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## Liquid Crystals

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### Mesomorphic and ferroelectric properties of novel optically active compounds derived from (R)-3-hydroxynonanoic acid

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## Mesomorphic and ferroelectric properties of novel optically active compounds derived from (*R*)-3-hydroxynonanoic acid

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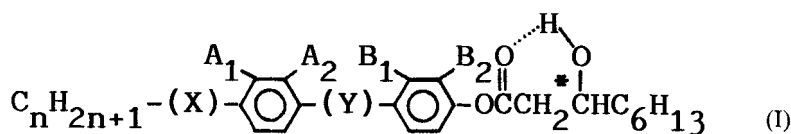
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Novel optically active compounds derived from (*R*)-3-hydroxynonanoic acid as shown in a general formula (I)



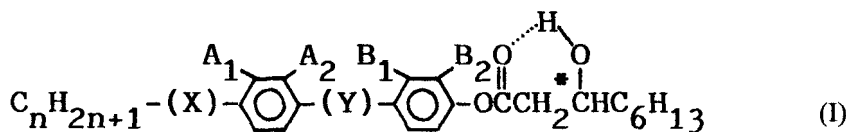
(*n*: 8, 10, or 12; X: -O-, -OCO-, or -COO-; Y: -OCO-, -COO-, -CH<sub>2</sub>O-, or -OCH<sub>2</sub>-; A<sub>1</sub>, A<sub>2</sub>, B<sub>1</sub>, or B<sub>2</sub>: -H or -Cl)

have been synthesized and their mesomorphic and ferroelectric properties have been investigated. The kind of mesophases and the transition temperatures depend strongly on the linkage groups and the substituents in the core. The compounds with an unsubstituted core show non-titled smectic mesophases (smectic *A* or *B*). The chiral smectic *C* phase appears in the compounds having a central ester linkage and a chloro-substituent as the A<sub>1</sub> or B<sub>1</sub> position and in the compound having a central -OCH<sub>2</sub>- linkage and a chloro-substituent at the A<sub>1</sub> position. The maximum spontaneous polarization (500 μC/m<sup>2</sup>) was observed in 4-dodecyloxy-3-chlorobenzoyloxyphenyl (*R*)-3-hydroxynonanoate. The thermal stability of each mesophase and the ferroelectric properties have been discussed from the structural point of view.

### 1. Introduction

Very many optically active smectogenic compounds have been synthesized since the invention of a high-speed switching device based on their ferroelectric properties [1]. The majority of their chiral sources are optically active alcohols and carboxylic acids with a protruding methyl branch attached to an asymmetric carbon. Yoshino *et al.* first showed that the spontaneous polarization (*P*<sub>s</sub>) was enhanced by replacing the methyl branch by a chloro-substituent [2]. Since then, optically active compounds with polar substituents such as fluoro, trifluoromethyl, or epoxide groups bound to an asymmetric carbon have also been used as chiral sources [3-5].

We have selected (*R*)-3-hydroxynonanoic acid as a new chiral source and synthesized the following compounds as shown in the general formula (I):



(*n*: 8, 10, or 12; X: -O-, -OCO-, or -COO-; Y: -OCO-, -COO-, -CH<sub>2</sub>O-, or -OCH<sub>2</sub>-; A<sub>1</sub>, A<sub>2</sub>, B<sub>1</sub>, or B<sub>2</sub>: -H or -Cl)

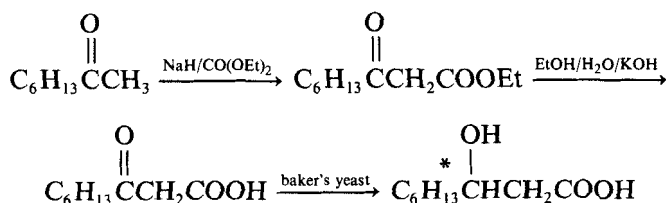
In these compounds the hydroxy group bound to the asymmetric carbon could interact with the neighbouring carbonyl group through intramolecular hydrogen bonding and form a six-membered ring which is thought to enhance the Ps and the thermal stability of the mesophases because of its chair-like form and steric hindrance around the asymmetric carbon.

In this paper, we discuss the effects of the chiral group, the linkage groups, and the substituents in the cores on the mesomorphic and the ferroelectric properties.

## 2. Experimental

### 2.1. Preparation of compounds

(*R*)-3-hydroxynonanoic acid was prepared by reducing the nonanoic acid-3-one, which was synthesized by reacting methylhexylketone with diethylcarbonate in DMF containing NaH followed by hydrolysis in EtOH/H<sub>2</sub>O/KOH solution, by using a baker's yeast (Scheme 1). The specific rotation ( $[\alpha]_D$ ) is  $-19.23^\circ$  and the optical purity calculated from the reference value ( $[\alpha]_D = -22.6^\circ$ ) [6] is about 85 per cent e.e. The compounds shown in the general formula (I) were synthesized by an esterification reaction of (*R*)-3-tetrahydropyranyloxynonanoic acid with the corresponding mesogenic phenols (II) using dicyclohexylcarbodiimide (DCC) as a condensation reagent followed by leaving the pyranil group by pyridinium *p*-toluenesulphonate (PPTS) (Scheme 2). All the final products were purified by using silica-gel column chromatography followed by recrystallization from ethylacetate several times. Their molecular structures were confirmed by I.R. and N.M.R. spectra.

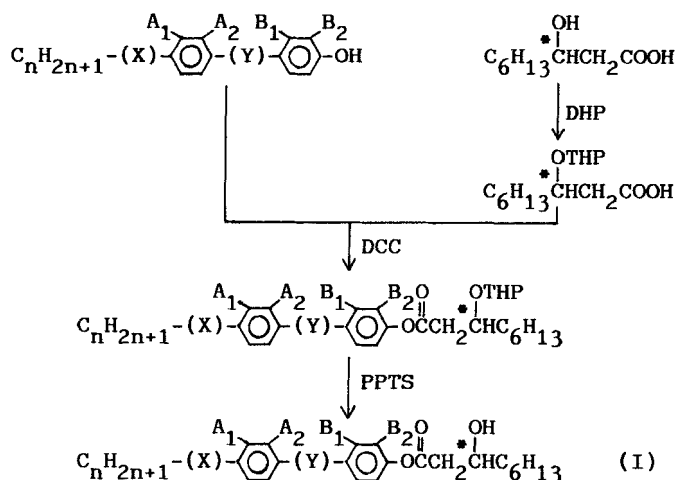


Scheme 1. Synthetic process of (*R*)-3-hydroxynonanoic acid.

The mesogenic phenols (II) were prepared via the well-known synthetic process shown in Scheme 3, by using *p*-hydroxybenzoic acids, hydroquinones, *p*-hydroxytoluene, and 4,4'-biphenol as starting materials.

### 2.2. Measurement of physical properties

An identification of the mesophases was carried out using a Nikon polarizing microscope equipped with a Mettler FP-52 heating stage. Transition temperatures were measured using a Daini Seikohsha SSC-560 differential scanning calorimeter



Scheme 2. Synthetic process of the compounds (I).

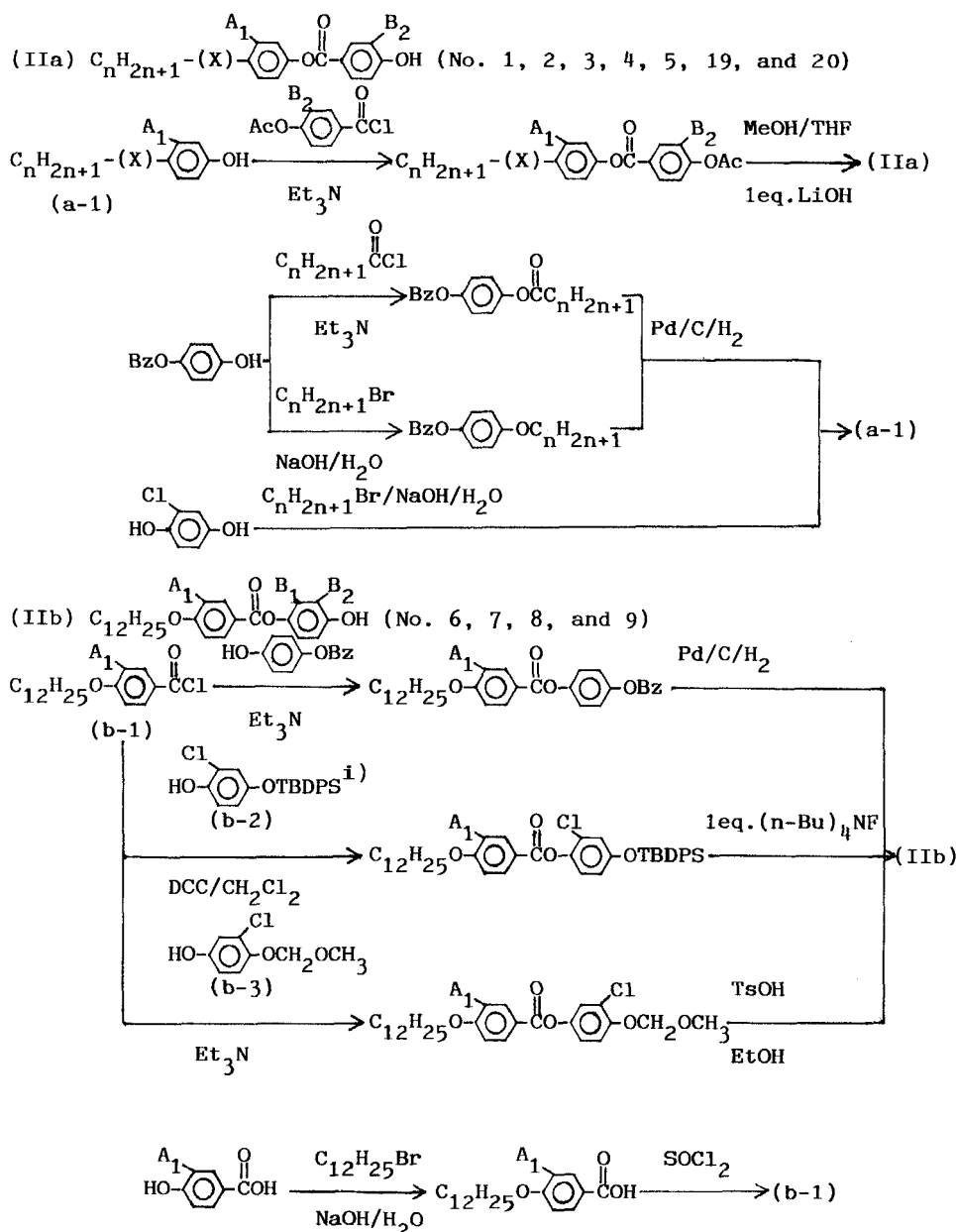
(D.S.C.) at a scanning rate of 2.5°C/min under an N<sub>2</sub> atmosphere. The spontaneous polarization (Ps) was determined by the triangular-wave method reported by Miyasato *et al.* [7]. The frequency, the maximum amplitude, and the cell thickness were 1.0 Hz, ±150 V and 50 μm respectively. The polarity (direction of Ps) was 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 helical twist sense was determined by observing the variation of pitch in the S<sub>C\*</sub> phase of the mixture with the reference compound.

### 3. Results and discussion

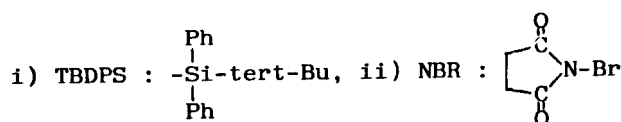
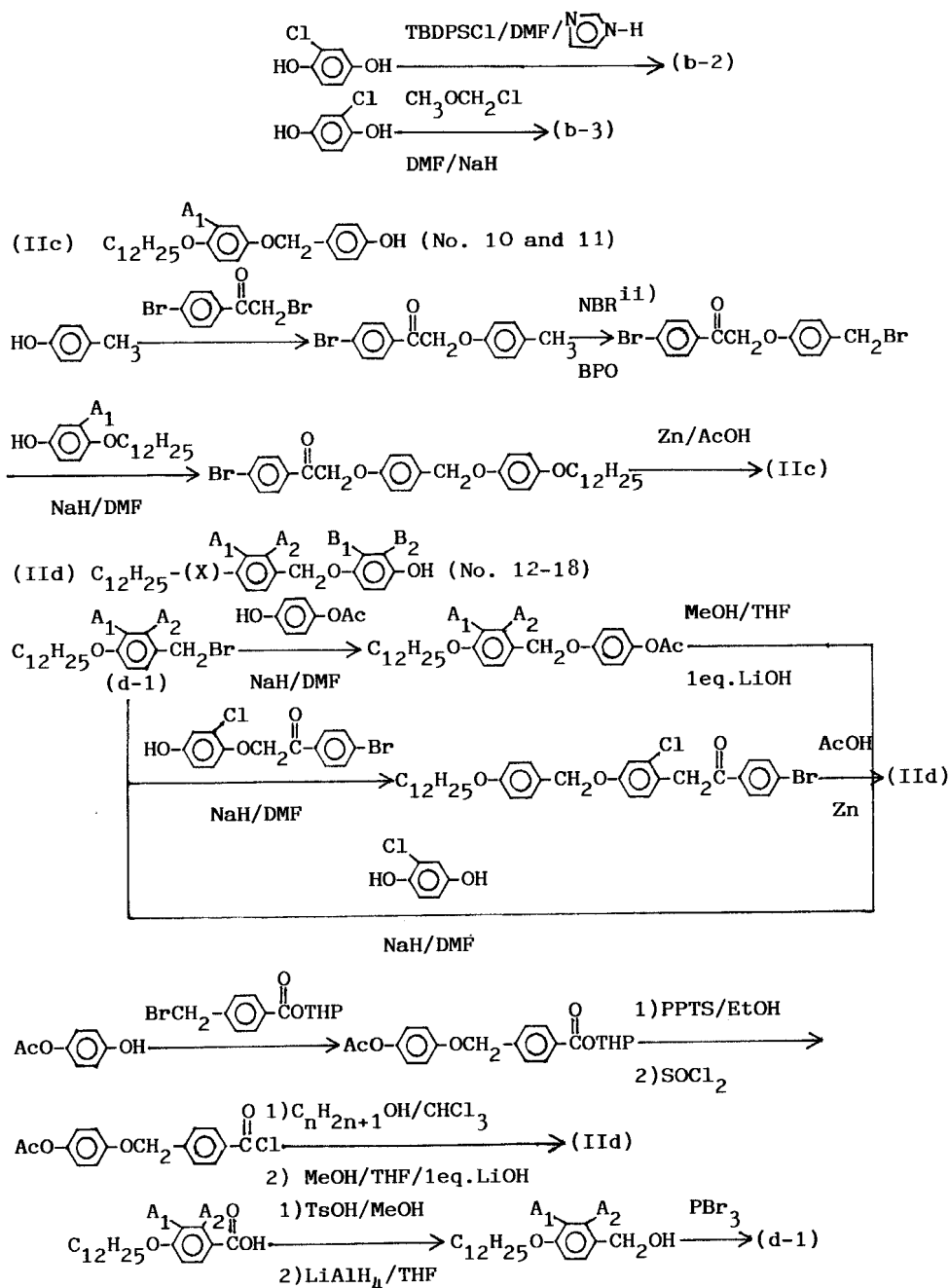
The phase sequences and the transition temperatures for the compounds (I) are summarized in the table. As can be seen in the table, no ferroelectric phases appear in the compounds having unsubstituted core structures (A<sub>1</sub>, A<sub>2</sub>, B<sub>1</sub> and B<sub>2</sub>: -H) and their isotropic-smectic (I-S) phase transition temperatures are much higher than those of the compounds whose chiral groups are the branched alkyl chains. For example, the I-S<sub>B</sub> transition temperature for No. 21 compound is 137°C, whereas the I-S<sub>G\*</sub> temperature for 4-((*S*)-3-methylpentanoyloxy)-4'-*n*-octyloxybiphenyl is 82°C [8]. Comparing with the chiral groups with a protruding methyl branch, the optically active 3-hydroxynonanoyloxy group, whose 3-hydroxy group could interact with the neighbouring carbonyl group through an intramolecular hydrogen bonding and form a chair-like six-membered ring, enhances the thermal stability of mesophases.

Some characteristic features can be associated with the mesophase and the molecular structure. That is, the I-S<sub>B</sub> transition is observed in the compounds having unsubstituted cores with the central linkage groups of a direct bond or an oxymethylene bond (-CH<sub>2</sub>O- or -OCH<sub>2</sub>-) (No. 10, 12, 17 and 21). The compound No. 18 having an unsubstituted core with a central -CH<sub>2</sub>O- linkage and a longer terminal hexadecyl ester chain shows not a I-S<sub>B</sub> but I-S<sub>A</sub> transition. If the central oxymethylene linkage is replaced by an ester linkage (-COO- or -OCO-), a SmA phase appears above the S<sub>B</sub> (Nos. 1, 2 and 19) and occasionally, the S<sub>B</sub> phase vanishes (Nos. 6 and 20). The chiral nematic (N\*) phase appears only in the compounds with a central ester linkage and a chloro-substituent (Cl-) at the position of B<sub>1</sub> or B<sub>2</sub> (Nos.

3, 7 and 8), where the compounds Nos. 3 and 7 show the  $SmC^*$  phase below the  $N^*$  phase. The compounds having the core with an central ester linkage and a Cl-substituent at  $A_1$  (Nos. 4 and 9) show I- $S_{C^*}$  transition. It is noteworthy that the compound having a core with a ester linkage and two Cl-substituents at  $B_1$  and  $B_2$  (No. 5) show no  $S_{C^*}$  phase but a  $S_A$ , although both corresponding analogues Nos. 4 and 3, which have a Cl-substituent at  $A_1$  and  $A_2$  respectively, show the  $S_{C^*}$  phase. In the case of the compounds with an oxymethylene linkage, the  $S_A$  phase appears instead of a  $S_B$  if a Cl-substituent is introduced into  $A_1$ ,  $B_1$  or  $B_2$  position in the core

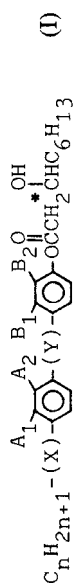


Scheme 3. Synthetic process of the compounds (IIa-d).



Scheme 3 (continued).

The phase sequences and the transition temperatures for the compounds (I).



No.	n	(X)	(Y)	A <sub>1</sub>	A <sub>2</sub>	B <sub>1</sub>	B <sub>2</sub>	mp	Cr	Phase transition temperature/°C†									
										S <sub>X</sub>	S <sub>B</sub>	S <sub>C</sub>	S <sub>A</sub>	C	I				
1	8	-O-	-OCO-	H	H	H	H	104	•	(80)	•	(100)	•	123	•				
2	12	-O-	-OCO-	H	H	H	H	106	•	(92)	•	(98)	•	123	•				
3	12	-O-	-OCO-	H	H	H	Cl	72	•	(63)	•	(71)	•	79	•				
4	12	-O-	-OCO-	Cl	H	H	H	104	•	(103)	•	(37)	•	116	•				
5	12	-O-	-OCO-	Cl	H	H	Cl	56	•	(46)	•	(65)	•	87	•				
6	12	-O-	-COO-	H	H	H	H	63	•	(62)	•	(52)	•	115	•				
7	12	-O-	-COO-	H	H	H	Cl	81	•	(74)	•	(77)	•	(77)	•				
8	12	-O-	-COO-	H	H	Cl	H	59	•	(89)	•	(45)	•	68	•				
9	12	-O-	-COO-	Cl	H	H	H	82	•	(103)	•	(47)	•	104	•				
10	12	-O-	-OCH <sub>2</sub> -	H	H	H	H	113	•	(89)	•	(59)	•	(107)	•				
11	12	-O-	-OCH <sub>2</sub> -	Cl	H	H	H	59	•	(77)	•	(80)	•	77	•				
12	12	-O-	-CH <sub>2</sub> O-	H	H	H	H	115	•	(89)	•	(59)	•	(104)	•				
13	12	-O-	-CH <sub>2</sub> O-	H	H	H	Cl	72	•	(89)	•	(47)	•	(51)	•				
14	12	-O-	-CH <sub>2</sub> O-	H	H	Cl	H	65	•	(89)	•	(47)	•	(61)	•				
15	12	-O-	-CH <sub>2</sub> O-	H	Cl	H	H	72	•	(89)	•	(59)	•	(50)	•				
16	12	-O-	-CH <sub>2</sub> O-	Cl	H	H	H	71	•	(77)	•	(86)	•	80	•				
17	12	-OCO-	-CH <sub>2</sub> O-	H	H	H	H	88	•	(77)	•	(86)	•	88	•				
18	16	-OCO-	-CH <sub>2</sub> O-	H	H	H	H	94	•	(61)	•	(71)	•	(88)	•				
19	10	-OCO-	-OCO-	H	H	H	H	89	•	(61)	•	(71)	•	118	•				
20	12	-OCO-	-OCO-	H	H	H	H	94	•	(81)	•	(80)	•	112	•				
21	10	-O-	-	H	H	H	H	102	•	(81)	•	(80)	•	137	•				

† mp; melting point, SmX; unidentified smectic phase, SmB; smectic B, Sm\*C; chiral smectic C, SmA; smectic A, Ch; cholesteric phase, Iso; isotropic liquid.

( ) indicate monotropic transition.

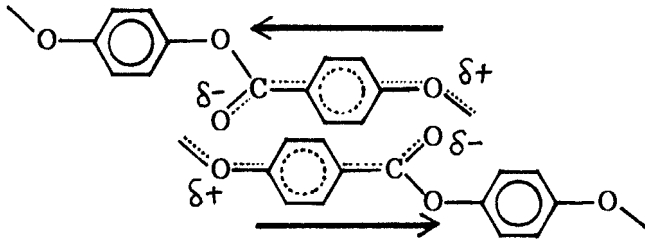
(Nos. 11, 13, 14 and 16) and, no mesophases can be observed in the compound with a Cl-substituent at  $A_2$  (No. 15). Among these compounds, only No. 11 shows a  $S_{C^*}$  phase below the  $S_A$ .

Some correlations can also be observed between the transition temperatures and the core structure in the molecule. The I-S transition temperature depends on the kind of linkage groups and little on the direction of the linkage in the core, and are, in the order of: direct bond > ester group > oxymethylene group. If a Cl-substituent is introduced into the core structure, the mesomorphic transition temperatures show a strong dependence on the kind of linkage group and on the position of the substituent in the core. When the hydrogen at  $A_1$  is replaced by a Cl, the I-S transition temperatures for the Nos. 4 and 9 compounds with an ester linkage become by 7° and 11°C lower respectively than those of the corresponding No. 2 and 6 analogues with the unsubstituted core, and the I-S transition temperatures for the Nos. 11 and 16 compounds with an oxymethylene linkage become by 30° and 24°C lower than those for the corresponding Nos. 10 and 12 analogues. On the other hand, when the H at  $B_1$  or  $B_2$  is replaced by a Cl, the large depression of the isotropic-mesomorphic transition temperatures occurs. That is, the I-N\* transition temperatures for the Nos. 8, 3 and 7 compounds with an ester linkage become as much as 47°, 44° and 38°C lower, respectively, than the I- $S_A$  transition temperatures for the corresponding analogues (Nos. 6 and 2), and the I- $S_A$  transition temperatures for the Nos. 14 and 13 compounds with an oxymethylene linkage are as much as 43° and 53°C lower than the I- $S_B$  transition temperatures for the corresponding analogue (No. 12).

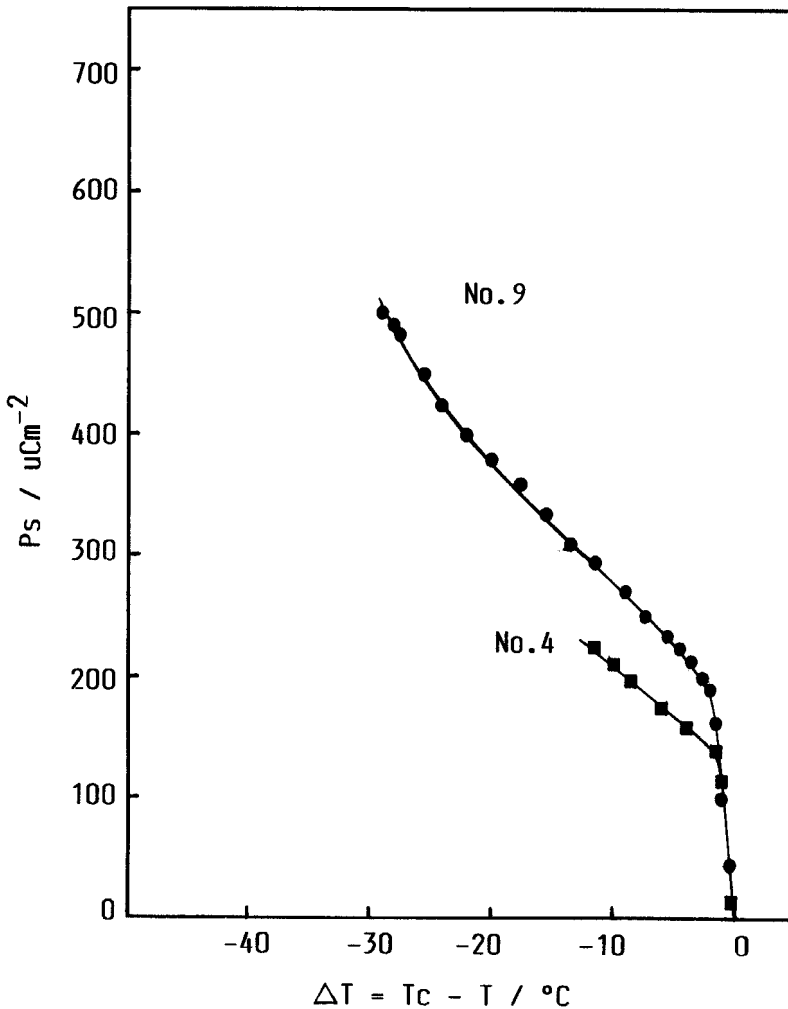
Taking these experimental results into account, we consider the correlation between the mesomorphic properties of the compounds (I) and their molecular structure as follows: Goodby has proposed that the structural characteristics for the compounds showing hexagonal  $S_B$  phase are (i) having one, or only short, terminal alkyl chains and often without terminal out-board dipole moments associated with them, and (ii) having distorted molecular structure that is often bent or curved [9]. He indicates that molecules with such structural characteristics tend to pack closely together and to form non-titled and ordered smectic phases like  $S_B$  and  $S_E$ , since their rotational molecular shapes become a 'tumble-boy' variety and their rotational molecular volumes are inter-penetrable. However, the molecular structures of compounds (I) with the  $S_B$  phase are different from those described by Goodby. It is also difficult to explain from these requirements that the  $S_A$  or the  $S_{C^*}$  phase appears instead of  $S_B$  when a Cl substituent is introduced into the core. The structural characteristics that promote a molecular arrangement that is packed closely, as pointed out by Goodby, are necessary for the appearance of highly ordered smectic phases. Most of the hydroxy groups bound to the asymmetric carbon could form a six-membered ring through the intramolecular hydrogen bonding, but some of them could participate in the intermolecular hydrogen bonding, and the bond between the optically active part and the core is considerably flexible because of its  $\sigma$ -bond nature. These facts may promote the molecular arrangement packed closely in the smectic layer. There is another characteristic difference between the central ester linkage and the oxymethylene linkage. The oxymethylene linkage is flexible because of its lack of double-bond nature, so it may promote dense packing among the cores. On the other hand, the ester linkage may conjugate with the neighbouring phenyl group to become more polarizable and the dipole-dipole interaction between these units may give impetus to



an anti-parallel packing shown in the following:



However, such dipole-dipole interactions are considered to restrict the packing arrangement between the cores and to suppress the ordered  $S_B$  phase, leading to enhancement of the thermal stability of the less ordered  $S_A$  and  $S_C$  phases, since the rigidity of the linkage groups might increase with decreasing the intermolecular distance.



Temperature dependence of the spontaneous polarization for the No. 4 (■) and No. 9 (●) compounds.

Gray and Toyne have summarized systematic studies on the relation between the substituents in the core structures and the thermal stability of mesophases for several compounds [10, 11]. They have pointed out that the following factors which affect the thermal stability of each mesophase must be considered when the substituents are introduced into the core: (i) the variation of the molecular width, (ii) the variation of the planarity of the molecule, and (iii) the variation of the size and the direction of the local dipole moments. McMillan and de Jeu have also indicated that the dipole-dipole interaction among the local dipoles play an important role in the appearance of  $S_C$  phase [12, 13].

The Cl substituent introduced into  $A_1$  could increase the molecular width without breaking the planarity of the core structure but it broadens the intermolecular distance; therefore, it may suppress the appearance of the  $N^*$  phase and highly ordered smectic phases, resulting in widening the temperature-range of less ordered  $S_A$  and  $S_{C^*}$  phases. And in the case of the compounds with an ester linkage (Nos. 4 and 9), the dipole moment of the Cl-substituent may affect the dipole-dipole interaction between the out-board dipoles and promote the appearance of  $S_{C^*}$  phase. On the other hand, the Cl substituent introduced into  $B_1$  or  $B_2$  could be located in a space around the ester linkage without destroying the linearity of the molecule, although it could distort the core due to its steric hindrance and break the planarity of the molecule so that the thermal stability of smectic phases may greatly decrease. In comparison with the oxymethylene linkage, the ester linkage has a comparatively large anisotropic polarizability which is condensed to enhance the thermal stability of the nematic phase. Therefore, the  $N^*$  phase can be observed in the Nos. 3, 7 and 8 compounds. It may be attributed to the effect of the Cl-substituent at  $B_2$  on the dipole-dipole interaction among the outboard dipoles that the  $S_{C^*}$  phase appears below the  $N^*$  phase in the Nos. 3 and 8.

The figure shows the temperature dependence of Ps of the representative compounds (Nos. 4 and 9). As can be seen in the figure, the magnitude of Ps is comparatively large in spite of locating the asymmetric carbon away from the core and the maximum value is  $500 \mu\text{C}/\text{m}^2$  ( $\Delta T = -28^\circ\text{C}$ ) of the No. 9 compound. This result can probably be explained by the facts that the hydroxyl group of the chiral part has a dipole moment contributing to the Ps and the internal bond rotation between the optical active part and the core may be restricted considerably by the six-membered ring formed through the intramolecular hydrogen bonding. The polarity and helix sense of these compounds are negative and right handed. These results are consistent with  $\alpha$ -chloroesters reported by Bahr *et al.* [14] and can be interpreted by the 'bent cylinder binding site' model for the magnitude and polarity of Ps proposed by Walba *et al.* [15].

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