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One-step Syntheses of *p*- and *m*-Xylylene-bridged Azacalixarenes and Their Rigid Molecular Skeletons

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Novel self-filled azacalixarenes were synthesized following a simple method. The structure of a *p*-xylylene-bridged compound was investigated by X-ray crystallographic analysis. Compound 1 : $C_{42}H_{44}O_4N_2$, monoclinic, space group C2/c, $a = 17.236$ (4), $b = 9.244$ (3), $c = 22.217$ (4) Å, $\beta = 101.23$ (1)°, D_{calc} 1.226 g/cm³, $V = 3472$ (1) Å³, $Z = 4$, $R = 0.042$. The final cycle of full-matrix least-squares refinement was based on 2201 observed reflections [$I > 3.00\sigma(I)$] and 284 variable parameters. Dynamic NMR and MM3 calculations were also employed to study the structures in solution. Azacalix[4] skeletons are rigidly fixed in shallow cone conformations and bridging xylylene units (*p*- and *m*-) are located in the cavities of the cyclic skeletons. Intra-cavity hydrogen bonds between OH and N atoms localize at low temperatures. The free energy of the localization was estimated to be 10.8 and 11.2 kcal mol^{-1} for *p*- and *m*-xylylene-bridged compounds, respectively.

Keywords: Azacalixarene, azacyclophane, hydrogen bond, self-filled structure

INTRODUCTION

Previously, we reported on the synthesis, structure, strong intramolecular hydrogen bonds, and inclusion properties of azacalixarenes [1]. This simple and convenient cyclization procedure promises wide application to build up sophisticated receptor molecules. On the other hand, in the field of cyclophane and calixarene chemistry, capped (and/or cupped) cyclophanes [2] and/or calixarenes derivatives which have arene-bridges on phenolic oxygen atoms have become of interest in terms of molecular structures, construction of guest selective molecules, and studies on the properties of a functional group embedded in a cavity [3]. In this report, one-step syntheses of azacalixarenes whose cavities are occupied by *p*- or *m*-xylylene units are described along with their structural features.

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RESULTS AND DISCUSSION

Synthesis

The compounds **1** and **2a** were easily synthesized following an one-step cyclization method [1]. One advantage of this reaction is to avoid the high dilution techniques usually employed in cyclophane synthesis. As described before, the template effect by hydrogen bonds between phenol and amine plays an important role in this cyclization reaction [1c]. The bis(hydroxymethyl)phenol derivative **4** was made to react with *p*- or *m*-xylylenediamine in refluxing xylene or toluene for 2–3 days. Small quantities of calix[*n*]arenes and/or oxacalix[n]arenes were generated as by-products in some cases. In the case of **2a**, the yields were satisfactory (41.5%) and isolation was very easy. Interestingly, starting from trimeric phenol derivative **5** (Fig. 1), a *disproportionation* reaction took place and the compound **2b**, which is a by-product of this reaction, was obtained in better yield than the desired compound **3**. The respective yields are very low compared to those of **1** and **2a**. Yamato *et al.*, reported a similar disproportionation in the synthesis of hydroxymetacyclophanes [4].

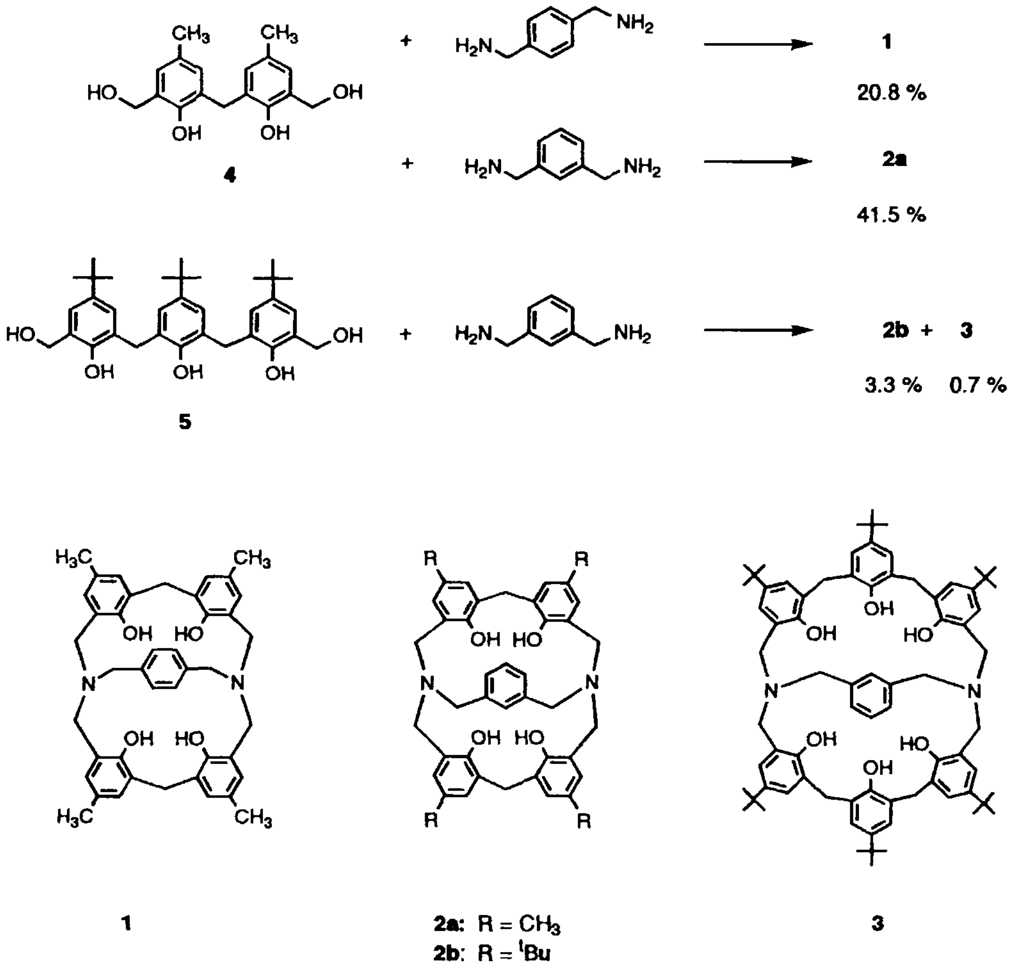


FIGURE 1 Synthetic scheme and structures of *N,N'*-xylylene-bridged azacalixarenes.

Structure in Crystalline State

The results of X-ray crystallographic analysis of compound **1** showed that the four phenol rings are arranged in a shallow saucer shape and that the bridging *p*-xylylene unit filled the molecular cavity (Fig. 2). The dihedral angle between the two benzene rings, C(1)—C(2)—C(3)—C(4)—C(5)—C(6) and C(7)—C(8)—C(9)—C(10)—C(11)—C(12) is estimated to be 155°, which is comparable to that of the hexahomotriazacalix[3]arene derivative [5]. On the other hand, the dihedral angle between the two aromatic rings, C(1)—C(2)—C(3)—C(4)—C(5)—C(6) and C(7*)—C(8*)—C(9*)—C(10*) — C(11*)—C(12*) is 119°. This value is similar to that of calix[n]arene [5]. The bridging *p*-xylylene unit is slightly bent: the dihedral angle between the two planes, C(13)—C(14)—C(15) and C(14)—C(15)—C(14*)—C(15*) is estimated to be ca. 5.3°. Both nitrogen atoms are oriented inward and the lone pairs can form favorable hydrogen bonds. Figure 3 shows the network of hydrogen bonds. The atomic distance O(1)···N(1) (2.69 Å) is shorter than O(2)···O(1*) (2.80 Å) and this feature affects the strength of the hydrogen bonds O(1)—H(21)···N(1) and O(2)—H(22)··· O(1*). Actually, the bond length of the phenolic hydroxyl group O(1)—H(21) is slightly longer (0.99 Å) than that of O(2)—H(22) (0.95 Å). Although the angle O(2)···H(22)···O(1*) (167°) is nearer to linear than O(1)—H(21)···N(1) (145°), the atomic distances mainly affect the strength of hydrogen bonds rather than the angles, as described below. Selected atomic distances, bond lengths and angles are summarized in Table I.

Structure in Solution

In order to obtain the conformational information and the hydrogen bond pattern in solution, variable-temperature ^{1}H NMR spectra were observed. Consequently, the spectra showed that both compounds **1** and **2** are fixed in rigid cone conformations as in the crystalline state. In the ^{1}H NMR spectra, the methylene signals of the diazacalix[4] skeleton (Ar—CH$_2$—Ar, Ar—CH$_2$ — N—CH$_2$—) appear as A_2X_2 patterns and broadening or shifting of the signals were not observed in the wide range of temperatures (−90 ∼ +180°C). This spectral properties suggest that the inversion of the phenol rings is inhibited: the bridged aromatic rings hinder the approach of the phenolic OH groups. On the other hand, both the aromatic and methylene signals of the bridging xylylene units of **1** and **2** remain sharp. Since the *m*- or *p*-xylylene bridging unit is surrounded by the four phenolic rings, the ^{1}H NMR signal of the aromatic protons of the xylylene units shifted to high magnetic regions (5.23 ppm for **1** and 5.8 – 5.9 ppm for **2a**). Although the azacalix [4] skeletons are rigidly fixed in cone structures, the movements of the bridging xylylene unit of **1** (rotation around CH$_2$—Ar—CH$_2$ axis) and **2** (flipping motion of *m*-xylylene unit) are very rapid (Fig. 4). Besides the aromatic ring inversion, three orientations of nitrogen lone pairs (inversion of nitrogen atoms) can be considered as shown in Figure 5. Since the signal of the methylene protons of the azacalixarene skeleton is independent of temperatures, this conformational change can be excluded. Of the three possible conformers, only *in-out* and *in-in* conformers can form hydrogen bonds between nitrogens and phenolic hydroxyl groups. Furthermore, at the low temperatures, the intracavity hydrogen bond pattern is symmetrical as described below. Therefore, the *in-in* conformer is the only possible conformer in solution, as in the crystalline structure. The MM3 calculations on **1** also exclude the presence of *in-out* and *out-out* conformers, because these are too strained than *in-in* conformer (26.7 and 27.2 kcalmol^{-1}, respectively) [6]. The calculations on **2** gave similar results.

In contrast to **1** and **2**, the compound **3** is a flexible molecule: the bridging xylylene unit and the methylenes adjacent to the nitrogens (Ar—CH$_2$—N—) appeared as a very broad

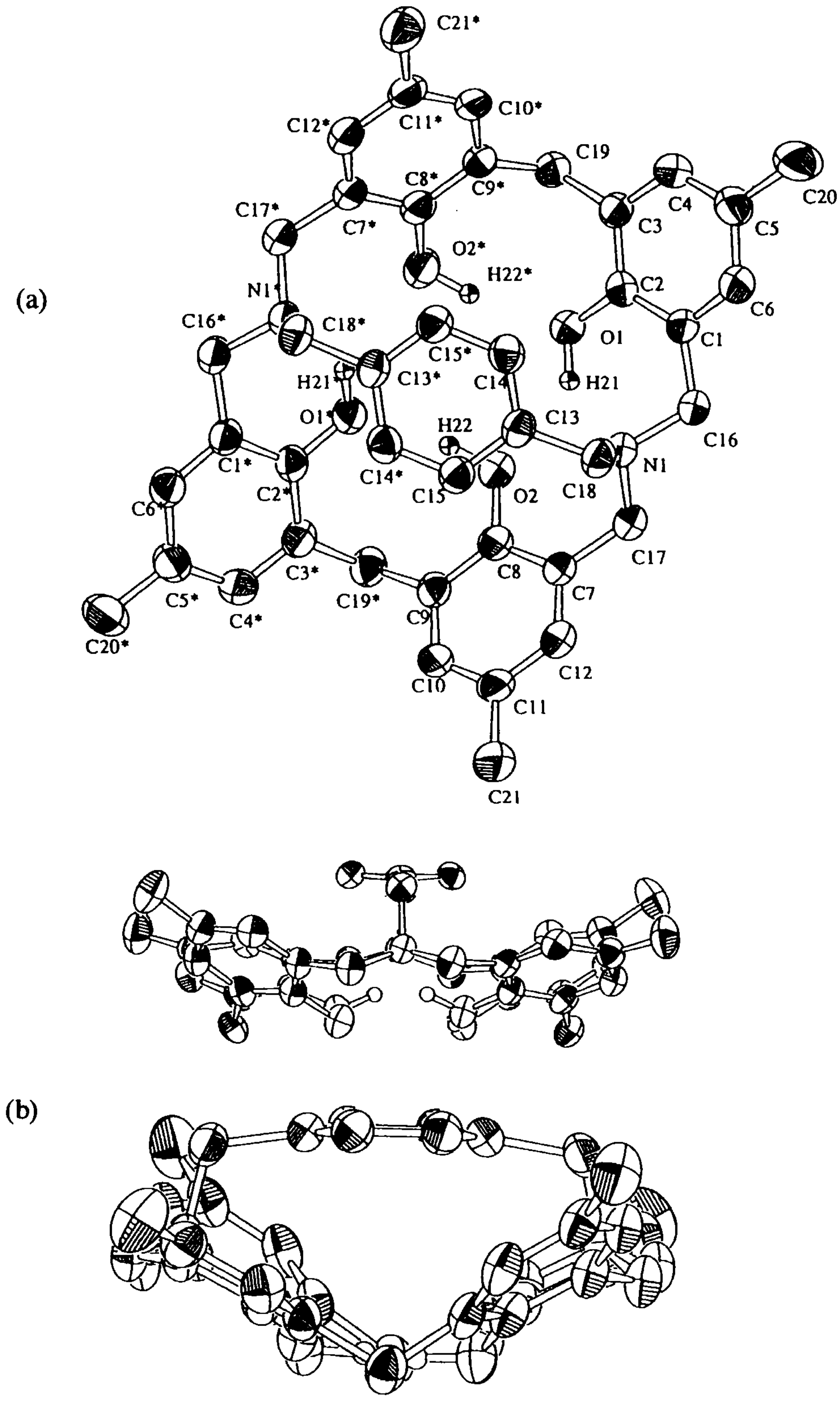


FIGURE 2 Crystal structure of compound 1, (a) top view; (b) side view.

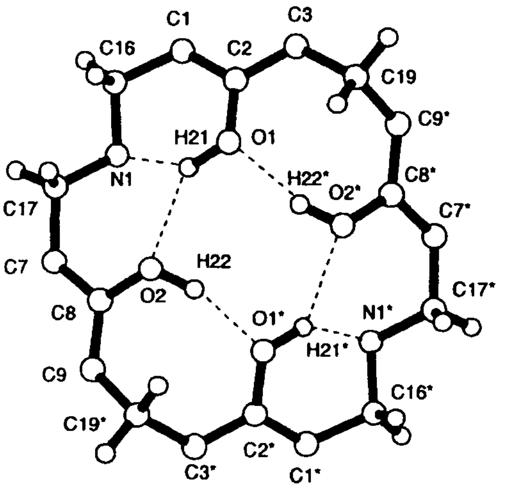


FIGURE 3 Hydrogen bond network in the cavity of 1.

TABLE I Selected atomic distances (Å), bond lengths (Å) and angles (°) of compound 1

Atoms	
O(1)—H(21)	0.99 (Å)
O(2)—H(22)	0.95
O(2)—H(21)	2.31
O(1)—H(22*)	1.87
N(1)—H(21)	1.82
O(1)—N(1)	2.69
O(1)—O(2)	2.96
N(1)—O(2)	2.99
O(2)—O(1*)	2.80
O(1)—H(21)—N(1)	145(°)
O(2)—H(22)—O(1*)	167

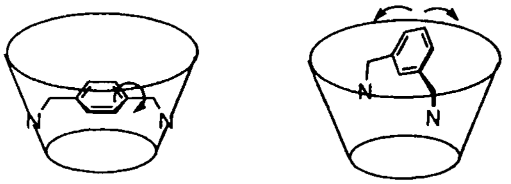
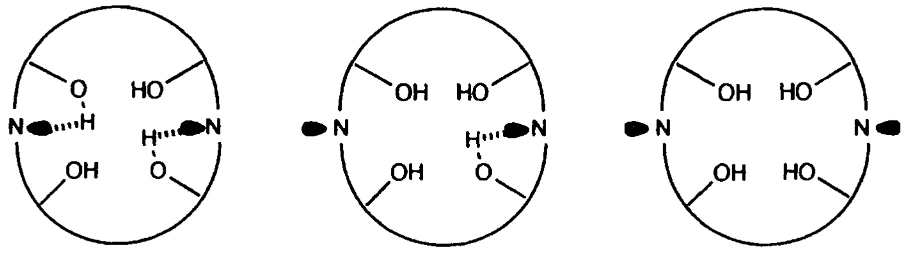


FIGURE 4 Restricted motions of xylylene bridging units in compounds 1 and 2.

signal in its NMR spectrum at room temperature in $CDCl_3$. On the other hand, the Ar—CH_2—Ar protons retain two pairs of doublets up to 60°C. At low temperatures (~ − 60°C), the aromatic and methylene protons split into complex patterns. The conformation at low temperatures could not be determined so far. These spectral results suggest that the inversion of aromatic rings (Ar—CH_2—N—) of **3** occurs.

Intramolecular Hydrogen Bonds

According to the crystal structure described above, the atomic distance O· · ·N is shorter than O· · ·O. Therefore the strength of the hydrogen bonds (OH· · ·N and OH· · ·O) should also be different. In fact, this is evidenced in the NMR (δ_{OH}) and IR (ν_{OH}) spectra. The IR spectra of **1** gave two bands (ν_{OH}): one of them appeared at 3240 cm^{-1} as a relatively sharp band and another appeared as a very broad band centered at 2800 cm^{-1}. The nature of the former band is similar to that of calix[4]arene (3164 cm^{-1}) or calix[8]arene (3258 cm^{-1}) [7], while the broad band is characteristic of azacalix[n]arenes [1]. Thus, the band at 3240 cm^{-1} results from O—H· · ·OH (· · · indicates a hydrogen bond), while the broad band results from O—H· · ·N vibration. In the ^1H NMR spectra, the OH signals of previously reported azacalixarenes appear around 11 ppm at room temperature and split into multiplets at low temperatures. For example, the OH signal of dihomoazacalix[4]arene appears in the range of 9.8–17.1 ppm as a multiplet at − 70°C [1]. On the other hand, the signals of the calixarene series appear around 10 ppm and do not show such remarkable low-field shifts even at low temperatures [6]. This phenomenon is ascribed to the localization of protons in the OH· · ·N· · ·OH cyclic array of hydrogen bonds in azacalixarenes. At room temperature, the OH signals of the compounds **1**, **2a**, **2b**, and **3** appear as singlets at 9.6, 11.1, 10.9, and 10.1 ppm, respectively ($CDCl_3$). In this series of compounds, the OH signal of **1** appears in a higher field than the other members of the azacalix[*n*]arene series. This is attributed to the fact that the OH· · ·N and OH· · ·O distances are elongated in the para-bridged system. In contrast to the aromatic and



in-in *in-out* *out-out*

FIGURE 5 Possible orientations of the nitrogen lone pairs of 1 and 2.

methylene proton signals, the OH signal is strongly dependent on temperatures (Fig. 6). At the low temperatures (−60°C in $CDCl_3$), the signal appeared as two relatively broad singlets with equal intensities (8.0 and 12.0 ppm for **1**, 9.2 and 13.4 ppm for **2b**, respectively). Considering the O···O and O···N atomic distances according to the crystal structure described above, the signal in a higher field corresponds to the O—H···OH signal (··· indicates a hydrogen bond) and that in a lower field corresponds to the O—H···N proton.

Since conformational changes can be ignored in this structure, the splitting of the OH signal should correspond to the localization of protons in the hydrogen bond network:

$$—O\cdots H\cdots O—\text{and}—O\cdots H\cdots N—$$
$$\rightarrow —OH\cdots O—\text{and}—OH\cdots N—$$

According to the coalescence temperature of the OH signal, the energy barrier of the proton transfer is estimated to be 10.8 $\mathrm{kcal mol^{-1}}$ for **1** and 11.2 $\mathrm{kcal mol^{-1}}$ for **2b**, respectively [8].

In the case of compound **3**, six OH peaks were observed in the range of 15.4 to 8.5 ppm at −60°C, as in the case of other azacalix[n]arenes [1]. The strong intramolecular OH···N hydrogen bonds are present but they are not symmetrical as in compounds **1** and **2**.

EXPERIMENTAL SECTION

General

All melting points were measured in Ar sealed tubes and were uncorrected. The ^{1}H NMR spectra were recorded on a JEOL-GSX 270 (270 MHz) NMR spectrometer. The FAB Mass Spectra were recorded on a JEOL JMS-SX/SX 102A, tandem mass spectrometer.

X-ray Crystallographic Analysis of 1

Crystal data: $C_{42}H_{44}O_4N_2$ (Formula weight 640.82), colorless prism, monoclinic (recrystallized from toluene). Crystal dimensions 0.45 × 0.25 × 0.20 mm, D_{calc} 1.226 g/cm^3, space group C2/c (#15) : $a = 17.236$ (4), $b = 9.244$ (3), $c = 22.217$ (4) Å, $\beta = 101.23$ (1)°, $V = 3472$ (1) Å^3, $Z = 4$, $F_{000} = 1368$.

All measurements were performed on a Rigaku AFC7R diffractometer with graphite monochromated Mo-Kα radiation ($\lambda = 0.71069$ Å), $\mu = 0.78\ \mathrm{cm^{-1}}$. The data were collected at a temperature of 25 ± 1°C using the ω-2θ scan technique to a maximum 2θ value of 55.0°. Of the 4372 reflections which were collected, 4232 were unique ($R_{int} = 0.020$). The data were corrected for Lorentz and polarization effects. The structure was solved using a direct method [9] and expanded using Fourier techniques [10].

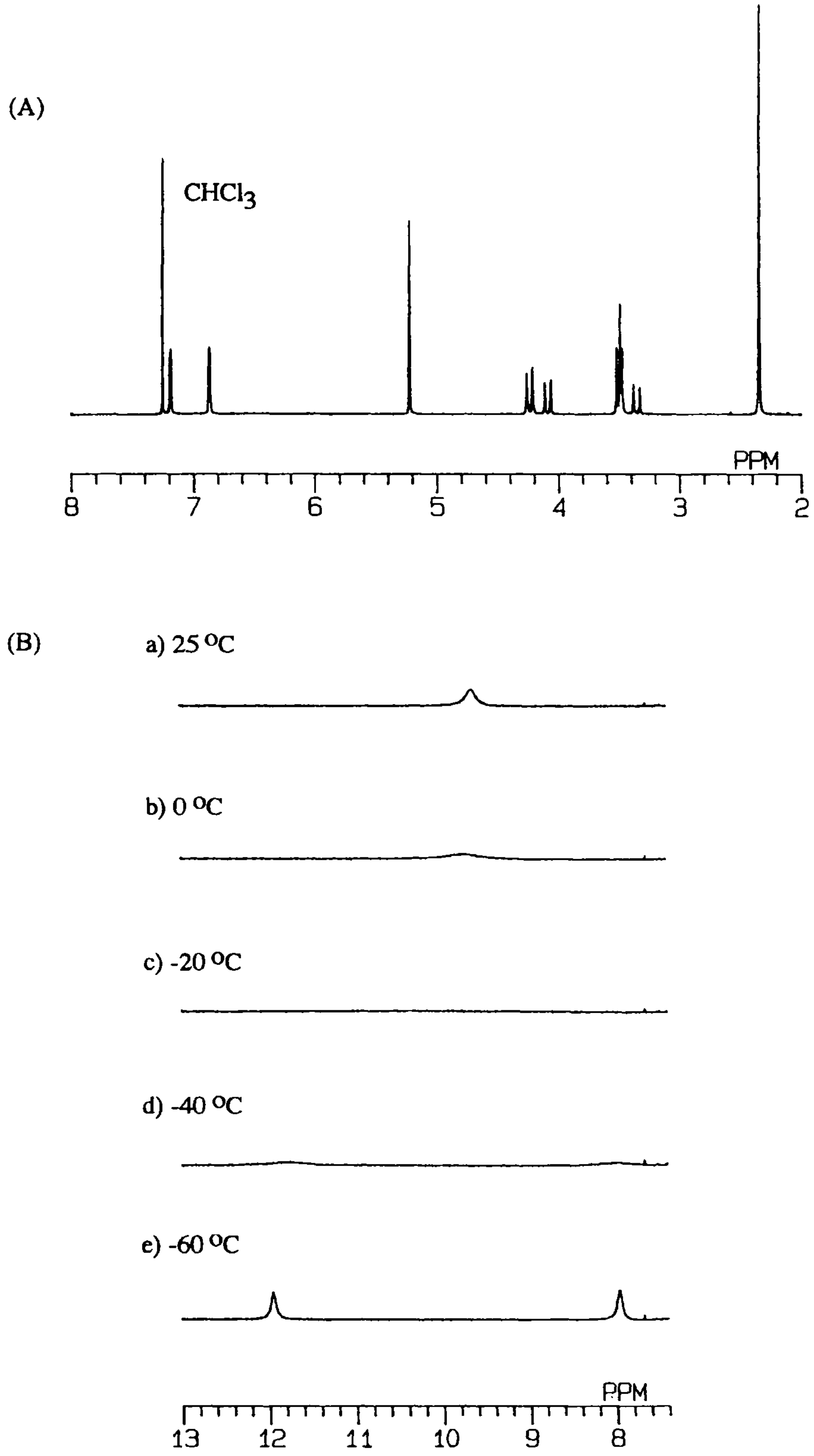


FIGURE 6 ^{1}H NMR spectrum (A) and temperature-dependent OH signal (B) of 1 in $CDCl_3$.

The non-hydrogen atoms were refined anisotropically; the hydrogen atoms, isotropically. The final cycle of full-matrix least-squares refinement was based on 2201 observed reflections [$I > 3.00\sigma(I)$] and 284 variable parameters. The final *R* factors were $R = \sum ||Fo| - |Fc|| / \sum |Fo| = 0.042$, $Rw = [\sum w(|Fo| - |Fc|)^2 / \sum w Fo^2]^{1/2} = 0.032$. The maximum and minimum peaks on the final difference Fourier map are 0.15 and $-0.14\,e^-/Å^3$, respectively. All calculations were performed using the teXscan [11] crystallographic software package from Molecular Structure Corporation.

SYNTHESIS AND CHARACTERIZATION

Compound 1

A solution of compound **4** (1.29 g, 4.47 mmol) and *p*-xylylenediamine (0.329 g, 2.42 mmol) in 150 cm^3 of xylene was heated under reflux with stirring for 2 days. After evaporating the solvent, the resultant resinous product was dissolved in CH_2Cl_2 and filtered off. The filtrate was concentrated and cyclohexane was added. The white powder thus precipitated was collected and the mother liquor was subjected to column chromatography (silica gel, CH_2Cl_2/acetone = 9/1, v/v). The slightly yellow powder thus obtained was recrystallized from toluene together with the white powder. White powder (302 mg, 21.1%). mp 270–271°C (dec); ^1H NMR (270 MHz, $CDCl_3$) δ 9.64 (bs, 4H, OH), 7.20 (d, $J = 2$ Hz, 4H, Ar—H), 6.88 (d, $J = 2$ Hz, 4H, Ar—H), 5.23 (s, 4H, Ar—H), 4.23, 3.50 (A_2X_2, $J = 13$ Hz, 8H, —CH_2—), 4.09, 3.35 (A_2X_2, $J = 13$ Hz, 4H, —CH_2—), 3.49 (s, 4H, —CH_2—), 2.35 (s, 12H, CH_3); FAB-MS, m/z 640 (M^+, 88%), 641 ($M^+ + 1$, 100%). Anal. Calcd for $C_{42}H_{44}N_2O_4$: C, 78.72; H, 6.92; N, 4.37. Found: C, 78.74; H, 6.92; N, 4.42.

Compound 2a

A solution of compound **4** (5.00 g, 17.3 mmol) and *m*-xylylenediamine (1.55 g, 11.4 mmol) in 300 cm^3 of toluene was heated under reflux for 3 days. After concentrating the solvent, the resultant white powder was collected by filtration. The white powder thus obtained was recrystallized from a $CHCl_3$-toluene mixture. The compound **2a** was obtained as a white powder (2.30 g, 41.5%). mp 295–296°C (dec); ^1H NMR (270 MHz, $CDCl_3$) δ 11.1 (bs, 4H, OH), 7.00 (d, $J = 2$ Hz, 4H, Ar—H), 6.76 (d, $J = 2$ Hz, 4H, Ar—H), 6.57 (s, 1H, Ar—H), 5.96 (s, 3H, Ar—H), 4.40, 3.40 (A_2X_2, $J = 13$ Hz, 8H, —CH_2—), 4.16, 3.26 (A_2X_2, $J = 13$ Hz, 4H, —CH_2—), 3.32 (s, 4H, —CH_2—), 2.26 (s, 12H, —CH_2); FAB-MS, m/z 640 (M^+, 89%), 641 ($M^+ + 1$, 100%). Anal. Calcd for $C_{42}H_{44}N_2O_4 \cdot 1/2H_2O$: C, 77.63; H, 6.98; N, 4.31. Found: C, 77.58; H, 6.80; N, 4.34.

Compound 2b and 3

A reaction product obtained from **5** (1.00 g, 1.86 mmol) and *m*-xylylenediamine (0.15 g, 1.13 mmol) was subjected to column chromatography on silica gel with CH_2Cl_2/MeOH = 90/10 as an eluent.

Compound **2b**: colorless needles from CH_2Cl_2–EtOH (3.3%). mp 273–275°C (dec); ^1H NMR (270 MHz, $CDCl_3$) δ 10.95 (bs, 4H, OH), 7.21 (d, $J = 2$ Hz, 4H, Ar—H), 6.94 (d, $J = 2$ Hz, 4H, Ar—H), 6.60 (s, 1H, Ar—H), 5.92–5.82 (m, 3H, Ar—H), 4.43, 3.41 (A_2X_2, $J = 13$Hz, 8H, —CH_2—), 4.20, 3.33 (A_2X_2, $J = 13$Hz, 4H, —CH_2—), 3.32 (s, 4H, —CH_2—), 1.31 (s, 36H, ^{t}Bu); FAB-MS, m/z 808 (M^+, 80%), 809, (M + 1, 100%). Anal. Calcd for $C_{54}H_{68}N_2O_4 \cdot H_2O$: C, 78.41; H, 8.53; N, 3.39. Found: C, 78.56; H, 8.46; N, 3.41. The water molecule included in the analytical sample was confirmed by ^1H-NMR spectrum.

Compound **3**: colorless powder from CH_2Cl_2–EtOH (0.7%). mp 248–251°C (dec); ^1H NMR (270 MHz, $CDCl_3$) δ 10.1 (bs, 6H, OH), 7.58 (s, 1H, Ar—H), 7.27 (s, 4H, Ar—H), 7.23 (s, 4H, Ar—H), 7.15–6.98 (AB_2, $J = 7$Hz, 3H, Ar—H), 6.86 (s, 4H, Ar—H), 4.37, 3.51 (A_2X_2, $J = 14$ Hz, 8H, —CH_2—), 4.8–2.5 (bs, 12H, —CH_2—), 1.29 (s, 18H, ^{t}Bu), 1.23 (s, 36H, ^{t}Bu); FAB-MS, m/z 1132 (M^+, 83%), 1133 (M + 1, 97%). Anal. Calcd for $C_{76}H_{96}N_2O_6$: C, 80.52; H, 8.54; N, 2.47. Found : C, 80.33, H, 8.49, N, 2.45.

Acknowledgments

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