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Preorganization Effect of a Polar Supermolecule on Dielectric Anisotropy in a Nematic Liquid Crystalline Phase

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We have prepared novel preorganized compounds in which 4-(4-fluorophenyl)phenyl and 4-(trifluoromethoxy)phenyl are connected via a rigid catechol unit or a flexible spacer and investigated their structural effects on the induced dielectric anisotropy in the mixture with a host material. The nonsymmetric bimesogenic compounds with the flexible spacer were found to be a dopant with negative dielectric anisotropy in host A composed of fluoro-substituted phenyl esters, whereas they were found to be a dopant with large positive dielectric anisotropy in host B (**6OCB**). The rigid U-shaped compound enhanced $\Delta\epsilon$ in both hosts A and B. We discuss effects of host−guest interaction on conformational change of the guest molecule in the nematic liquid crystalline phase.

Introduction

Liquid crystal displays (LCD) have rapidly become an indispensable man−machine interface in our life. Numerous efforts have sought to improve LCD performance. Reducing the driving voltage is an important goal for LCD improvement. Liquid crystalline materials with high dielectric anisotropy ($\Delta\epsilon$) are known to decrease the threshold voltage (Vth) of the electrooptical response of a dielectrically positive liquid crystal mixture. Consequently, they decrease the driving voltage of a twisted-nematic (TN) display. On the other hand, a high voltage holding ratio (VHR) of liquid crystalline materials is necessary for thin film transistor (TFT) LCDs. A compound possessing a polar group, such as −CN, decreases the VHR. Thus, the general molecular design for liquid crystalline materials introduces fluorine atoms at a ring, a side chain, or a linkage group of a liquid crystalline compound on the basis of the prediction from molecular modeling of electrooptical properties that fluorine reduces the threshold voltage.[1−5] Supermolecular liquid crystalline materials have attracted much attention from the perspective of design of a self-organizing system.[6] Many kinds of dimeric and trimeric mesogenic molecules have been reported.[7,8] Coles et al. reported the phase transition behavior and electrooptical properties of siloxane bimesogenic liquid crystals.[9−11] We have reported novel preorganized systems, e.g., U-shaped molecules,[12] binaphthyl derivatives,[13] and λ-shaped molecules.[14] The preorganized supermolecules induced unusual ordering in the supramolecular liquid crystalline phase. Furthermore, we recently found that a U-shaped compound in which two mesogenic groups with partially substituted fluorine atoms connected via catechol markedly reduced the threshold voltage.[15]

In the present study, we have designed novel preorganized compounds in which 4-(4-fluorophenyl)phenyl and 4-(trifluoromethoxy)phenyl are connected via a rigid catechol unit or a flexible spacer. Herein, we report their structural effects on the induced dielectric anisotropy in the mixture with a host material. In addition, we report the unusual dependency of dielectric anisotropy induced by the compound possessing a flexible spacer on the host structure.

Experimental Section

Preparation of Materials. The compound 1-[[6-[[4-(trifluoromethoxy)phenyl]oxy]hexyl]oxy]-2-[[6-[[4-(4-fluorophenyl)phenyl]oxy]hexyl]oxy]benzene (**1**) was prepared by synthesis outlined in Scheme 1. Purification of final products was carried out using

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(1) Goto, Y.; Ogawa, T.; Sawada, S.; Sugimori, S. *Mol. Cryst. Liq. Cryst.* **1991**, *209*, 1.

(2) Kirsch, P.; Bremer, M. *Angew. Chem., Int. Ed.* **2000**, *39*, 4216.

(3) Matsui, S.; Kondo, T.; Sago, K. *Mol. Cryst. Liq. Cryst.* **2004**, *411*, 127.

(4) Kusumoto, T.; Saito, Y.; Nagashima, Y.; Negishi, M.; Takehara, S.; Iwashita, Y.; Takeuchi, K.; Takatsu, H. *Mol. Cryst. Liq. Cryst.* **2004**, *411*, 155.

(5) Pauluth, D.; Tarumi, K. *J. Mater. Chem.* **2004**, *14*, 1219.

(6) (a) Goodby, J. W.; Mehl, G. H.; Saez, I. M.; Tuffin, R. P.; Mackenzie, G.; Auzely-Velty, R.; Benvegu, T.; Plusquellec, D. *Chem. Commun.* **1998**, 2057. (b) Saez, I. M.; Goodby, J. W. *J. Mater. Chem.* **2005**, *15*, 26.

(7) Imrie, C. T.; Luckhurst, G. R. *Handbook of Liquid Crystals*; Demus, D., Goodby, J. W., Gray, G. W., Spiess, H.-W., Vill, V., Eds.; Wiley-VCH: Weinheim, 1998, Vol 2B, Chapter X, pp 801−833.

(8) Imrie, C. T.; Henderson, P. A. *Curr. Opin. Colloid Interface Sci.* **2002**, *7*, 298.

(9) Redmond, H.; Coles, H. J.; Wischerhoff, E.; Zentel, R. *Ferroelectrics* **1993**, *148*, 323.

(10) Robinson, W. K.; Carboni, C.; Kloess, P.; Perkins, S. P.; Coles, H. J. *Liq. Cryst.* **1998**, *25*, 301.

(11) Pivnenko, M. N.; Lehmann, P.; Komitov, L.; Coles, H. J. *Liq. Cryst.* **2005**, *32*, 173.

(12) Yoshizawa, A.; Yamaguchi, A. *Chem. Commun.* **2002**, 2060.

(13) Rokunohe, J.; Yoshizawa, A. *J. Mater. Chem.* **2005**, *15*, 275.

(14) Yamaguchi, A.; Nishiyama, I.; Yamamoto, J.; Yokoyama, H.; Yoshizawa, A. *J. Mater. Chem.* **2005**, *15*, 280.

(15) Yoshizawa, A.; Ogasawara, F.; Manabe, K.; Segawa, S.; Narumi, T. *Jpn. J. Appl. Phys.* **2004**, *43*, L1549.

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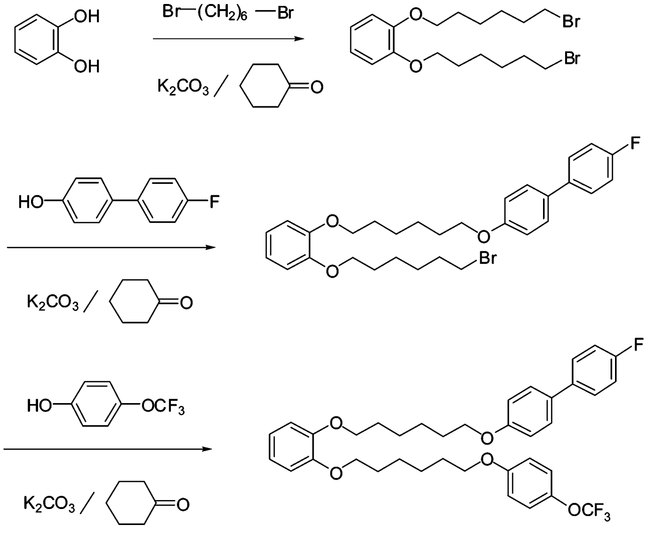
Scheme 1. Synthetic Route for Compound 1



column chromatography over silica gel (63−210 μm) (Kanto Chemical Co., Inc.) using dichloromethane or a dichloromethane−ethyl acetate mixture as the eluent, followed by recrystallization from ethanol. Structures of the final products were elucidated using infrared (IR) spectroscopy (FTS-30, Bio-Rad Laboratories, Inc.) and proton nuclear magnetic resonance spectroscopy (JNM-GX270, JEOL). Elemental analysis (1110, CE Instruments) was obtained for each final compound.

1-[[6-[[4-(Trifluoromethoxy)phenyl]oxy]hexyl]oxy]-2-[[6-[[4-(4-fluorophenyl)phenyl]oxy]hexyl]oxy]benzene, 1. Potassium carbonate (3.59 g, 26 mmol) was added to a solution of 1,2-dihydroxybenzene (1.43 g, 13 mmol) and 1,6-dibromohexane (9.52 g, 39 mmol) in cyclohexanone (15 mL). The reaction mixture was stirred at 140 °C for 6 h. After filtration of the precipitate, the solvent was removed by evaporation. The residue was purified by column chromatography on silica gel with (7:3) dichloromethane−hexane. 1,2-Bis[(6-bromohexyl)oxy]benzene was obtained (4.36 g, 10 mmol, 76%).

Potassium carbonate (1.38 g, 10 mmol) was added to a solution of 1,2-bis[(6-bromohexyl)oxy]benzene (4.36 g, 10 mmol) and 4-fluoro-4′-hydroxybiphenyl (1.88 g, 10 mmol) in cyclohexanone (15 mL). The reaction mixture was stirred at 70 °C for 6 h. After filtration of the precipitate, the solvent was removed by evaporation. The residue was washed with ethanol (50 mL) and purified by column chromatography on silica gel with (6:4) dichloromethane−hexane. 1-[(6-Bromohexyl)oxy]-2-[[6-[[4-(4-fluorophenyl)phenyl]oxy]hexyl]oxy]benzene was obtained (0.48 g, 0.9 mmol, 9%).

Potassium carbonate (69 mg, 0.50 mmol) was added to a solution of 1-[(6-bromohexyl)oxy]-2-[[6-[[4-(4-fluorophenyl)phenyl]oxy]hexyl]oxy]benzene (134 mg, 0.25 mmol) and 4-(trifluoromethoxy)phenol (89 mg, 0.50 mmol) in cyclohexanone (15 mL). The reaction mixture was stirred at 140 °C for 6 h. After filtration of the precipitate, the solvent was removed by evaporation. The residue was purified by column chromatography on silica gel with dichloromethane. Recrystallization from ethanol gave the desired product (106 mg, 0.17 mmol, 66%). ^{1}H NMR (270 MHz, solvent $CDCl_3$, standard TMS) δ_H/ppm: 7.50−7.42 (m, 4H, Ar−*H*), 7.09 (d, 2H, Ar−*H*, $J = 9.2$ Hz), 7.08 (dd, 2H, Ar−*H*, $J = 8.8$ Hz, 8.8 Hz), 6.93 (d, 2H, Ar−*H*, $J = 8.9$ Hz), 6.89 (t, 2H, Ar−*H*, $J = 8.6$ Hz), 6.87 (d, 2H, Ar−*H*, $J = 9.2$ Hz), 6.84 (d, 2H, Ar−*H*, $J = 9.2$ Hz), 4.00 (t, 4H, Ar−OCH_2−, $J = 6.5$ Hz), 3.99 (t, 2H, Ar−OCH_2−, $J = 6.5$ Hz), 3.92 (t, 2H, Ar−OCH_2−, $J = 6.5$ Hz), 1.87−1.52 (m, 16H, aliphatic-*H*). IR (KBr) ν_{max}/cm^{-1}: 2945, 2859, 1607, 1506, 1476, 1162, 1123. Anal. Calcd for $C_{37}H_{36}F_4O_5$: C, 69.4. Found: C, 69.3.

Compounds **2**−**4** were obtained using a method similar to that for compound **1**. Analytical data for the compounds are listed below.

1-[[6-[[4-(Trifluoromethoxy)phenyl]oxy]hexyl]oxy]-4-[[6-[[4-(4-fluorophenyl)phenyl]oxy]hexyl]oxy]benzene, 2. ^{1}H NMR (270 MHz, solvent $CDCl_3$, standard TMS) δ_H/ppm: 7.52−7.42 (m, 4H, Ar−*H*), 7.12 (d, 2H, Ar−*H*, $J = 9.2$ Hz), 7.08 (dd, 2H, Ar−*H* $J = 8.8$ Hz, 8.8 Hz), 6.94 (d, 2H, Ar−*H*, $J = 8.9$ Hz), 6.86 (d, 2H, Ar−*H*, $J = 9.2$ Hz), 6.83−6.79 (m, 4H, Ar−*H*), 4.00 (t, 2H, Ar−OCH_2−, $J = 6.5$ Hz), 3.95 (t, 2H, Ar−OCH_2−, $J = 6.5$ Hz), 3.92 (t, 2H, Ar−OCH_2−, $J = 6.6$ Hz), 3.91 (t, 2H, Ar−OCH_2−, $J = 6.5$ Hz), 2.05−1.50 (m, 16H, aliphatic-*H*). IR (KBr) ν_{max}/cm^{-1}: 2953, 2878, 1511, 1501, 1164, 1116. Anal. Calcd for $C_{37}H_{36}F_4O_5$: C, 69.4. Found: C, 69.2.

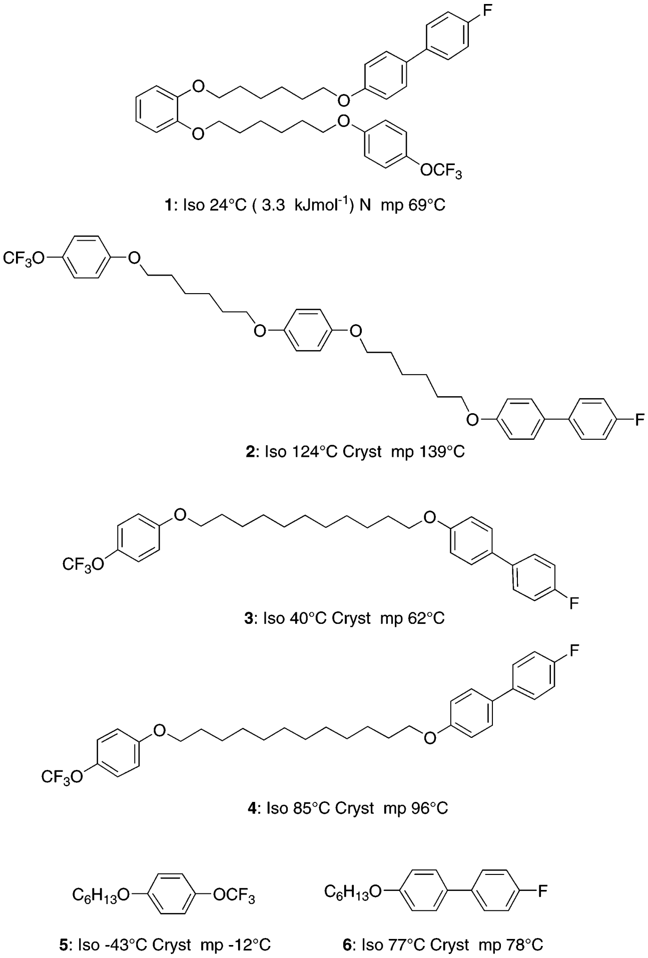
1-[[4-(Trifluoromethoxy)phenyl]oxy]-11-[[4-(4-fluorophenyl)phenyl]oxy]undecane, **3.** ^{1}H NMR (270 MHz, solvent $CDCl_3$, standard TMS) δ_H/ppm: 7.52−7.42 (m, 4H, Ar−*H*), 7.12 (d, 2H, Ar−*H*, $J = 9.2$ Hz), 7.08 (dd, 2H, Ar−*H* $J = 8.8$ Hz, 8.8 Hz), 6.95 (d, 2H, Ar−*H*, $J = 8.9$ Hz), 6.86 (d, 2H, Ar−*H*, $J = 9.2$ Hz), 3.99 (t, 2H, Ar−OCH_2−, $J = 6.5$ Hz), 3.93 (t, 2H, Ar−OCH_2−, $J = 6.4$ Hz), 1.85−1.32 (m, 18H, aliphatic-*H*). IR (KBr) ν_{max}/cm^{-1}: 2935, 2920, 2852, 1609, 1498, 1474, 1161, 1106. Anal. Calcd for $C_{30}H_{36}F_4O_3$: C, 69.4. Found: C, 69.1.

1-[[4-(Trifluoromethoxy)phenyl]oxy]-12-[[4-(4-fluorophenyl)phenyl]oxy]dodecane, **4.** ^{1}H NMR (270 MHz, solvent $CDCl_3$, standard TMS) δ_H/ppm: 7.52−7.42 (m, 4H, Ar−*H*), 7.12 (d, 2H, Ar−*H*, $J = 9.2$ Hz), 7.08 (dd, 2H, Ar−*H* $J = 8.8$ Hz, 8.8 Hz), 6.95 (d, 2H, Ar−*H*, $J = 8.9$ Hz), 6.86 (d, 2H, Ar−*H*, $J = 9.2$ Hz), 3.99 (t, 2H, Ar−OCH_2−, $J = 6.5$ Hz), 3.93 (t, 2H, Ar−OCH_2−, $J = 6.6$ Hz), 1.85−1.31 (m, 20H, aliphatic-*H*). IR (KBr) ν_{max}/cm^{-1}: 2935, 2919, 2851, 1607, 1501, 1475, 1164, 1107. Anal. Calcd for $C_{31}H_{38}F_4O_3$: C, 69.9. Found: C, 69.8.

4-(Trifluoromethoxy)-1-(hexyloxy)benzene, 5. Potassium carbonate (0.55 g, 4.0 mmol) was added to a solution of 4-(trifluoromethoxy)phenol (0.36 g, 2.0 mmol) and 1-bromohexane (0.33 g, 2.0 mmol) in cyclohexanone (15 mL). The reaction mixture was stirred at 140 °C for 3 h. After filtration of the precipitate, the solvent was removed by evaporation. The residue was purified by column chromatography on silica gel with dichloromethane (0.32 g, 1.2 mmol, 62%). ^{1}H NMR (270 MHz, solvent $CDCl_3$, standard TMS) δ_H/ppm: 7.12 (d, 2H, Ar−*H*, $J = 9.2$ Hz), 6.86 (d, 2H, Ar−*H*, $J = 9.2$ Hz), 3.93 (t, 2H, Ar−OCH_2−, $J = 6.6$ Hz), 1.50−1.31 (m, 8H, aliphatic-*H*), 0.91 (t, 3H, −CH_3, $J = 7.0$ Hz). IR (neat) ν_{max}/cm^{-1}: 2967, 2935, 2862, 1508, 1471, 1163.

4-Fluoro-4′-(hexyloxy)biphenyl, 6. Potassium carbonate (0.69 g, 5.0 mmol) was added to a solution of 4-fluoro-4′-hydroxybiphenyl (0.94 g, 5.0 mmol) and 1-bromohexane (0.99 g, 6.0 mmol) in cyclohexanone (20 mL). The reaction mixture was stirred at 100 °C for 4 h. After filtration of the precipitate, the solvent was removed by evaporation. The residue was purified by column chromatography on silica gel with dichloromethane. Recrystallization from ethanol gave the desired product (0.43 g, 1.6 mmol, 32%). ^{1}H NMR (270 MHz, solvent $CDCl_3$, standard TMS) δ_H/ppm: 7.51−7.41 (m, 4H, Ar−*H*), 7.08 (dd, 2H, Ar−*H* $J = 8.8$ Hz, 8.8 Hz), 6.94 (d, 2H, Ar−*H*, $J = 8.9$ Hz), 3.99 (t, 2H, Ar−OCH_2−, $J = 6.5$ Hz), 1.85−1.32 (m, 8H, aliphatic-*H*), 0.91 (t, 3H, −CH_3, $J = 7.0$ Hz). IR (KBr) ν_{max}/cm^{-1}: 2960, 2938, 2859, 1608, 1501, 1162.

Physical Properties. Transition temperatures were determined by thermal optical microscopy using a polarizing microscope (BX-51, Olympus Optical Co. Ltd.) equipped with a temperature control unit (LK-600PM, Japan High Tech). The heating and cooling rates were 5 °C min^{-1}. Temperatures and enthalpies of transition were investigated using differential scanning calorimetry (DSC) (DSC 6200, Seiko Instruments Inc.). Dielectric measurements were



1: Iso 24°C (3.3 kJmol^{-1}) N mp 69°C

2: Iso 124°C Cryst mp 139°C

3: Iso 40°C Cryst mp 62°C

4: Iso 85°C Cryst mp 96°C

5: Iso -43°C Cryst mp -12°C

6: Iso 77°C Cryst mp 78°C

Figure 1. Molecular structures and transition temperatures of the materials.

performed using an impedance analyzer (HP 4284A, Hewlett-Packard Co.) with a temperature control unit at a frequency of 1 kHz.[16] A sample was contained in a homogeneous configuration cell (5.0±0.5 μm), where the inner surfaces had been coated with polyimide aligning agent and had been buffed unidirectionally (E. H. C. Co., Ltd.). The dielectric measurements were performed using the single cell method and carried out three times at each measured value. The experimental error was within ±2%.

Results and Discussion

Figure 1 shows molecular structures and transition temperatures of the newly designed compounds and the corresponding monomeric compounds. The U-shaped compound **1** showed a nematic (N) phase on cooling, along with marked hysteresis in transition behavior between the cooling and heating cycles. On the other hand, the rodlike compound **2**, in which two mesogenic groups are connected via 1,4-dihydroxybenzene, and compounds **3** and **4**, in which the two mesogenic groups are connected via a flexible spacer, showed no liquid crystalline phase.

We used two host materials to investigate dielectric anisotropy of the compounds: a nematic mixture composed of alkoxyphenylbenzoate and fluoro-substituted phenyl esters (host A) and 4-(hexyloxy)-4′-cyanobiphenyl (**6OCB**, host B) (see Figure 2).

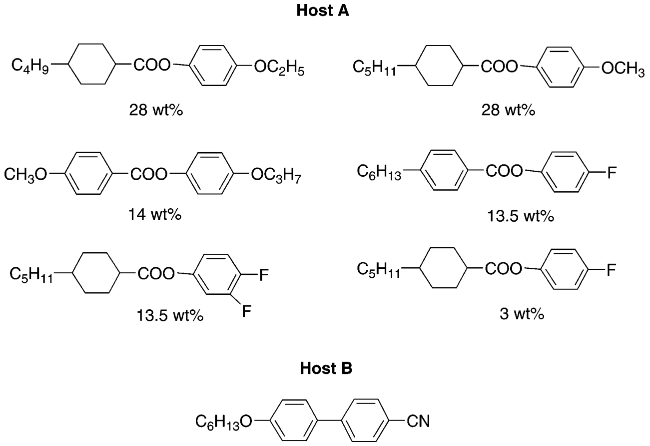


Figure 2. Components of the host nematic liquid crystals. Host A: Iso 49 °C N, mp 8 °C. Host B (**6OCB**): Iso 77 °C N, mp 57 °C.

Table 1. Transition Temperature, Parallel Component ($\epsilon_{\|}$) and Perpendicular Component ($\epsilon_{\perp}$) of Dielectric Constant,[a] and Dielectric Anisotropy ($\Delta\epsilon$) of a Mixture Consisting of Host A and 5 mol % of Each Compound[b]

		$T_{IN} - 10$ °C			$T_{IN} - 20$ °C		
compd	T_{IN} (°C)	$\epsilon_{\|}$	$\epsilon_{\perp}$	$\Delta\epsilon$	$\epsilon_{\|}$	$\epsilon_{\perp}$	$\Delta\epsilon$
host A	49	5.5	4.7	0.8	5.7	4.8	0.9
1	45	6.4	5.2	1.2	6.9	5.4	1.5
2[c]							
3	48	4.9	4.3	0.6	5.1	4.4	0.7
4	48	4.9	4.4	0.5	5.1	4.4	0.7
5:**6** (1:1 mixture)[d]	42	5.8	4.9	0.9	6.2	5.0	1.2

[a] Dielectric measurements were performed at a frequency of 1 kHz. [b] The mole fraction was calculated assuming the average molecular weight of 306.5 for host A. [c] Compound **2** was not miscible with host A. [d] 5 mol % of each compound was doped with host A.

The transition temperature, the parallel and perpendicular component of the dielectric constant, and the dielectric anisotropy of a mixture consisting of host A and 5 mol % of each compound are listed in Table 1.

Isotropic−nematic transition temperature (T_{IN}) of a mixture of compound **1** and host A is lower by 4 °C than that of host A. On the other hand, T_{IN} of a mixture of compound **3** and host A is comparable to that of host A. These results indicate that compound **1** forms a U-shaped structure and that compound **3** forms a rodlike structure in host A. The dielectric anisotropy of the mixture consisting of host A and compound **1** is greater than that of host A, but the dielectric anisotropy of a mixture consisting of host A and compound **3** is less than that of host A. The difference in induced dielectric anisotropy between compounds **1** and **3** results from a change of the parallel component of the dielectric constant. The parallel component of the mixture with compound **1** increased; however, that of the mixture with compound **3** decreased. No significant difference exists in the physical properties between compound **3** with an odd-numbered spacer and compound **4** with an even-numbered spacer in host A. Compound **1** was found to induce larger dielectric anisotropy in the mixture than the binary mixture of the corresponding polar monomesogenic compounds **5** and **6**. Differences in $\Delta\epsilon$ of the mixture from that of host A at $T_{IN} - 20$ °C are +0.6 for compound **1** and +0.3 for the binary mixture.

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(16) Uchida, T.; Takahashi, Y. *Mol. Cryst. Liq. Cryst.* **1981**, *72*, 133.

Table 2. Parallel Component ($\epsilon_{||}$) and Perpendicular Component ($\epsilon_{\perp}$) of Dielectric Constant[a] and Dielectric Anisotropy ($\Delta\epsilon$) of a Mixture Consisting of Host A and 5 mol % of Each Compound at $T_{IN} - 20$ °C[b]

compd	$\epsilon_{\|\|}$	$\epsilon_{\perp}$	$\Delta\epsilon$
host A	5.7	5.0	0.7
1	6.2	4.7	1.5
4	5.1	4.6	0.5
5:6 (1:1 mixture)[c]	6.0	5.0	1.0

[a] Dielectric measurements were performed at a frequency of 300 Hz. [b] The mole fraction was calculated assuming the average molecular weight of 306.5 for host A. [c] 5 mol % of each compound was doped with host A.

Table 3. Transition Temperature, Parallel Component ($\epsilon_{||}$) and Perpendicular Component ($\epsilon_{\perp}$) of Dielectric Constant,[a] and Dielectric Anisotropy ($\Delta\epsilon$) of a Mixture Consisting of Host B and 5 mol % of Each Compound

		$T_{IN} - 10$ °C			$T_{IN} - 20$ °C		
compd	T_{IN} (°C)	$\epsilon_{\|\|}$	$\epsilon_{\perp}$	$\Delta\epsilon$	$\epsilon_{\|\|}$	$\epsilon_{\perp}$	$\Delta\epsilon$
host B	77	15.8	6.6	9.2	16.9	6.1	10.8
1	68	15.5	6.5	9.0	17.1	5.7	11.4
2	76	14.8	7.6	7.2	—[b]	—[b]	—[b]
3	70	17.4	6.9	10.5	18.3	6.5	11.8
4	69	17.1	6.3	10.8	18.3	6.2	12.1
5:6 (1:1 mixture)[c]	69	15.2	6.3	8.9	16.2	5.6	10.6

[a] Dielectric measurements were performed at a frequency of 1 kHz. [b] Phase separation occurred. [c] 5 mol % of each compound was doped with host B.

We performed the dielectric measurement using lower frequency, i.e., 100, 200, 300, and 600 Hz. The measurement could not be performed at 100 and 200 Hz, probably due to a reorientational effect induced by prove voltage. Results of the measurements at 300 Hz are shown in Table 2. There is no considerable difference in the obtained values between 300 Hz and 1 kHz.

Physical properties were also observed in a mixture consisting of host B and 5 mol % of each compound. Those results are listed in Table 3.

The T_{IN} of a mixture of compound **1** and host B is lower by 9 °C than that of host B. The T_{IN} of a mixture of compound **3** and host B is lower by 7 °C than that of host B. These suggest that compound **3** with a flexible spacer is not a rodlike structure. On the other hand, T_{IN} of a mixture of compound **2** and host B is comparable to that of host B, indicating that compound **2** with a rigid phenyl ring in the spacer exists as a rodlike structure in host B. Compound **1** induces larger dielectric anisotropy in the mixture with host B at $T_{IN} - 20$ °C than the binary mixture of compounds **5** and **6**. Differences in $\Delta\epsilon$ of the mixture from that of host B at $T_{IN} - 20$ °C are +0.6 for compound **1** and −0.2 for the binary mixture. Both compounds **3** and **4** induce larger dielectric anisotropy in the mixture with host B than compound **1**. The differences in $\Delta\epsilon$ of the mixture from that of host B at $T_{IN} - 20$ °C are +1.0 for compound **3** and +1.3 for compound **4**. The induced larger dielectric anisotropy results from a marked increase of the parallel component of the dielectric constant. On the other hand, the dielectric anisotropy of a mixture consisting of host B and compound **2** is smaller than that of host B; the difference in $\Delta\epsilon$ of the mixture from that of host B is −2.0 at $T_{IN} - 10$ °C. A marked difference exists in the induced dielectric anisotropy between compound **3**, which has a flexible spacer, and compound **2**, which has a rigid ring in the spacer.

Table 4. Parallel Component ($\epsilon_{||}$) and Perpendicular Component ($\epsilon_{\perp}$) of Dielectric Constant[a] and Dielectric Anisotropy ($\Delta\epsilon$) of a Mixture Consisting of Host B and 5 mol % of Each Compound at $T_{IN} - 20$ °C

compd	$\epsilon_{\|\|}$	$\epsilon_{\perp}$	$\Delta\epsilon$
host B	17.0	6.8	10.2
1	17.2	6.0	11.2
4	18.2	6.3	11.9
5:6 (1:1 mixture)[b]	16.3	6.2	10.1

[a] Dielectric measurements were performed at a frequency of 100 Hz. [b] 5 mol % of each compound was doped with host B.

We performed the dielectric measurement using lower frequency, i.e., 100 Hz, 200, 300, and 600 Hz. The dielectric measurement of a mixture of host B and compound **2** at $T_{IN} - 10$ °C could not be performed at 100, 200, and 300 Hz. Results of the measurements of a mixture of host B and each dopant at $T_{IN} - 20$ °C using 100 Hz as prove frequency are shown in Table 4.

The dielectric anisotropy of a uniaxial liquid crystalline phase can be described as

$$\Delta\epsilon = (NhFS)(\epsilon_0)^{-1}[\Delta\alpha - \mu^2 F(2k_B T)^{-1}(1 - 3\cos^2\beta)] \quad (1)$$

where F and h are the reaction field and cavity field factors that account for the field dependent interaction of a molecule with its environment, N is the number density, S is the order parameter, μ is the dipole moment, $\Delta\alpha$ is the molecular polarizability anisotropy, and β is the angle between the dipole moment vector and the effective orientation axis of the liquid crystal molecule.[17,18]

Compound **1** induces larger dielectric anisotropy in the mixture with each host than the binary mixture of compounds **5** and **6**. The order parameter of the mixture can affect the dielectric anisotropy. Differences in $\Delta\epsilon$ of a mixture consisting of compound **1** and host B from that of host B are −0.2 at $T_{IN} - 10$ °C and +0.6 at $T_{IN} - 20$ °C; this is thought to result from the difference in the order parameter between them. However, the marked enhancement of dielectric anisotropy of compound **1** can result from an increase in the effective dipole moment in the system, i.e., the dipole moment along the director that constitutes the coupling between μ and β. The destabilization of T_{IN} by compound **1** implies that the conformation of compound **1** in the mixture is a U-shaped structure. The preorganized U-shaped structure of compound **1** can produce a larger effective dipole moment in the system than the binary mixture of compounds **5** and **6**.

On the other hand, compounds **3** and **4** show unusual dependency of dielectric anisotropy on the host structure. Extrapolated values of compounds **3** and **4** from the observed $\Delta\epsilon$ at $T_{IN} - 20$ °C in the mixture with host A are −2.2. However, those in the mixture with host B are +19.9 and

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(17) (a) Maier, W.; Meier, G. *Z. Naturforsch. A* **1961**, *16*, 262. (b) Dunmur, D.; Toriyama, K. *Handbook of Liquid Crystals;* Demus, D., Goodby, J. W., Gray, G. W., Spiess, H.-W., Vill, V., Eds.; Wiley-VCH: Weinheim: 1998; Vol 1, Chapter VII, pp 231−252.

(18) In eq 1, F denotes the reaction field factor $\{F = 1/(1 - f\alpha); f = (\epsilon - 1)/2\pi\epsilon_0 a^3(2\epsilon + 1)\}$ and h the cavity factor $\{h = 3\epsilon/(2\epsilon + 1)\}$. The macroscopic dielectric constant is used for ϵ.

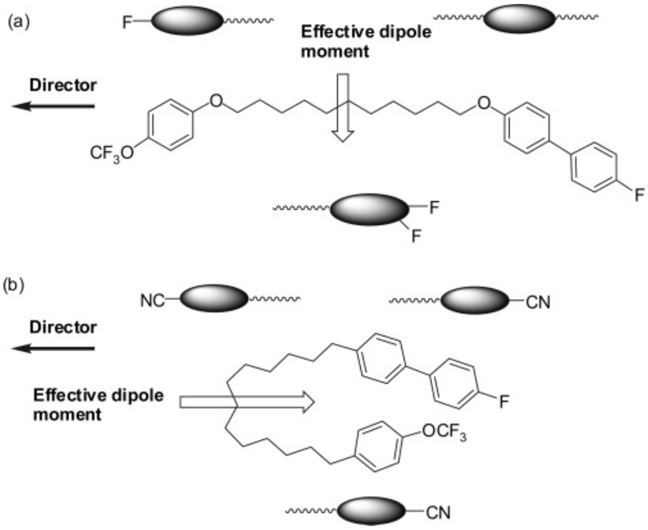

Figure 3. A molecular conformation model for compound **3** in the mixture with host A (a) and that with host B (b).

+21.4, respectively. The marked difference in $\Delta\epsilon$ results from a change of the parallel component of the dielectric constant. The significant increase of the parallel component of the mixture with host B was observed. Thus, the difference in $\Delta\epsilon$ can be caused by the β term: the conformational change between a bend-shaped structure in host A and a U-shaped structure in host B, as shown in Figure 3. These are consistent with the phase transition behavior for a mixture consisting of compound **3** and each host. The dielectric anisotropy and the transition behavior of the mixture would be similar to those of a mixture consisting of compound **2** if compound **3** adopted a bend structure in the mixture with host B. The conformational change for the present flexible system results from the host−guest intermolecular interaction.

It is noticed that there is a possibility that the doped molecule reoriented by prove voltage at the dielectric measurement. The measurements using lower frequency clarify that there is no intrinsic influence of the prove voltage on the measurement at 1 kHz.

Conclusion

The rigid U-shaped compound **1** enhances $\Delta\epsilon$ in both hosts A and B. The preorganized system is thought to be a new approach to induce large positive dielectric anisotropy in liquid crystalline materials without introducing a large dipole moment. The nonsymmetric bimesogenic compounds with a flexible spacer, compounds **3** and **4**, were found to be a dopant with negative dielectric anisotropy in host A composed of fluoro-substituted phenyl esters, whereas they were found to be a dopant with large positive dielectric anisotropy in host B (**6OCB**). The results indicate that the preorganized U-shaped compound maintains its rigid structure in different host materials. However, the flexible compound changes its conformation because of interaction with its surrounding host molecules.

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