

## Synthesis and Structure of [2]Catenated *tertiary* Octamide and Octamine

Nobuhiro Watanabe, Yoshio Furusho, Nobuhiro Kihara, Toshikazu Takata,\* Kazushi Kinbara,<sup>†</sup> and Kazuhiko Saigo<sup>†</sup>

Department of Applied Chemistry, Graduate School of Engineering, Osaka Prefecture University,  
1-1 Gakuen-cho, Sakai, Osaka 599-8531

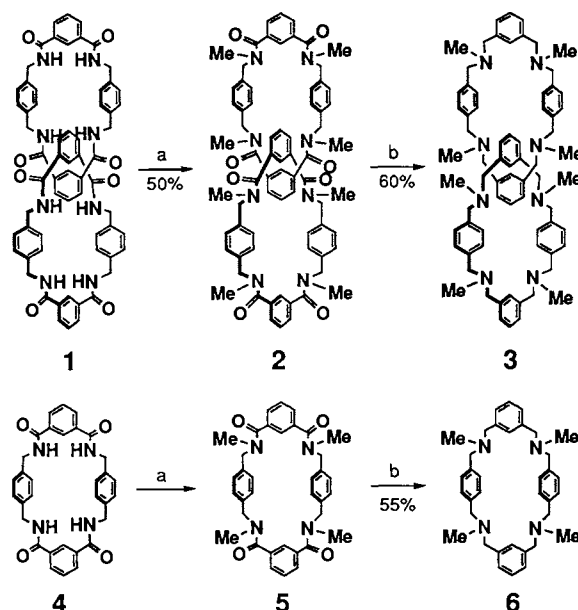
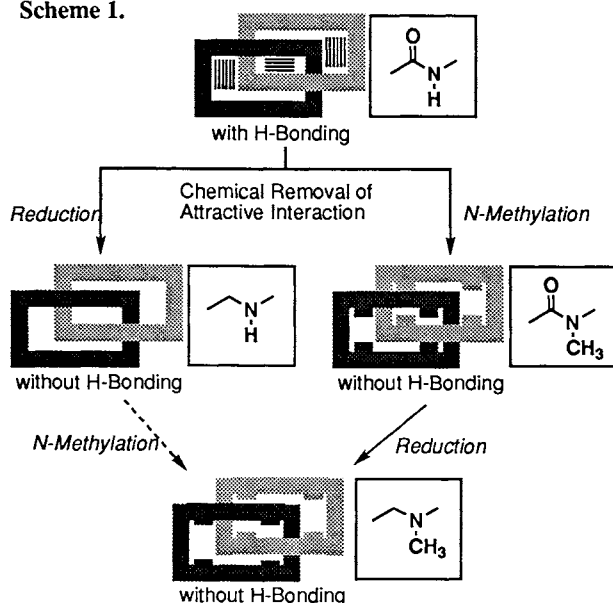
<sup>†</sup>Department of Chemistry and Biotechnology, Graduate School of Engineering, The University of Tokyo,  
7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656

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Treatment of [2]catenated *sec.* octamide (**1**) with methyl iodide under an alkaline condition gave the corresponding *N*-methylated *tert.* octamide (**2**) which was reduced to [2]catenated *tert.* octamine (**3**). The structures of **2** and **3** were studied by X-ray crystal structure and <sup>1</sup>H NMR analyses.

Mechanically interlocked molecules such as catenane and rotaxane are one of the typical supramolecular compounds with unique topological bonding and high freedom of their components.<sup>1-4</sup> The recent sophisticated supramolecular syntheses, taking an advantage of template direction of metal cation,  $\pi$ - $\pi$  stacking interaction, or hydrogen bonding, have allowed us to obtain them in a hundred milligram to a gram scale.<sup>2</sup> From a viewpoint of designing catenane- or rotaxane-based materials with novel properties, it is important to remove the attractive interactions between their components<sup>3</sup> which act as a driving force for the formation of mechanically interlocked molecules but often restrict the mobility.<sup>5</sup> To synthesize mechanically interlocked molecules with high mobility between the components, chemical removal of the template direction used in the directed synthesis should be needed, unless "statistical method" is chosen. We recently reported that borane reduction of [2]catenated *sec.* octamide (**1**)<sup>6</sup> to [2]catenated *sec.* octamine is an effective way to high mobility catenane (Scheme 1).<sup>3</sup> In this paper, we report another way to high mobility catenane along with the structural and mobile features of catenanes formed.

Scheme 1.

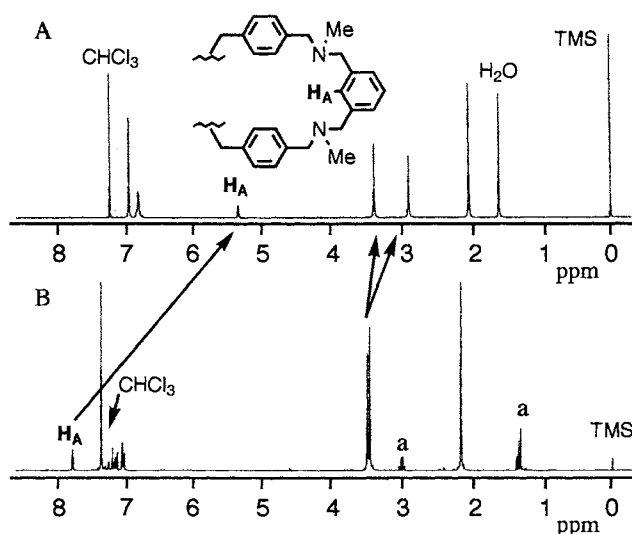


Scheme 2. (a)  $\text{CH}_3\text{I}$ ,  $\text{KOH}$  /  $\text{DMSO}$ , rt, 6 days. (b)  $\text{BH}_3$ -THF, reflux, 24 h.

Successive treatment of **1** with  $\text{CH}_3\text{I}$  /  $\text{KOH}$  in  $\text{DMSO}$  successfully caused complete *N*-methylation of the eight amide groups to afford octamethylated [2]catenane (**2**) in 50% yield.<sup>7</sup> **2** was characterized by FAB mass, IR, and <sup>1</sup>H NMR spectroscopy. Disappearance of  $\nu_{\text{N-H}}$  ( $3316\text{ cm}^{-1}$  for **1**) in the IR spectrum of **2** in addition to the characteristic mass spectral pattern unambiguously indicated that all the amide groups of **1** were *N*-methylated. <sup>1</sup>H NMR (270 MHz,  $\text{DMSO}-d_6$ , 295 K) signals of **2** were extremely broadened as compared with those of **1** at room temperature. Elevating the temperature (403 K), the signals became very sharp: the signal pattern was quite simple like **5**, but slightly different from **5** in chemical shift.

Macrocyclic tetramide **4** as the single ring model of **1** was similarly *N*-methylated to afford tetramethylated macrocycle (**5**). <sup>1</sup>H NMR (270 MHz,  $\text{DMSO}-d_6$ ) signals of **5** were similarly broadened at 295 K and became sharp at higher temperature, like the case of **2**. Thus, the signal broadening observed in **2** and **5** at room temperature can be attributed to the *s-cis* - *s-trans* isomerism of the amide groups, although it cannot be ruled out that the circumrotation of the ring components of **5** is restricted by the steric hindrance of the *N*-methyl groups.

Although the chemical removal of hydrogen bonding of **1** was successfully achieved by the repeated *N*-methylation, the enhanced mobility of the produced catenane **2** was not clearly confirmed. So, the conversion of the amide functionality of **2** to



**Figure 1.**  $^1\text{H}$  NMR spectra (270 MHz,  $\text{CDCl}_3$ , 298 K) of (A) **3** and (B) **6**. "a" denotes signals of triethylamine hydrochloride.

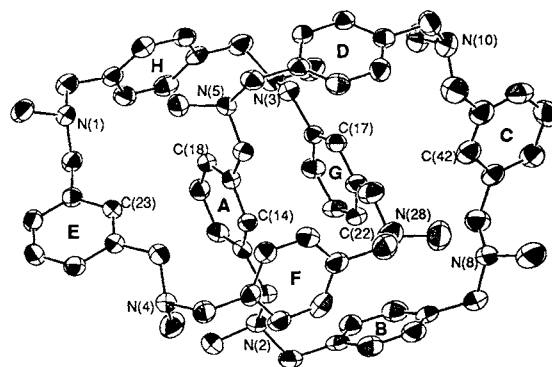
the amine functionality was carried out. The corresponding [2]catenated *tert.* octamine (**3**)<sup>8</sup> was obtained in 60% yield by borane reduction in refluxing THF, according to the procedure for **1** reported previously.<sup>3</sup> Macrocyclic tetramine (**6**) was also obtained in 55% yield by similar borane reduction of **5**.

The structure of **3** was determined by the  $^1\text{H}$  NMR, IR, and FAB mass spectrometry as well as the elemental analysis. The  $^1\text{H}$  NMR spectrum of **3** showed neither coalescence nor chemical shift change even at  $-30^\circ\text{C}$ , undoubtedly indicating the desired mobility of the components much higher than that of **1** and/or **2**. This was coincided in the NMR signal pattern as simple as that of **6** as illustrated in Figure 1.

Characteristic differences in  $^1\text{H}$  NMR between the catenane **3** and the macrocycle **6** can be seen not only in the benzyl methylene chemical shifts but also in the chemical shifts of isolated aromatic protons of their *m*-substituted phenyl moieties ( $\text{H}_\text{A}$ , Figure 1). The specially large high-field shift of the aromatic proton (from *ca.* 7.8 ppm (**3**) to *ca.* 5.3 ppm (**6**)) was eventually accounted for by an influence of  $\text{CH} - \pi$  interaction which was confirmed unequivocally by the X-ray crystal structure analysis of **3**<sup>9</sup> (Figure 2). There were six  $\text{CH} - \pi$  interactions (between aromatic CH and benzene ring)<sup>10</sup> and one  $\pi - \pi$  interaction (between two benzene rings: A and G) in crystal state of **3**. All  $\text{H}_\text{A}$  protons participate  $\text{CH} - \pi$  interaction. Thus, the big high-field shift of  $\text{H}_\text{A}$  mentioned above are attributed to  $\text{CH} - \pi$  interaction working also in the solution.

Thus, we could demonstrate in this paper that *N*-methylation followed by reduction of [2]catenated *sec.* octamide (**1**) having strong hydrogen bonding between the components to [2]catenated *tert.* octamine (**3**) can be another effective route to catenane with high mobility.

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**Figure 2.** ORTEP drawing of **3** by X-ray crystal structure analysis. Hydrogen atoms are omitted for clarity.

Science Foundation which is greatly acknowledged.

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- 7 Preparation of **2**. To a suspension of KOH (400 mg, 73 mmol) in DMSO (4.0 mL) was added **1** (250 mg, 0.23 mmol) and then immediately methyl iodide (0.50 mL, 7.8 mmol). The mixture was stirred for 2 days. After usual work-up, this procedure was repeated three times to give completely *N*-methylated [2]catenane (**2**) in 50% yield. White solid, mp  $280-282^\circ\text{C}$  (from methanol); IR (KBr)  $\nu_{\text{C=O}}$  1627  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (270 MHz, DMSO- $d_6$ , 403 K)  $\delta$  7.27 (t,  $J = 8$  Hz, 4H, isophthaloyl 1Hx4), 7.18 (d,  $J = 8$  Hz, 8H, isophthaloyl 2Hx4), 7.09 (s, 16H, *p*-xylylene), 6.69 (br s, 4H, isophthaloyl 1Hx4), 4.37 (s, 16H, benzyl), 2.61 (s, 24H, *N*-methyl); FAB-MS (matrix: *m*-nitrobenzyl alcohol)  $m/z$  1178  $[(\text{M}+\text{H})^+]$ , 589  $[(\text{M}/2+\text{H})^+]$ .
- 8 Physical and spectral of **3**: mp  $205-207^\circ\text{C}$  (from  $\text{CHCl}_3\text{-MeOH}$ );  $^1\text{H}$  NMR (270 MHz,  $\text{CDCl}_3$ )  $\delta$  6.98 (s, 16H, *p*-xylylene 4Hx4), 6.80–7.00 (m, 12H, isophthaloyl 3Hx4), 5.40 (br.s, 4H, isophthaloyl 1Hx4), 3.43 (s, 16H, benzyl of xylylene), 2.92 (s, 16H, benzyl of isophthaloyl), 2.05 (s, 24H, *N*-methyl); FAB-MS (matrix: *m*-nitrobenzyl alcohol)  $m/z$  1066  $[(\text{M}+\text{H})^+]$ .
- 9 Crystal data of **3**:  $\text{C}_{72}\text{H}_{88}\text{N}_8$ ,  $M_r = 1065.50$ , Triclinic,  $P\bar{1}$ ,  $a = 10.182$  (1),  $b = 13.597$  (2),  $c = 23.078$  (3) Å,  $\alpha = 92.73$  (1),  $\beta = 93.63$  (1),  $\gamma = 108.33$  (1),  $V = 3019.2$  (7) Å<sup>3</sup>,  $Z = 2$ ,  $D_c = 1.172$  Mg  $\text{m}^{-3}$ ,  $R = 0.079$  and  $wR = 0.089$  for 6596 observed reflections ( $I > 1.50 \sigma(I)$ ).
- 10 The  $\text{CH} - \pi$  interaction between H of aromatic carbon and benzene ring was observed between C(14)-F, C(17)-D, C(18)-H, C(22)-B, C(23)-A, and C(42)-C (see, Figure 2).