Chemical Modification of Amide-Based Catenanes and Rotaxanes II. Synthesis of *tertiary* Amine [2]Catenanes and [2] Rotaxanes via *N*-Methylation Followed by Borane Reduction of *secondary* Amide [2]Catenanes and [2]Rotaxanes and Mobility of Their Components

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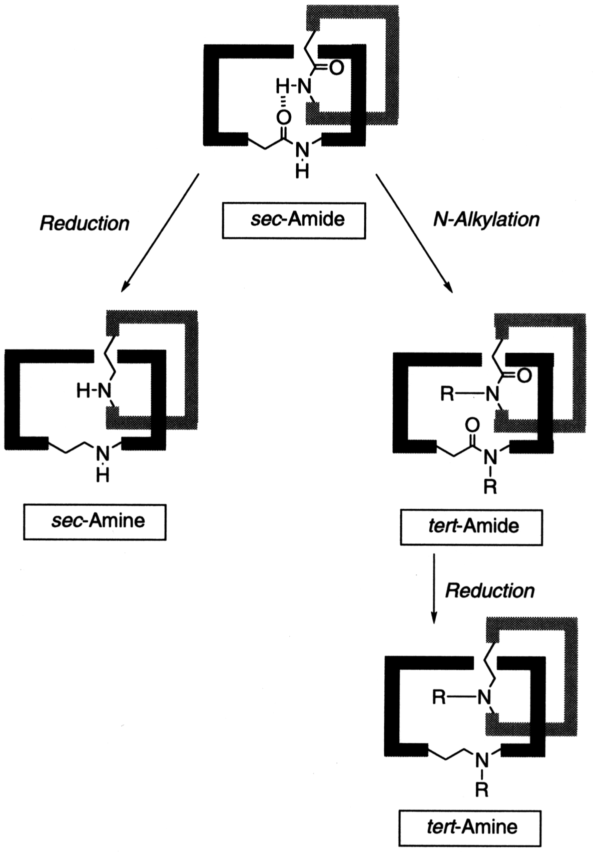
Secondary amide [2]catenane **1a** was converted to the corresponding *tertiary* amide [2]catenane **1b** by repetitive treatment with a methylating system of CH_3I and KOH in DMSO. The amide functions of **1b** were reduced with borane in refluxing THF to give the corresponding *tertiary* amine [2]catenane **1c**. Their structures were characterized by NMR, IR, and FAB-MS spectroscopies. An X-ray crystallographic analysis of **1c** showed that its solid-state structure was stabilized by a CH–π interaction between the *p*-xylylene and *m*-xylylene units, together with a π–π stacking interaction between the two *m*-xylylene units. A variable temperature ^{1}H NMR study suggested that **1c** had components of highly enhanced mobility in $CDCl_3$, even at lower temperature, although a much weaker interaction, such as the CH–π interaction, existed between their components in solution. *Tertiary* amine [2]rotaxane **3c** was obtained from the corresponding *secondary* amide [2]rotaxane **3a** by a procedure similar to that used for **1a**. The ^{1}H NMR spectra indicated that the mobility of the components of **3c** is sufficiently high even at lower temperature.

Mechanically interlocked molecules, such as catenanes and rotaxanes, are becoming ordinary compounds for chemists.[1] Several types of these compounds are easily accessible by recent sophisticated supramolecular syntheses, effectively utilizing the template direction of a metal cation, a π–π stacking interaction, or hydrogen bonding.[2] The mechanical bonds of catenanes and rotaxanes have a high degree of freedom in relative motion of the components.[3,4] From their structural features, it is easily anticipated that catenane- or rotaxane-based polymer materials exhibit special properties. For example, a poly[2]catenane may have a very large loss modulus, a low activation energy for viscous flow, and rapid stress relaxation.[4] We emphasized in a preceding paper[3c] that the design of catenane- or rotaxane-based polymer materials should meet two criteria to obtain such special properties: (1) high mobility of the mechanical bonds is necessary, and (2) the linkage between two adjoining topological units should be rigid and compact. From this viewpoint, we synthesized a *secondary* amine [2]catenane by borane reduction of *secondary* amide [2]catenane **1a**[5]. Our observation that no hydrogen bonding existed in the *secondary* amine [2]catenane in $CDCl_3$ clearly showed the highly enhanced mobility of the components in the [2]catenane in comparison with **1a**.[3a] We also demonstrated that borane reduction was an efficient way to catenanes or rotaxanes endowed with high mobility of the components and was well-tolerant to a modification of the backbone structure.[3c] *N*-Methylation is a simple chemical modification to remove hydrogen-bonding interaction of *secondary* amide groups. Geerts reported that the *N*-methylation of Vögtle's amide-based [2]catenanes did not enhance the mobility of the components, due to a steric hindrance of the *N*-methyl groups.[4] There is another way to remove the hydrogen bonding of *secondary* amide groups, that is, *N*-alkylation followed by reduction to *tertiary* amino groups (Scheme 1). This method seems to be suitable for creating polymer materials, because *tertiary* amino groups are more stable than *secondary* ones.

In this paper, we describe the synthesis of *tertiary* amine [2]catenane **1c** and [2]rotaxane **3c** from the corresponding *secondary* amides, **1a** and **3a**, via the *N*-methylation-reduction procedure. Further, the mobility of the components of those compounds is discussed based on ^{1}H NMR spectroscopic results, in comparison with that of *tertiary* amide [2]catenane **1b** and [2]rotaxane **3b**.

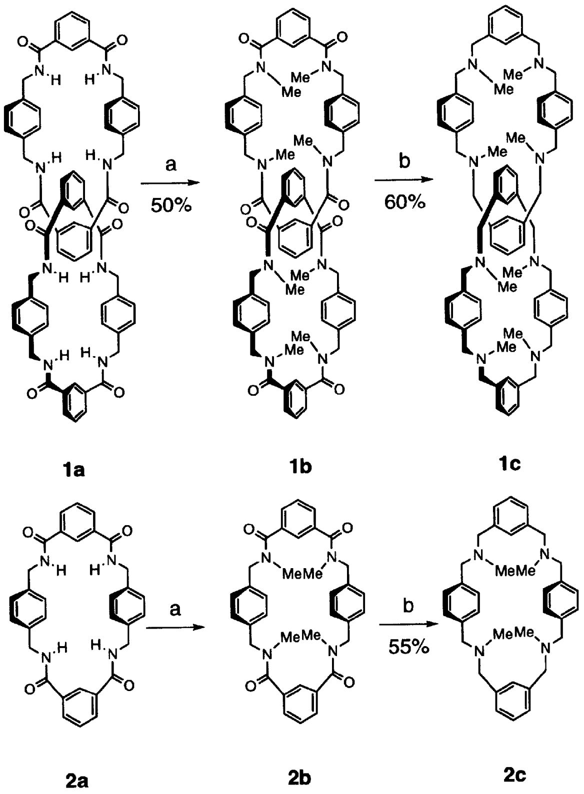
Results and Discussion

***Tertiary* Amide and *Tertiary* Amine [2]Catenanesw:** **1a**[5] was treated with an excess of CH_3I and KOH in DMSO for *N*-methylation. This procedure was repeated three times until the



Scheme 1.

eight amide groups of **1a** were completely *N*-methylated to give the desired *tertiary* amide [2]catenane **1b** in 50% yield (Scheme 2). **1b** was characterized by FAB mass, IR, and ^{1}H NMR spectroscopies. The FAB mass spectrum of **1a** had the characteristic features of interlocked molecules, such as a lack of fragmentation between M + H and M/2 + H, indicating that the *N*-methylated product retained the [2]catenane skeleton. The fragmentation pattern, together with the disappearance of the absorption band around 3316 cm^{-1} ($\nu_{\text{N-H}}$ for **1a**) in the IR spectrum, unambiguously supported that all of the amide groups were *N*-methylated. At room temperature, the ^{1}H NMR (270 MHz, DMSO-d_6, 295 K) spectrum of **1b** was greatly broadened. Upon elevating the measuring temperature up to 403 K, the signals became sharp, and the signals of the *N*-methyl and benzylic protons appeared as singlets at 2.61 and 4.37 ppm, respectively, as shown in Fig. 1.



Scheme 2. (a) CH_3I, KOH/DMSO, rt 6 days. (b) BH_3•THF, reflux, 24 h

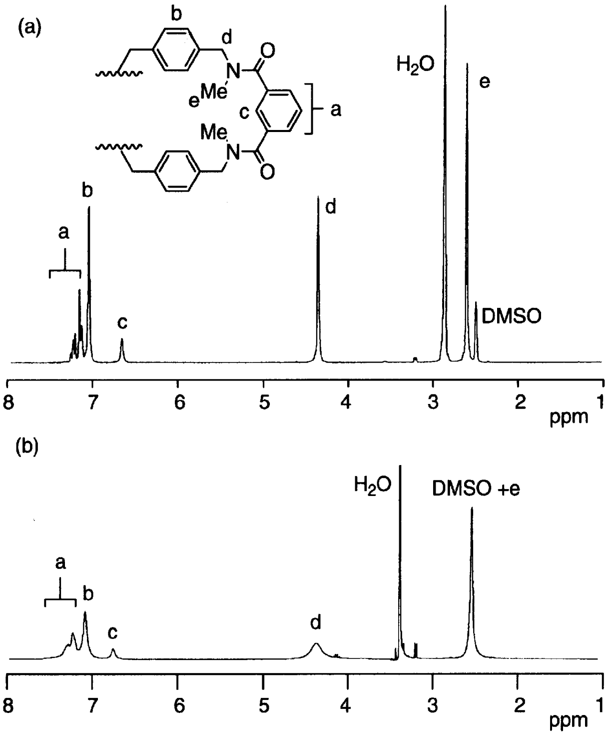


Fig. 1. ^{1}H NMR (270 MHz, DMSO-d_6) of **1b** at (a) 403 K and (b) 295 K.

In a similar manner to that for **1a**, monomacrocycle **2a** was *N*-methylated to afford *N*, *N*′, *N*″, *N*‴-tetramethylated monomacrocycle **2b**. The ^{1}H NMR (270 MHz, DMSO-d_6, 295 K) spectrum of **2b** was again greatly broadened at room temperature and became sharp at higher temperature (403 K). The spectral pattern was almost the same as that of **1b** at 403 K, but the two patterns slightly differed in their chemical shifts. Therefore, the signal broadening of the spectra at room temperature could be attributed to the *s-cis* – *s-trans* isomerism of the *tertiary* amide groups, although a possibility that the steric hindrance of the *N*-methyl groups on both rings restricts their circumrotation could not be ruled out. Thus, the chemical removal of hydrogen bonding was achieved by the complete *N*-methylation of **1a**, whereas the mobility of the produced *tertiary* amide [2]catenane **1b** could not be evaluated precisely because of the *s-cis* – *s-trans* isomerism of the amide groups.

The transformation of the *tertiary* amide groups to the *tertiary* amine ones was carried out by borane reduction. The corresponding *tertiary* amine [2]catenane **1c** was obtained in 60% yield. The FAB mass and ^{1}H NMR spectroscopies unambiguously supported the [2]catenane structure of **1c**. In the ^{1}H NMR (270 MHz, $CDCl_3$) spectrum at room temperature, all of the aliphatic signals were observed as singlets. The simple ^{1}H NMR spectrum suggested that the macrocyclic component rotated completely through the other faster than on the ^{1}H NMR time scale. The high mobility of **1c** was retained even at lower temperature down to –30 °C, that is, neither coalescence nor remarkable broadening of the signals was observed.

The *tertiary* amide monomacrocycle **2b** was treated with borane in THF in a similar manner to that for **1b**, to give the corresponding *tertiary* amine monomacrocycle **2c** in 55% yield. In the ^{1}H NMR spectra, **2c** gave a signal pattern similar to that of **1c**. However, a characteristic difference in the chemical shift was observed: the signals of the *m*-xylylene units, especially those at the 2-position (signal c) and the benzylic position (signal e) of **1c**, shifted remarkably to a higher magnetic field in comparison with those of **2c**, as shown in Fig. 2. The same phenomenon was observed in the case of several *secondary* amine [2]catenanes. This ^{1}H NMR behavior of [2]catenanes was explained in terms of a CH–π interaction working between their components, which was clearly confirmed by an X-ray crystal structure analysis of **1c**, as described below.

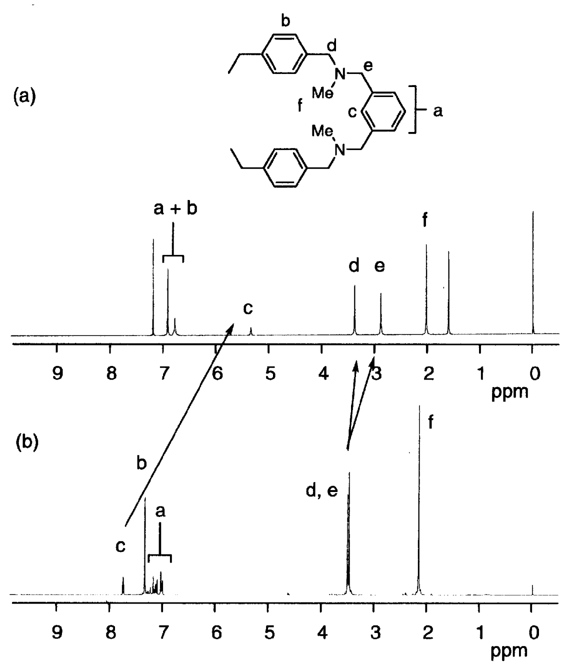


Fig. 2. ^{1}H NMR (270 MHz, $CDCl_3$, 295 K) of (a) **1c** and (b) **2c**.

The X-ray crystallographic analysis of **1c** showed that the two macrocyclic components adopt almost the same conformation (Fig. 3 and Table 1). The two *p*-phenylene units (D (H) and

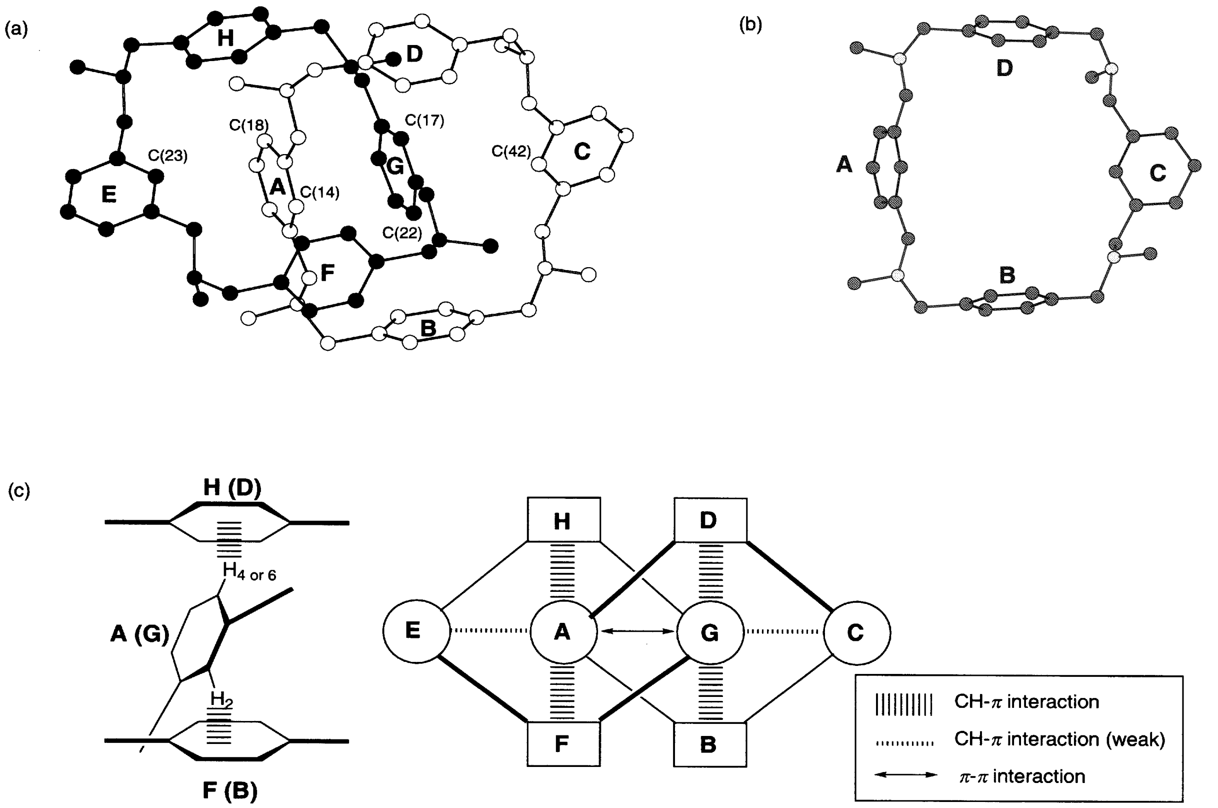


Fig. 3. Chem 3D drawings of the single crystal structure of (a) **1c** and (b) one of the two macrocyclic components in the solid state. Hydrogen atoms are omitted for clarity. (c) Schematic diagrams of intramolecular CH–π and π–π interactions.

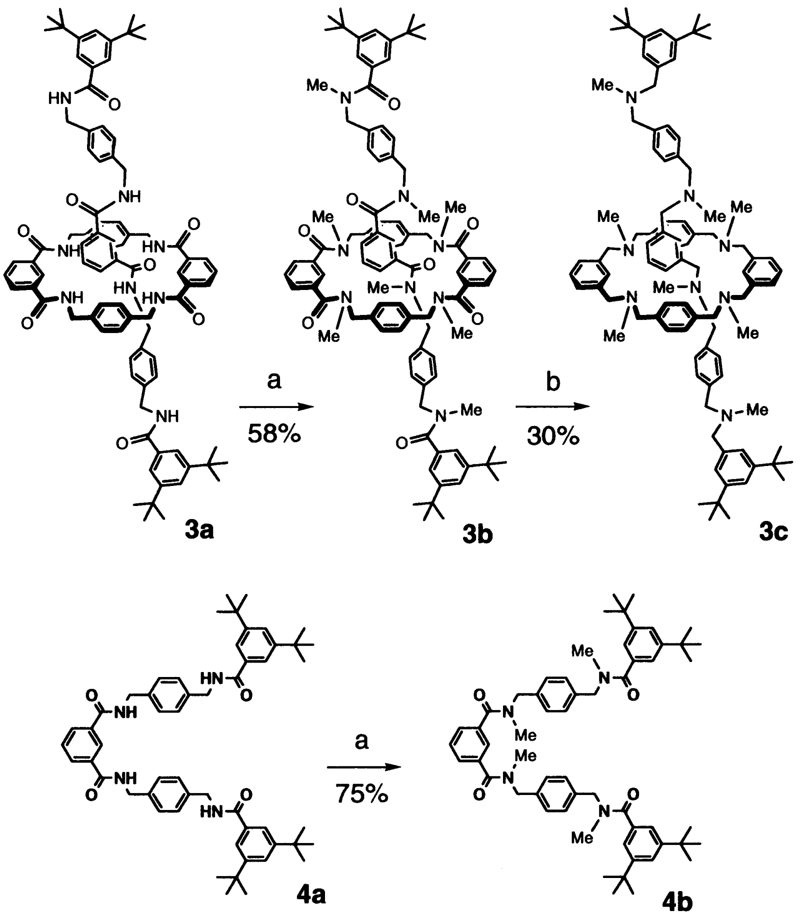
Table 1. Centroid–Centroid Separations for Pairs of Aromatic Rings of **1c** (Fig. 3)

Interaction	Mode	Distance/Å	Angle/deg a)
A···F	CH–π	5.117	82.21
A···H		4.846	83.97
G···B		4.861	89.58
G···D		4.969	89.71
C···G		5.287	89.08
E···A		5.186	78.07
A···G	π–π	3.518	0.63

a) Defined by the two mean planes of the aromatic rings.

B (F)) are almost perpendicular to the mean plane of the macrocyclic component (defined by four nitrogen atoms). One *m*-phenylene unit (A (G)) is almost perpendicular, and the other (C (E)) is parallel to the mean plane. The "parallel" *m*-xylylene (A (G)) unit is threaded through the center of the other macrocyclic component. The [2]catenane framework is stabilized by one π–π interaction and six CH–π interactions. The π–π interaction works between the two "perpendicular" *m*-xylylene units. The hydrogen atoms of the two "perpendicular" *m*-xylylene units (A and G) participate in two CH–π interactions: H_2 of the ring A is very close to the ring F, while $H_{4\ \mathrm{or}\ 6}$ of the ring A is close to the ring H(A(centroid)···F(centroid) = 5.117 Å (82.21 deg), A(centroid)···H(centroid) = 4.846 Å (83.97 deg)); similarly, the hydrogen atoms of the ring G participate in two CH–π interactions with the ring B and D(G(centroid)···D(centroid) = 4.969 Å (89.71 deg), G(centroid)···B(centroid) = 4.861 Å (89.58 deg)). Each of the "parallel" *m*-xylylene units (C and E) forms the CH–π interaction with the "perpendicular" *m*-xylylene units (G and A, respectively), although they are not strong C(centroid)···G(centroid) = 5.287 Å (89.08 deg), E(centroid)···A(centroid) = 5.186 Å (78.07 deg)). Thus, the fact that all the four H_2 of the *m*-xylylene units participate in the CH–π interaction is consistent with the large high-field shift in the ^1H NMR spectrum (Fig. 2).

***Tertiary* Amide and *Tertiary* Amine [2]Rotaxanes:** The *secondary* amide [2]rotaxane **3a**[3c] was treated with CH_3I and KOH in DMSO in a similar manner to that for **1a**, to afford the *tertiary* amide [2]rotaxane **3b** in 58% yield (Scheme 3). **3b** was characterized by FAB mass, IR, and ^1H NMR spectroscopies. The FAB mass spectrum of **3b** showed a typical fragmentation pattern of mechanically-bonded molecules, that is, the absence of a fragment peak between M(rotaxane) + H and M(axis) + H. Thus, **3b** retained the [2]rotaxane skeleton. At room temperature, the ^1H NMR (270 MHz, DMSO-d_6, 295 K) spectrum of **3b** was greatly broadened. The signals became assignable to each proton of **3b** at 353 K, as shown in Fig. 4.



Scheme 3. (a) CH_3I, KOH/DMSO, rt, 5 days. (b) BH_3•THF, reflux, 24 h

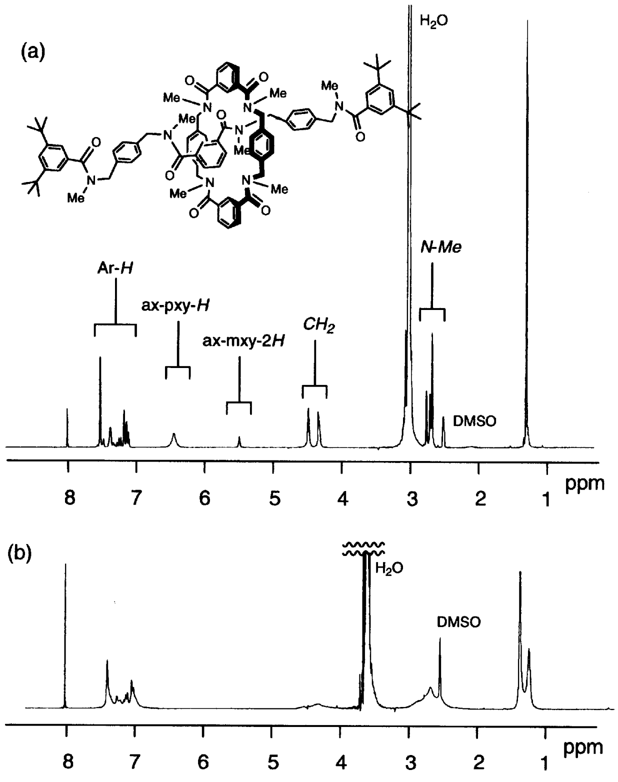


Fig. 4. ^{1}H NMR (270 MHz, $CDCl_3$) of **3b** at (a) 403 K and (b) 295 K.

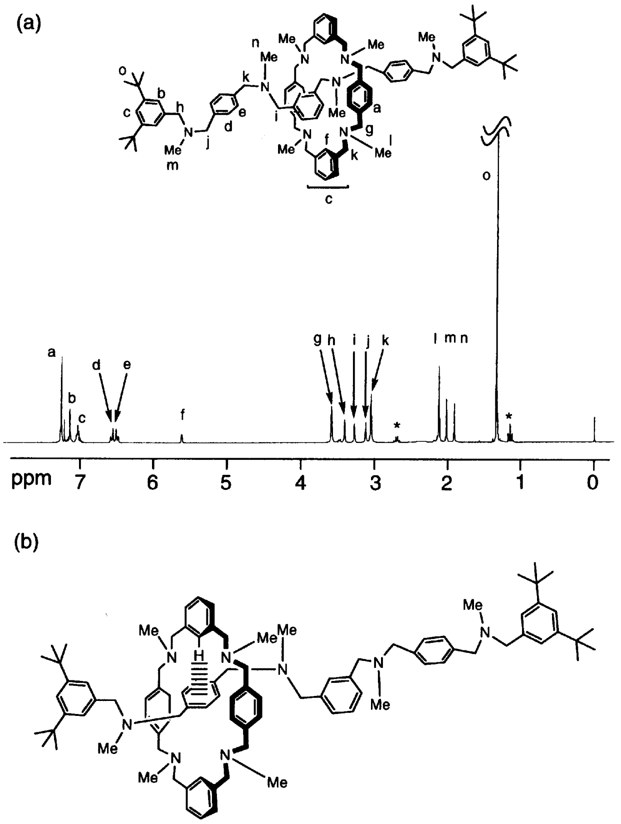


Fig. 5. (a) ^{1}H NMR spectra (270 MHz, $CDCl_3$) of **3c** at 295 K. The signals with asterisk are those of triethylamine. (b) The intramolecular CH–π interaction between the macrocyclic and the axle components of **3c**.

Similarly, axle **4a**[3c] was treated with CH_3I and KOH in DMSO to afford *N*,*N*′,*N*′′,*N*′′′-tetramethylated axle **4b**. The ^{1}H NMR (270 MHz, DMSO-d_6) spectrum of **4b** was again extremely broadened at room temperature and became sharp at higher temperature (403 K). Therefore, the broadening of their spectra could be attributed to the *s-cis* – *s-trans* isomerism of the amide groups, although it could not be ruled out that the steric hindrance of the *N*-methyl groups on their components restricted their relative motion, that is, shuttling of the ring component and/or pirouetting of the axle.

The reduction of **3b** was carried out by the same procedure as that described above, and the corresponding *tertiary* amine [2]rotaxane **3c** was obtained in 30% yield. The structure of **3c** was determined by the IR, NMR, and FAB mass spectra, which were completely consistent with the proposed structure. The ^{1}H NMR (270 MHz, $CDCl_3$, 295 K) spectrum of **3c** showed sharp signals, and suggested that the macrocyclic component underwent smooth shuttling on the ^{1}H NMR time scale, as shown in Fig. 5. In addition, no coalescence was confirmed, even at 243 K. The signal of *m*-xylylene-2H of the macrocyclic component appeared at a specially higher magnetic field (5.64 ppm) at 295 K, similarly to the case of the *tertiary* amine [2]catenane **1c**. It can be presumed here that the protons of *m*-xylylene-2H of the macrocyclic component of **3c**, in analogy with **1c**, served as proton donors to the *p*- and *m*-xylylene units to form CH–π interaction, as illustrated in Fig. 5b. Although a weak interaction, such as the CH-π interaction, was observed, the macrocyclic component moved smoothly on the axle component, even at lower temperature, which is apparent from the fact that no coalescence of the signals was observed.

Summary

N-Methylation followed by borane reduction of the *secondary* amide groups was demonstrated to efficiently yield *tertiary* amide catenanes and rotaxanes, as proved with respect to a wide range of amide compounds.[6] The thus-obtained *tertiary* amine [2]catenane **1c** and [2]rotaxane **3c**, had a much more enhanced mobility, even at low temperature, in comparison with that of **1a** and **3a**. An X-ray single-crystal structure analysis showed that the solid-state structure of **1c** was stabilized by the CH–π interaction between the components. Although the CH–π interaction was observed in **1c** and **3c** in solution, this kind of interaction was too weak to restrict the mobility of the components. Therefore, the present approach from *secondary* amide catenanes and rotaxanes was proved to be an effective way to catenanes and rotaxanes having components of high mobility.

Experimental

General: The melting points were measured on a Yanagimoto micro melting-point apparatus and were uncorrected. IR spectra were recorded on a JASCO FT-IR model 230 spectrometer. ^{1}H NMR (270 MHz) measurements were performed in $CDCl_3$ or $(CD_3)_2SO$ on a JEOL JNM-GX-270 spectrometer, where the chemical shifts were determined with respect to $CHCl_3$ (δ 7.26) or DMSO-d_6(δ 2.50). For recycling preparative HPLC, a JAICO LC-908 system using columns JAIGEL 1 (20 mmϕ × 600 mm) and JAIGEL 2 (20 mmϕ × 600 mm). FABMS measurements were performed on a Finnigan TSQ-70 instrument

***Tertiary* Amide [2]Catenane (1b):** To a suspension of KOH (400 mg, 73 mmol) in DMSO (4.0 mL) was added **1a** (250 mg, 0.23 mmol) and then immediately methyl iodide (0.50 mL, 7.8 mmol). The mixture was stirred for 2 days. After the usual workup, this procedure was repeated three times to give completely *N*-methylated [2]catenane **1b** in 50% yield. Mp 280–282 °C (from MeOH); IR (KBr) 1627 ($\nu_{C=O}$) cm^{-1}; ^{1}H NMR (270 MHz, DMSO-d_6, 403 K) δ 7.27 (4H, t, J = 8 Hz, isophthaloyl-5*H*), 7.18 (8H, d, J = 8 Hz, isophthaloyl-4,6*H*), 7.09 (16H, s, *p*-xylylene-*H*), 6.69 (4H, br s, isophthaloyl-2*H*), 4.37 (16H, s, *p*-xylylene-C*H*$_2$), 2.61 (24H, s, *N-Me*); FABMS (matrix: mNBA) *m*/*z* 1178 [(M + H)$^+$], 589 [(M/2 + H)$^+$]. HRMS (FAB): found *m*/*z* 1177.6534. Calcd for $C_{72}H_{73}N_8O_8$ (M + H) 1177.5551.

***Tertiary* Amine [2]Catenane (1c):** A THF solution of borane (1.0 M, 10 mL, 10 mmol) was added to **1b** (80 mg, 0.068 mmol) and the mixture was refluxed for 2 days. Water was added to quench the excess of borane and the mixture was evaporated to dryness. To the residue was added a 6 M aqueous HCl solution (M = mol dm^{-3}). After being refluxed for 6 h, the solution was made alkaline with aqueous 10% NaOH and then extracted with dichloromethane. The extract was washed with water, dried over anhydrous $MgSO_4$, and evaporated to dryness to give the crude product **1c**. Purification was performed with a recycling preparative GPC (eluent: $CHCl_3$ containing 0.02% triethylamine) to afford **1c** as a white solid in 60% yield. Mp 205–207 °C; ^{1}H NMR (270 MHz, $CDCl_3$) δ 6.98 (16H, s, *p*-xylylene-*H*), 7.0–6.8 (12H, m, *m*-xylylene-4,5,6-*H*), 5.40 (4H, br s, *m*-xylylene-2*H*), 3.43 (16H, *s*, *p*-xylylene-C*H*$_2$), 2.92 (16H, s, *m*-xylylene-C*H*$_2$), 2.05 (24H, s, *N-Me*); FABMS (matrix: mNBA) *m*/*z* 1066 [(M + H)$^+$], 533 [(M/2 + H)$^+$]. Found: C, 78.11; H, 8.00; N, 10.07%. Calcd for $C_{72}H_{88}N_8 \cdot 0.2CHCl_3$: C, 78.08; H, 8.05; N, 9.92%.

Crystallographic Data for 1c: A single crystal suitable for X-ray analysis was grown from a solution of $CHCl_3$–MeOH. Intensity data were collected on a Mac Science MXC18 diffractometer equipped with a graphite monochromator by using Cu$K\alpha$ radiation (λ = 1.54178 Å) at 190 K with the 2θ-ω scan method. Structure solution and refinements were performed by using the SIR92 program package. Crystal data for **1c** ($C_{72}H_{88}N_8$, FW = 1065.50): crystal dimensions 1.0 × 0.50 × 0.15 mm, triclinic, $P\bar{1}$, a = 10.182(1), b = 13.597(2), c = 23.078(3) Å, α = 92.73(1), β = 93.63(1), γ = 108.33(1)°, V = 3019.2(7) Å^3, Z = 2, ρ_{calcd} = 1.172 g cm^{-3}, μ = 4.931 mm^{-1}, θ_{max} = 49.65°, 9317 reflections measured, 6596 observed ($I > 1.5(\sigma(I))$), number of parameters 874, R = 0.079, R_W = 0.089, residual electron density +0.84/–0.38 e/Å^3. 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 number 153728. The details of structures have been deposited as Document No. 74007 at the Office of the Editor of Bull. Chem. Soc. Jpn.

***Tertiary* Amide Monomacrocycle (2b):** In a similar manner to that for **1b**, **2b** was obtained by repetitive *N*-methylation of the corresponding secondary amide monomacrocycle **2a** as a white solid. The **2a** which was collected from the reaction mixture of the preparation of **1a** contained cyclic and linear oligomers, and was used without purification. Mp 147–151 °C; IR (KBr) 1633 cm^{-1} ($\nu_{C=O}$) cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$, 403 K) δ 7.6–7.4(6H, m, isophthaloyl-4,5,6*H*), 7.43 (s, 2H, isophthaloyl-2*H*), 7.22 (8H, s, *p*-xylylene-*H*), 4.58 (8H, s, *p*-xylylene-C*H*$_2$), 2.82 (12H, s, *N-Me*); FABMS (matrix: mNBA) 589 [(M+H)$^+$].

***Tertiary* Amine Monomacrocycle (2c):** In a similar manner to that for **1c**, **2c** was obtained from **2b** in 55% yield. ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.83 (2H, s, *m*-xylylene-2*H*), 7.40 (8H, s, *p*-xylylene-*H*), 7.19 (2H, t, J = 8 Hz, *m*-xylylene-5*H*), 7.08 (4H, d, J = 8 Hz, *m*-xylylene-4,6*H*), 3.56 (8H, s, C*H*$_2$), 3.52 (8H, s, C*H*$_2$), 2.19 (12H, s, *N-Me*).

***Tertiary* Amide [2]Rotaxane (3b):** In a similar manner to that for **1b**, **3b** was obtained from **3a** in 58% yield. ^{1}H NMR (270 MHz, DMSO-d_6, 403 K) δ 7.6–7.1 (24H, m, Ar-*H*), 6.48 (8H, br s, Ar-*H*, axis-*p*-xylylene-*H*), 5.51 (2H, br s, isophthaloyl-2*H*), 4.49 (8H, s, macrocyclic (mc) -*p*-xylylene-C*H*$_2$), 4.35 (4H, s, axis-*p*-xylylene-C*H*$_2$), 4.33 (4H, s, axis-*p*-xylylene-C*H*$_2$), 2.74 (6H, s, axis-*N-Me*), 2.69 (6H, s, axis-*N-Me*), 2.66 (12H, s, mc-*N-Me*), 1.25 (36H, s, *t*-C_4H_9); FABMS (matrix: mNBA) *m*/*z* 1480. [(M + H)$^+$], 891 [(axis + H)$^+$]; HRMS (FAB): found *m*/*z* 1479.0364. Calcd for $C_{94}H_{110}N_8O_8$ (M$^+$) 1478.8447.

***Tertiary* Amine [2]Rotaxane (3c):** In a similar manner to that for **1c**, **3c** was obtained from **3b** in 30% yield. For the assignment of the ^{1}H NMR spectrum of **3c**, a partially deuterated **3c** (**3c**-d_{16}) was also synthesized from **3b** by the use of BD_3 (generated from $NaBD_4$ and I_2 in situ). The final assignment described below was achieved with the results of NOE experiments. ^{1}H NMR (270 MHz, $CDCl_3$, 295 K) δ 7.31 (2H, t, J = 2 Hz, endcap-Ar-*H*), 7.29 (8H, s, mc-*p*-xylylene-*H*), 7.17 (4H, d, J = 2 Hz, endcap-Ar-*H*), 7.3–7.1 (10 H, m, axis- and mc-Ar-*H*), 6.60 (4H, d, J = 8 Hz, axis-*p*-xylylene-H_{out}), 6.53 (4H, d, J = 8 Hz, axis-*p*-xylylene-H_{in}), 5.64 (2H, br, s, mc-*m*-xylylene-2*H*), 3.61 (8H, s, mc-*p*-xylylene-C*H*$_2$), 3.43 (4H, s, endcap-C*H*$_2$ (absent in the spectrum **3c**-d_{16})), 3.30 (4H, s, axis-*m*-xylylene-C*H*$_2$ (absent in the spectrum **3c**-d_{16})), 3.15 (4H, s, axis-*p*-xylylene-C*H*$_{2out}$), 3.08 (8H, s, mc-*m*-xylylene-C*H*$_2$ (absent in the spectrum **3c**-d_{16})), 3.08 (4H, s, axis-*p*-xylylene-C*H*$_{2in}$), 2.13 (12H, s, mc-*N-Me*), 2.04 (6H, s, axis-*N-Me*$_{out}$), 1.93 (6H, s, axis-*N-Me*$_{in}$), 1.34 (36H, s, *t*-C_4H_9); FABMS (matrix: mNBA) *m*/*z* 1368. [(M + H)$^+$], 836 [(axis + H)$^+$]. HRMS (FAB). found *m*/*z* 1367.9969. Calcd for $C_{94}H_{127}N_8$ (M + H$^+$) 1368.0184.

***Tertiary* Amide Axis (4b):** In a similar manner to that for **1b**, **4b** was obtained from **4a** in 75% yield. ^{1}H NMR (270 MHz, $CDCl_3$, 295 K) δ 7.6–7.2 (18H, m, Ar-*H*), 4.76 (4H, br s, benzylic-*H*), 4.51 (4H, br s, benzylic-*H*), 3.1–2.8 (12H, m, *Me*), 1.4–1.2 (36H, m, *t*-C_4H_9); FABMS (matrix: mNBA) *m*/*z* 891 [(M + H)$^+$].

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