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The effects of a second branched alkyl chain and double chiral centres on the phase transition and spontaneous polarization of a chiral smectic liquid crystal

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The effects of a second branched alkyl chain, lateral substitution, and double chiral centres on the phase transition and spontaneous polarization of the ferroelectric liquid crystal having a 2-methylalkanoyl group have been investigated. The introduction of another branched alkyl chain away from the 2-methylalkanoyl group causes a sharp S_C^*–S_A transition peak and also enhances the ferroelectric properties in the S_C^* phase. Since the order within the layers is liquid-like in the S_C^* phase, the alkyl chain branching away from both the chiral centre and a polar group affects the overall motion of the molecule in the S_C^* phase. In the system of a compound with double chiral centres, the existence of the chiral centre in the 2-methylalkanoyl group affects the phase transition temperatures and the magnitude of the spontaneous polarization in the S_C^* phase. On the other hand, the existence of the chiral centre in the 2-methylbutyl group only affects the stability of a more highly ordered smectic phase appearing below the S_C^* phase.

1. Introduction

To control the physical properties of a ferroelectric liquid crystal via its molecular structure is a most attractive problem both from basic interest and in view of possible applications. Much work has been carried out to establish correlations between physical properties and molecular structure [1]. We have previously reported the effects of dipole moment, alkyl chain length, lateral substitution, and core structure on the phase transition and spontaneous polarization of ferroelectric liquid crystals [2–4]. At present, it is difficult to give quantitative descriptions for the intermolecular interactions in the S_C^* phase. Therefore, it is necessary to investigate the molecular motions and microscopic environment of molecules in smectic phases [5–8]. Since the order within the layers is liquid-like in a S_C^* phase, molecular motions play an important role in the intermolecular interactions.

Our recent ^{13}C NMR study of a ferroelectric liquid crystal revealed that the discontinuity concerning the overall fluctuation occurs at the S_C^*–S_A transition [9]. The influence of alkyl chain branching on smectic phase formation has been discussed by Coates [10] and Matsunaga *et al.* [11]. By introducing another branched alkyl chain into a S_C^* molecule, it is expected that the overall motion in the S_C^* phase will be influenced. Here we report on the effects of a second branched alkyl chain and double chiral centres on the phase transition and spontaneous polarization of a chiral smectic liquid crystal.

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2. Experimental

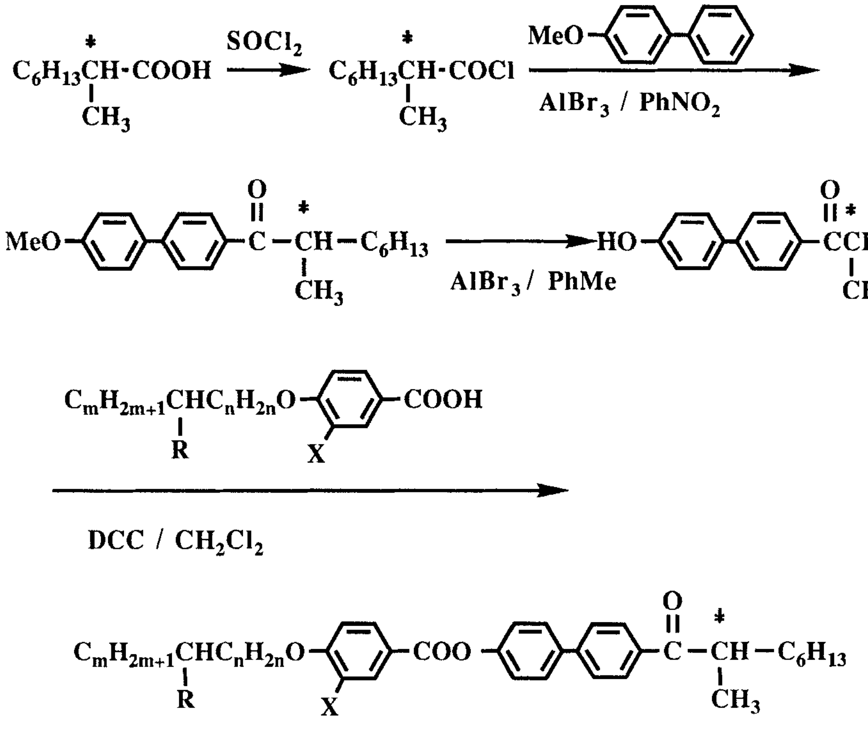
2.1. *Synthesis*

The route for the synthesis of the materials is presented in scheme 1.

2.1.1. *Synthesis of 4-hydroxy-4′-((S)-2-methyloctanoyl)biphenyl*

Commercially available (*S*)-2-methyloctanoic acid (89 per cent enantiomer excess, Nippon Mining Co., Ltd.) was used as the starting material. To thionyl chloride (8·98 g, 75·5 mmol) placed in a flask was added (*S*)-2-methyloctanoic acid (8·93 g, 56·4 mmol). The mixture was stirred at room temperature for 1 hour and then at 70°C for 2 hours. The excess thionyl chloride was distilled off yielding the (*S*)-2-methyloctanoyl chloride (9·80 g, 55·5 mmol, 98 per cent).

Into a flask was charged commercially available 4-methyloxybiphenyl (1·0 g, 5·4 mmol), which was dissolved in 3 ml of nitrobenzene under an atmosphere of nitrogen. To the solution was added dropwise a mixture of (*S*)-2-methyloctanoyl chloride (1·5 g, 8·1 mmol) and aluminium bromide (2·2 g, 8·1 mmol) which had been previously stirred under ice cooling at room temperature for 5 min. Then, the reaction mixture was stirred at 40°C for 9 hours. The reaction mixture was then poured into 50 ml of acidic ice water (pH 1) and extracted with chloroform (3 x 40 ml). The combined organic layers were washed with water (4 x 50 ml) and dried over anhydrous magnesium sulphate. The drying agent and solvent were removed and the residue purified by column chromatography on silica gel using first hexane as eluent and then a 1 : 1 hexane/toluene mixture. Recrystallization from ethanol gave the 4-methyloxy-4′-((*S*)-2-methyloctanoyl)biphenyl (430 mg, 25 per cent).



Scheme 1. Synthetic route to the 4-(2-methyloctanoyl)-4′-biphenyl 3-*X*-4-alkyloxybenzoates.

400 mg (1·2 mmol) of the above 4-methyloxy-4′-((*S*)-2-methyloctanoyl)biphenyl was dissolved in 6 ml of dried toluene in a flask. Aluminium bromide (1·3 g, 50 mmol) was added to the solution under ice cooling for 5 min. The reaction solution was then stirred under ice cooling for 6 hours, at room temperature for 60 hours, and at 40°C for 11 hours. The reaction mixture was poured into ice water (100 ml) and extracted with toluene (2 × 40 ml). The combined organic layers were washed with water (2 × 40 ml) and dried over anhydrous magnesium sulphate. Column chromatography on silica gel using toluene as eluent and then using a 1 : 1 toluene/diethyl ether mixture as eluent gave the desired product (200 mg, 54 per cent). 90 MHz ^{1}H NMR ($CDCl_3$) δ 7·98 (d, 2 H), 7·60 (d, 2 H), 7·50 (d, 2H), 6·92 (d, 2 H), 6·00 (brs, 1 H), 3·48 (m, 1 H), 2·00–0·75 (m, 16 H). IR (KBr): 3250, 2900, 1650, 1585, 1170 cm^{-1}. $[\alpha]^{25D}$: +6·0° (c 4·26, $CHCl_3$). The absolute configuration of the asymmetric carbon of the product was estimated from that of the asymmetric carbon of the starting material.

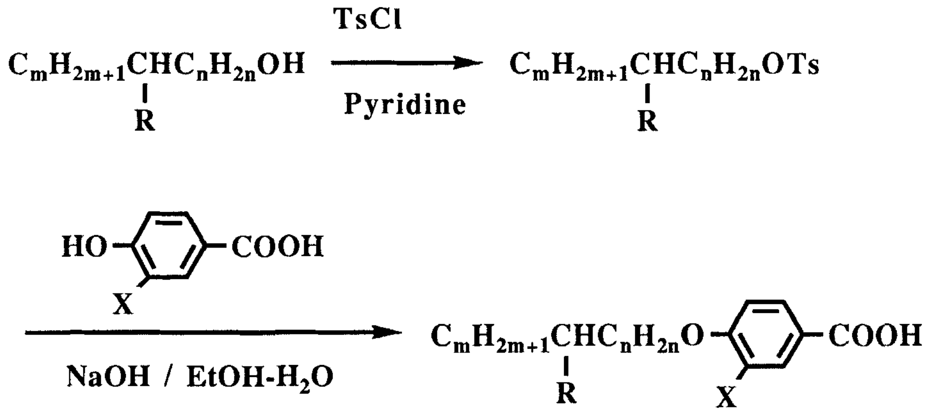
Racemic (±)-4-hydroxy-4′-(2-methyloctanoyl)biphenyl was prepared from the racemic (±)-2-methyloctanoic acid in a similar method to that for the 4-hydroxy-4′-((*S*)-2-methyloctanoyl)biphenyl.

2.1.2. *Synthesis of 3-X-4-alkyloxybenzoic acid*

A typical route of the synthesis of 3-*X*-4-alkyloxybenzoic acid is shown in scheme 2. 4-((*S*)-2-methylbutyloxy)benzoic acid was purchased from Teikoku Chemical Industry Co., Ltd. 4-Butyloxybenzoic acid and 4-octyloxybenzoic acid were purchased from Kanto Chemical Co., Inc. The other materials were prepared by the method shown in scheme 2. Racemic (±)-4-(2-methylbutyloxy)benzoic acid was prepared from racemic (±)-2-methylbutanol as a starting material. The structures of the obtained substituted benzoic acids were confirmed by means of IR and NMR spectral analysis.

2.1.3. *Synthesis of 4-((S)-2-methyloctanoyl)-4′-biphenyl 4-((S)-2-methylbutyloxy) benzoate*

A solution of 4-((*S*)-2-methylbutyloxy)benzoic acid (1·04 g, 5·0 mmol), 4-hydroxy-4′-((*S*)-2-methyloctanoyl)biphenyl (1·55 g, 5·0 mmol), *N*,*N*′-dicyclohexylcarbodiimide (1·05 g, 5·1 mmol), 4-dimethylaminopyridine (0·10 g), in dichloromethane (10 ml) was stirred at room temperature for 10 hours. After filtration to remove the precipitate, the filtrate was concentrated under reduced pressure. The residue was purified by column chromatography on silica gel using toluene as eluent followed by recrystallization from



Scheme 2. Synthetic route to the 3-*X*-4-alkyloxybenzoic acids.

ethanol (2 x 30 ml). 1·15 g (2·3 mmol, 46 per cent) of the desired product was obtained. 90 MHz ^{1}HNMR (CDCl$_3$): δ 8·16 (d, 2 H), 8·06 (d, 2 H), 7·84 (d, 4 H), 7·48 (d, 2 H), 7·00 (d, 2 H), 3·95 (d, 1 H), 3·92 (d, 1 H), 3·48 (m, 1 H), 2·13–0·80 (m, 25 H), IR (KBr): 2920, 1730, 1673, 1595, 1270 cm^{-1}.

The other final ester products were prepared by the same esterification of a number of 3-*X*-4-alkyloxybenzoic acids with 4-hydroxy-4′-(2-methyloctanoyl)biphenyl. The structures of the final products were confirmed by means of IR and ^{1}HNMR spectral analysis. The purity of the compounds was determined by thin layer chromatography. Smectic A–isotropic coexistence ranges of the compounds were less than 1°C.

2.2. *Measurements*

The liquid crystal transition temperatures and enthalpies were determined by differential scanning calorimetry using a Seiko DSC-200 calorimeter. The liquid crystal transition temperatures were also observed by polarizing optical microscopy using a Mettler FP82 heating stage.

Cells (purchased from EHC Co., Ltd.) of 2·5 μm thickness aligned by rubbing, after coating the ITO deposited glass plates with a polyimide film, were used for measurements of the spontaneous polarization and tilt angle. The spontaneous polarization was measured by the triangular wave method [12] and the tilt angle was derived from the optical switching angle of the sample.

^{13}C NMR measurements were carried out using a JEOL GSX-270 spectrometer at 67·9 MHz with proton dipolar decoupling. The ^{13}C CP/MAS NMR spectra were observed at a spinning speed of 4·5 kHz and at a contact time of 5·0 ms. The temperature was calibrated by observing the S$_A$ to isotropic phase transition.

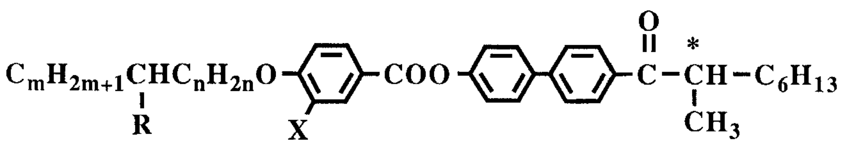
3. Results and discussion

The transition temperatures, spontaneous polarization, and tilt angle of the 4-(2-methyloctanoyl)-4′-biphenyl 3-*X*-4-alkyloxybenzoates were investigated. Their structural formulae are given in figure 1.

3.1. *Alkyl chain branching*

The transition temperatures measured for the butyloxy **1**, (*S*)-2-methylbutyloxy **2a**, 3-methylbutyloxy **3** derivatives are listed in table 1.

Compound **2a** gives an S$_A$–I transition temperatures lowered by 41°C compared to that of compound **1**. The S$_A$–I transition temperature given by compound **3** is higher



1: R=H, X=H, m=2, n=1, 2: R=CH$_3$, X=H, m=2, n=1

3: R=CH$_3$, X=H, m=1, n=2, 4: R=H, X=Cl. m=2, n=1

5: R=CH$_3$, X=Cl, m=2, n=1

Figure 1. Structures of the 4-(2-methyloctanoyl)-4′-biphenyl 3-*X*-4-alkyloxybenzoates.

Table 1. Transition temperatures (°C) and enthalpies of transition (kJ mol^{-1}) determined† for the 4-((*S*)-2-methyloctanoyl)-4′-biphenyl 4-alkyloxybenzoates.

Compound	Alkyl group	C		S_X‡		S_C^*		S_A		I
1	$CH_3(CH_2)_3$	●	85·1			●	(69·9)	●	146·2	●
ΔH§			24·4						4·2	
2	$CH_3CH_2CH(CH_3)CH_2$	●	67·3	●	(30·9)	●	69·8	●	104·6	●
ΔH			20·9		2·3		0·3		3·0	
3	$CH_3CH(CH_3)CH_2CH_2$	●	64·4	●	(30·6)	●	75·4	●	123·2	●
ΔH			25·5		3·1		0·3		3·3	

† The transition temperatures and enthalpies of S_A–I, S_C^*–S_A, and S_X–S_C^* were determined on cooling by DSC at a rate of 2·0°C min^{-1}, those of crystal to smectic phases were determined on heating.

‡ Higher ordered smectic phase not yet identified.

§ Transition enthalpy of the S_A–S_C^* transition for compound **1** was too small to be evaluated.

than that of compound **2a**, even though it is lower than that of compound **1**. The S_A–I transition entropies observed for compounds **1**, **2a**, and **3** are 10·0 J mol^{-1} K^{-1}, 7·9 J mol^{-1} K^{-1}, and 8·3 J mol^{-1} K^{-1} respectively. Favourable entropy changes observed for compounds **2a** and **3** can be explained on the basis of their packing entropy. The higher S_A–I transition temperature of compound **1** indicates that the S_A–I transition of this system is governed by the enthalpy term.

For compounds **1**, **2a**, and **3** the introduction of another branched alkyl chain gives slight temperature changes at the S_C^*–S_A transition. An important difference between the DSC thermograms of compound **1** and those of compounds **2a** and **3** is observed. The thermograms of cooling of compounds **1** and **3** are shown in figure 2. The peak height at the S_C^*–S_A transition is enhanced by the introduction of the alkyl chain branch away from the chiral centre. The branched alkyl chain may affect the intermolecular interaction in the S_C^* phase. The thermal stability of the higher ordered smectic phase increases upon introduction of the second alkyl chain branch. Compounds **2a** and **3** give lower crystal–smectic transition temperatures compared to that of compound **1**. It is necessary to obtain microscopic information concerning the relationship between molecular structure and phase transition properties. ^{13}C cross polarization and magic angle spinning (CP/MAS) NMR spectroscopy provides useful information concerning each carbon of the molecule in both the smectic and crystal phases [8]. In order to investigate the microscopic environment of a biphenyl benzoate liquid crystal at the C–S_C^* transition, the ^{13}C CP/MAS NMR spectra in the S_C^* and C phases for 4-((*S*)-2-methyloctanoyl)-4′-biphenyl 4-octyloxybenzoate were obtained. This compound shows a favourable temperature range of the S_C^* phase. The NMR spectra obtained are shown in figure 3. Chemical shifts of typical carbons in the S_C^* and C phases are also given in table 2. In the crystal phase, the aromatic carbon C10 gives doublet peaks. Larger shifts are observed for the carbons C7 (4·0 ppm) and C8 (−1·6 ppm) in the alkyloxy chain attached to the benzene ring. Observed shifts for the carbons in the chain attached to the benzene ring are larger than those for the carbons attached to the biphenyl ring. Similar results for 4-((*S*)-2-methyloctanoyl)phenyl 4′-nonylbiphenyl-4-carboxylate [8] and 4-heptyloxyphenyl 4′-((*S*)-2-methylbutyl)biphenyl-4-carboxylate [13] are reported. Following the approach of Hayamizu *et al.* [13], there may be two mechanisms that can explain the appearance of the doublet for the aromatic carbon C10. The first is the slowing down of an internal flip motion of the benzene ring around

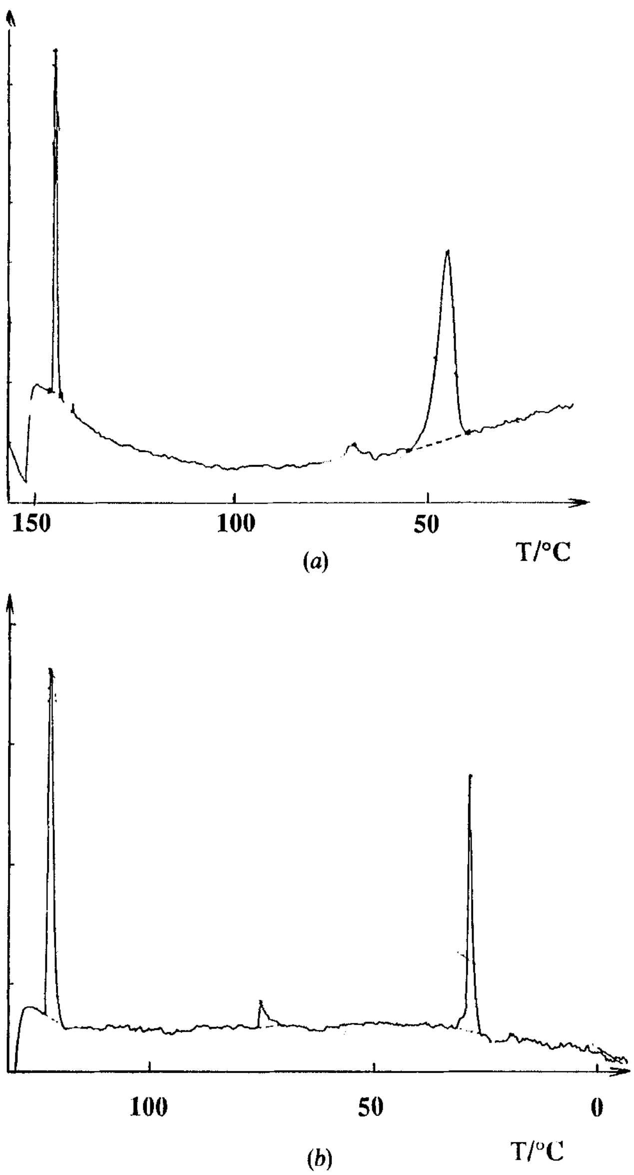


Figure 2. DSC cooling curves for (*a*) compound **1** and (*b*) compound **3**. Cooling rate 2°C min^{-1}.

the O–C9–C12–C13 axis. A second possibility may be the slowing down of a segmental motion of the alkoxy side chain. But there is not clear evidence for the slowing down of the segmental motion for the alkoxy carbon C8 both in the line width and the peak intensity. Therefore, splitting of the chemical shift for the aromatic carbon C10 suggests the slowing down of the internal motion of the benzene ring around O–C9–C12–C13 axis. The origin of the large shifts for the carbons C7 and C8 may be the stretched ordering of the alkyloxy chain in the crystal phase. NMR results indicate that the internal motion of the benzene ring and the ordering of the alkyloxy chain are related to the thermal stability of the higher ordered smectic phase and the crystal-smectic

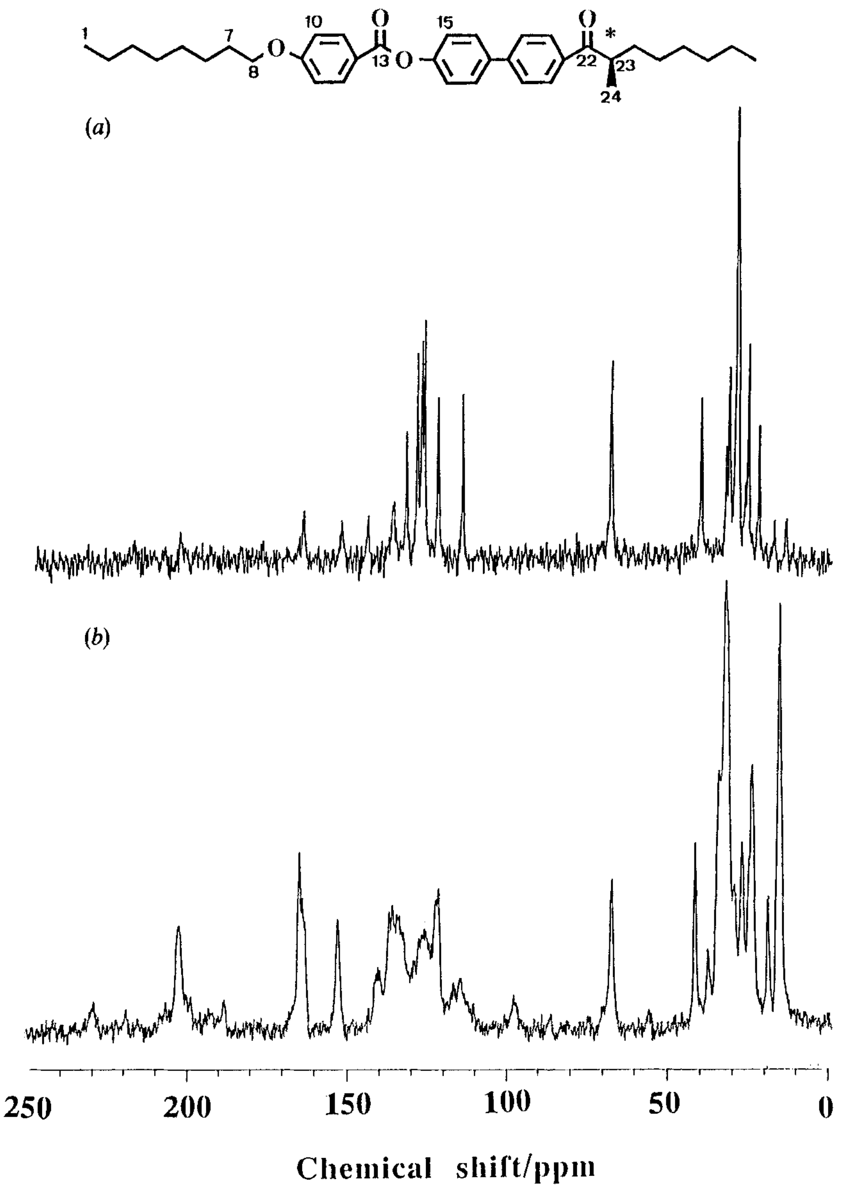


Figure 3. The ^{13}C NMR spectra of 4-((*S*)-2-methyloctanoyl)-4′-biphenyl 4-octyloxybenzoate in (*a*) the S_C^* phase at 90°C and (*b*) in the crystal phase at 52°C.

Table 2. ^{13}C chemical shifts (ppm) obtained for 4-((*S*)-2methyloctanoyl)-4′-biphenyl 4-octyloxybenzoate in the S_C^* (90°C) and C (52°C) phases.

	Aromatic		Ester	Alkyloxy		Alkanoyl		
Phase	C10	C15	C13	C7	C8	C22	C23	C24
S_C^*	115·1	122·8	164·3	33·5	68·7	203·0	41·1	17·9
C	114·8 116·8	121·7	164·6	37·5	67·1	202·6	41·4	18·7

transition. By the introduction of the branching methyl group to the alkyloxy chain, the molecular packing of the alkyloxy chain becomes less rigid and the flexibility of the benzene ring increases.

The temperature dependence of the spontaneous polarization and that of tilt angle observed for compounds **1**, **2a**, and **3** are shown in figures 4 and 5, respectively. Compounds **2a** and **3** give higher values of the spontaneous polarization and tilt angle compared to those of compound **1** in the temperature range of the S_C^* phase. The spontaneous polarization, tilt angle, and ratio $P_s/\sin\theta$ obtained at 10°C below the S_C^*–S_A transition for compounds **1**, **2a**, and **3** are listed in table 3. The ferroelectric properties in the S_C^* phase are strongly affected by the introduction of another alkyl chain branching away from the 2-methyloctanoyl group. There is the possibility that the first order nature of the S_C^*–S_A transition can cause an apparent increase in the spontaneous polarization. Since compounds **2a** and **3** show an exothermic DSC peak at the S_C^*–S_A transition, the enhanced polarization of compounds **2a** and **3** could be related to a first order S_C^*–S_A transition.

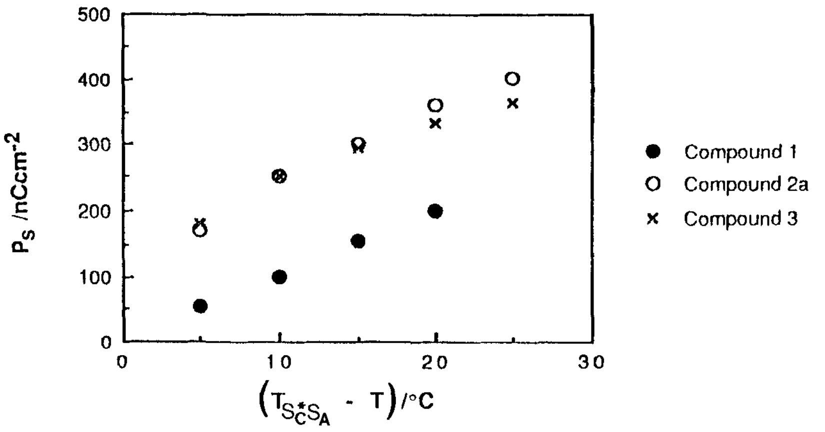


Figure 4. The temperature dependence of the spontaneous polarization observed for compounds **1**, **2a**, and **3**.

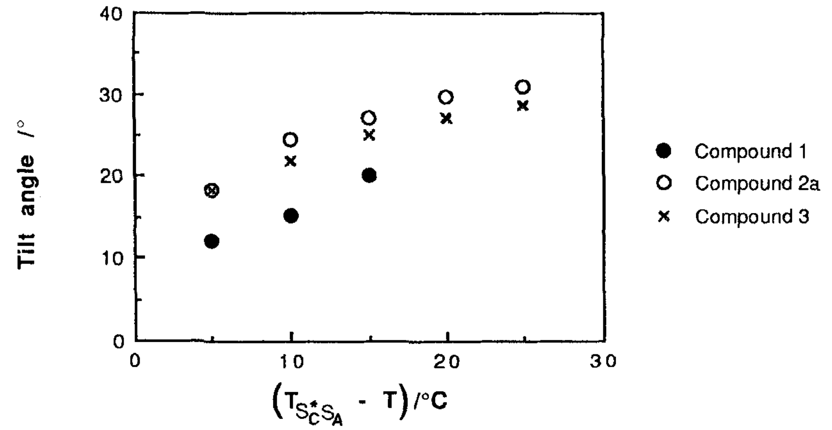


Figure 5. The temperature dependence of the tilt angle observed for compounds **1**, **2a**, and **3**.

Table 3. The spontaneous polarization, tilt angle, and ratio $P_s/\sin\Theta$ obtained† for compounds **1**, **2a**, and **3**.

Compound	P_s/nC cm^{-2}	Θ/°	$P_s/\sin\Theta$/nC cm^{-2}
1	−100	15·2	−381
2a	−250	24·4	−605
3	−251	22·0	−670

† Obtained at 10°C below the S_C^*–S_A transition.

Let us consider the effect of the alkyl chain branching on the intermolecular interaction in the S_C^* phase. X-ray studies of S_C phases reveal a diffraction pattern very similar to that of the S_A phase, i.e. there is an inner ring corresponding to the lamellar thickness, and a diffuse outer ring associated with the unstructured nature of the layers [14]. In our preliminary X-ray measurements of 4-((*S*)-2-methyloctanoyl)phenyl 4′-nonylbiphenyl 4-carboxylate in the S_A and S_C^* phases, similar results have been obtained [15]. Our recent ^{13}C NMR study of the compound indicates the discontinuity concerning the overall fluctuation at the S_A–S_C^* transition [9]. On the bases of these spectroscopic studies, even in a S_C^* phase, the order within the layers is liquid-like and molecular motion plays an important role in the intermolecular interaction. The alkyl chain branching influence the overall motion in the S_C^* phase. Our results suggest the existence of cooperative overall motion related to the appearance of the ferroelectricity in the S_C^* phase.

3.2. *Effect of lateral substitution*

The effect of lateral substitution on the benzene ring of this system on the physical properties was investigated. The physical properties of a laterally substituted S_C^* liquid crystal strongly depend on the position of the lateral substituent [3, 16–17]. In this work, we restricted our investigation to the 3-substituted-4-alkyloxybenzoate system.

The phase transition temperatures measured for 3-chloro-4-butyloxybenzoate (**4**), 3-chloro-4-((*S*)-2-methyloxy)benzoate (**5**), and 4-butyloxybenzoate (**1**) are listed in table 4. Compound **4** gives a S_A–I transition temperature 40°C lower than that of compound **1**. The S_C^*–C transition of compound **4** was not detectable in cooling to 0°C by DSC, nor by optical microscopy at a cooling rate of 2°C min^{-1}. Compound 4 gives a crystal-smectic transition temperature 25°C lower than that of compound **1**. The effect of lateral substitution on the benzene ring on the phase transition is similar to that of

Table 4. Transition temperatures (°C) and enthalpies of transition (kJ mol^{-1}) determined† for the 4-((*S*)-2-methyloctanoyl)-4′-biphenyl 3-X-4-alkyloxybenzoates.

Compound	X	Alkyl	C		S_C^*		S_A		I
1	H	$CH_3(CH_2)_3$	●	85·1	●	(69·9)	●	146·2	●
ΔH				24·4				4·2	
4	Cl	$CH_3(CH_2)_3$	●	58·2	●	63·8	●	107·3	●
ΔH				25·2		0·3		3·2	
5	Cl	$CH_3CH_2CH(CH_3)CH_2$	●	68·0	●	(44·4)	●	(64·7)	●
ΔH				27·1		0·9		1·8	

† The transition parameters were determined on cooling by DSC at a rate of 2·0°C min^{-1}, except for crystal to smectic or isotropic transitions which were determined on heating.

alkyl chain branching. Compound **5** gives a S_A–I transition temperature 44°C lower than that of compound **4**. The S_A–S_C^* transition temperature of compound **5** is depressed. In DSC measurements, a remarkable difference in the peak height at the S_C^*–S_A transition between compounds **4** and **5** are observed as shown in figure 6. A large enhancement of the S_C^*–S_A transition enthalpy for compound **5** is observed.

The temperature dependence of the spontaneous polarization observed for compounds **1**, **4**, and **5** is shown in figure 7. The enhanced polarization of compound **4** and especially that of compound **5** is observed. The spontaneous polarization, tilt

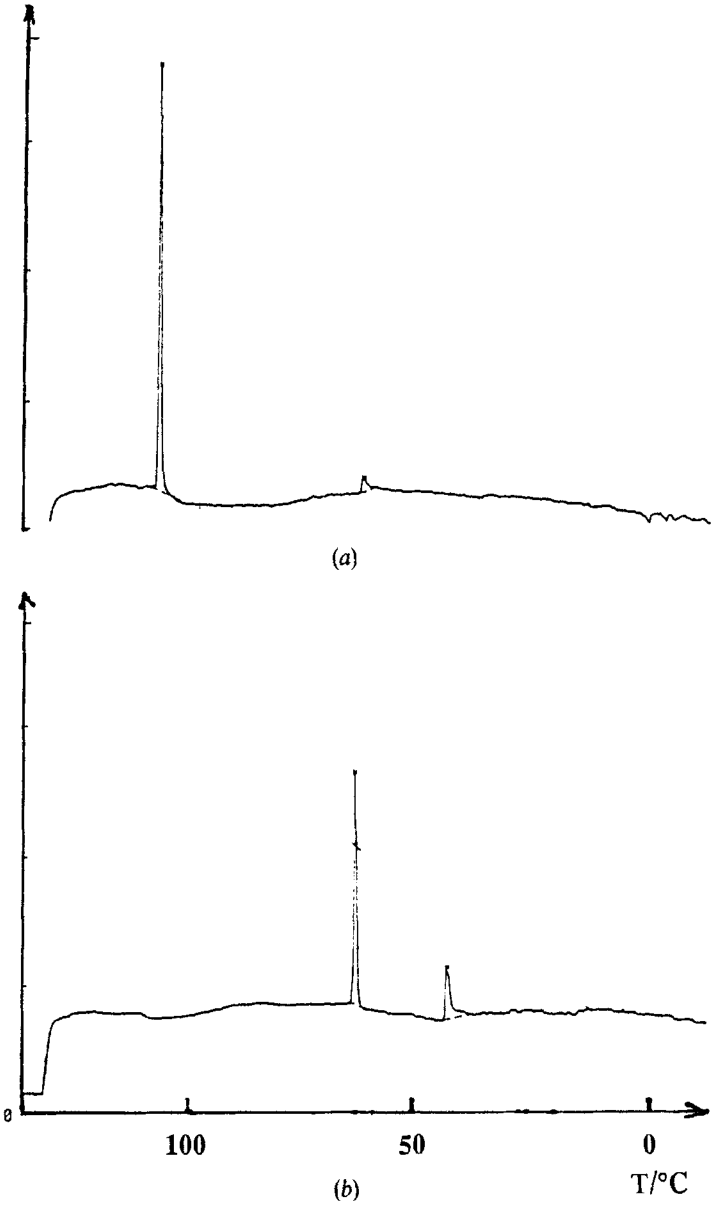


Figure 6. DSC cooling curves for (*a*) compound **4** and (*b*) compound **5**. Cooling rate 2°C min^{-1}.

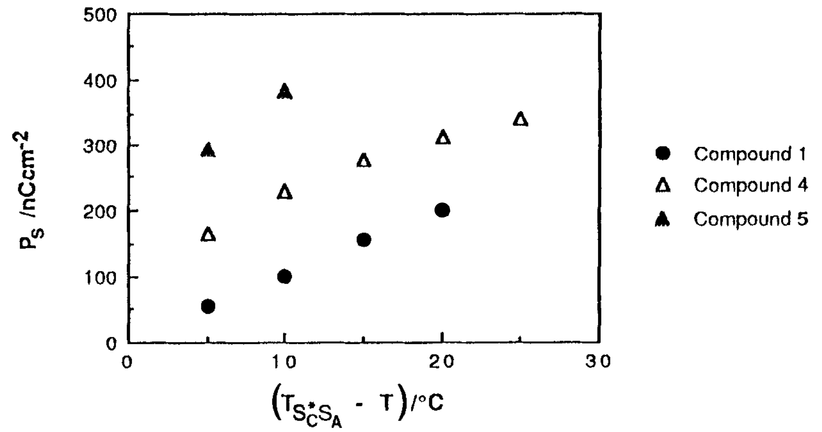


Figure 7. The temperature dependence of the spontaneous polarization observed for compounds **1**, **4**, and **5**.

Table 5. The spontaneous polarization, tilt angle, and ratio $P_s/\sin\Theta$ obtained† for compounds **1**, **4**, and **5**.

Compound	P_s/nC cm^{-2}	Θ/°	$P_s/\sin\Theta$/nC cm^{-2}
1	−100	15·2	−381
4	−229	26·6	−511
5	−385	30·8	−752

† Obtained at 10°C below the S_C^*–S_A transition.

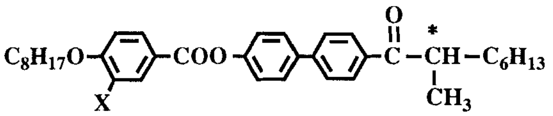
angle, and ratio $P_s/\sin\theta$ obtained at 10°C below the S_A–S_C^* transition for compounds **1**, **4**, and **5** are listed in table 5. Comparing the ferroelectric properties of compounds 1 and 4, the chlorosubstitution to the benzene ring increases the values of the spontaneous polarization and tilt angle. In order to characterize the chlorosubstitution effect on the spontaneous polarization, the physical properties of 4-((*S*)-2-methyloctanoyl)-4′-biphenyl 3-*X*-4-octyloxy benzoate were investigated. The structural formula, bond moment C–X [18], van der Waals radius of X [18], and polarization observed at 10°C below the S_A–S_C^* transition are given in table 6. The magnitude of the spontaneous polarization depends on the value of van der Waals radius of X and does not depend on the value of bond moment of C–X. The higher value of polarization of compound **4** compared to that of compound **1** may be caused, not by the electrostatic effect of the chlorosubstituent on the molecular dipole moment, but, by the steric effect on molecular motion.

The magnitude of P_0 ($=P_s/\sin\Theta$) observed for compound **5** is described by

$$P_0(\text{compound } \mathbf{5}) \sim P_0(\text{compound } \mathbf{1}) + \{P_0(\text{compared } \mathbf{2a}) - P_0(\text{compound } \mathbf{1})\} + \{P_0(\text{compound } \mathbf{4}) - P_0(\text{compound } \mathbf{1})\}. \quad (1)$$

This demonstrates the additivity of the steric effects on the spontaneous polarization in the S_C^* phase. The remarkable high value of the spontaneous polarization observed for compound **5** is interpreted by the effects of the 2-methylbutyloxy group and of the chlorosubstituent on the overall motion in the S_C^* phase.

Table 6. Bond moment of C–X [18], Van der Waals radius of X [18], and spontaneous polarization observed for the compounds under investigation.

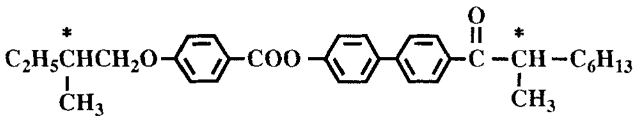


X	Bond moment/D	Van der Waals radius/Å	P_s/nC cm^{-2}
H	0·4	1·20	−155
F	1·41	1·47	−156
Cl	1·46	1·75	−235

3.3. *Effect of the double chiral centres on the physical properties*

In order to characterize the chiral effect of a compound having double asymmetric carbons, the system of compound **2** shown in table 7 were investigated. The phase transition temperatures and spontaneous polarizations obtained for compounds **2a**, **2b**, **2c**, and **2d** are listed in table 7. The S_C^* (or S_C)–A_A transition temperature, thermal stability of the higher ordered smectic phase (S_X), crystal-smectic transition temperature (melting point), and spontaneous polarization of compounds **2a**, **2b**, **2c**, and **2d** are strongly influenced by the molecular chirality of the asymmetric carbon in the 2-methyloctanoyl group.

Table 7. Structure and absolute configurations of the asymmetric carbons of compound **2**.



Compound	2-Methylbutyl	2-Methyloctanoyl
2a	S	S
2b	±	S
2c	S	±
2d	±	±

Table 8. Transition temperatures (°C)† and spontaneous polarization‡ obtained for compounds **2a**, **2b**, **2c**, and **2d**.

Compound	C		S_X§		S_C^* (or S_C)		S_A		I	P_s/nC cm^{-2}
2a	●	67·3	●	(30·9)	●	69·8	●	104·6	●	−250
2b	●	63·1	●	(30·6)	●	69·1	●	105·2	●	−252
2c	●	81·6			●	(60·2)	●	103·1	●	−1
2d	●	82·2			●	(62·1)	●	105·1	●	—

† The transition temperatures were determined on cooling by DSC at a rate of 2·0°C min^{-1}, except for crystal to smectic transition temperatures which were determined on heating.

‡ Obtained at 10°C below the S_C^*–S_A transition.

§ Higher ordered smectic phase not yet identified.

Comparing the physical properties of compounds **2a** and **2c** the S_C^*–S_A transition temperature of compound **2c** is lower by 9·6°C than that of compound **2a**. Additionally, in the S_C^* phase, the magnitude of the spontaneous polarizations of compounds **2a** and **2c** are 250 nC cm^{-2} and 1 nC cm^{-2}, respectively. The tilt angle observed at 10°C below the S_C^*–S_A transition for compounds **2a** and **2c** are 24·4° and 13·2°, respectively. For compound **2a**, the S_C^*–S_X transition is observed on cooling at 30·9°C (2·3 kJ mol^{-1}), whereas for compound **2c**, the S_C^*–C transition is observed at 31·3°C (11·8 kJ mol^{-1}).

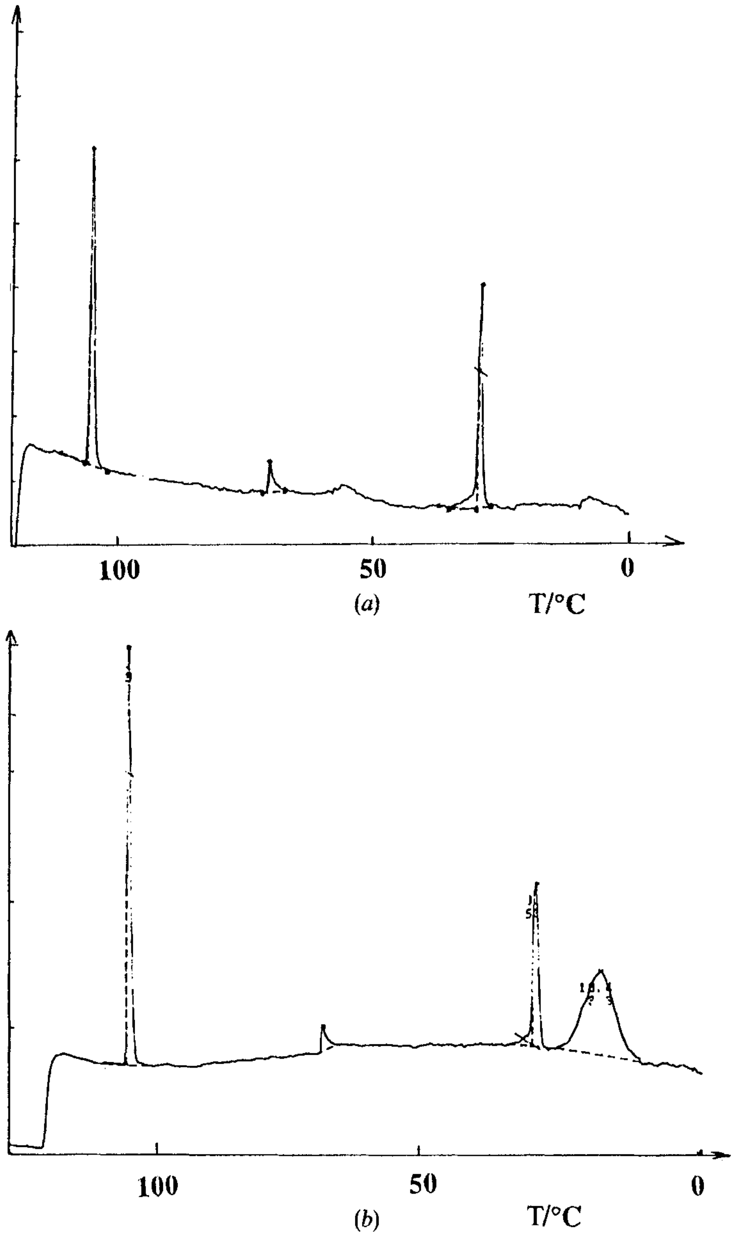


Figure 8. DSC cooling curves for (*a*) compound **2a** and (*b*) compound **2b**. Cooling rate 2°C min^{-1}.

The difference in the phase transition temperatures is also observed for the system of 3-methylbutyloxy benzoate with one asymmetric carbon. The phase sequence of compound **3** is I (123·2°C) S_A (75·4°C) S_C^* (30·6°C) S_X (see table 1). On the other hand, the phase sequence of 4-(($\pm$)-2-methyloctanoyl)-4′-biphenyl 4-(3-methylbutyloxy)benzoate determined on cooling cycle by DSC is I (122·8°C) S_A (68·8°C) S_C (17·8°C) C. The introduction of another alkyl chain branching to a S_C^* molecule may affect the cooperative overall motion discussed in § 3.1. So that the effect of the chiral centre in the 2-methyloctanoyl group on physical properties may be clearly observed.

In order to investigate the effect of the molecular chirality of the 2-methylbutyloxy group on the physical properties, the transition temperatures and spontaneous polarization of compound **2b** are compared with those of compound **2a**. The S_A–I, S_C^*–S_A, and S_X–S_C^* transition temperatures of compound **2b** are similar to those of compound **2a**. There is no difference in the magnitude of spontaneous polarization between compounds **2a** and **2b**. The existence of the molecular chirality of the asymmetric carbon in the 2-methylbutyloxy group does not play an important role in the intermolecular interaction in the S_C^* phase. The cooperative overall motion in the S_C^* phase may depend on the molecular structure adjacent to a chiral centre. An important difference between the thermograms of compound **2a** and of compound **2b** is observed as shown in figure 8. Compound **2b** shows a broad exothermic peak (5·5 kJ mol^{-1}) at 18°C on cooling. The molecular packing of the 2-methylbutyloxy group and the internal motion of the 4-(2-methylbutyloxy)benzene group in the higher ordered smectic phase may be influenced by the chiral centre in the 2-methylbutyloxy group.

4. Conclusions

The effects of another branched alkyl chain, lateral substitution, and double chiral centres on the physical properties in chiral smectic liquid crystals having the 2-methyloctanoyl group have been investigated. By introducing another branched alkyl chain away from the 2-methyloctanoyl group, a sharp S_C^*–S_A transition peak and remarkable enhancement of ferroelectric properties in the S_C^* phase are observed. The effects of the lateral substitution to the benzene ring on the physical properties are similar to those of the introduction of the alkyl chain branching. The compound having both the second alkyl chain branch and the lateral substituent shows the additivity of the steric effects on the physical properties. These results suggest that the introduction of another branched alkyl chain or of a lateral substituent to a S_C^* molecule influences an overall motion of the molecule in the S_C^* phase. The motion may be the cooperative motion related to the appearance of the ferroelectricity. In the system of a compound with double chiral centres, the existence of the chiral centre in the 2-methyloctanoyl group affects the phase transition temperatures and the magnitude of the spontaneous polarization in the S_C^* phase. On the other hand, the existence of the chiral centre in the 2-methylbutyl group only affects the stability of a higher ordered smectic phase which appears below the S_C^* phase.

In order to characterize the nature of the molecular motion in the S_C^* phase, spectroscopic studies of a thermally stable S_C^* liquid crystal having double chiral centres is in progress.

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References

[1] Reviews on ferroelectric liquid crystals see, for example: (*a*) MEYER, R. B., 1977, *Molec. Crystals liq. Crystals*, **40,** 33. (*b*) PATEL, J. S., and GOODBY, J. W., 1987, *Opt. Engng.*, **26,** 373. (*c*) BLINC, R., FILIPIC, C., LEVSTIK, A., ZEKS, B., and CARLSSON, T., 1987, *Molec. Crystals liq. Crystals*, **151,** 1.

[2] YOSHIZAWA, A., NISHIYAMA, I., FUKUMASA, M., HIRAI, T., and YAMANE, M., 1989, *Jap. J. appl. Phys.*, **28,** L1269.

[3] HIRAI, T., FUKUMASA, M., NISHIYAMA, I., YOSHIZAWA, A., SHIRATORI, N., YOKOYAMA, A., and YAMANE, M., 1991, *Ferroelectrics*, **114,** 251.

[4] SHIRATORI, N., NISHIYAMA, I., YOSHIZAWA, A., and HIRAI, T., 1990, *Jap. J. appl. Phys.*, **29,** L2086.

[5] SELINGER, J., OSREDKHAR, R., ZAGAR, V., and BLINC, R., 1977, *Phys. Rev. Lett.*, **38,** 411.

[6] LALANNE, J. R., BUCHERT, J., DESTRADE, C., NGUYEN, H. T., and MARCEROU, J. P., 1989, *Phys. Rev. Lett.*, **62,** 3046.

[7] POON, C. D., and FUNG, B. M., 1989, *Liq. Crystals*, **5,** 1159.

[8] YOSHIZAWA, A., KIKUZAKI, H., HIRAI, T., and YAMANE, M., 1989, *Jap. J. appl. Phys.*, **28,** L1988.

[9] YOSHIZAWA, A., KIKUZAKI, H., HIRAI, T., and YAMANE, M., 1990, *Jap. J. appl. Phys.*, **29,** L1153.

[10] COATES, D., 1987, *Liq. Crystals*, **2,** 63.

[11] MATSUNAGA, Y., and MIYAJIMA, N., 1990, *Molec. Crystals, liq. Crystals*, **178,** 157.

[12] MIYASATO, K., ABE, S., TAKEZOE, H., FUKUDA, A., and KUZE, E., 1983, *Jap. J. appl. Phys.*, **22,** L661.

[13] HAYAMIZU, K., YANAGISAWA, M., and YAMAMOTO, O., 1989, *Liq. Crystals*, **4,** 273.

[14] GRAY, G. W., 1979, *The Molecular Physics of Liquid Crystals*, edited by G. R. Luckhurst and G. W. Gray (Academic Press), chap. 12.

[15] YOSHIZAWA, A. (unpublished results).

[16] COATES, D., 1987, *Liq. Crystals*, **2,** 423.

[17] FURUKAWA, K., TERASHIMA, K., ICHIHASHI, M., SAITO, S., MIYAZAWA, K., and INUKAI, T., 1988, *Ferroelectrics*, **85,** 451.

[18] THE CHEMICAL SOCIETY OF JAPAN, 1984, *Kagaku Binran* (Maruzen), II, p. 714.