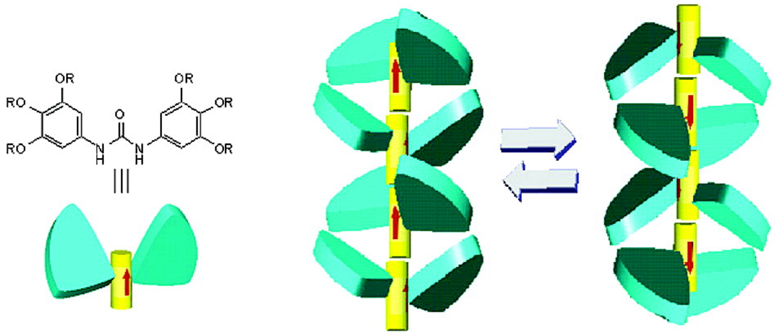
Article

A Ferroelectrically Switchable Columnar Liquid Crystal Phase with Achiral Molecules: Superstructures and Properties of Liquid Crystalline Ureas

Keiki Kishikawa, Shoichiro Nakahara, Yohei Nishikawa, Shigeo Kohmoto, and Makoto Yamamoto

J. Am. Chem. Soc., **2005**, 127 (8), 2565-2571• DOI: 10.1021/ja046100c • Publication Date (Web): 05 February 2005



Journal of the American Chemical Society is published by the American Chemical Society. 1155 Sixteenth Street N.W., Washington, DC 20036

J|A|C|S
ARTICLES

A Ferroelectrically Switchable Columnar Liquid Crystal Phase with Achiral Molecules: Superstructures and Properties of Liquid Crystalline Ureas

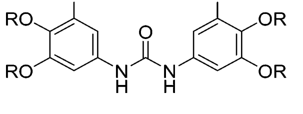
Keiki Kishikawa,* Shoichiro Nakahara, Yohei Nishikawa, Shigeo Kohmoto, and Makoto Yamamoto

Contribution from the Department of Applied Chemistry and Biotechnology, Faculty of Engineering, Chiba University, 1-33 Yayoi-cho, Inage-ku, Chiba 263-8522, Japan

Received July 1, 2004; Revised Manuscript Received December 27, 2004; E-mail: kishikawa@faculty.chiba-u.jp

Abstract: Novel columnar liquid crystalline compounds *N*,*N*′-bis(3,4,5-trialkoxylphenyl)ureas **1a**−**c** (R = *n*-C_8H_{17}, *n*-$C_{12}H_{25}$, and *n*-$C_{16}H_{33}$) were synthesized, and their phase transitions were measured by differential scanning calorimetery. The superstructures were investigated by X-ray diffraction, polarized light optical microscopy, and IR spectroscopy. The compounds exhibited both rectangular and hexagonal columnar phases in which the urea molecules in each column were stacked in one direction with strong hydrogen bonds. To confirm the ferroelectric switching, optoelectronic experiments were carried out, and the hexagonal columnar phases of **1b** and **1c** gave a sharp peak of spontaneous polarization in response to an applied triangular wave electric field (0.1−18 Hz). This is the first example of ferroelectrically switchable columnar liquid crystal phases generated by achiral molecules.

Ferroelectric liquid crystals (FLCs) are polar fluid and of great interest in the fields of physics, physical chemistry, materials chemistry, and optoelectronics.[1,2] In general, FLC phases are generated by chiral molecules, and introduction of chirality had been thought to be essential in both rodlike[2] and disklike molecules.[3] In 1996, an FLC phase generated by achiral banana-shaped molecules[4] was found by Niori et al., and scientists the world over have been searching for a new type of achiral liquid crystalline molecules for an FLC generation.[5] After the discovery, several attempts were also made using bowlic,[6] conical,[7] and badminton-shuttlecock[8] shaped molecules to find the other type of FLC phases in the highly ordered phases, columnar phases. Those molecules in mesophases generate one-directional stacking in the columns. However, the adjacent columns are aligned in an antiparallel arrangement to cancel out the macroscopic dipoles of the columns, which suppresses the ferroelectric ordering in bulk.[9] Thus, realization of FLC phases without chirality is a tough scientific challenge even in these days. Although switching behaviors were observed in columnar phases of achiral vanadyl liquid crystalline complexes, they concluded that the switching probably originated in the ionic/charges relaxations, not in the polar switching.[10] Though a switching behavior was also reported in a benzene derivative possessing three amide and three alkyne substituents, the polar structure was not maintained after removal of the applied electric field, and current response peaks were not reported.[11] In this article, we report the first example of ferroelectrically switchable fluid columnar liquid crystalline compounds generated by achiral molecules. The current response peaks that indicated an energy barrier between two polar structures were observed. In this study, the word “ferroelectric” was used as “polar switchable”.



1a: R = *n*-C_8H_{17}
1b: R = *n*-$C_{12}H_{25}$
1c: R = *n*-$C_{16}H_{33}$

To achieve ferroelectric columnar phases, stabilization of the one-directional stacking of molecules in the column and reduction of the intercolumnar dipole−dipole interaction are

---

(1) Hall, A. W.; Hollingshurst, J.; Goodby, J. W. In *Handbook of Liquid Crystal Research*; Collings, P. J., Patel, J., Eds.; Oxford University Press: New York 1997; Chapter 2.

(2) Kelly, S. M.; Lagerwall, S. T.; Miyachi, K.; Fukuda, A. In *Handbook of Liquid Crystals*; Demus, D., Goodby, J., Gray, G. W., Spiess, H.-W., Vill, V., Eds.; Wiley-VCH: New York, 1998; Vol. 2B, Chapter 6.

(3) Chandrasekhar, S. In *Handbook of Liquid Crystals*; Demus, D., Goodby, J., Gray, G. W., Spiess, H.-W., Vill, V., Eds.; Wiley-VCH: New York, 1998; Vol. 2B, Chapter 8.

(4) Niori, T.; Sekine, F.; Watanabe, J.; Furukawa, T.; Takezoe, H. *J. Mater. Chem.* **1996**, *6*, 1231.

(5) (a) Link, D. R.; Natale, G.; Shao, R.; Maclennan, J. E.; Korblova, N. A.; Walba, D. M. *Science* **1997**, *278*, 1924. (b) Heppke, G.; Moro, D. *Science* **1998**, *279*, 1872. (c) Pelzl, G.; Diele, S.; Weissflog, W. *Adv. Mater.* **1999**, *11*, 707. (d) Shen, D.; Pegenau, A.; Diele, S.; Wirth, I.; Tschierske, C. *J. Am. Chem. Soc.* **2000**, *122*, 1593. (e) Walba, D. M.; Körblava, E.; Shao, R.; Maclennan, J. E.; Link, D. R.; Glaser, M. A.; Clark, N. A. *Science* **2000**, *288*, 2181.

(6) (a) Lei, L. *Mol. Cryst. Liq. Cryst.* **1983**, *91*, 77. (b) Malthete, J.; Collet, A. *J. Am. Chem. Soc.* **1987**, *109*, 7544. (c) Jákli, A.; Saupe, A. *Liq. Cryst.* **1997**, *22*, 309.

(7) (a) Xu, B.; Swager, T. M. *J. Am. Chem. Soc.* **1993**, *115*, 1159. (b) Serrette, A. G.; Swager, T. M. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 2342. (c) Xu, B.; Swager, T. M. *J. Am. Chem. Soc.* **1995**, *117*, 5011.

(8) Badminton-shuttle cock: (a) Sawamura, M.; Kawai, K.; Matsuo, Y.; Kanie, K.; Kato, T.; Nakamura, E. *Nature* **2002**, *419*, 702. (b) Matsuo, Y.; Muramatsu, A.; Hamasaki, R.; Mizoshita, N.; Kato, T.; Nakamura, E. *J. Am. Chem. Soc.* **2004**, *126*, 432.

(9) Tschierske, C. *Science* **2002**, *419*, 681.

(10) (a) Kilian, D.; Knawby, D.; Athanassopoulou, M. A.; Trzaska, S. T.; Swager, T. M.; Wrobel, S.; Haase, W. *Liq. Cryst.* **2000**, *27*, 509. (b) Haase, W.; Kilian, D.; Athanassopoulou, M. A.; Knawby, D.; Swager, T. M.; Wróbel, S. *Liq. Cryst.* **2002**, *29*, 133.

(11) Bushey, M. L.; Nguyen, T.-Q.; Nuckolls, C. *J. Am. Chem. Soc.* **2003**, *125*, 8264.

10.1021/ja046100c CCC: $30.25 © 2005 American Chemical Society

Scheme 1. Synthesis of **1** from 3,4,5-Trialkoxyaniline (**2**)

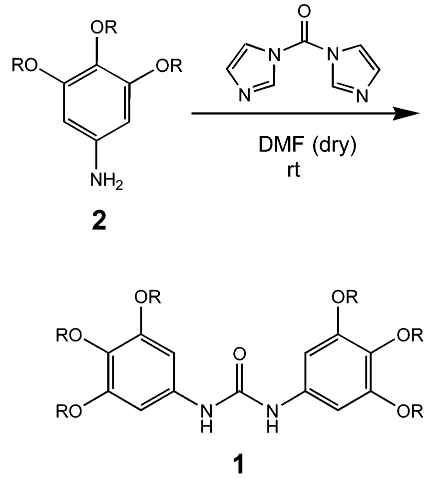


Table 1. Phase Behavior of **1a**−**c**[a]

Compound	Phase behavior
1a	$\mathbf{Cr} \underset{160\ (-0.2)}{\overset{161\ (0.4)}{\rightleftarrows}} \mathbf{Col_r} \underset{163\ (-2.6)}{\overset{167\ (2.7)}{\rightleftarrows}} \mathbf{Col_h} \underset{183\ (-2.2)}{\overset{188\ (2.4)}{\rightleftarrows}} \mathbf{I}$
1b	$\mathbf{Cr} \underset{92\ (-11.0)}{\overset{110\ (14.0)}{\rightleftarrows}} \mathbf{Col_r} \underset{147\ (-0.5)}{\overset{149\ (0.7)}{\rightleftarrows}} \mathbf{Col_h} \underset{174\ (-3.0)}{\overset{178\ (3.5)}{\rightleftarrows}} \mathbf{I}$
1c	$\mathbf{Cr} \xrightarrow{80\ (h_1)^b} \mathbf{X} \xrightarrow{82\ (h_2)^b} \mathbf{Col_r}$; $\mathbf{Col_r} \xrightarrow[74\ (-20.0)]{} \mathbf{Cr}$; $\mathbf{Col_r} \underset{137\ (-0.2)}{\overset{139\ (0.3)}{\rightleftarrows}} \mathbf{Col_h} \underset{164\ (-2.8)}{\overset{168\ (3.7)}{\rightleftarrows}} \mathbf{I}$

[a] The transition temperatures (°C) and enthalpies (in parentheses, kcal/mol) were determined by DSC (5 °C/min) and are given above and below the arrows. Cr, Col$_r$, Col$_h$, and Iso indicate crystal, rectangular columnar, hexagonal columnar, and isotropic phases, respectively. X phase indicates an unidentified phase. [b] The peaks could not be removed. $h_1 + h_2 = 15.9$ kcal/mol.

important for reduction of the repulsive interaction between the columns in the ferroelectric arrangement. On the basis of this idea, the simple ureas (**1**) were designed. The molecules have the following features: (1) the molecules have intermolecular hydrogen bonding in the direction of the column axis and (2) the polar site is introduced at the molecular center and six long alkyl chains are arranged at the outside of the mesogenic core, which makes a long distance between the polar centers of the neighboring columns to decrease the intercolumnar dipole−dipole interaction.

Results and Discussion

Synthesis of Compounds 1a−c and Their Phase Identification. Compounds **1** were synthesized from *N*,*N'*-carbonyldiimidazole and the corresponding 3,4,5-trialkoxyaniline, which was prepared from pyrogallol in three steps (Scheme 1).[12] The phase behaviors are shown in Table 1. All of **1a** (R = n-C_8H_{17}), **1b** (R = n-$C_{12}H_{25}$), and **1c** (R = n-$C_{16}H_{33}$) exhibited hexagonal and rectangular columnar liquid crystal phases (Col$_h$ and Col$_r$ liquid crystal phases). The Col$_h$ phases of **1a**, **1b**, and **1c** exhibited focal conic textures with smooth surfaces (Figure 1a) in the homogeneously aligned sample in polarized optical microscopy (POM). In the homeotropically aligned sample, dendric textures (Figure 1b) were observed. From the C_6 symmetry, the upper phases of **1** were estimated to be hexagonal columnar phases.[13] In the Col$_r$ phases of **1a**, **1b**, and **1c**, mosaic textures[14] (Figure 1c) were observed in the homeotropically aligned sample. Focal conic textures with many arc lines (filament-like, Figure 1d) were observed in the homogeneously aligned sample. In the DSC measurement of **1a** (Figure 2a), very sharp peaks were observed at the Col$_r$−Col$_h$ and Col$_h$−isotropic transitions and the Col$_r$ phase was observed in a narrow temperature range. Compound **1b** (Figure 2b) and **1c** (Figure 2c) generated a Col$_r$ phase in a wide temperature range. The transition enthalpy in the Col$_r$−Col$_h$ transition decreased with increase in alkyl chain length. On the other hand, the transition enthalpy in the crystal (Cr)−Col$_r$ and Col$_h$−isotropic transitions increased with increase in alkyl chain length. In the Cr−Col$_r$ and Col$_r$−Col$_h$ transitions, the values of transition enthalpies of **1a** are quite different from those of **1b** and **1c**. In the Col$_r$ phase of **1a**, the intercolumnar distance is so short that the interaction between the columns is larger than that of **1b** or **1c**, and it is thought that the packing structure is similar to that of the crystal phase.

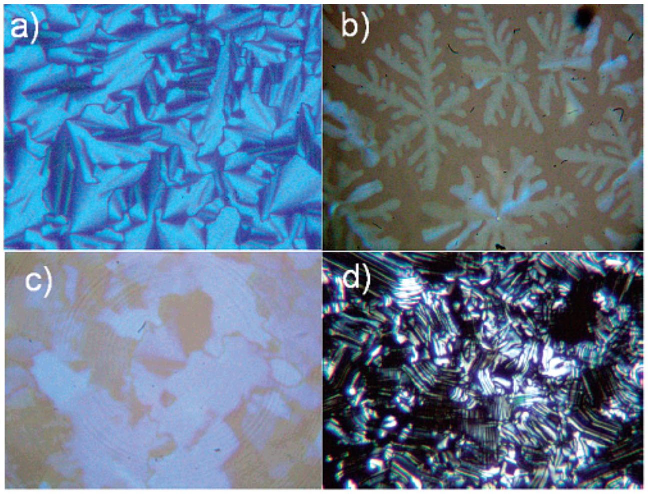


Figure 1. Microphotographs of **1a** in the Col$_h$ and Col$_r$ phases. (a) The focal conic textures (Col$_h$, 180 °C), (b) the dendric textures (Col$_h$, 180 °C), (c) mosaic textures (Col$_r$, 165 °C), and (d) arced focal conic (filament-like) textures (Col, 160° C_r).

X-ray Diffraction and IR Spectroscopy of 1a−c. The Col$_h$ phases of **1** showed one sharp $d(100)$ peak, and their $d(110)$ peaks in XRD (Figure 3a) were not observed clearly. On the other hand, the Col$_r$ phases showed two sharp peaks as the $d(200)$ and $d(110)$ peaks. The XRD peak patterns indicated that these phases belonged to Col$_r$ ($C2/m$) phases (Figure 3b).[15] In all cases, the XRD charts had a broad halo at 4.5−4.6 and 9.3−9.6 Å.[16] The diffuse band at 4.5−4.6 Å indicates disordered conformation of the alkyl chains, which is indicative of liquid crystal phases. The broad peak at 9.3−9.6 Å corresponds to

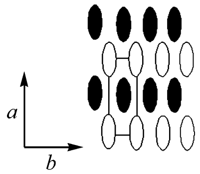
---

(12) Percec, V.; Ahn, C.-H.; Bera, T. K.; Ungar, G.; Yeardley, D. J. P. *Chem.−Eur. J.* **1999**, *5*, 1070.

(13) (a) Bouligand, Y. *J. Phys.* **1980**, *41*, 1307. (b) Baehr, C.; Ebert, M.; Frick, G.; Wendorff, J. H. *Liq. Cryst.* **1990**, *7*, 601.

(14) Destrade, C.; Foucher, P.; Gasparoux, H.; Nguyen, H.-T.; Levelut, A. M.; Malthete, J. *Mol. Cryst. Liq. Cryst.* **1984**, *106*, 121.

(15) The following arrangement of the polar columns is postulated as one of the models:



(16) XRD charts of **1a** and **1b** and the analysis of all columnar phases are shown in the Supporting Information.

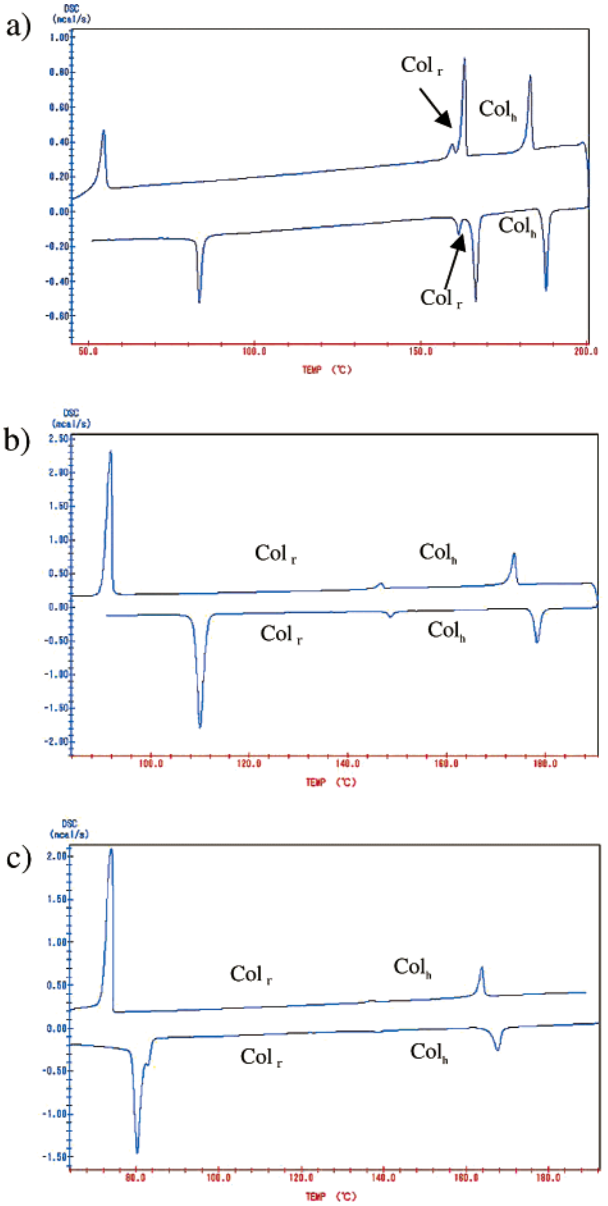


Figure 2. DSC charts of (a) **1a**, (b) **1b**, and (c) **1c** (rate: 5 °C/min). The farthest left peak of **1a** is a transition between crystals.

twice the repeat distance of the linearly hydrogen bonded ureas.[17] There was no indication of a chiral superstructure in XRD. On the basis of the repeat distances (9.3−9.6 Å), the z values (= the number of the molecules in one unit lattice) were calculated to give the slightly larger values. This can be explained by the assumption that their specific gravities are probably smaller than 1. To investigate the intermolecular hydrogen bonds, IR spectroscopy was performed. The N−H stretching vibration of **1b** at 160 °C (Col$_h$) and 120 °C (Col$_r$) appeared at 3338 and 3319 cm^{-1}, respectively, and these wavenumbers are smaller than those of free NH stretching wavenumbers of ureas (3427−3444 cm^{-1}).[18] The C═O stretching wavenumbers at 160 and 120 °C were 1647 and 1643 cm^{-1}, respectively, and these values are also smaller than those of the free C═O stretching vibration of ureas (around 1660 cm^{-1}).

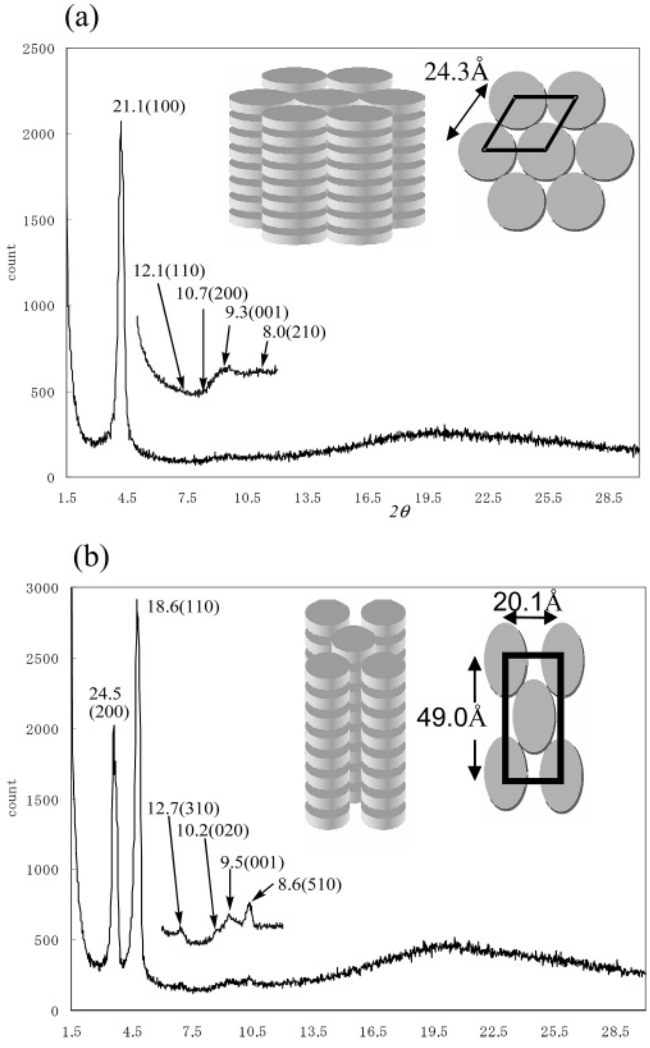


Figure 3. XRD of **1b** and the superstructures: (a) 160 °C (Col$_h$) and (b) 120 °C (Col$_r$).

These results indicate that intermolecular hydrogen bonding interacts strongly between the molecules in the Col$_h$ and Col$_r$ phases. Table 2 shows the XRD data of **1a**−**c**.

Single-Crystal X-ray Diffraction of 1d (R = CH$_3$). To estimate the packing structures of the ureas **1a**−**c**, *N*,*N*′-bis-(3,4,5-trimethoxyphenyl)urea (**1d**) was synthesized and the single-crystal X-ray diffraction was performed. The structure solved is shown in Figure 4. The molecule has a C_2 symmetric conformation, and its two benzene rings are not in a plane (Figure 4a). In the crystal packing, one-dimensional stacking of the urea molecules was observed (Figure 4b). The repeat distance in the stacking was 4.7 Å. Twice this distance (= 9.4) agrees to the repeat distances (= 9.3−9.6 Å) in the XRD experiments. It is assumed that the strong intermolecular hydrogen bonding and the intermolecular steric repulsion between the trimethoxyphenyl groups generate the twisted conformation.

Models for the Packing Structure in the Columnar Phases. From the CPK models of **1** (Figure 5), the polar (urea) part is only at the center and surrounded by six long alkyl chains. To have one-directional packing of the molecules in the column with the intermolecular hydrogen bonds, rotation of the N−Ar single bond is necessary to reduce the intermolecular steric repulsion. Accordingly, it is assumed that the C_2 symmetric conformation observed in Figure 4a is the best one to pack the

---

(17) Nguyen, T. L.; Fowler, F. W.; Lauher, J. W. *J. Am. Chem. Soc.* **2001**, *123*, 11057.

(18) Simic, V.; Bouteiller, L.; Jalabert, M. *J. Am. Chem. Soc.* **2003**, *125*, 13148.

Table 2. XRD Data of **1a**, **1b**, and **1c**

compd	temp (°C)	phase	*d*, obsd (Å)	*d*, (calcd) (Å)	Miller index	*z*
1a	170	**Col$_h$**[a]	19.0	19.0	100	2.3
			-[b]	11.0	110	
		$a = 21.9$	9.5	9.5	200	
		$c = 9.3$	9.3	–	001	
			4.6	–	–	
	165	**Col$_r$**	23.4	23.4	200	4.6
		(*C*2/*m*)	16.0	16.0	110	
		$a = 46.8$	11.9	11.7	400	
		$b = 17.0$	9.5	–	001	
		$c = 9.5$	8.0	8.0	220	
			4.7	–	–	
1b	160	**Col$_h$**	21.1	21.1	100	2.2
			12.1	12.1	110	
		$a = 24.3$	10.7	10.6	200	
		$c = 9.3$	9.3	–	001	
			8.0	8.0	210	
			4.5	–	–	
	120	**Col$_r$**	24.5	24.5	200	4.3
		(*C*2/*m*)	18.6	18.6	110	
		$a = 49.0$	12.7	12.7	310	
		$b = 20.1$	10.2	10.1	020	
		$c = 9.5$	9.5	9.3	001	
			8.6	8.8	510	
			4.5	–	–	
1c	145	**Col$_h$**	24.7	24.7	100	2.5
			–[b]	14.3	110	
		$a = 28.5$	12.4	12.4	200	
		$c = 9.6$	9.6	–	001	
			9.3	9.3	210	
			4.6	–	–	
	100	**Col$_r$**	28.8	28.8	200	4.9
		(*C*2/*m*)	22.6	22.6	110	
		$a = 57.6$	15.2	15.2	310	
		$b = 24.6$	12.4	12.4	020	
		$c = 9.6$	11.2	11.3	220	
			9.6	–	001	
			4.6	–	–	

[a] The phase was identified from the C_6 symmetry and the similarity to the other Col$_h$ phases. [b] The peak was not measured.

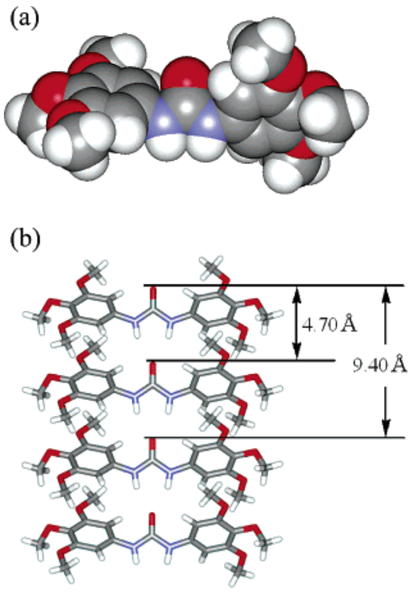


Figure 4. X-ray structure of **1d** (a) and (b). One-dimensional aggregates (space group: *C*2/*c* (#15), $a = 31.171(2)$ Å, $b = 4.6971(7)$ Å, $c = 13.591(2)$ Å, $b = 108.445(8)°$, $V = 1887.7(4)$ Å^3, $Z = 4$, $R = 0.036$, $R_w = 0.070$, GOF = 1.87).

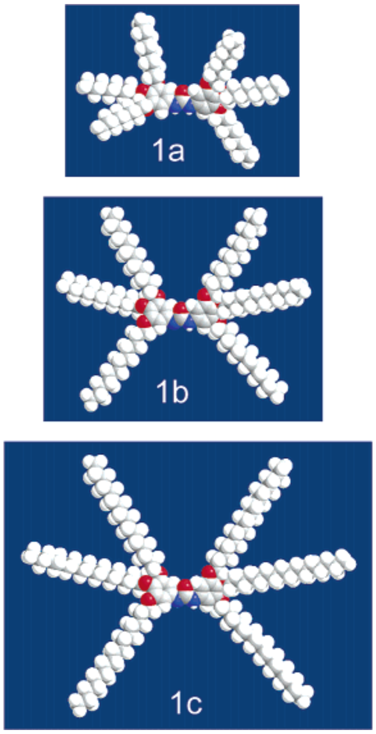


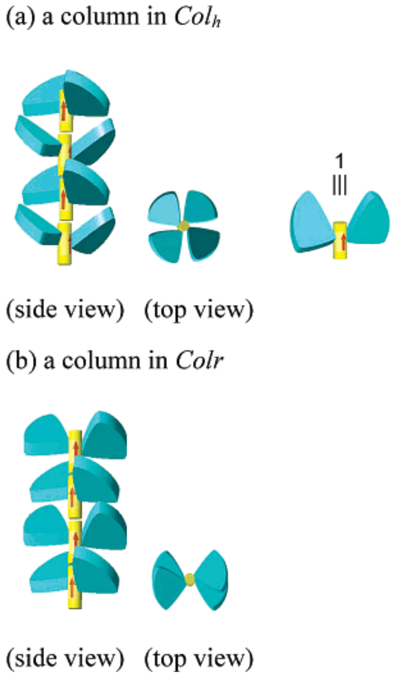
Figure 5. CPK models of **1a**, **1b**, and **1c**. The red, blue, gray, and white spheres indicate oxygen, nitrogen, carbon, and hydrogen atoms, respectively.

molecules in one direction with strong intermolecular hydrogen bonds. Further, the neighboring two molecules in the column stack in a twisted parallel arrangement to reduce the steric repulsion. The repeat distances 9.3–9.6 Å in the XRD experiments indicated that the molecules were piled up with an alternately crossed manner in the column (Figure 4). The two benzene rings in the molecule are in a C_2 symmetry, and the angle between the neighboring two molecules in the column is almost 90° in the Col$_h$ phase to give a circle as the cross section of the column (Scheme 2a). On the other hand, in the Col$_r$ phase, the corresponding angle in the column is smaller than 90° to give an oval as the cross section (Scheme 2b).

The Electrooptical Investigation of 1a–c. The electrooptical investigations of **1a**, **1b**, and **1c** were carried out in a transparent sandwich-type capacitor cell consisting of two glass plates coated with indium tin oxide (ITO) and polyimide (voltage: 200 V$_{pp}$, cell gap: 5 μm, area: 1 cm^2). The repolarization current in response to an applied triangular wave field was measured. The Col$_h$ phase of **1a** showed one broad peak, and the spontaneous polarization (P_s) was 1100 nC/cm^2 (Figure 6a). In the case of **1b**, the Col$_h$ phase showed one peak, and the P_s was 1570 nC/cm^2 (Figure 6b). The result of **1c** in the Col$_h$ phase is shown in Figure 6c. One sharp peak was observed at ca. ±10 V, and the P_s was 1260 nC/cm^2. The peak became sharper with increase in alkyl chain length. In the cases of these Col$_h$ phases, the focal conic textures were observed before starting the switching experiment (Figure 7a). As the switching proceeded, the textures disappeared, and it maintained a homeotropic (dark) texture while the triangular wave voltage was applied (Figure 7b). The dark texture was maintained after the electric field was switched off. Accordingly, in these Col$_h$ phases the directions of the columns were switched in the vertical direction to the glass surface and the direction was maintained without applying the electric field.

The Col$_r$ phases did not show clear switching peaks. Small granule textures (homogeneously aligned small domains) at 0.4

Scheme 2. Schematic Representation (Side and Top Views) of One-Directionally Packed Molecules in the $\mathrm{Col_h}$ (a) and $\mathrm{Col_r}$ (b) Phases



Hz became dark with a higher voltage (30−50 V, Figure 7c) and bright at 0 V (Figure 7d), and this phenomenon occurred repeatedly. This might originate in the instability of ferroelectric arrangement of columns in a high voltage and relaxing-back of the molecules to the antiparallel arrangement at 0 V.

Comparison of Our Results with Haase's Results in the Switching Experiment. In switching experiments, separation of polar switching and ion/charge relaxation is often difficult. Haase et al. reported that reversal current peaks were observed in the switching experiment of vanadyl liquid crystalline complexes.[10] They concluded that the peak originated in ion/charge relaxation. To confirm that the reversal current peaks in our experiments originate in a polar switching, our results were compared with Haase's results.

In their switching experiment, no electrooptical switching was observed in the liquid crystal phase, which meant that the molecules did not change their directions during the switching process. In our case, the homogeneous textures changed to a homeotropic texture by applying the voltage as aforementioned, which meant that the direction of the columns changed from parallel to perpendicular to the glass surface.

The area of the current response peak (P_s) against the frequency was investigated in the $\mathrm{Col_h}$ phase of **1c** at 160 °C. Figure 8 indicates the P_s ($\mathrm{nC/cm^2}$) at 0.1−18 Hz (100 $\mathrm{V_{pp}}$). A large broad peak (**A**) and a small broad peak (**B**) were observed at 0.1 Hz (Figure 9a). Peak **A** decreased with increase in frequency (Figure 9b), and disappeared at high frequency (more than 1.0 Hz). The area of peak **B** was almost constant (approximately 1.2×10^3 $\mathrm{nC/cm^2}$) from 0.1 to 18 Hz. However, the peak top moved to the right with increase in frequency. At 20 Hz, the peak could not be separated from the current peak top. This indicated the polar switching could not follow the frequency (20 Hz) of the triangular wave voltage. In an ionic/charges relaxation observed by Haase et al., one broad peak was observed by applying the triangular wave voltage only at low frequencies (below 1 Hz). From the comparison with their experiment, peak **A** might originate in an ionic/charge relaxation. Therefore, it is strongly assumed that peak **B**, which was

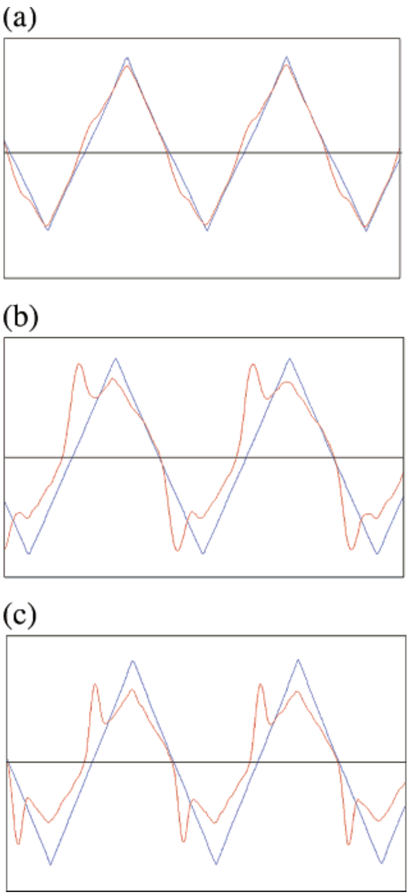


Figure 6. Switching experiment of **1a** (a), **1b** (b), and **1c** (c) in the $\mathrm{Col_h}$ phase with triangular wave voltage. The blue and red lines indicate the voltage (200 $\mathrm{V_{pp}}$, 6.0 Hz (4.3 Hz in the case of **1a**)) and current, respectively (cell area: 1 cm × 1 cm, cell gap: 5 μm). The peak areas of the current gave the spontaneous polarizations of **1a**, **1b**, and **1c** (1100, 1570, and 1260 $\mathrm{nC/cm^2}$, respectively).

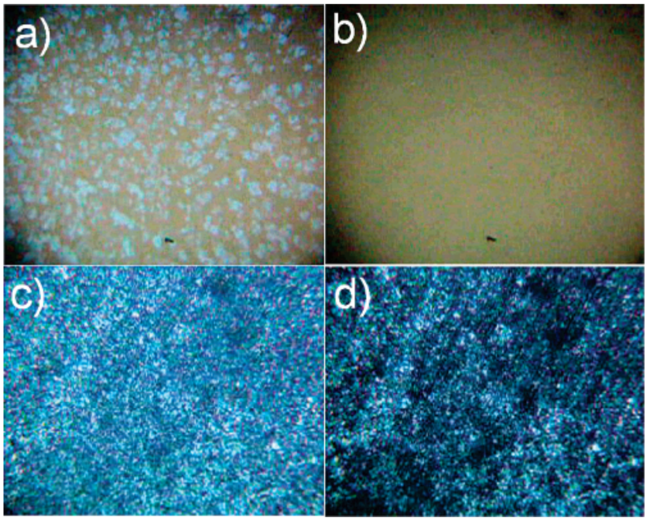


Figure 7. Microphotographs of **1a** in the electrooptical switching. The textures of (a) $\mathrm{Col_h}$ phase (T = 185 °C) at 0 V before applying a triangular wave field, (b) $\mathrm{Col_h}$ phase (T = 185 °C) after applying a triangular wave field, (c) $\mathrm{Col_r}$ phase (T = 165 °C) at 0 V, (d) $\mathrm{Col_r}$ (T = 165 °C) at +50 V. (Voltage: 100 $\mathrm{V_{pp}}$, frequency: 0.4 Hz, cell area: 1 cm × 1 cm, cell gap: 5 μm).

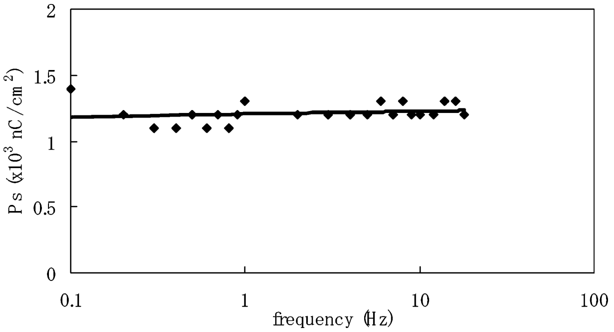


Figure 8. Peak area in the current response against the frequency (Hz) in the liquid crystal phase of **1c**. (Voltage: 100 V_{pp}, cell area: 1 cm × 1 cm, cell gap: 5 μm, T = 160 °C.)

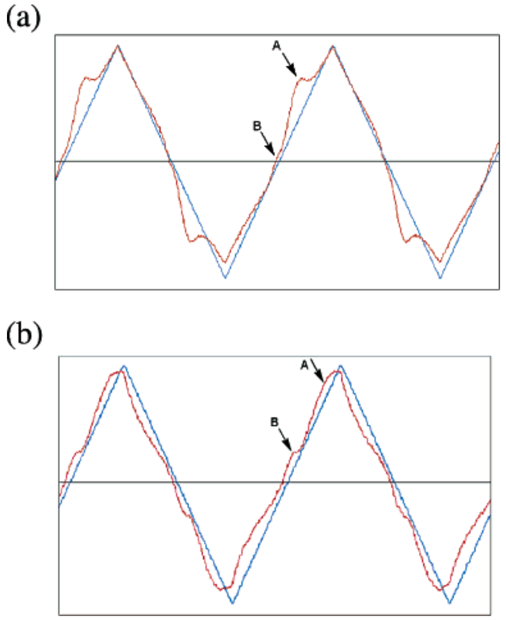


Figure 9. Two peaks in the current response at 0.1 (a) and 0.6 Hz (b) in the liquid crystal phase of **1c**. (Voltage: 100 V_{pp}, T = 160 °C, cell area: 1 cm × 1 cm, cell gap: 5 μm.)

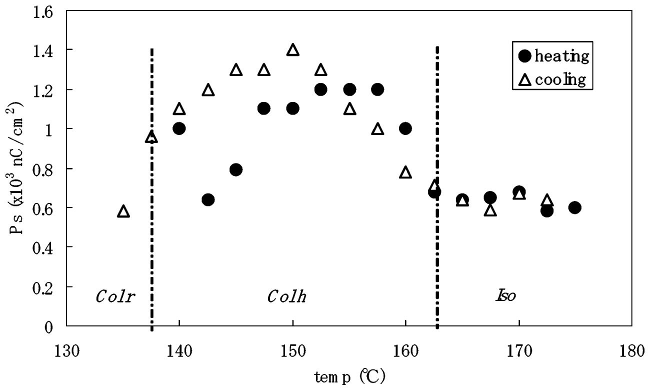


Figure 10. Peak area in the current response against the temperature in the liquid crystal and isotropic liquid phases of **1c**. (Voltage: 100 V_{pp}, frequency: 6.0 Hz, cell area: 1 cm × 1 cm, cell gap: 5 μm.)

observed up to 18 Hz, does not originate in an ionic/charge relaxation.

Then the area of the current response peak (P_s) of **1c** against the temperature was investigated at 6.0 Hz (Figure 10). In the Col_r phase, the peak was not observed. In the Col_h phase, the switching peak was observed and had a maximum value (1.4 × 10^3 nC/cm^2 at 150 °C on cooling and 1.2 × 10^3 nC/cm^2 at 155 °C on heating). At high temperature (above 162.5 °C), the peak area decreased even in the Col_h phase and was almost constant (0.65 × 10^3 nC/cm^2) up to 175 °C (isotropic liquid phase). The patterns of the plots on heating and cooling were similar to each other, although there was only small difference between the temperatures and the maximum values. This result was also different from the spontaneous polarization against the temperature in Haase's switching experiment. In their case, the shape of the line on heating was quite different from that on cooling. They said that the behavior was atypical of FLCs. In our case, the behavior observed is almost typical of FLCs. Jákli and Saupe also reported a similar result in a ferroelectric columnar phase of a chiral bowlic compound,[6c] in which they proposed a shift of domain for the polar switching mechanism because of the appearance of birefringence. In our experiment, no birefringence appeared. Although small current response peaks were observed even in the isotropic liquid phase, it could be explained by the assumption that there were partially hydrogen-bonded linear arrangements of the urea molecules in the isotropic liquid phase. It is thought that the spontaneous polarization becomes lower or disappears at higher temperature in the isotropic phase.

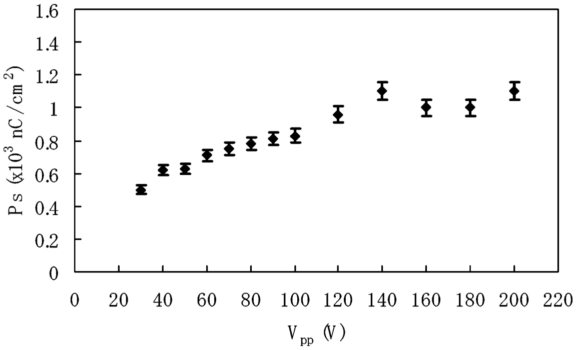


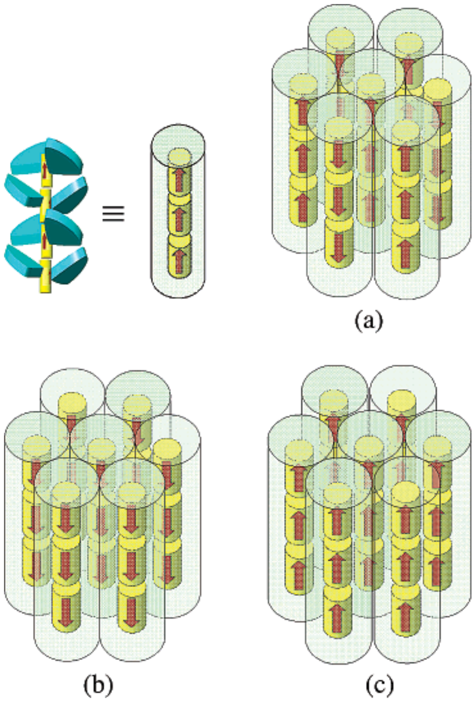
Figure 11. Peak area in the current response against the applied triangular wave voltage in the liquid crystal phases of **1c** at 160 °C. (Frequency: 6.0 Hz, cell area: 1 cm × 1 cm, cell gap: 5 μm.)

The P_s against the applied voltage at 160 °C and 6 Hz was plotted in Figure 11. The value increased with increase in voltage up to 100 V_{pp}, and the P_s value was constant from 120 to 200 V_{pp}. This meant that all columns change their direction at more than 120 V_{pp}, and part of the columns did not change them at lower voltage (up to 100 V_{pp}).

The relaxation experiment of the Col_h phases of **1c** was performed at 160 °C with a rectangular wave voltage (2 Hz, 0 to +20 V). The current response peak was observed after switching the voltage from +20 to 0 V. It took 0.15 s for the relaxation. In the switching experiment, the polar directions of the columns are aligned by the applied voltage, and after removal of the applied voltage each column can change its polar direction by keeping its homeotropic alignment. After the relaxation, the ratio of the opposite direction becomes 50:50 and the polarity of the domain disappears.

Model for the Switching Experiment. Each column has a one-dimensional polar organization of the molecules because of the strong hydrogen bonding. At 0 V (before applying the voltage), the sample has a poly-domain structure. In each domain, the columns are arranged in parallel, although each column directs either of the opposite directions randomly (Scheme 3a). After applying the voltage, the directions of all columns are organized in one direction (Scheme 3b or c). In

Scheme 3. Schematic Representation of the Columns in the Switching Experiment[a]



[a] (a) Columns at 0 V and (b, c) columns in an applied field.

each column, the hydrogen bonds interact between the adjacent molecules and stabilize the polar packing. There is a small energy barrier between the two polar states. However, the energy barrier is not large enough to fix the polar direction of the column. After switching off the applied voltage, the conformational changes of the urea molecules take place thermally without changing the column direction. The polar state (Scheme 3b or c) goes back to the nonpolar state in Scheme 3a. Accordingly, the ferroelectric switching between the two polar states (Scheme 3b and c) is observed, if the switching speed is high enough compared with the relaxation time. However, the following two models cannot be ruled out as the nonpolar state: (i) polar columns direct the opposite directions regularly (antiferroelectric arrangement) and (ii) the urea molecules in one column direct the opposite directions with a regular repeat distance (or at random).

Conclusion

We could achieve a ferroelectric switching in columnar phases by stabilization of the one-directional stacking of molecules in the column and reduction of the intercolumnar dipole–dipole interaction. Thus far, polar columns generated by one-directionally stacked molecules have been studied solely to realize ferroelectric columnar liquid crystals. This study indicates that it is also important to reduce the intercolumnar dipole–dipole interaction for realization of ferroelectric columnar liquid crystals. The long intercolumnar distance between the polar sites is important to reduce the interaction. In the $\mathrm{Col_h}$ phases, the hydrogen bonding in the molecular stacking overwhelmed the intercolumnar dipole–dipole and steric interactions. On the other hand, in the $\mathrm{Col_r}$ phases in which the intercolumnar distance in the *b*-axis (= *b*) was shorter than the *a* value in the $\mathrm{Col_h}$ phases, the steric interaction between the neighboring two columns may be so large that the columns in the *b*-axis direction might be organized in a syn-parallel manner and the aligned columns might be organized in an antiparallel arrangement in the *a*-axis direction to cancel out the dipoles.[15]

In these liquid crystalline compounds, the energy barrier between the two polar states was too small to maintain the polar organization. To achieve bistablity in columnar liquid crystals, interaction between molecules in the column or between molecules and glass surface should be stronger. Further, the temperature range of the liquid crystals should be decreased. In bistable columnar liquid crystals, the polarity of each column can be controlled independently, which is useful as a high-density memory device.

Acknowledgment. This work was supported by Tokuyama Science Foundation and the Ministry of Education, Science, Sports and Culture, Grant-in-Aid for Scientific Research (B), 2003, 15350108 and Exploratory Research, 2004, 16655090.

Supporting Information Available: The synthetic routes of **1a**–**c** and their spectral data, XRD charts of **1a** and **1c**, and a microphotograph of **1b** ($\mathrm{Col_h}$). This material is available free of charge via the Internet at http://pubs.acs.org.

JA046100C