December, 1987] *Bull. Chem. Soc. Jpn.*, ***60***, *4239—4243 (1987)*

Thermal and Ferroelectric Properties of (*S*)-2-Methylbutyl Esters of α-Substituted 4-(4-Alkoxybenzoyloxy)cinnamic Acid

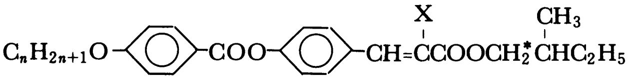
Jun Nakauchi,* Yoshitaka Kageyama, Mioko Uematu, and Shunsuke Minami
Tokyo Research Laboratory, Mitsubishi Rayon Co. Ltd., Noborito, Tama-ku, Kawasaki, Kanagawa 214

(Received May 26, 1987)

Three homologous series of (*S*)-2-methylbutyl esters of α-substituted 4-(4-alkoxybenzoyloxy)cinnamic acid **Ia** (α-H), **Ib** (α-CH_3), and **Ic** (α-CN) have been synthesized and their thermal and ferroelectric properties have been investigated. The mesomorphic transition temperatures for the homologous series (**Ia**, **Ib**, and **Ic**) depend on the α-substituents as well as the terminal alkoxyl chain length. In comparison with Schiff base analogues, the transition temperatures from the isotropic phase to smectic A for all the homologous series are a little lower; however, their transition temperatures from the smectic A phase to chiral smectic C show significantly different features. The thermal stability of the chiral smectic C phase has been discussed from the view point of the local intermolecular dipole-dipole interaction in the homologous series (**Ia**, **Ib**, and **Ic**) and the Schiff base analogues. The spontaneous polarization for the homologous series is in the order of the homologues: **Ib**>**Ia**>**Ic** and their polarity is negative for **Ia** and **Ib** and positive for **Ic** homologues, respectively. These results have also been discussed in terms of the α-substituent effect on the spontaneous polarization.

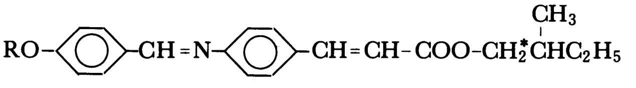
Since the discovery of ferroelectricity in smectic liquid crystals containing a chiral group in the molecular structure (Sm*C phase),[1] extensive studies have been carried out not only from a fundamental point of view, but for practical applications as well. However, the relation between the ferroelectricity in the Sm*C phase and the molecular structure has not been well understood so far. Two plausible reasons are the limited number of compounds which have been investigated regarding their physical properties and the drastic change of the thermal stability in the mesophase frequently caused by altering the molecular structure slightly. Thererofe, the synthesis of various novel compounds with the Sm*C phase and the measurement of their fundamental physical propertries are necessary in order to elucidate the relationship between the ferroelectricity and the molecular structure.

From this point of view, the following homologous series (**Ia**, **Ib**, and **Ic**) of general formula:



(**Ia** : X = -H, n = 5—16 ; **Ib** : X = -CH_3, n = 5—16 ;
Ic : X = -CN, n = 7—12)

have been synthesized and their thermal and ferroelectric properties have been investigated. These compounds have a characteristic molecular structure in the sense that the -CH=N- linkage of well-known Schiff base analogues ((*S*)-2-methylbuthyl 4-(4-alkoxybenzylideneamino)cinnamate)



is replaced with a -COO- linkage. Such a mesogen unit was reported to be a suitable structure for the Sm*C phase,[2] and some compounds shown in the above formula (**Ia** : n=5—14, **Ic** : n=5—12) have already been synthesized; their thermal porperties and polarity were reported by Goodby et al.[3-5] However, the effect of the α-substituents on the mesomorphic thermal stability and other ferroelectric properties have not been discussed so far.

In the present paper, we compare the physical properties of the homologous series (**Ia**, **Ib**, and **Ic**) with those of the Schiff base analogues reported by P. Keller et al.[6] and Ph. Martinot-Lagarde et al.,[7,8] and discuss the effect of the molecular structure on the thermal stabilty in the mesophase and the ferroelectricity in the Sm*C phase.

Experimental

Preparation of Materials. All the reagents purchased from Tokyo Kasei Co. Ltd. were used without further purification. *p*-Hydroxy-α-methylcinnamic acid was prepared by a Perkin reaction according to the literature.[9] (*S*)-2-Methylbutyl esters of α-substituted *p*-hydroxycinnamic acid were synthesized by an esterification reaction of *p*-hydroxy-α-substituted cinnamic acid with (*S*)-2-methyl-1-butanol using a Soxhlet extractor. Their specific rotations ($[\alpha]_D$) measured in diethyl ether at 23 °C were +5.35°, +3.59°, and +8.16° for α-H, α-CH_3, and α-CN derivatives, respectively. (*S*)-2-Methylbutyl esters of α-substituted 4-(4-alkoxybenzoyloxy)cinnamic acid were synthesized by a reaction of (*S*)-2-methylbutyl esters of α-substituted *p*-hydroxycinnamic acid with *p*-alkoxybenzoyl chloride and triethylamine in the diethyl ether solution. The crude products obtained were purified twice by recrystallization from their solution with diethyl ether and pentane. Their elementary analysis data are listed in Table 1.

Measurements of Physical Properties. An identification of the mesophase was carried out using a Nikon polarizing microscope equipped with a Mettler FP-52 heating stage. Transition temperatures were measured using a Daini Seikosha SSC-560 differential scanning calorimeter (DSC) at a scanning rate of 2.5 °C min^{-1} under an N_2 atomsphere.

The spontaneous polarization (*Ps*) was determined by a triangular-wave method reported by Miyasato et al.[10] The frequency, the maximum amplitude and the cell thickness were 1.0 Hz, ±70 V and 50 μm, respectively.

The tilt angle (θ/°) and the polarity (the direction of *Ps*)

Table 1. Elemental Analyses for Homologous Series **Ia**, **Ib**, and **Ic**

(**Ia** Homologues)

Carbon No.	Calcd (%)		Found (%)	
n	C	H	C	H
5	73.56	7.60	73.73	7.83
6	73.95	7.81	74.13	8.07
7	74.31	8.02	74.40	8.29
8	74.65	8.21	74.65	8.44
9	74.97	8.39	75.10	8.45
10	75.27	8.56	75.34	8.79
11	75.56	8.72	75.61	8.96
12	75.83	8.87	75.77	9.14
14	76.33	9.15	76.19	9.27
16	76.78	9.40	76.85	9.62

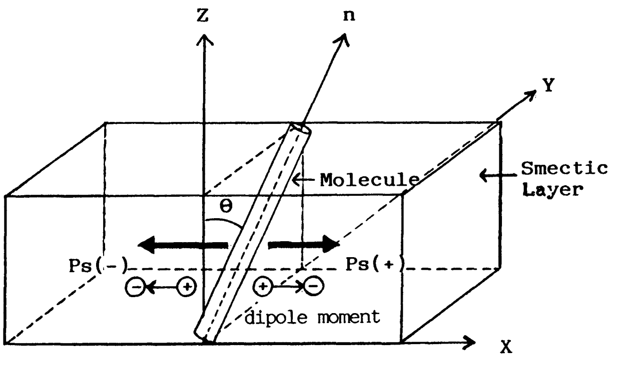
(**Ib** Homologues)

Carbon No.	Calcd (%)		Found (%)	
n	C	H	C	H
5	73.95	7.81	74.28	7.93
6	74.31	8.02	74.35	8.19
7	74.65	8.21	74.60	8.41
8	74.97	8.39	75.08	8.56
9	75.27	8.56	75.55	8.79
10	75.56	8.72	75.55	8.80
11	75.83	8.87	75.86	8.90
12	76.08	9.01	76.22	9.14
14	76.56	9.28	76.54	9.38
16	76.99	9.52	77.19	9.78

(**Ic** Homologues)

Carbon No.	Calcd (%)			Found (%)		
n	C	H	N	C	H	N
7	72.93	7.39	2.93	72.96	7.53	2.89
8	73.29	7.59	2.85	73.27	7.79	2.84
9	73.64	7.77	2.77	73.58	7.98	2.69
10	73.96	7.95	2.70	73.90	8.17	2.64
11	74.27	8.12	2.62	74.16	8.36	2.49
12	74.55	8.28	2.56	74.34	8.57	2.49

were determined by applying a *D.C.* field to a specimen placed between crossed polarizers and by observing the direction of extinction by rotating the stage. The polarity is defined by the direction that the molecules are tilted with respect to the layer normal, as shown in following picture.



Results and Discussion

Figures 1, 2, and 3 show the mesomorphic trends of each homologous series (**Ia**, **Ib**, and **Ic**). A normal odd-even alternation for the isotropic (Iso) to smectic A (SmA) and for SmA to chiral smectic C (Sm*C) can clearly be seen in **Ia** homologues, though it is ambiguous in **Ib** and **Ic** homologues. In all the homologous series investigated, cholesteric (Ch) appears in the lower alkoxyl chain homologues, whose number of the carbon in terminal alkoxyl chain are n=5, n=6, and n=9 for **Ia**, **Ib**, and **Ic** homologues, respectively. The Sm*C phase of **Ia** and **Ic** homologues injected at decyloxy and heptyloxy derivatives appears as a monotropic transition from SmA, except for enantiotropic undecyloxy and dodecyloxy derivatives of **Ia** homologues. On the other hand, the Sm*C phase of **Ib** homologues

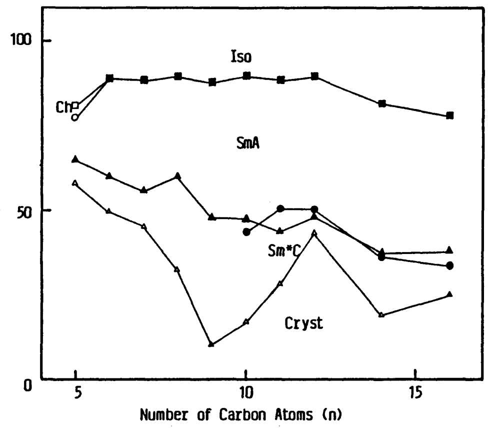


Fig. 1. Plots of the transition temperatures against the number of carbon atoms (n) in the n-alkoxyl chain of (S)-2-methylbutyl 4-(4-alkoxybenzoyloxy)-cinnamates (**Ia** homologues): Iso-Ch (-□-); Iso-SmA (-■-); Ch-SmA (-○-); SmA-Sm*C (-●-); SmA-Cryst or Sm*C-Cryst (-△-); melting point (-▲-).

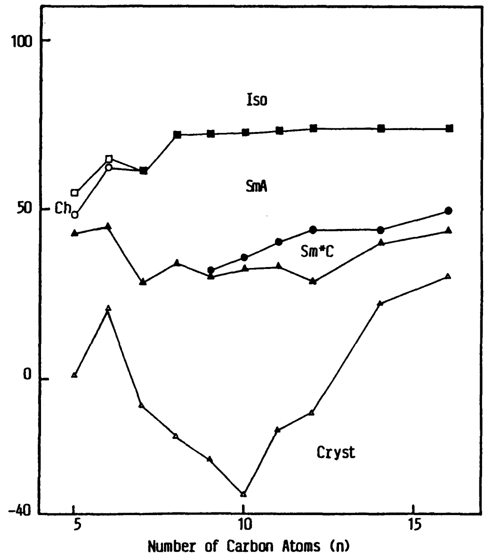


Fig. 2. Plots of the transition temperatures against the number of carbon atoms (n) in the n-alkoxyl chain of (S)-2-methylbutyl 4-(4-n-alkoxybenzoyloxy)-α-methylcinnamates (**Ib** homologues): Iso-Ch (-□-); Iso-SmA (-■-); Ch-SmA (-○-); SmA-Sm*C (-●-); SmA-Cryst or Sm*C-Cryst (-△-); melting point (-▲-).

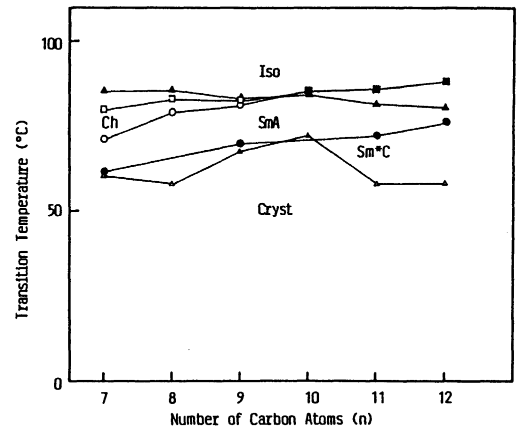


Fig. 3. Plots of the transition temperatures against the number of carbon atoms (n) in the n-alkoxyl chain of (S)-2-methylbutyl 4-(4-n-alkoxybenzoyloxy)-α-cyanocinnamates (**Ic** homologues): Iso-Ch (-□-); Iso-SmA (-■-); Ch-SmA (-○-); SmA-Sm*C (-●-); SmA-Cryst or Sm*C-Cryst (-△-); melting point (-▲-).

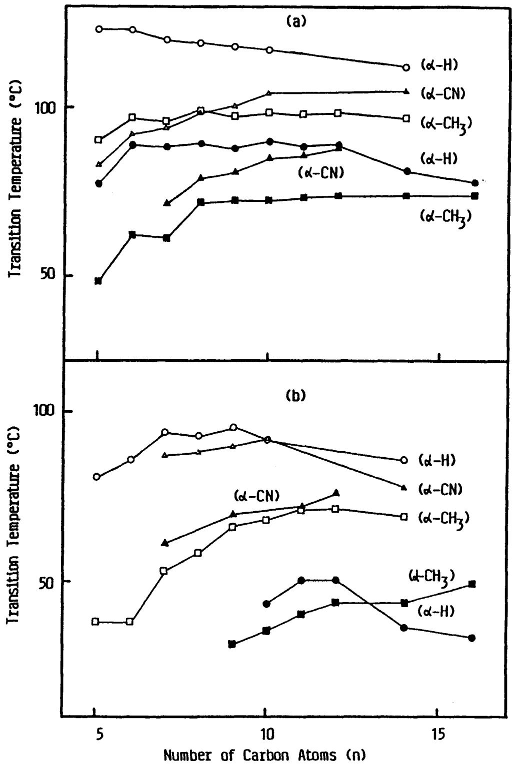
injected at nonyloxy derivative appears as an enantiotropic one from SmA with a wider temperature range than those of **Ia** and **Ic** homologues. Plots of the transition temperatures from SmA to Sm*C against the number of carbon atoms in the alkoxyl chain in **Ia** homologues are "parabolic" as Goodby et al. referred to;[11] however, this trend was not seen in **Ib** and **Ic** homologues.

In order to compare the thermal stability of SmA and Sm*C phase for homologous series (**Ia**, **Ib**, and **Ic**) with those for the Schiff base analogues reported by Keller et al.,[6] the transition temperatures from Iso to SmA and from SmA to Sm*C against the carbon number of the terminal alkoxyl chain are plotted in Figs. 4a and 4b, respectively. As is evident from Fig. 4a, the transition temperatures from the Iso phase to SmA for each homologues with different α-substituents are a little lower than those for the Schiff base analogues. This trend is attributed to the effect of replacing the -CH=N- linkage in the core with the -COO- linkage on the thermal stability for SmA phase.[12]

On the other hand, the thermal stability of the Sm*C phase for the homologous series (**Ia**, **Ib**, and **Ic**) is significantly different from those for the Schiff base analogues. That is, the transiton temperatures from SmA phase to Sm*C for the Schiff base analogues decrease in the order of the analogues: α-H$>\alpha$-CN$>\alpha$-CH_3. However, those for the homologous series decrease in the order of the homologues (α-CN$>\alpha$-H$\approx\alpha$-CH_3 (**Ic**>**Ia**≈**Ib**)), respectively.

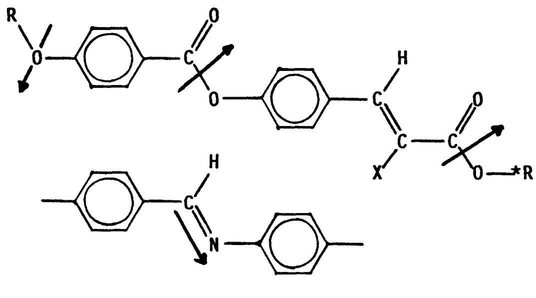
According to McMillan's theory,[13] if a molecule has both central and out-board dipole moments, the transition temperature from SmA to Sm*C depends on the local intermolecular dipole-dipole interaction among these dipole moments.

In the homologous series (**Ia**, **Ib**, and **Ic**), the central dipole corresponds to the dipole of the ester linkage of



Figs. 4a and 4b. Plots of the transition temperatures from Iso phase to SmA (4a) and from SmA phase to Sm*C (4b) against the number of carbon atoms in the n-alkoxyl chain of the homologous series **Ia** (-●-), **Ib** (-■-), and **Ic** (-▲-), and those of the Schiff base analogues α-H (-○-), α-CH_3 (-□-), and α-CN (-△-).

the core (6.34×10^{-30} C m)[14] and the out-board dipoles correspond to dipoles of the ether linkage (4.27×10^{-30} C m)[14] and the ester linkage of the cinnamoyl moiety including the α-substituent. It is noteworthy that the direction of the dipole moment of the homologous series (-COO-: 6.34×10^{-30} C m) to the molecular axis is quite defferent from that of the Schiff base analogues (-CH=N-: 5.24×10^{-30} C m),[14] if the molecule has the all trans configulation, as shown in the following schemes



These facts indicate that the different dependence of the SmA-Sm*C transition temperature on the α-substitution between the homologous series (**Ia**, **Ib**, and **Ic**) and the Schiff base analogues can be attributed to a difference in the local intermolecular dipole-dipole interaction caused by replacing the central linkage -CH=N- with -COO-.

The temperature dependence of the spontaneous polarization in the Sm*C of the homologous series **Ia**, **Ib**, and **Ic** are shown in Figs. 5, 6, and 7, respectively. As is evident from the figures, the spontaneous polarization of the homologous series is in the order of the homologues (**Ib**>**Ia**>**Ic**) and shows a maximum at certain alkoxyl chain length in each homologues. The maximum value was observed in the **Ib** homologue with a terminal dodecyloxyl chain (60 μC m^{-2}). These facts show that spontaneous polarization strongly depends on the α-substituents in the cinnamoyl moiety as well as the terminal alkoxyl chain length.

The polarities of the spontaneous polarization in the homologous series are negative for **Ia** and **Ib** homologues and positive for **Ic** homologues, respectively. The alternation of polarity between **Ia**, **Ib**, and **Ic**, which was observed in the Schiff base analogues,[8] has already been reported and interpreted as tilt variations between the core and the terminal chain by Goodby et al.[5] To confirm the tilt variations among the homologous series, the tilt angles for the dodecyloxy homologues for **Ia**, **Ib**, and **Ic** were measured. Figure 8 shows the temperature dependence of the tilt angle in the Sm*C phase for **Ia**, **Ib**, and **Ic** homologues. The tilt angle measured by the optical method corresponds to the angle of the core in the molecule tilted to the smectic layer. Therefore, the core of the **Ic** homologue has the most tilted structure among three homologues. This result seems to be in conflict with the speculation of Goodby et al. However, in the present study, the thickness of the smectic layer has not been measured yet; hence, the tilt variations between the core and the terminal chain are not clear at this stage.

According to Meyer et al.,[1] the spontaneous polari-

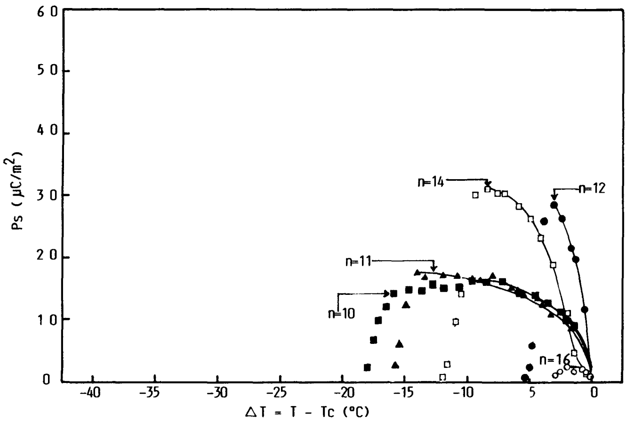


Fig. 5. Temperature dependence of the spontaneous polarization of **Ia** homologues. The cell thickness, the frequency and the maximum amplitude of applied voltage are 50 μm, 1.0 Hz, and ±70 V, respectively.

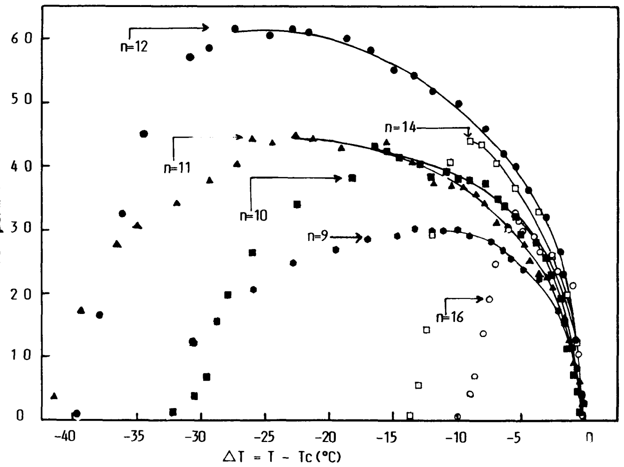


Fig. 6. Temperature dependence of the spontaneous polarization of **Ib** homologues. The cell thickness, the frequency and the maximum amplitude of applied voltage are 50 μm, 1.0 Hz, and ±70 V, respectively. The deviation of the plots from the curve satisfied the relation: Ps∝$(\Delta T)^a$ at the lower temperature side is probably due to the applied voltage not enough to reverse the spontaneous polarization completely.

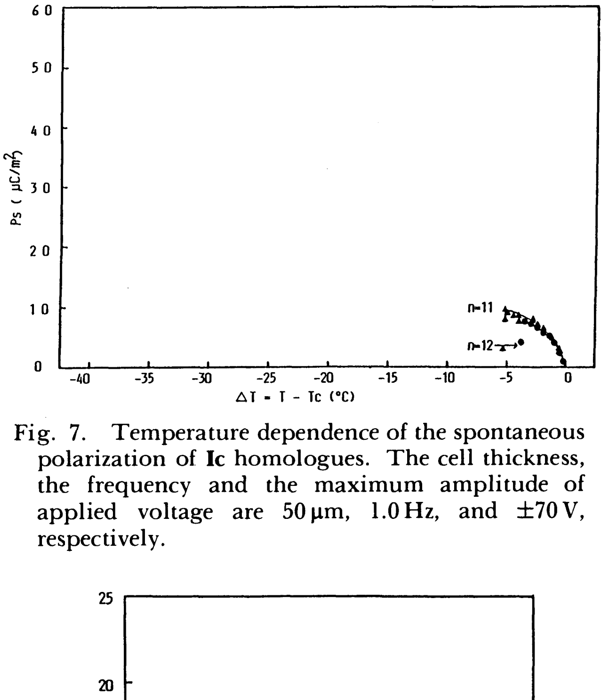


Fig. 7. Temperature dependence of the spontaneous polarization of **Ic** homologues. The cell thickness, the frequency and the maximum amplitude of applied voltage are 50 μm, 1.0 Hz, and ±70 V, respectively.

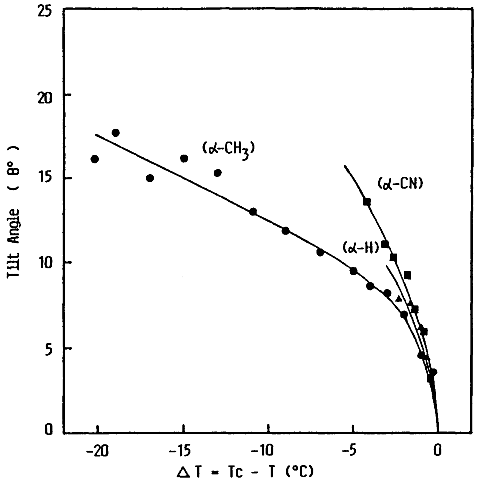
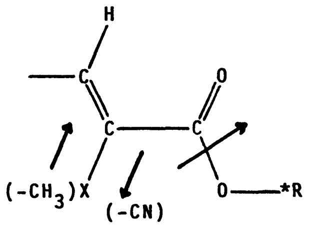


Fig. 8. Temperature dependence of the tilt angle for the homologous series **Ia** (-▲-), **Ib** (-●-), and **Ic** (-■-).

zation originates from the perpendicular component of the dipole moment in the polar group attached to the asymmetric carbon atom. The structure of the cinnamoyl moiety adjecent to the asymmetric carbon for the homologous series (**Ia**, **Ib**, and **Ic**) are schematically pictured as follows.



The contribution of the α-substituent to the dipole moment or the 2-methylbutoxycarbonyl group is inverse between **Ib** and **Ic** homologues. In comparison with the unsubstituted homologues **Ia**, **Ib** homologues have an electron-releasing methyl group so that the dipole moment of the ester group in the cinnamoyl moiety is enhanced, thus leading to the increase of spontaneous polarization. On the other hand, **Ic** homologues have a strong electron-withdrawing cyano group (13.01×10^{-30} C m)15) with the opposite direction of the dipole moment to that of the dipole moment of the ester group in the cinnamoyl moiety (6.34×10^{-30} C m); hence the perpendicular component of the net dipole moment to the molecular axis decreases and has the opposite direction to those of **Ia** and **Ib** homologues. The **Ic** homologues have a smaller spontaneous polarization with opposite polarity.

The authors thank Dr. Toshio Yoshihara for his helpful discussion.

References

1) R. B. Meyer, L. Liebelt, L. Strzelecki, and P. Keller, *J. de Physique,* **36**, L-69 (1975).

2) J. W. Goodby and T. M. Leslie, "Liquid Crystals and Ordered Fluids," Plenum, New York (1984), Vol. 4, p. 1.

3) J. W. Goodby, *Science,* **231**, 350 (1986).

4) J. W. Goodby, E. Chin, T. M. Leslie, J. M. Geary, and J. S. Patel, *J. Am. Chem. Soc.,* **108**, 4729 (1986).

5) J. W. Goodby and E. Chin, *J. Am. Chem. Soc.,* **108**, 4736 (1986).

6) P. Keller, L. Liebert, and L. Strzelecki, *J. de Physique,* **37**, C3-27 (1976).

7) Ph. Martinot-Lagarde, *J. de Physique,* **37**, C3-129 (1976).

8) Ph. Martinot-Lagarde, R. Duke, and G. Durand, *Mol. Cryst. Liq. Cryst.,* **75**, 249 (1981).

9) J. R. Johnson, "Organic Reaction," ed by R. Adams, W. E. Bachman, J. R. Johnson, L. F. Fieser, and H. R. Snyder, Robert E. Krieger Pub., Huntington, New York (1978), Vol. 1, p. 210.

10) K. Miyasato, S. Abe, H. Takezoe, A. Fukuda, and E. Kuze, *Jpn. J. Appl. Phys.,* **22**, L661 (1983).

11) J. W. Goodby and G. W. Gray, *Mol. Cryst. Liq. Cryst.,* **48**, 127 (1978).

12) G. W. Gray, "The Molecular Physics of Liquid Crystals," ed by G. R. Luckhurst and G. W. Gray, Academic Press., London, New York, San Francisco (1979), Chap. 1.

13) W. L. McMillan, *Phys. Rev. A,* **8**, 1921 (1973).

14) R. T. Klingbiel, D. J. Genova, T. R. Criswell, and J. P. Van Meter, *J. Am. Chem. Soc.,* **96**, 7651 (1974).

15) V. I. Minkin, O. A. Osipov, and Yu. A. Zhdanov, "Dipole Moments in Organic Chemistry," Plenum Press., New York, London (1970), p. 226.