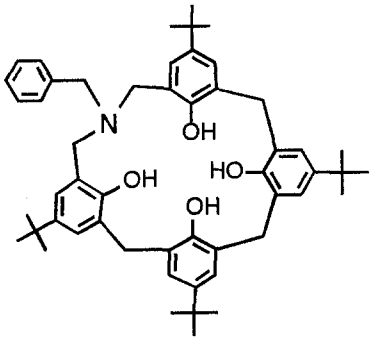
In the case of hexahomotriazacalix[3]arene (**1**), *O*-alkylation by picolyl chloride was easily achieved with sodium hydride as a base in DMF (78%). However, even without *O*-alkylation, functional groups can be introduced into the azacalixarene structures by the one-step procedure described here. Attachment of various side arms to bifunctional azacalixarene systems should allow the construction of new macrocyclic host molecules with multi-binding sites.

3.2.2. *Alkali Metal Ion Complex Formation*

As previously reported, the hexahomotriazacalix[3]arene (**1**) has cation binding ability toward alkali and alkaline-earth metal ions [1]. Moreover, compound **1** showed pH-dependent and effective extraction of uranyl ion in the presence of a high concentration of NaCl. However, dihomoazacalix[4]arene (**2**) and tetraho-modiazacalix[4]arene (**3**) have poor cation affinity: the extraction of alkali and alkaline-earth metal ions from a neutral aqueous solution into the organic phase was not observed. In order to increase the cation affinity, we introduced picolyl side arms on the bridging nitrogen atoms of the hexahomotriazacalix[3]arene structure.



1



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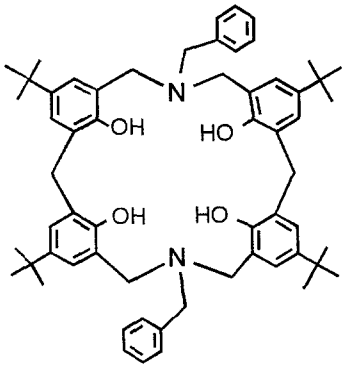

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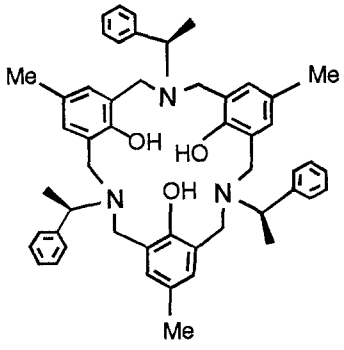

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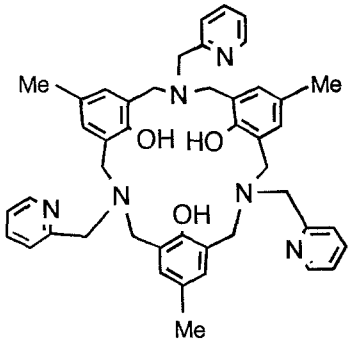
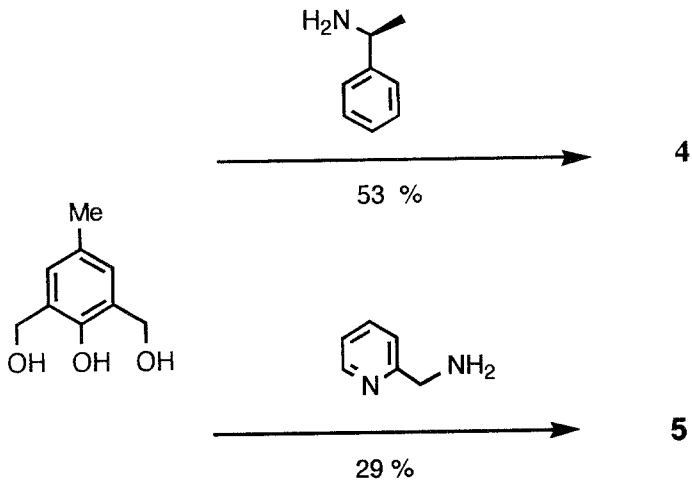


5

Fig. 1. Structures of azacalixarenes.



Scheme 2. Syntheses of compounds **4** and **5**.

Synthesis of the ligand, **5**, was easily achieved by the direct coupling reaction between picolylamine and 2,6-bis(hydroxymethyl)-4-methylphenol. The structure and the synthetic scheme of **5** are shown in Figure 1 and Scheme 2, respectively. Liquid–liquid alkali metal picrates extraction experiments were carried out using **5** as a ligand. Figure 2 shows the plots of extraction ratios, E (%), vs. ionic radii of alkali metal ions. Compared to compound **1**, the extraction ratios became 50–60 times greater. However, the ion selectivity decreased remarkably, showing the flexibility of the picolyl side arms. Similar to **1**, compound **5** showed affinity to K^+ ion, but Cs^+ was extracted in greater amounts than Rb^+. This result may be due to the change in the ligand to metal ratio of the complex.

3.2.3. *A Chiral Molecule*

Although syntheses of calixarenes which have no plane of symmetry have been reported, optical resolutions were unsuccessful because of the rapid inversion of aromatic rings at room temperature [8]. The first chiral resolution was shown to have an asymmetrically substituted calixarene fixed in a cone conformation by *O*-alkylation [9].

On the other hand, chiral side arms can easily be introduced into the hexahomotriazacalix[3]arene structure starting from a chiral benzylamine derivative: *S*-(−)-α-methylbenzylamine ($[\alpha]_D^{20} = -39°$). Optical rotation of the isolated chiral azacalixarene, **4**, was $[\alpha]_D^{24} = -67.9 \pm 0.5°$ ($c = 0.25, CHCl_3$). The synthetic scheme and structure are shown in Scheme 2 and Figure 1, respectively. Starting from various kinds of chiral primary amines, this synthetic method can be applied to other chiral azacalix[n]arene systems.

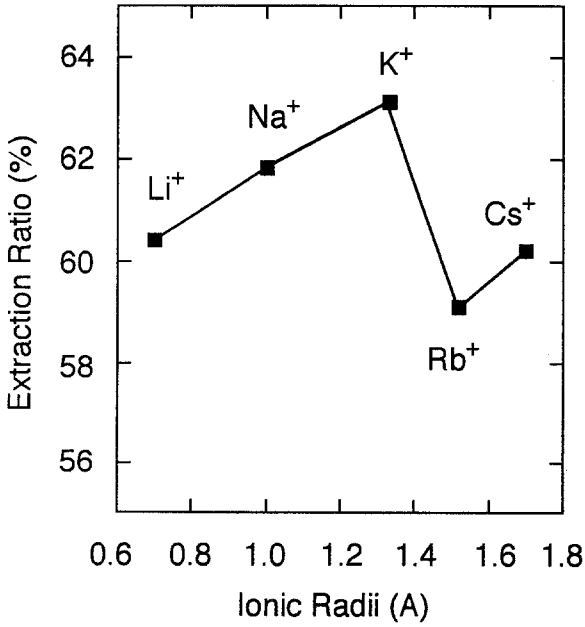


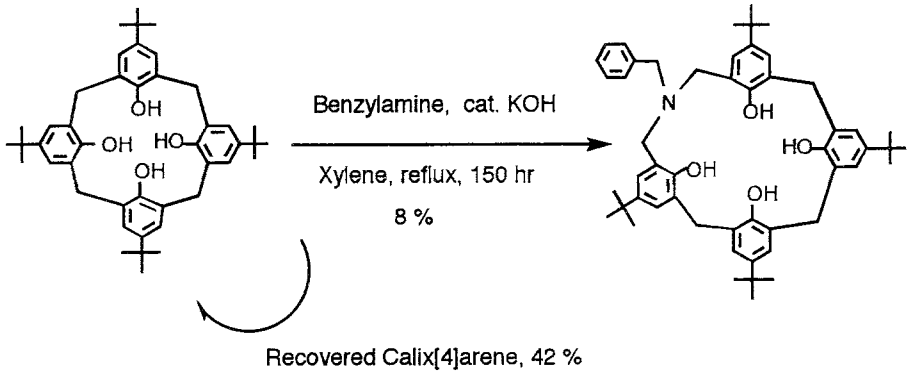
Fig. 2. Plots of extraction ratios (%) of alkali metal picrates from aqueous to organic phase.

3.3. CONVERSION OF CALIX[4]ARENE INTO DIHOMOAZACALIX[4]-ARENE

Considering the reaction pathway of calix[n]arene formations [11a] and the transformations of calix[8]arene or calix[6]arene into calix[4]arene [11b, c], we expected the generation of dihomoazacalix[4]arene (**2**) by nitrogen atom insertion into calix[4]arene. Indeed, when a mixture of *p-tert*-butylcalix[4]arene, paraformaldehyde, and benzylamine was heated in refluxing xylene in the presence of catalytic amounts of base (KOH) for 150 h, dihomoazacalix[4]arene (**2**) was obtained in 8% yield (Scheme 3), and 42% of the starting *p-tert*-butylcalix[4]arene was recovered. Even in the presence of a larger excess of benzylamine, the isolated azacalixarene was only compound **2**, while other possible $(aza)_n$calixarenes were not isolated. Calix[4]arene is stable enough in refluxing xylene, even in the presence of a base, and the ring opening–closing reaction hardly occurs. This might be one of the reasons for the low rate of nitrogen insertion into calix[4]arene. Under similar conditions, the reaction starting from *p-tert*-butylcalix[8]arene gave a complex mixture, and azacalixarenes were not isolated.

3.4. CLATHRATE FORMATION

All azacalixarenes are readily soluble in organic solvents except methanol and ethanol. Dihomoazacalix[4]arene (**2**) formed clathrate compounds with various solvent molecules (Table I). Among these clathrate compounds, **2**·CH_3NO_2 and **2**·DMF were yellow crystals, while the others were colorless. Interestingly, from



Scheme 3. Conversion of *p-tert*-butylcalix[4]arene into dihomoazacalix[4]arene (**2**).

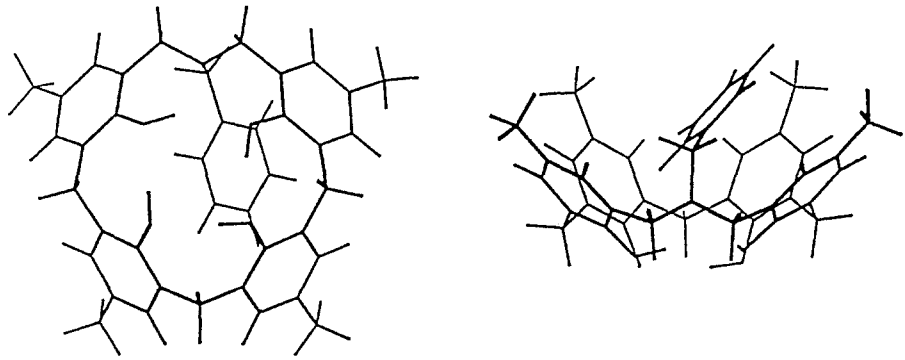
a solution of **2** in a DMF/DMSO mixture, the **2**·DMF complex was selectively obtained as yellow plates. Hydrogen bonding between the host and alcohols seems to be possible, but ethanol and methanol did not form clathrates with **2**, probably because of the insolubility of the host in alcohols. At this stage, the driving forces of clathrate formation are unclear, but they seem to be unrelated to several factors (size-fit, hydrogen bonding, n–π, π–π interactions).

3.5. HYDROGEN BONDS IN THE CAVITY

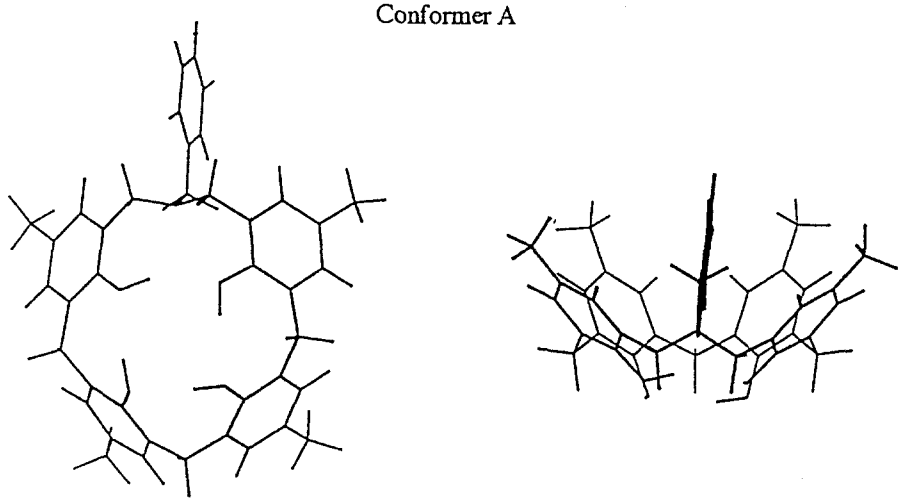
3.5.1. *MM3 Calculations*

Previously, we showed that the conformations of **2** and **3** are fixed in the 'cone' conformation in solution: in spite of the elongation of one methylene bridge of calix[4]arene into an azamethylene bridge, the cone conformer of **2** is more stable than that of calix[4]arene [2]. Unfortunately, the X-ray crystallographic analysis of the **2**·DMF complex was unfruitful. Only the cone conformation and inclusion of a DMF molecule in the crystal lattice were confirmed. Further attempts at X-ray crystallographic analysis are being made. To support the results of the experiments and predict the optimal structure of derivatives of **2**, MM3 calculations were carried out [12]. The calculations started from their conformational isomers, i.e., cone, partial cone, 1,2-, and 1,3-alternate.

The stability of these conformations, expressed in terms of their steric energy is as follows: cone < 1,2-alternate ≅ 1,3-alternate ≅ 2-partial cone < 2,3-alternate < 1-partial cone. Among all optimal structures, the 'cone' conformation was the most stable. The phenolic OH groups formed a cyclic array of hydrogen bonds. When bulky isopropyl groups are introduced at the *p*-position of aromatic rings adjacent to the —CH_2—N—CH_2-bridge, the 'cone' conformation is the most stable, and the benzyl group is located outside the molecule (Figure 3) [12]. The NMR spectrum of **2** showed that the position of the benzyl group is on the outer side of the molecule; thus, the results of the calculations coincide with the NMR spec-



Conformer A



Conformer B

Fig. 3. Optimal structures of *p*-tetramethyldihomoazacalix[4]arene by MM3 calculations. Left: bottom view from OH side. Right: side view from benzyl side arm.

tra. Interestingly, the side arm benzyl groups of *p*-tetrabromo, *p*-tetramethyl and unsubstituted compounds are located inside the cavity in their optimal structures. Inside benzyl conformers of *p*-tetrabromo, *p*-tetramethyl and unsubstituted compounds are more stable than their outside conformers by 8.3, 8.9 and 6.2 kcal mol^{-1} ($\Delta\Delta G^0$), respectively (Figure 3, conformer A and B). If these conformers actually exist, functionalized benzyl groups can interact with a guest molecule in the cavity. To confirm the existence of such a 'self-filled' conformer, the syntheses and con-

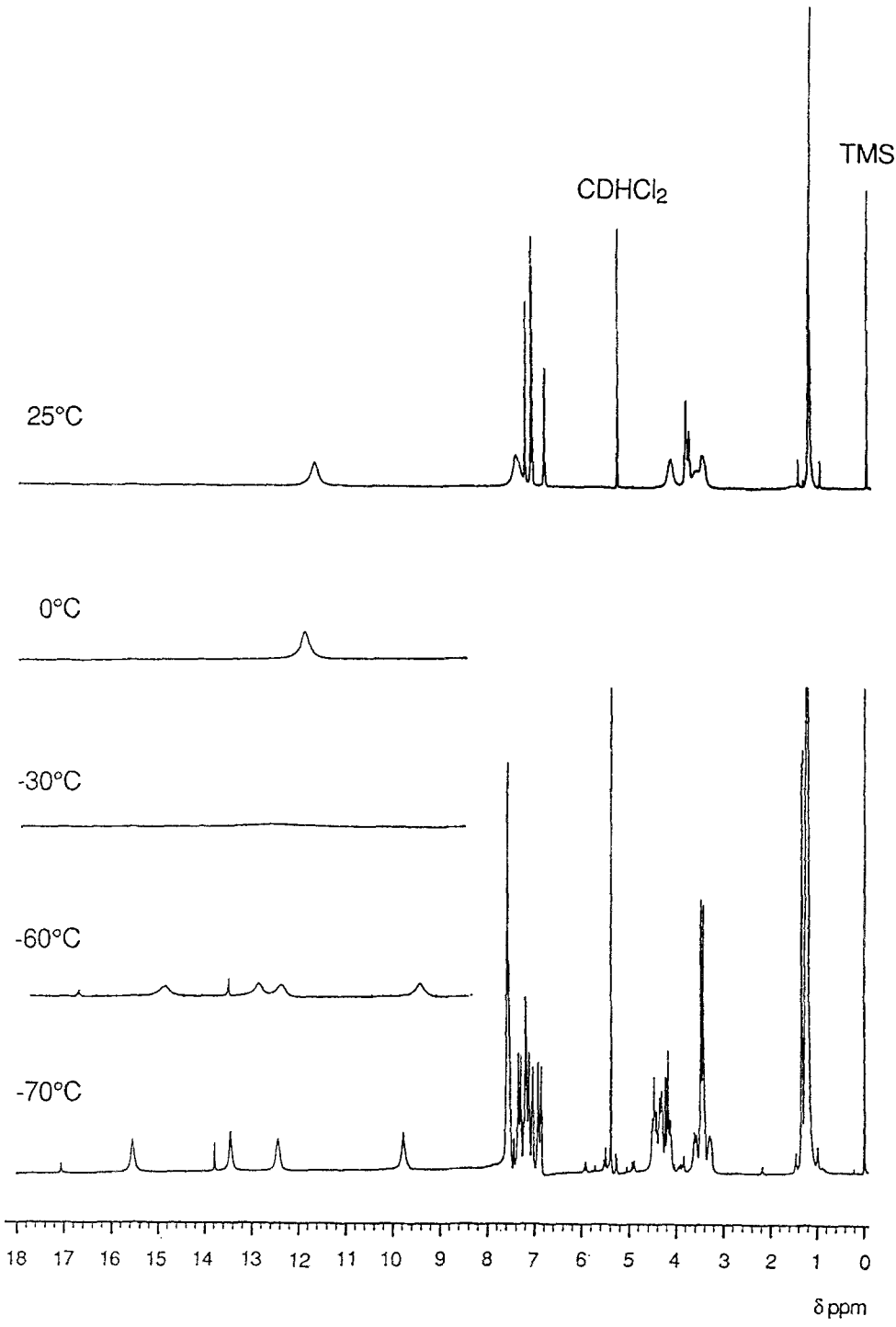


Fig. 4. Temperature-dependent ^{1}H-NMR (270 MHz, CD_2Cl_2) spectra of **2**.

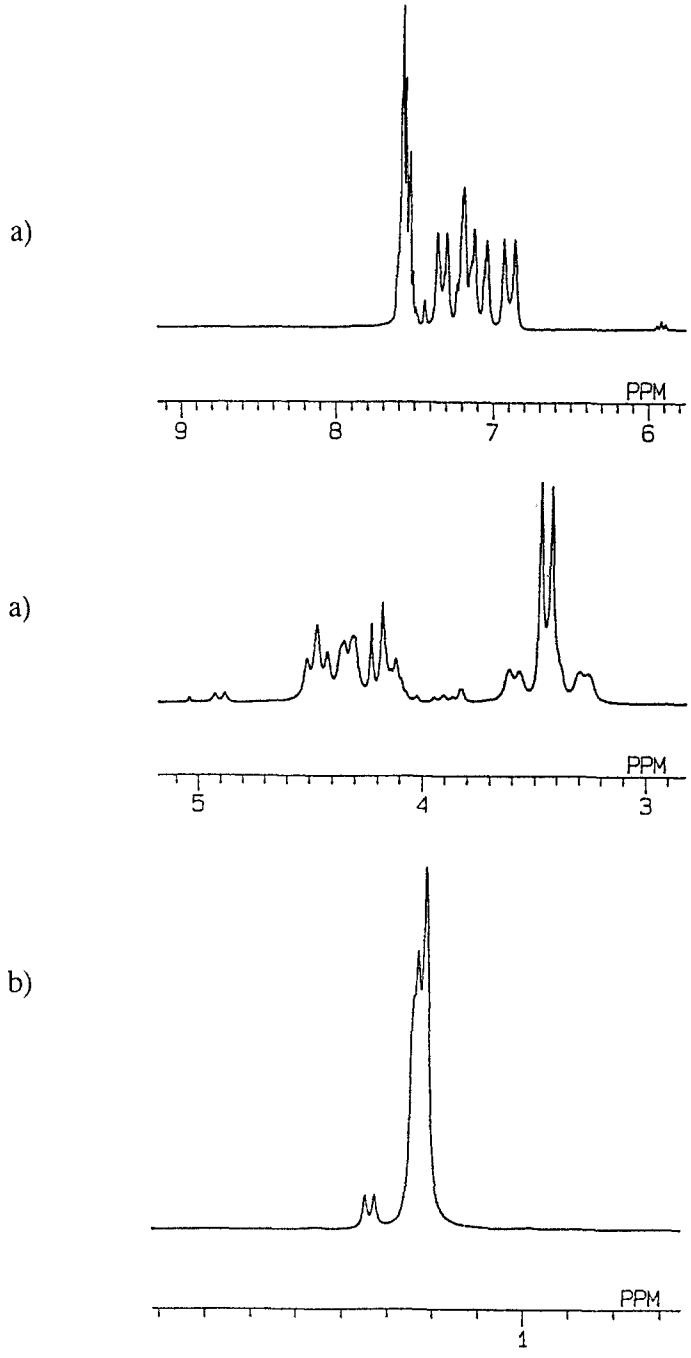


Fig. 5. Expanded ^{1}H-NMR (270 MHz, CD_2Cl_2) spectra of **2**: (a) aromatic and benzylic protons at -70°C, (b) *tert*-butyl protons at -80°C.

formational analyses of *p*-tetrabromo- and *p*-tetramethyldihomoazacalix[4]arenes are currently in progress.

3.5.2. *Variable Temperature NMR Measurements*

In contrast to the sharp OH signals of calix[*n*]arenes in ^{1}H-NMR spectra [10a], the OH signals of azacalixarenes appear as relatively broad singlets at lower fields than those of calix[*n*]arenes. The nitrogen lone pairs form favorable hydrogen bonds with the phenolic OH protons and thus weaken the phenolic O—H bonds. This intramolecular acid–base system provides the strong hydrogen bonds [1, 2]. The phenolic OH signal of **2** appears at 11.6 ppm as a broad singlet in $CDCl_3$ at 25°C. At low temperatures, the signal coalesced at circa -30° and finally appeared as six singlets in ^{1}H-NMR spectra below -60°C. The sharp singlets at 17.1 and 13.8 ppm are small, while the singlets at 15.6, 13.5, 12.5 and 9.8 ppm have equal intensities and are relatively broad (Figure 4). The splittings of the OH signal is concomitant with the splitting of aromatic, benzyl and *tert*-butyl proton signals. A small doublet of *tert*-butyl protons shows the existence of a minor conformational isomer at -70°C and the two small sharp singlets (17.1 and 13.8 ppm) should correspond to that minor conformational isomer. The four OH signals (15.6, 13.5, 12.5 and 9.8 ppm) originate from the four OH groups of the major conformer. Probably, the four OH groups are in different spacial arrangements. This speculation agrees with the splitting pattern of aromatic protons: they split into eight singlets, showing that the circumstances surrounding each aromatic proton are different. Moreover, all methylene protons are nonequivalent and the major *tert*-butyl protons split into three singlets at -80° (Figure 5). At the present stage, the interpretation of the splitting pattern of benzyl protons is difficult, but these results show that the major conformer of **2** is the 1,2-alternate, and the minor signals correspond to those of a cone conformation. These results are different from those of the MM3 calculations, in which the most stable conformation is the 'cone' of C_s symmetry (without considering the cyclic array of the OH groups). The MM3 calculations showed that the difference in free energy (ΔG^0) between the cone and the 1,2-alternate conformations is 10.0 kcal mol^{-1}. Further conformational analyses of **2** by calculations and dynamic NMR studies are in progress. Similar splittings of OH groups were also observed in **1** and **3**, but were not as remarkable as those in **2**.

References

1. H. Takemura, K. Yoshimura, I. U. Khan, T. Shinmyozu, and T. Inazu: *Tetrahedron Lett.* **33**, 5775 (1992).
2. I. U. Khan, H. Takemura, M. Suenaga, T. Shinmyozu, and T. Inazu: *J. Org. Chem.* **58**, 3158 (1993).
3. H. Takemura, M. Suenaga, K. Sakai, H. Kawachi, T. Shinmyozu, Y. Miyahara, and T. Inazu: *J. Incl. Phenom.* **2**, 207 (1984).
4. T. Shinmyozu, N. Shibakawa, K. Sugimoto, H. Sakane, H. Takemura, K. Sako, and T. Inazu: *Synthesis* 1257 (1993).

5. Islam Ullah Khan: *Azacalixarenes: Novel Macrocyclic Host Molecules*, Thesis, Kyushu University, Japan (1993).
6. (a) P. Neri and S. Pappalardo: *J. Org. Chem.* **58**, 1048 (1993). (b) S. Kanamathareddy and C. D. Gutsche: *J. Org. Chem.* **57**, 3160 (1992). (c) J. S. Rogers and C. D. Gutsche: *J. Org. Chem.* **57**, 3152 (1992). (d) A. Casnati, P. Minari, A. Pochini, and R. Ungaro: *J. Chem. Soc., Chem. Commun.* 1413 (1991).
7. (a) V. Balzani and J.-M. Lehn: *Angew. Chem. Int. Ed. Engl.* **30**, 190 (1991). (b) H. Tsukube, K. Takagi, T. Higashiyama, T. Iwachido, and N. Hayama: *Tetrahedron Lett.* **26**, 881 (1985). (c) H. Tsukube, H. Minatogawa, M. Munakata, M. Toda, and K. Matsumoto: *J. Org. Chem.* **57**, 542 (1992).
8. (a) V. Böhmer, F. Marschollek, and L. Zetta: *J. Org. Chem.* **57**, 3200 (1987). (b) H. Casablanca, J. Royer, A. Satrallah, A. Taty-C and J. Vicens: *Tetrahedron Lett.* **28**, 6595 (1987).
9. (a) S. Shinkai, T. Arimura, H. Satoh, and O. Manabe: *J. Chem. Soc., Chem. Commun.* 1495 (1987). (b) S. Shinkai, T. Arimura, H. Kawabata, K. Araki, K. Iwamoto, and T. Matsuda: *J. Chem. Soc., Chem. Commun.* 1734 (1990). (c) T. Arimura, H. Kawabata, T. Matsuda, T. Muramatsu, H. Satoh, K. Fujio, O. Manabe, and S. Shinkai: *J. Org. Chem.* **56**, 301 (1991). (d) S. Shinkai, T. Arimura, H. Kawabata, H. Murakami, and K. Iwamoto: *J. Chem. Soc., Perkin Trans. 1* 2429 (1991).
10. (a) G. J.-C. Bünzli and J. M. Harrowfield: in *Calixarenes*, J. Vicens and V. Böhmer (Eds.), Kluwer Academic Publishers, the Netherlands (1990), pp. 211–231. (b) N. Sabbatini, M. Guardini, A. Mecati, V. Balzani, R. Ungaro, E. Ghidini, A. Casnati, and A. Pochini: *J. Chem. Soc., Chem. Commun.* 878 (1990).
11. (a) C. D. Gutsche: in *Calixarenes*, J. F. Stoddart (Ed.), Monographs in Supramolecular Chemistry, Royal Society of Chemistry, Great Britain (1989), pp. 50–59. (b) C. D. Gutsche, M. Iqbal, and D. Stewart: *J. Org. Chem.* **51**, 742 (1986). (c) B. Dhawan, S.-I. Chen, and C. D. Gutsche: *Macromol. Chem.* **188**, 921 (1987).
12. MM3 calculations were carried out with a MM3 ('92) program in its ANCHOR II implementation. ANCHOR II is a molecular design support system for SUN computers from Fujitsu Limited. Trade Mark of Fujitsu Limited and Kureha Chemical Company, 1992. In these calculations, the memory size of the hardware was limited, thus, molecules larger than *p*-diisopropyldihomoazacalix[4]arene were not considered for the model.