A Catenated Cyclic Octamine: A Noncovalently Bonded Molecular System without Attractive Interaction between the Two Units

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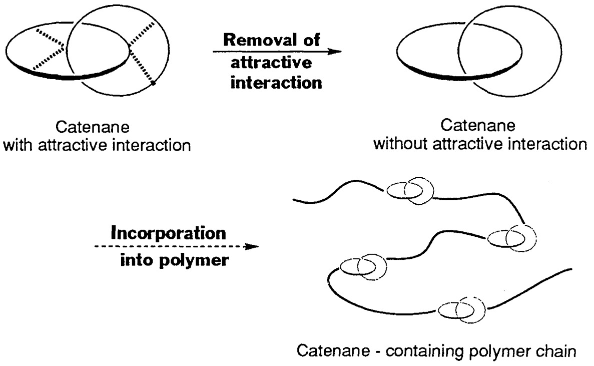
A novel [2]catenane consisted of two cyclic tetramine units (**6**) was prepared and characterized in terms of mobility of the units. The preparation of **6** was performed by reduction of the corresponding cyclic octamide-type [2]catenane (**3**) with borane. Varying temperature NMR study indicated that the units of **6** actually move or rotate quite freely unlike those of **3**, evidently suggesting a noncovalently bonded molecule without attractive interaction[1] between the two units.

Application of molecular architecture in supramolecular chemistry to syntheses of molecules and materials containing noncovalently bonded systems such as catenanes and rotaxanes is of current interest in new materials development.[2, 3] Cyclic units of catenanes as noncovalently bonded molecules have extremely high freedom in motion in comparison with covalently bonded molecules, especially when some interaction (mainly attractive interaction) between them is removed. If such topologically bonded systems with high mobility are introduced into polymer backbone,[2] the polymers endowed with the highly mobile units should be quite interesting particularly from the viewpoint of their potential rheological and mechanical properties.

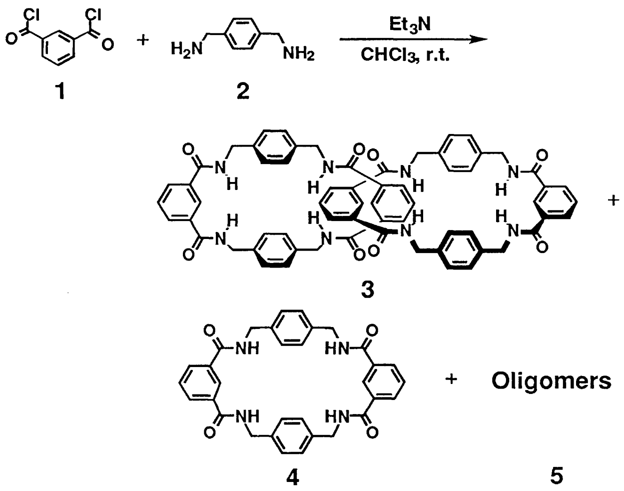
Scheme 1



Among several conditions required to reflect most effectively the characteristics of the [2]catenane units on polymer properties, a most important thing is that the sufficiently high mobility of the two rings is secured. To accomplish it, interactions such as attractive interaction worked between the two rings must be removed. Although a variety of catenanes has recently been synthesized,[3] a limited number of catenanes has been reported which satisfy a few conditions essential for the above mentioned application, such as high stability, simple structure, and easy and high yield preparation. We have chosen the Leigh's catenane **3**[4,5] as a precursor of the interaction-free catenane, which can be readily derived from commercially available starting materials in a relatively high yield. This paper discloses the preliminary results on the successful synthesis and characterization of a [2]catenanated cyclic octamine **6** having little interaction between the two rings.

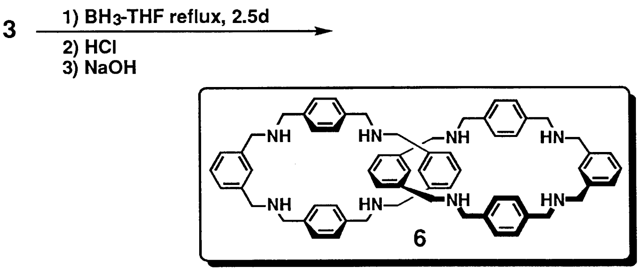
Cyclic octamide-type [2]catenane **3** was prepared in 20% yield by the reaction of isophthaloyl chloride with *p*-xylylenediamine in amylene-stabilized chloroform at room temperature, according to the Leigh's report.[4] Besides **3**, formation of a mixture of linear and cyclic oligomers (**5**)[6] including monocyclic tetramide (**4**)[7] was confirmed. The structures of **3**[8] and **4**[9] were determined by the IR, NMR, and FAB-MS spectra.

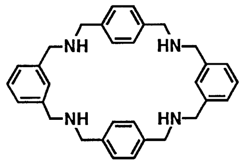
Scheme 2



Reduction of **3** (213 mg, 0.2 mmol) was carried out with excess borane (BH$_3$-THF solution, 18 mmol) for 2.5 d in refluxing THF. The reaction was terminated by addition of water at 0 °C to decompose excess borane, after no IR change at the carbonyl region was observed. Hydrolysis by addition of 6M HCl (30 mL) to the residual white solid obtained by evaporation diminished IR B-H absorption (2541 and 2468 cm^{-1}) of the reaction mixture completely. Treatment of the mixture with excess alkali (NaOH pellet, up to pH > 13) under cooling yielded white solid. The solid material was subjected to benzene extraction to afford 185 mg of **6** as white solid (77% yield).[10]

The structure of **6** was determined by the IR, NMR and FAB-MS spectra which were completely consistent with the proposed structure.[11] The FAB-MS result unambiguously showed that **6** still has the [2]catenane skeleton, while the IR spectrum revealed the disappearance of the amide carbonyl group. The ^{1}H NMR spectrum well supported the structure of **6**, in which N-H signal appeared at ca. 1.6 ppm corresponding to *free* amine N-H region. This result suggested that the N-H protons of **6** do not participate in some interaction like hydrogen bonding between the two rings, in contrast to that of **3**, indicating that the two rings of **6** can freely move or rotate. In the ^{1}H NMR spectra,





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two kinds of benzylic proton signals of monocyclic tetramine 7^{12} prepared for comparison appeared as singlet at 3.70 ppm, while those of **6** gave two singlets at 3.50 and 3.34 ppm, respectively.

To confirm the highly enhanced mobility of **6** compared with **3**, ^{1}H NMR spectra of **3**, **6**, and **7** were compared at varying temperatures. **3** showed its coalescence temperature around 0 °C (solv. CDCl$_3$: DMSO = 1 : 1, 270 MHz). By the NMR measurements at different magnetic fields (270 and 500 MHz[13]), activation parameters could be calculated as shown in Figure 1 which suggested that the rings of **3** can only slowly rotate in a rate at 400 Hz at 0 °C. In contrast to it, no coalescence could be observed down to -60 °C in the case of **6** (solv. CDCl$_3$, 270 MHz). In the ^{1}H NMR of **6** at -60 °C, three kinds of aromatic protons of the *m*-xylylene moiety separately appeared at a higher magnetic field (7.15 ~ 6.45 ppm), although benzylic and amine proton signals were only slightly shifted. However, no such shift was observed in the case of **7** under the same conditions. Therefore, this phenomenon is considered as characteristic of the catenane structure, although the reason is not clear at present time.

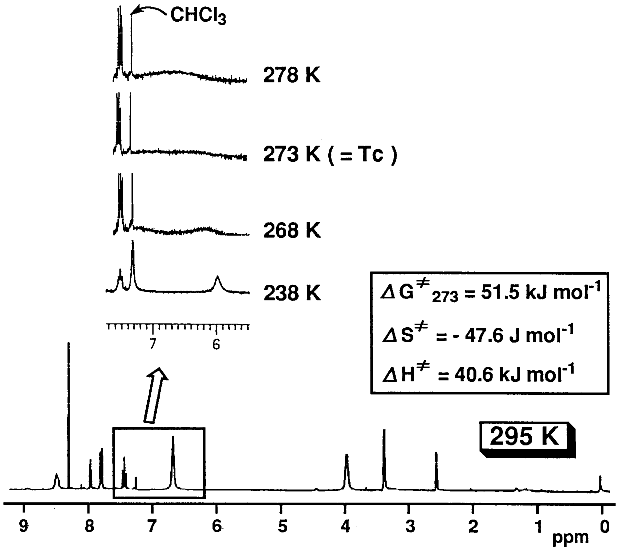

Figure 1. Varying temperature ^{1}H NMR study of **3** [DMSO:CDCl$_3$ = 1 : 1 (v/v), 270 MHz]. Activation parameters were calculated from the results of the NMR measurements at both 270 and 500 MHz.

Thus, this paper has presented a new [2]catenane without attractive interaction between the two ring units. The results of this work would provide some fundamental bases of novel polymer materials being able to make the most of the catenane unit incorporated. Further study including application of **6** to novel host, star molecule nuclei, and so on is under active progress.

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References and Notes

1 The term "without attractive interaction" used in this paper means "without attractive interaction enough to hinder the circumrotation of the two rings", but not "without any attractive interaction including van der Waals interaction".

2 J.-L. Weidmann, J.-M. Kern, J.-P. Sauvage, Y. Geerts, D. Muscat, and K. Müllen, *J. Chem. Soc., Chem. Comm.*, **1996**, 1243 and references cited therein; Y. Geerts, D. Muscat, and K. Müllen, *Macromol. Chem. Phys.*, **196**, 3425 (1995); J. A. Preece and J.F. Stoddart, *Macromol. Symp.*, **98**, 527 (1995).

3 A review: D.B. Amabilino and J.F. Stoddart, *Chem. Rev.*, **95**, 2725 (1995).

4 A.G. Johnston, D.A. Leigh, R.J. Prichard, and M.D. Deegan, *Angew. Chem. Int. Ed. Engl.*, **34**, 1209 (1995).

5 A.G. Johnston, D.A. Leigh, R.J. Prichard, L. Nezhat, J.P. Smart, and M.D. Deegan, *Angew. Chem. Int. Ed. Engl.*, **34**, 1912 (1995).

6 The oligomeric mixture (**5**) contained monocyclic octamide and linear polyamide.

7 It had been impossible to obtain pure cyclic tetramine **4**, however, recently Leigh *et al.* have found unique preparation of pure **4** via rotaxane: A.G. Johnston, D.A. Leigh, A. Murphy, J.P. Smart, and M.D. Deegan, *J. Am. Chem. Soc.*, **118**, 10662 (1996). In this experiment, we have obtained **4** as a mixture containing 27% of **5**.

8 **3**: IR (KBr) 3316, 3062, 1640 cm^{-1}; ^{1}H NMR (DMSO, 270 MHz) 8.31 (s, 8H, CONH), 7.97 (s, 4H, isophthaloyl 2-H), 7.80 (dd, 8H, isophthaloyl 4,6-H, $J_{4,5}$=7.0 Hz, $J_{2,4}$=1.0 Hz), 7.42 (t, 4H, isophthaloyl 5-H, $J_{5,4}$=$J_{5,6}$=8.0 Hz), 6.66 (brs, 16H, xylylene), 3.92 (brs, 16H, benzyl CH$_2$); FAB-MS (matrix: *m*-nitrobenzyl alcohol) m/z 1065 [(M+H)$^+$].

9 **4**: IR (KBr) 3298, 3062, 1644 cm^{-1}; ^{1}H NMR (DMSO, 270 MHz) 9.14 (t, 4H, CONH, J=4.6 Hz), 8.38 (s, 2H, isophthaloyl 2-H), 8.02 (dd, 4H, isophthaloyl 4,6-H, $J_{4,5}$=8.0 Hz, $J_{2,4}$=2.0 Hz), 7.55 (t, 2H, isophthaloyl 5-H, $J_{5,4}$=$J_{5,6}$=8.0 Hz), 7.28 (s, 8H, xylylene), 4.45 (d, 8H, benzyl CH$_2$, J=5.5 Hz); FAB-MS (matrix: *m*-nitrobenzyl alcohol) m/z 533 [(M+H)$^+$].

10 A variety of chromatographic purifications on silica gel, alumina, and polystyrene gel was unsuccessful probably due to the strong adsorption of **6** to such stationary phases under any conditions. Only purification could be performed with octahydrochloride of **6** (obtained as white needle in 97% crude yield). Namely, purification by column chromatography on Sephadex LH-20 using chloroform-methanol mixed solvent as eluent resulted in a satisfactory isolation, although completely pure **6** has not been obtained yet.

11 **6**: IR (KBr) 3422 cm^{-1}; ^{1}H NMR (CDCl$_3$, 270 MHz) 7.29 ~ 6.87 (m, 32H, aromatic), 3.50 (sharp s, 16H, benzyl CH$_2$), 3.34 (s, 16H, benzyl CH$_2$), 1.56 (brs, 8H, NH): Two benzylic proton signals were not distinguished (methylenes attached to *m*-substituted or *p*-substituted benzene ring); FAB-MS (matrix: glycerine) m/z 953 [(M+H)$^+$].

12 The monocyclic tetramine **7** was obtained from **4** by a similar method of **6** from **3** (41% yield). The structure was spectroscopically identified with **7** previously obtained by independent preparation: D. Chen and A.E. Martell, *Tetrahedron*, **47**, 6895 (1991). **7**: IR (KBr) 3304 cm-1; ^{1}H NMR (CDCl$_3$) 7.26 - 7.14 (m, 16H, ArH), 3.70 (sharp s, 16H, benzyl CH$_2$), 2.08 (brs, 4H, NH).

13 The coalescence temperature at 500 MHz was 283 K.