Hexagonal Columnar Superstructure Generated by Compact Liquid-crystalline Molecules Possessing Disk-shape, C_3-Symmetry, and Ionic Bonding Sites

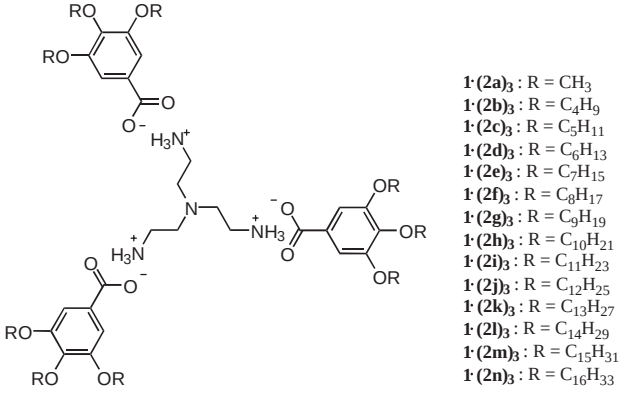
Masaki Katoh,[1] Satoshi Uehara,[2] Shigeo Kohmoto,[2] and Keiki Kishikawa*[2]
[1]*Quality Materials Science, Graduate School of Science and Technology, Chiba University, 1-33 Yayoi-cho, Inage-ku, Chiba 263-8522*
[2]*Department of Applied Chemistry and Biotechnology, Faculty of Engineering, Chiba University, 1-33 Yayoi-cho, Inage-ku, Chiba 263-8522*

(Received January 16, 2006; CL-060058; E-mail: kishikawa@faculty.chiba-u.jp)

Small C_3-symmetric supramolecules, 1:3 complexes of tri(2-aminoethyl)amine (**1**) and 3,4,5-trialkoxybenzoic acid (**2c**–**2n**, R = $(CH_2)_{n-1}CH_3$, n = 5–16) generated a stable hexagonal columnar phase. The phase behaviors, stoichiometry, supramolecular structure, and superstructure were investigated.

Recently, hexagonal columnar superstructures generated by disklike molecules are often utilized for realization of highly functionalized materials.[1] Therefore, simple and novel methods for the creation of them by disklike molecules are extremely desired. However, those molecules have become larger and more complex to realize their high functionality. Owing to their complexity, it is very difficult to understand the essential intermolecular interactions necessary for their aggregations. We strongly believe that the studies on small, simple, and symmetric mesogens are very important to understand the minimum interactions required for construction of the superstructures. Based on this concept, we designed and synthesized one of the simplest supramolecular liquid-crystalline molecules (**1**·(**2c**)$_3$–**1**·(**2n**)$_3$) which generated stable hexagonal columnar superstructures, and their properties were investigated. In our design, 1) a disk-shape, 2) C_3-symmetry, and, 3) three ionic bonding sites were introduced into a small molecule to generate a hexagonal columnar superstructure. It was expected that the C_3-symmetric disk-shaped molecules were piled up by rotating 60 degrees to generate a rigid columnar molecular aggregate. The three ionic parts could be arranged in a C_3-symmetric manner, which acted as a strong attractive force between the adjacent disklike molecules in the column.

The supramolecular compounds (**1**·(**2a**)$_3$–**1**·(**2n**)$_3$) (Scheme 1) were synthesized by concentration of a 1:3 mixture of tri(2-aminoethyl)amine (**1**) and the corresponding 3,4,5-trialkoxybenzoic acid (**2a**–**2n**)[2] in chloroform, respectively.



1·(**2a**)$_3$: R = CH_3
1·(**2b**)$_3$: R = C_4H_9
1·(**2c**)$_3$: R = C_5H_{11}
1·(**2d**)$_3$: R = C_6H_{13}
1·(**2e**)$_3$: R = C_7H_{15}
1·(**2f**)$_3$: R = C_8H_{17}
1·(**2g**)$_3$: R = C_9H_{19}
1·(**2h**)$_3$: R = $C_{10}H_{21}$
1·(**2i**)$_3$: R = $C_{11}H_{23}$
1·(**2j**)$_3$: R = $C_{12}H_{25}$
1·(**2k**)$_3$: R = $C_{13}H_{27}$
1·(**2l**)$_3$: R = $C_{14}H_{29}$
1·(**2m**)$_3$: R = $C_{15}H_{31}$
1·(**2n**)$_3$: R = $C_{16}H_{33}$

Scheme 1. Structure of **1**·(**2**)$_3$.

The phase identification was performed by using a polarized optical microscope (POM) equipped with a hot-stage. Although complexes **1**·(**2a**)$_3$ and **1**·(**2b**)$_3$ did not show any liquid-crystal phase, the other complexes (**1**·(**2c**)$_3$–**1**·(**2n**)$_3$) exhibited enantiotropic hexagonal columnar phases. These phase behaviors were plotted against the number (n) of carbons in the alkyl chain (Figure 1a). Their clearing points indicated an odd–even effect[3] from n = 6 to 14. The clearing point of the complexes with an odd number is higher than those with its next (even) numbers. The microphotograph is shown in Figure 1b and it is the typical texture of hexagonal columnar liquid-crystalline phase.[4]

To confirm the most suitable molar ratio (**1**:**2** = 1:3), the miscibility experiment was performed on the mixture of **1** and

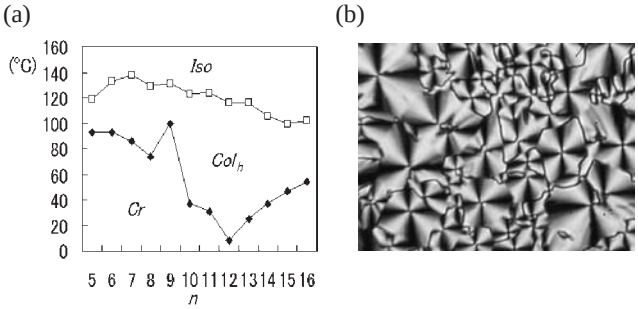


Figure 1. (a) Phase behaviors of **1**·(**2c**)$_3$–**1**·(**2n**)$_3$ plotted against n (*Iso*: isotropic phase, Col_h: hexagonal columnar phase, and *Cr*: crystal phase).[5] (b) The polarized optical microphotograph of **1**·(**2c**)$_3$ (114 °C, ×200).

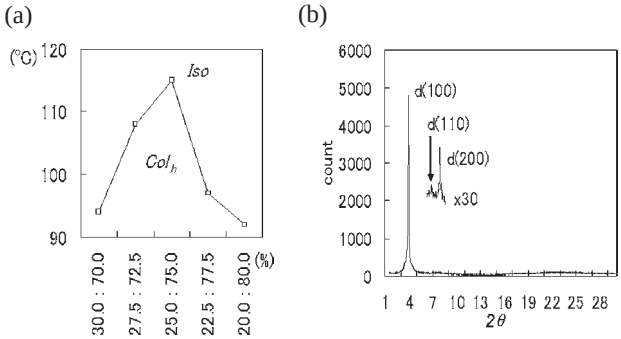


Figure 2. (a) Plots of the isotropic–liquid crystal transition temperature on cooling (5 °C/min) against the molar ratio of **1** and **2c** (*Iso*: isotropic phase, Col_h: hexagonal columnar phase). (b) XRD chart of **1**·(**2c**)$_3$ (100 °C).

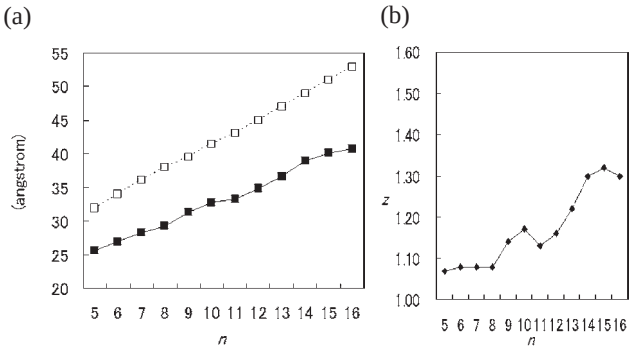


Figure 3. (a) The diameters of **1**·(**2**)$_3$ in molecular modeling (open square) and the column diameters (a, closed square) were plotted against n.[5] (b) The z values of the hexagonal columnar phases were plotted against the number n.[5]

2c (Figure 2a). The mixtures of **1** and **2c** were prepared with the molar ratio from 30:70 to 20:80 stepped by 2.5 mol %. The mixtures showed the hexagonal columnar phase. At the ratio of 75.0:25.0, the highest transition temperature was observed. From the plots, stability of the liquid-crystal phase was very sensitive to the ratio of the mixture, and the ratio of **1**:**2** = 1:3 was the most suitable for the liquid-crystal phase.

Triazine and melamine were applied as the core compounds. However, the 1:3 mixtures did not exhibit any liquid-crystal phase and macroscopic segregation was observed.

X-ray diffraction (XRD) of **1**·(**2c**)$_3$ was performed (Figure 2b).[5] It gave a sharp d_{100} peak. The d_{110} and d_{200} peaks were also obtained as small peaks. The XRD indicated that the phase had a disordered hexagonal columnar superstructure.

The d_{100} peaks of **1**·(**2**)$_3$ in this series except **1**·(**2a**)$_3$ and **1**·(**2b**)$_3$ were measured by XRD. In Figure 3a, the diameter a ($=2 \times d_{100}/\sqrt{3}$) is plotted against the number of carbons in the alkyl chain (closed squares) and the diameters obtained by molecular modeling are also plotted (open squares). The short diameters were explained by intercolumnar interdigitation of the alkyl chains. It was assumed that the intracolumnar spacing was smaller than the averaged distance of the molten alkyl chains (ca. 4.5 Å), because triaminoethylamine molecules pile up by avoiding the intermolecular steric repulsion. Based on $c = 4.0$ Å, the z values (the number of disk-shaped complexes in the unit cell) are about 1 ($z = 1.07$–1.32) (Figure 3b). The estimated value 4.0 Å was assumed to be suitable as the intracolumnar spacing from the z values (ca. 1) of the small complexes ($n = 5$–8). It strongly suggested that the 1:3 complex was packed as one disk unit in the column. The increase in the z value originated in the difference of densities between aromatic and aliphatic parts. The complex possessing longer chains had a larger z value. However, the expected dimeric periodicity could not be observed in their XRD charts. This suggested that the positional relation between the adjacent molecules in the column was not rigid.

The model of **1**·(**2c**)$_3$ is shown in Figure 4a. The complexes have a disk shape, and have a space between the two trialkoxybenzoates. The self-organization is depicted in Figure 4b. The 1:3 mixtures of **1** and **2** (**A**) generate the disk-shaped complexes (**B**). They pile up by rotating about 60 degrees around the central axis of the column (**C**) and the columns are organized into the hexagonal columnar superstructure (**D**). The alkyl chains interdigitate between the columns or turn back to fill the space. From the models, the complexes with the longer chains ($n > 9$) had steric repulsion between the adjacent trialkoxybenzoate. This might be the reason that the z values are constant in the cases of $n = 5$–8 and increased from $n = 9$.

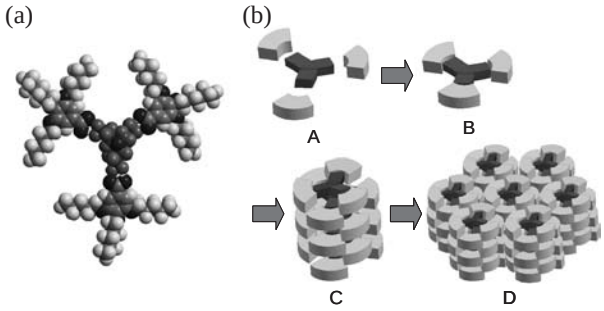


Figure 4. (a) The molecular model of **1**·(**2c**)$_3$ (R = n-C_5H_{11}). (b) The schematic representation of self-organization of **1** and **2**.

We demonstrated that the small and simple C_3-symmetric supramolecules consisting of **1** and **2** with ratio of 1:3 generated the stable columnar phases. These simple molecules indicated the existence of several effects, such as an odd–even effect, highly amine–acid ratio dependent phase stability, effect of the chain length on the z value, and steric repulsion between the acid components. Further study on the effect of the molecular structures and the molar ratio is now in progress.

This work was supported by Science Foundation and the Ministry of Education, Culture, Sports, Science and Technology, Grant-in-Aid for Scientific Research (B), 2003, No. 15350108 and Exploratory Research, 2004, No. 16655090.

References and Notes

1 N. Steinke, W. Frey, A. Baro, S. Laschat, C. Drees, M. Nimtz, C. Hägele, F. Giesselmann, *Chem.—Eur. J.* **2006**, *12*, 1026; A. Fechtenkötter, K. Saalwächter, M. A. Harbison, K. Müllen, H. W. Spiess, *Angew. Chem., Int. Ed.* **2005**, *44*, 4739; A. Grafe D. Janietz, T. Frese, J. H. Wendorff, *Chem. Mater.* **2005**, *17*, 4979; Y. Kamikawa, M. Nishii, T. Kato, *Chem.—Eur. J.* **2004**, *10*, 5942; Y. Ishida, S. Amano, K. Saigo, *Chem. Commun.* **2003**, 2338; V. Percec, M. N. Holerca, S. Uchida, W.-D. Cho, G. Ungar, Y. Lee, D. J. P. Yeardley, *Chem.—Eur. J.* **2002**, *8*, 1106; G. Ungar, V. Percec, M. N. Holerca, G. Johansson, J. A. Heck, *Chem.—Eur. J.* **2000**, *6*, 1258.

2 A. G. Serrette, C. K. Lai, T. M. Swager, *Chem. Mater.* **1994**, *6*, 2252.

3 *Liquid Crystals*, 2nd ed., ed. by S. Chandrasekhar, Cambridge University Press, Cambridge, U.K., **1992**; K.-U. Jeong, S. Jin, J. J. Ge, B. S. Knapp, M. J. Graham, J. Ruan, M. Guo, H. Xiong, F. W. Harris, S. Z. D. Cheng, *Chem. Mater.* **2005**, *17*, 2852; K. Moriya, H. Mizusaki, M. Kato, T. Suzuki, S. Yano, M. Kajiwara, K. Tashiro, *Chem. Mater.* **1997**, *9*, 255.

4 *Smectic and Columnar Liquid Crystals*, ed. by P. Oswald, P. Pieranski, CRC Press, Boca Raton, **2006**; *Textures of Liquid Crystals*, ed. by I. Dierking, Wiley-VCH GmbH & Co., Weinheim, **2003**, p. 207, Plate 107; C. Destrade, P. Foucher, H. Gasparoux, H. T. Nguyen, A. M. Levelut, J. Malthête, *Mol. Cryst. Liq. Cryst.* **1984**, *106*, 121.

5 See the Supporting Information.

Published on the web (Advance View) February 18, 2006; DOI 10.1246/cl.2006.322