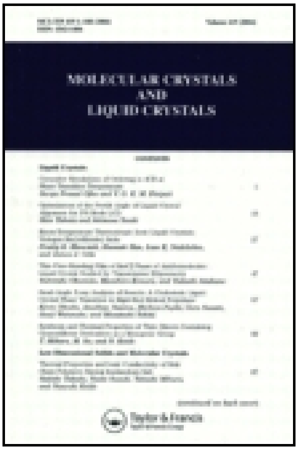

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Field-Induced Smectic A to Smectic C Transition in Ferroelectric Liquid Crystals with a Chiral Group on Each End of the Core

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Field-Induced Smectic A to Smectic C Transition in Ferroelectric Liquid Crystals with a Chiral Group on Each End of the Core

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The smectic A to chiral smectic C transition was studied in dichiral ferroelectric liquid crystals with an optically active alkanoyl group on one end of the core and another chiral group on the other end. Two electric current peaks were observed when a triangular-wave electric field was applied to the dichiral compounds in the smectic A phase. Texture observation and induced tilt angle measurement under an electric field revealed that these two current peaks are attributable to an electric-field-induced smectic A to smectic C phase transition. Differential scanning calorimetry and spontaneous polarization measurement showed that the smectic A to chiral smectic C transition of the dichiral compounds is first-order. The field-induced transition is attributed to the large spontaneous polarization and the first-order property of the transition.

Keywords: Ferroelectric liquid crystal, electric-field-induced phase transition, first-order transition, spontaneous polarization, tilt angle

1. INTRODUCTION

We have synthesized dichiral compounds with an optically active alkanoyl group on one end of the core and a chiral group derived from an optically active acid on the other end, and have shown that they exhibit very large spontaneous polarization *Ps*.[1–3] The study on the temperature dependences of *Ps* suggests that the smectic A (SmA) to chiral smectic C (SmC*) phase transition of the dichiral compounds is first-order.[3]

A theoretical prediction that the SmA-SmC* phase transition of a ferroelectric liquid crystal (FLC) is second-order[4] has been supported by many experimental results. Recent work, however, has shown that some FLCs with large *Ps* have a first-order SmA-SmC* transition, and that these compounds exhibit an electric-field-induced SmA-SmC* transition.[5]

This paper describes new types of FLCs that have a first-order SmA-SmC* transition and show an electric-field-induced SmA-SmC* transition.

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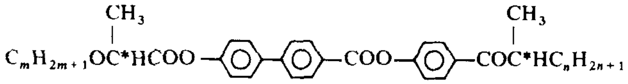
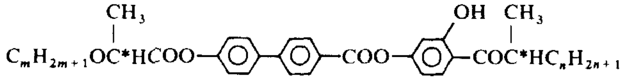
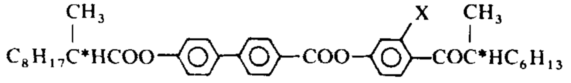
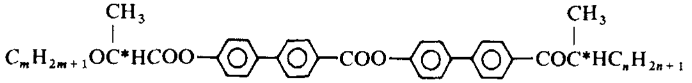
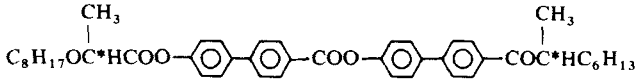
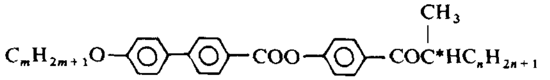
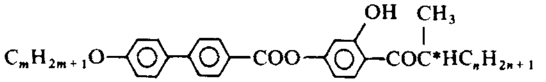
TABLE I

Compounds Investigated

Compound	Chemical Structure	Absolute Configuration	
A(*m*, *n*)		R	S
B(*m*, *n*)		R	S
C(*X*)		S	S
D(*m*, *n*)		R	S
E		S	S
F(*m*, *n*)			S
G(*m*, *n*)			S

2. EXPERIMENTAL

The dichiral compounds investigated are listed in Table I. Monochiral compounds with an alkanoyl group were also investigated for comparison. The phase transition temperatures on cooling are summarized in Table II.

The optical textures were observed using a Nikon XTP-11 polarizing microscope and the spontaneous polarization was measured by the triangular wave method,[6] using a sample cell which consists of two ITO-coated glass plates with rubbed polyimide. The cell spacing was 10 μm and the electrode area was 100 mm^2. The liquid crystals were injected into the cell in the isotropic phase and cooled slowly.

Differential scanning calorimetry (DSC) thermograms were obtained on a Perkin-Elmer DSC-7 using a 5-mg sample. DSC runs were taken during cooling at five different rates, ranging from 10°C/min to 1°C/min. The enthalpy change, ΔH, for SmA-SmC* transitions was evaluated and plotted against the cooling rate. A least-square straight-line fit of the ΔH data gave the enthalpy change ΔH_0 at zero cooling rate.

TABLE II

Phase Transition Temperatures for Compounds Investigated

Compound	m.p./° C	I–S_A/° C	S_A–S_C^*/°C	S_C^*–S_X/°C
A(6, 2)	52	106	50	–
A(6, 4)	79	79	67	–
A(8, 4)	43	80	65	–
A(4, 6)	92	76	70	–
A(8, 6)	80	75	72	–
A(10, 6)	64	75	70	–
B(4, 2)	55	56	25	–
B(6, 2)	52	63	23	–
B(6, 4)	47	40	32	–
B(6, 5)	45	40	31	–
B(8, 5)	48	39	34	–
B(4, 6)	45	42	28	–
B(5, 6)	37	49	35	–
B(8, 6)	43	44	36	–
B(6, 8)	47	43	35	–
B(8, 8)	40	46	39	–
C(H)	79	75	67	–
C(OH)	46	27	15	–
D(6, 6)	103	193	172	97
D(8, 6)	97	187	169	86
E	106	190	166	79
F(10, 2)	74	182	119	63
F(8, 6)	79	153	139	65
G(10, 2)	62	151	97	–
G(8, 6)	33	132	96	–

3. RESULTS

3.1. Two Current Peaks Observed Under the Application of a Triangular-wave Electric Field

When a triangular-wave electric field was applied to one of the dichiral compounds with a three-ring core (compounds *A*, *B* and *C*) in the SmA phase, two current peaks were observed, one in the positive field and the other in the negative. An example of compound *B*(4, 6) is shown in Figure 1. As the temperature approaches the SmA-SmC* transition temperature (28.3°C), the two current peaks approach each other toward zero field, and unify at the SmA-SmC* transition temperature. The field strengths where the two peaks are observed vary linearly with $\Delta T = T - T_c$, where T_c is the SmA-SmC* transition temperature (Figure 2).

To elucidate this phenomenon, texture observation and induced tilt angle measurement of compound *B*(4, 6) in the SmA phase were done under an electric field. The induced tilt angles were proportional to the applied field *E* in a small field region (Figure 3), suggesting an electroclinic effect.[7] In this region, the texture characteristic of the SmA phase remained unchanged. When the field exceeded a certain threshold value E_{th}, a steep rise in the induced tilt angles and the texture change from SmA to SmC* were observed. The threshold field E_{th} is plotted against ΔT in Figure 4.

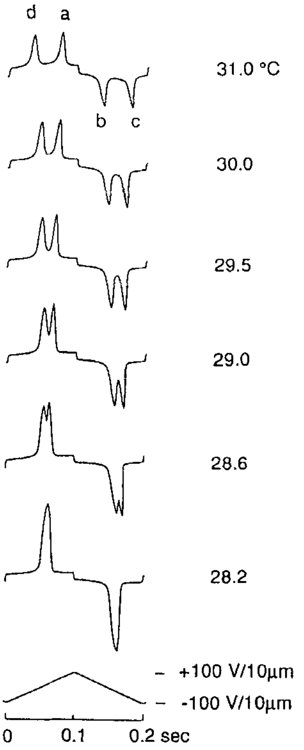


FIGURE 1 Examples of two current peaks observed when a triangular-wave electric field was applied to the dichiral compounds in SmA phase for compound *B*(4, 6) in a 10 μm cell. The curve at the bottom is the applied field, ± 10 V·μm^{-1}, 50 Hz.

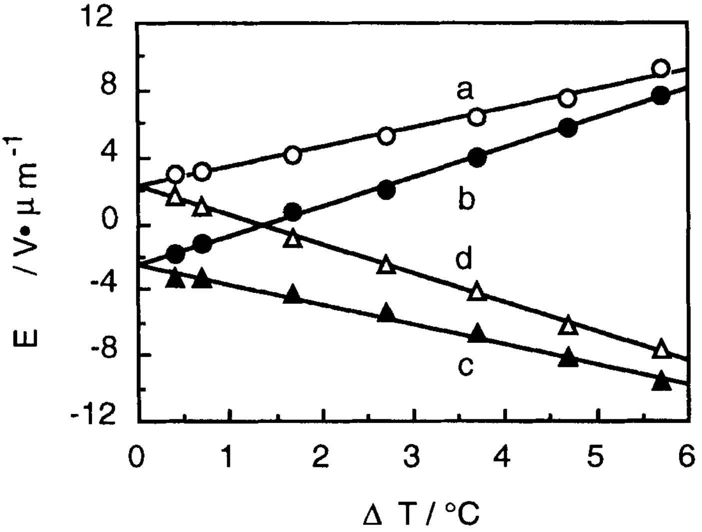


FIGURE 2 Relation between temperature and field strength at which the two peaks were observed. Experimental conditions are the same as in Figure 1. Labels on each line (*a*, *b*, *c*, *d*) correspond to those on each peak in Figure 1. $\Delta T = T - T_c$, where T_c is the SmA-SmC* transition temperature.

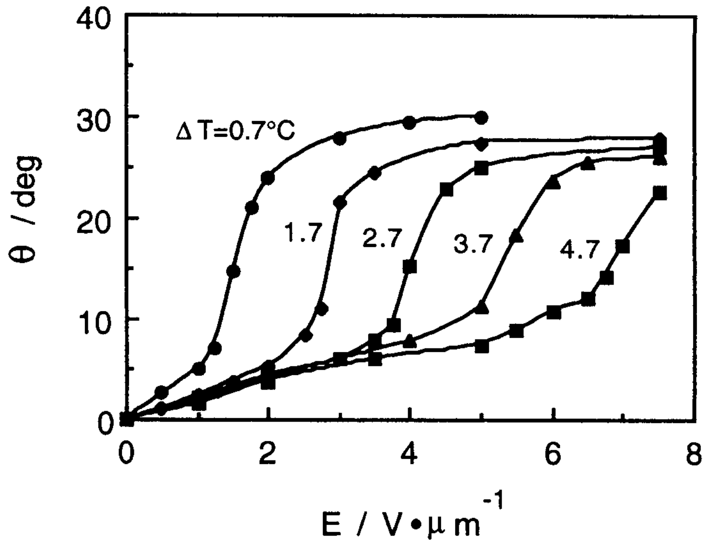


FIGURE 3 Relation between induced tilt angle and field strength for dichiral compound *B*(4, 6) at various temperatures.

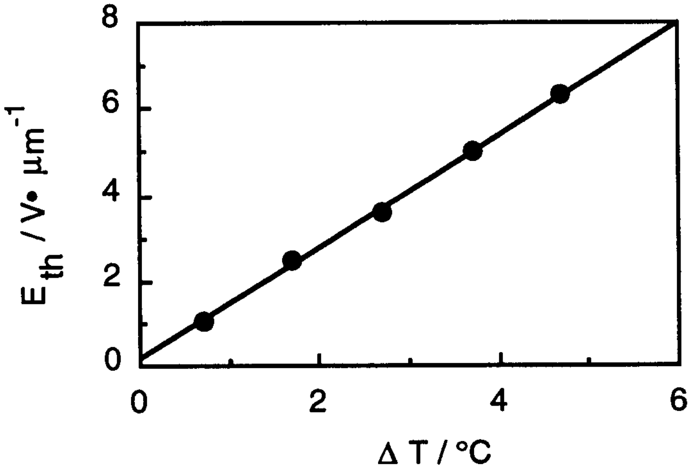


FIGURE 4 Relation between temperature and threshold field strength for dichiral compound *B*(4, 6).

Comparing Figure 3 with Figure 1, it is apparent that E_{th} is almost equal to the field strength where current peak (a) in Figure 1 starts to rise, and that the end point of the steep rise in Figure 3 is nearly equal to the field strength at which peak (a) is maximum. Comparing Figure 4 with Figure 2, E_{th} values are found to be equal to the average of the field strengths at which the two peaks (a) and (b) are observed.

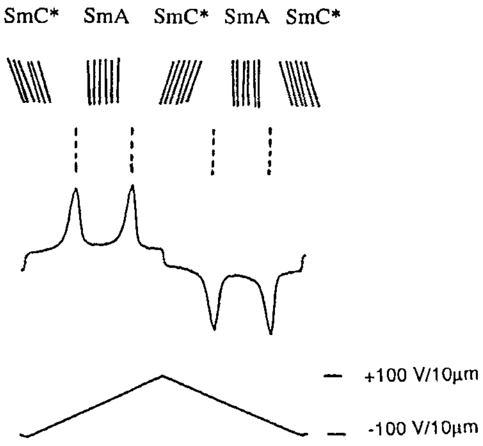


FIGURE 5 Illustration of field-induced SmA to SmC* phase transition. Rods represent the liquid crystal molecules.

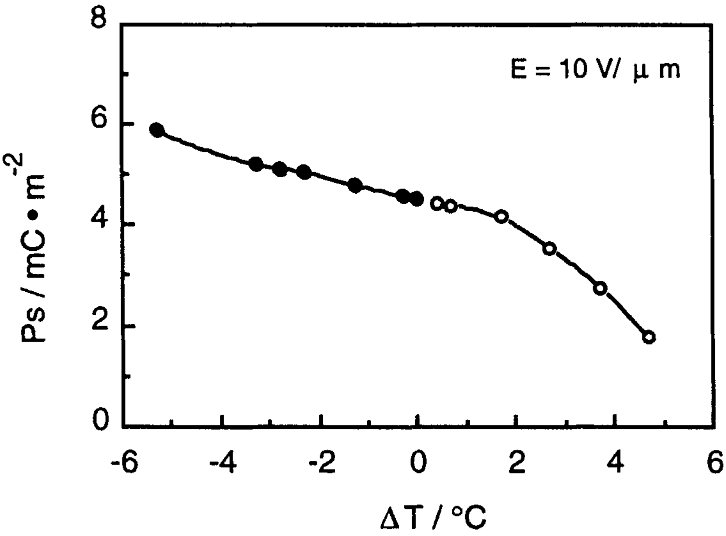


FIGURE 6 Temperature dependences of the area of the two peaks (∘) and spontaneous polarization (•) for compound *B*(4, 6).

The facts described above show that the two current peaks in Figure 1 are observed at a field strength where an electric-field-induced SmA-SmC* transition takes place. In other words, current peak (a) is attributed to the transition from SmA to one of the two stable states of the SmC* phase, and peak (c) is related to the transition from SmA to the other state of the SmC* phase. Peaks (b) and (d) are due to the respective reverse transitions. These processes are illustrated in Figure 5.

The areas of the two peaks in Figure 1 found by integration are plotted against ΔT in Figure 6, in which the *Ps* in the inherent SmC* phase is also shown. A smooth curve

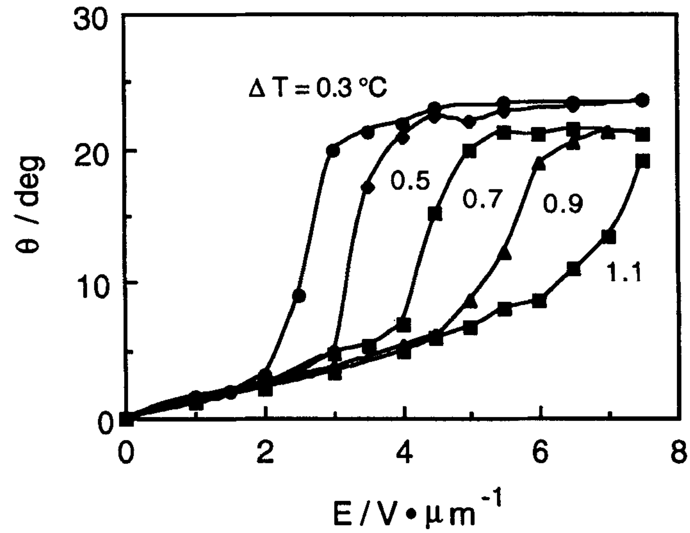


FIGURE 7 Relation between field strength and induced tilt angle for dichiral compound *E* with a four-ring core.

was obtained throughout both the SmA and SmC* phase regions. This means that the current associated with the transition from one state of the induced SmC* phase to the other through the SmA phase corresponds to the polarization reversal current characteristic of the SmC* phase.

Field-induced SmA-SmC* transition currents were not clearly observed for dichiral compounds with a four-ring core, such as compounds *D* and *E*, and for some three-ring dichiral compounds having a short alkanoyl group, such as compound *A*(6, 2). A steep rise in induced tilt angles was nevertheless observed for these compounds when an electric field was applied (Figure 7).

3.2. Relationship Between Field Strength and Shift in SmA-SmC* Transition Temperature

As described above, an induced SmA-SmC* transition takes place when an electric field is applied to the dichiral compounds in the SmA phase at a temperature near the SmA-SmC* transition. In other words, the SmA-SmC* transition temperature rises under an electric field. The average field strength, E_{av}, at which peaks (a) and (b) are observed in Figure 1 is equal to E_{th}, where the induced transition takes place. Consequently, one can get an E–T phase diagram by plotting the induced transition temperatures against E_{av} or E_{th}. Examples are given in Figure 8.

The slope of the line dividing the SmA and SmC* phases in Figure 8 is equal to the SmA-SmC* transition temperature shift per unit field strength, $\Delta T/E$, which indicates the ease of field-induced SmA-SmC* transition. The $\Delta T/E$ values for the dichiral compounds are summarized in Table III.

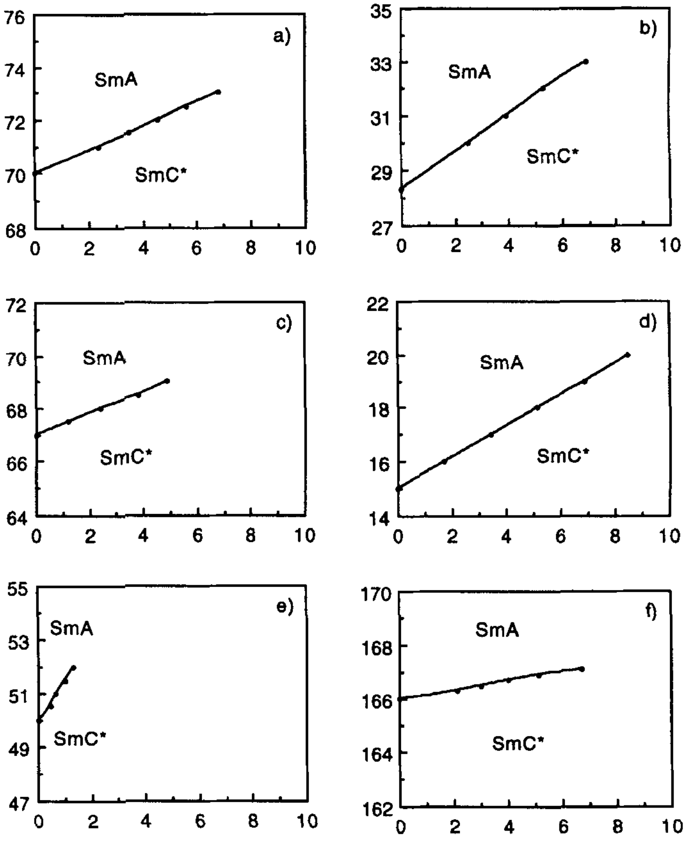


FIGURE 8 E-T phase diagrams for a) compound $A(4,6)$, b) compound $B(4,6)$, c) compound C(H), d) compound C(OH), e) compound $A(6,2)$ and f) compound E. The ordinate is temperature T(°C) and the abscissa is field strength E(V/μm).

3.3. DSC Study of the SmA-SmC* Transition in Dichiral Compounds

The field-induced SmA-SmC* transition is generally considered to be related to the order of the transition. Consequently, it is important to determine the order of the SmA-SmC* transition for the dichiral compounds and it was investigated by DSC. The enthalpy change ΔH_0 for the SmA-SmC* transition at zero cooling rate was obtained by extrapolation (Figure 9). The ΔH_0 thus obtained is considered to be the true latent heat, free from specific heat contributions.[8] The results are summarized in Table III.

SmA-SmC* transitions for dichiral compounds A to E have a definite ΔH_0 value. This means that the transitions are accompanied by latent heat; that is, they are first-order.

TABLE III

$\Delta T/E$, ΔH_0, ΔPs and Ps for dichiral compounds

Compound	$\Delta T/E/^\circ\mathrm{C}\cdot\mu\mathrm{m}\cdot\mathrm{V}^{-1}$	$\Delta H_0/\mathrm{KJ}\cdot\mathrm{mol}^{-1}$	$\Delta Ps/\mathrm{mC}\cdot\mathrm{m}^{-2}$	Ps#/$\mathrm{mC}\cdot\mathrm{m}^{-2}$
A(6,2)	1.4	0.1	1.88	3.50
A(6,4)	0.39	0.7	2.58	4.57
A(8,4)	0.48	0.4	2.19	4.07
A(4,6)	0.44	1.0	3.16	–
A(8,6)	0.36	1.0	2.80	5.12
A(10,6)	0.40	0.8	2.32	4.18
B(4,2)	0.82	0.3	2.70	–
B(6.2)	1.02	0.2	2.73	4.40
B(6,4)	0.66	1.0	5.10	7.70
B(6,5)	0.58	1.0	4.60	6.50
B(8,5)	0.90	1.0	5.56	–
B(4,6)	0.68	0.7	4.50	6.63
B(5,6)	0.62	0.8	4.30	6.60
B(8,6)	0.53	1.1	4.10	6.65
B(6,8)	0.56	1.1	3.95	5.60
B(8,8)	0.51	0.9	3.36	5.85
C(H)	0.40	0.8	1.53	3.60
C(OH)	0.58	0.6	2.85	4.70
D(6,6)	–	0.7	0.30	2.75
D(8,6)	–	0.8	0.25	2.50
E	0.17	0.7	0.30	1.78
F(10,2)	–	0	0	0.50
F(8,6)	–	0	0	1.08
G(10,2)	–	0	0	0.57
G(8,6)	–	0	0	1.46

Measured at 10°C below the SmA-SmC* transition temperature.

Dichiral compounds *A*, *B*, and *C* are characterized by the fact that the Ps at the SmA-SmC* transition is not zero.[3] The jumps in *Ps* at the SmA-SmC* transition, ΔPs, for these compounds was shown in Table III. The jump in *Ps* at the transition is characteristic of the first-order transition, and is consistent with the result of the DSC study.

At first, the temperature dependences of *Ps* for the four-ring core dichiral compounds *D* and *E* appeared to show a rise from zero, that is, they have second-order characteristics.[3] Closer examination, however, revealed that there is a small jump in *Ps* at the SmA-SmC* transition.

The ΔH_0 of SmA-SmC* transitions for monochiral compounds with an alkanoyl group, compounds *F* and *G*, are practically zero. Therefore, their SmA-SmC* transitions are second-order, just as are most of the FLCs. The curves of their temperature dependences of *Ps* show a slow rise from zero,[3] as expected.

The ΔH_0 of the SmA-SmC* transition for dichiral compounds *A* and *B* is strongly influenced by the length of both the terminal groups. ΔH_0 increases rapidly with increasing carbon numbers *m* and *n*, and becomes nearly constant when both *m* and *n* are six or more. The magnitude of ΔH_0 for these compounds seems to correlate with the width of the SmA phase (Figure 10). As *m* and *n* increase, the SmA phase becomes narrower and ΔH_0 of the SmA-SmC* transition increases.

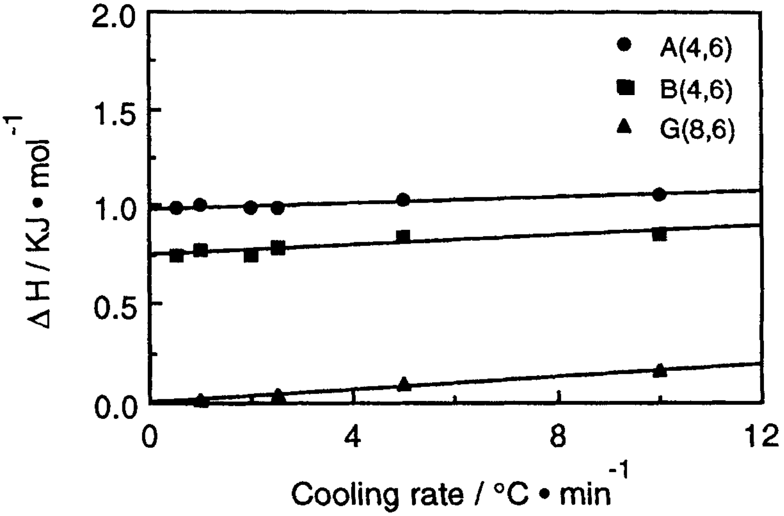


FIGURE 9 Change in ΔH with cooling rate for SmA-SmC* transition of monochiral and dichiral compounds.

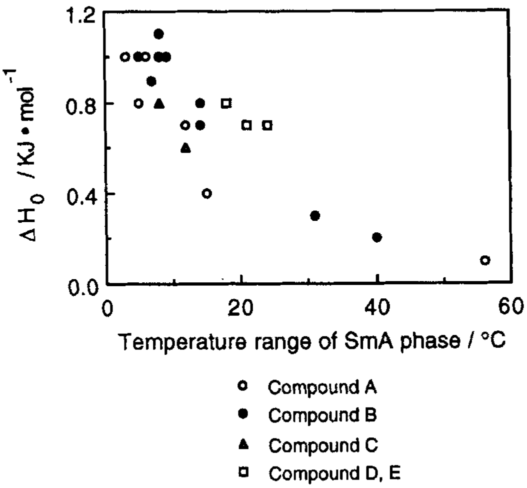


FIGURE 10 ΔH_0 versus width of SmA phase for dichiral compounds.

4. DISCUSSION

A Clausius–Clapeyron type equation,

$$\Delta T/E = \Delta Ps/\Delta S,$$

where ΔS is the entropy change at the transition, has been established for the field-induced shift of a first-order ferroelectric-paraelectric transition in solid ferroelec-

TABLE IV

Observed and Calculated $\Delta T/E$

Compound	Observed $\Delta T/E$	Calculate $\Delta T/E$
A(6, 4)	0.39	0.69
A(4, 6)	0.44	0.62
B(6, 4)	0.66	0.84
B(4, 6)	0.68	1.04
B(8, 6)	0.53	0.71
C(H)	0.40	0.37
C(OH)	0.58	0.86

trics.[9] This equation explains the linear relationship between ΔT and E observed in the dichiral compounds. However, the $\Delta T/E$ values estimated using this equation and the equation $\Delta S = \Delta H/Tc$ were found to be larger than the measured values (Table IV). Although the errors in measuring ΔPs, ΔT and ΔH are partly responsible, the reason for this discrepancy is not clear and is being studied.

The $\Delta T/E$ values obtained for dichiral compounds *A*, *B* and *C* with a three-ring core are larger than the values reported by Bahr *et al.*[5] The $\Delta T/E$ value for compound *E*, on the other hand, is smaller than those obtained by them. It can be deduced using the equation described above that these primarily result from the magnitude of ΔPs of the dichiral compounds, that is, ΔPs for the dichiral compounds with a three-ring core is considerably larger and ΔPs for compound *E* with a four-ring core is smaller than ΔPs of the compounds investigated by Bahr.

In general, $\Delta T/E$ values decrease with increasing length of the terminal groups in compounds with the same core and the same chiral center. In other words, the induced SmA-SmC* phase transition for the dichiral compounds with shorter terminal groups occurs more easily than those with longer terminal groups. Generally speaking, the increase in the terminal carbon numbers in the dichiral compounds causes an increase in both ΔPs and ΔH, but the rate of increase for ΔH is greater than for ΔPs.

Comparison of compound *A*(4, 6) and *B*(4, 6), or compound *C*(H) and *C*(OH), shows that the presence of a hydroxyl group in the core leads to an increase in $\Delta T/E$ value. This is attributed to the fact that the presence of a hydroxyl group results in a considerable increase in ΔPs but does not considerably influence ΔH.

When a triangular-wave electric field was applied, two current peaks were not clearly observed for dichiral compounds with a four-ring core (compounds *D* and *E*) and for some dichiral compounds with a three-ring core having a short alkanoyl group such as compound *A*(6, 2). As shown in Table III, the dichiral compounds with a four-ring core exhibit smaller *Ps* than their analogous compounds with a three-ring core. The dichiral compounds with a three-ring core and a short alkanoyl group have a smaller *Ps* than their analogues with a longer alkanoyl group. These results suggest that the magnitude of *Ps* determines whether the field-induced transition currents are clearly observed or not.

In general the enthalpy change ΔH_0 of the SmA-SmC* phase transition for the dichiral compounds increases as the lengths of the two terminal groups increase. At the same time, the increase in the length of the terminal group tends to enhance *Ps*. In other words, the increase in *Ps* is essentially related to a greater structural change at the transition and hence with the enhancement of the first-order property of the transition, which is profoundly correlated with the field-induced SmA-SmC* phase transition.

The two current peaks attributed to the field-induced SmA-SmC* transition under the application of a triangular-wave electric field were first reported by Dupont *et al.*[10] They observed at the same time the electric current due to the electoclinic response, which appears at near zero voltage. In our dichiral compounds, however, no clear electric current attributable to electroclinic response was observed. One reason for this is presumably in the fact that the first-order property of the dichiral compounds is considerably stronger than the compounds investigated by Dupont *et al.* This results in a lowering of the electroclinic response relative to the phase transition current. Another reason is probably the rather high viscosity of the dichiral compounds, which leads to a broadening of the response current.

5. CONCLUSION

Two current peaks were observed when a triangular-wave electric field was applied to the SmA phases of dichiral compounds having an optically active alkanoyl group on one end of the core and a chiral group derived from an optically active acid on the other end. These peaks were attributed to transitions from the SmA phase to field-induced SmC* phase. The field-induced SmA-SmC* transition is related to the first-order character of the transition.

Field-induced transition currents were not clearly observed for dichiral compounds with a four-ring core or those with a three-ring core having a short alkanoyl group, despite the first-order character of the SmA-SmC* transition. In this regard the magnitude of the *Ps* value seems to play an important role.

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