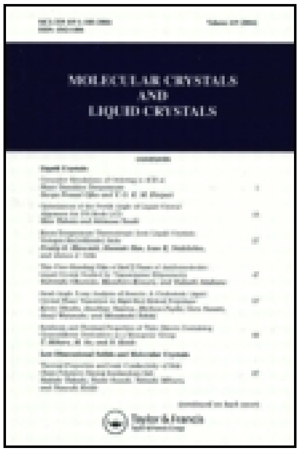


Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

Physical Properties of Some Chiral Smectic Liquid Crystals Having 1-Methyl-Alkoxy-Phenyl Group

T. Inukai [a] , S. Saitoh [a] , H. Inoue [a] , K. Miyazawa [a] , K. Terashima [a] & K. Furukawa [a]
[a] Fine Chemicals Division, Chisso Corporation, 2 Kamariya, Kanazawa-ku, Yokohama, Japan

Version of record first published: 20 Apr 2011.

To cite this article: T. Inukai , S. Saitoh , H. Inoue , K. Miyazawa , K. Terashima & K. Furukawa (1986): Physical Properties of Some Chiral Smectic Liquid Crystals Having 1-Methyl-Alkoxy-Phenyl Group, Molecular Crystals and Liquid Crystals, 141:3-4, 251-266

To link to this article: http://dx.doi.org/10.1080/00268948608079613

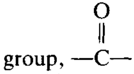
Mol. Cryst. Liq. Cryst., 1986, Vol. 141, pp. 251–266
0026-8941/86/1414-0251/$20.00/0

Physical Properties of Some Chiral Smectic Liquid Crystals Having 1-Methyl-Alkoxy-Phenyl Group

T. INUKAI, S. SAITOH, H. INOUE, K. MIYAZAWA, K. TERASHIMA, and K. FURUKAWA

Fine Chemicals Division, Chisso Corporation, 2 Kamariya, Kanazawa-ku, Yokohama 236, Japan

(*Received July 31, 1986; in final form August 11, 1986*)

The liquid crystalline compounds having an optically active 1-methyl-alkoxy-phenyl group were synthesized. They show some abnormality, i.e., firstly rather high value of spontaneous polarization for the structural feature lacking a strongly polar group,  $\overset{\mathrm{O}}{\overset{\|}{—\mathrm{C}—}}$, in the vicinity of the chiral center, and secondly the sense of twist in the S_C^* phase that is opposite to what was originally expected. We report the characteristics of these compounds.

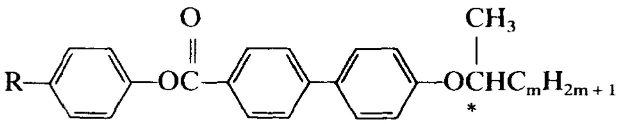
Keywords: mesophase, ferroelectric, 1-methyl-alkoxy-phenyl compounds, spontaneous polarization, sense of twist, tilt angle

INTRODUCTION

In the preceding paper[1] we reported the sense and magnitude of spontaneous polarization and twisting power in S_C^* phase of diverse types of liquid crystalline compounds. It was found there that the compounds having an optically active 1-methyl-alkoxy-phenyl group show some abnormality, i.e., firstly rather high values of spontaneous polarization for the structural feature lacking a strongly polar group in the vicinity of the chiral center, and secondly the sense of twist in the S_C^* phase that is opposite to what was originally expected. Now we report more extensive study of this type of compounds in effort of better understanding of the phenomena.

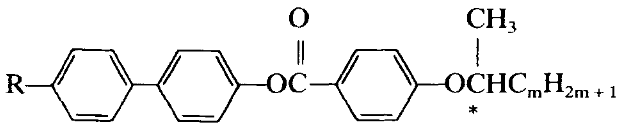
RESULTS AND DISCUSSION

The types of compounds studied are as follows



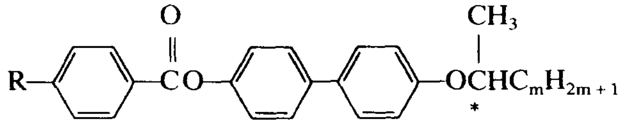
(I)

(IA, R = n-Alkyl; IB, R = n-Alkoxy)



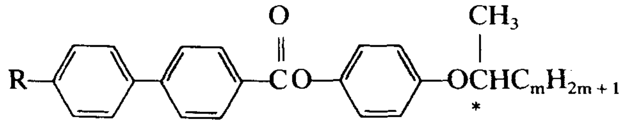
(II)

(IIA, R = n-Alkyl; IIB, R = n-Alkoxy)



(III)

(IIIA, R = n-Alkyl; IIIB, R = n-Alkoxy)



(IV)

(IVA, R = n-Alkyl; IVB, R = n-Alkoxy)

in which m is mostly 6 and occasionally 3.

1. S *p*-n-Alkylphenyl- and *p*-n-alkoxyphenyl ester of 4′-(1-methylalkoxy)-biphenyl-4-carboxylic acids (IA, IB)

The transition temperatures of the compounds IA(m = 6) and IB(m = 6) are plotted against the chain length in Figures 1 and 2. The spontaneous polarization (Ps) plotted against $T - Tc$ is shown in Figures 3 and 4; T is the temperature at which measurement was carried out and Tc is the upper limit of S_C^* phase. The tilt angle

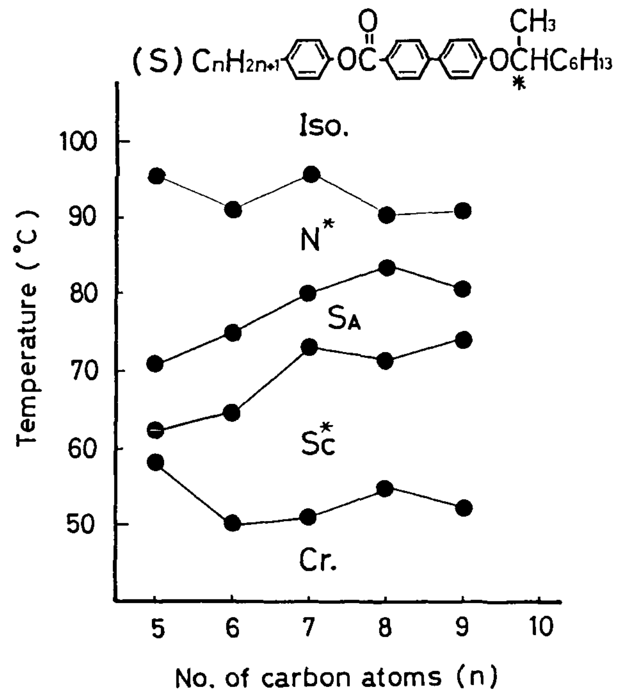
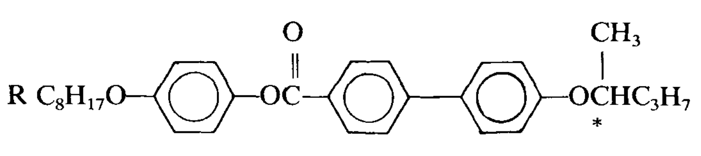


FIGURE 1 Plots of transition temperatures against the number of carbon atoms (n) of compounds IA (m = 6).

versus $T-Tc$ is shown in Figures 5 and 6. The Ps and tilt angle of compounds IA (m = 6) tend to become nil at $T-Tc = 0$ (S_C^* – S_A transition temperature), whereas those of compounds IB have lower temperature dependence and seem not to disappear at $T - Tc = 0$ (S_C^* – N* transition temperature).

Incidentally R *p*-n-octyloxyphenyl ester of 4′-(1-methyl-butyloxy)-biphenyl-4-carboxylic acid (IB, R = n—$C_8H_{17}O$—, m = 3) shows the same phase transition series as that of IB (m = 6).



$$\mathrm{Cr.}\ \underset{71.8^\circ C}{\text{———}}\ S_c^*\ \underset{89.8^\circ C}{\text{———}}\ N^*\ \underset{137.4^\circ C}{\text{———}}\ I$$

Its Ps is 76 nC/cm^2 at $T - Tc = -30$°C, which is smaller compared

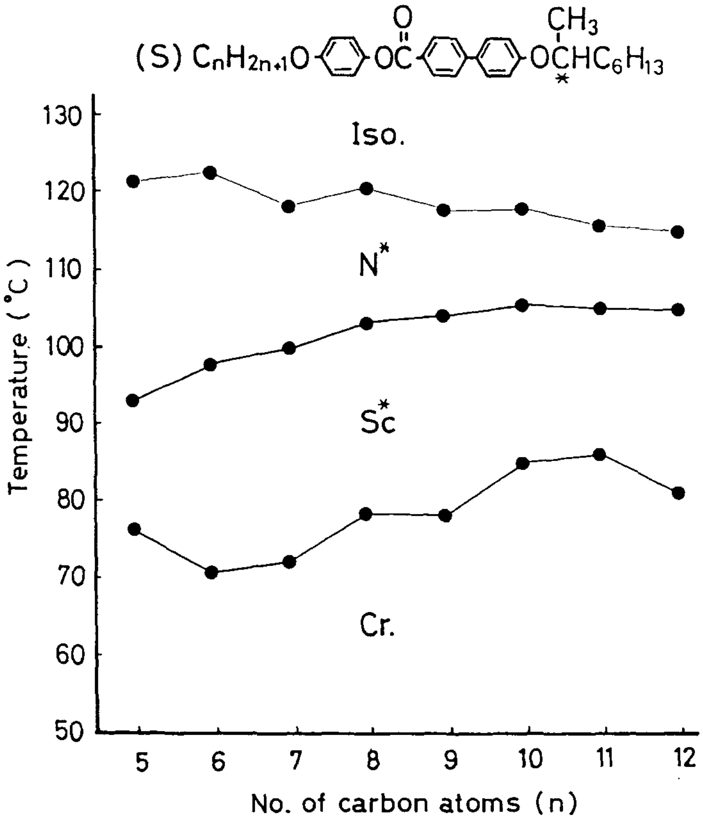


FIGURE 2 Plots of transition temperatures against the number of carbon atoms (n) of compounds IB (m = 6).

with that of corresponding compound of IB (R = n-$C_8H_{17}O$—,m = 6), but the tilt angle is almost the same (41° at $T - Tc = -30°C$).

2. 4′-Alkyl- and 4′-alkoxy-4-biphenylyl esters of *p*-(1-methyl-alkoxy)-benzoic acids. (IIA, IIB)

The phase transition temperatures, Ps and tilt angles of IIA (m = 6) are shown in Table I.

Figure 7 shows the plots of transition temperatures of compound IIB (m = 6) against chain length. Their Ps and tilt angle are plotted in Figure 8. The Ps is almost temperature independent and is about half of that of IB. The tilt angle stays at 45° throughout the temperature range of $T - Tc = -5°C$ to $-30°C$. The results with 1-methylbutyloxy analogues (IIB, m = 3) are shown in Table II.

The behavior of these compounds with respect to phase transition series, Ps, and tilt angle is very similar to that of the m = 6 analogues.

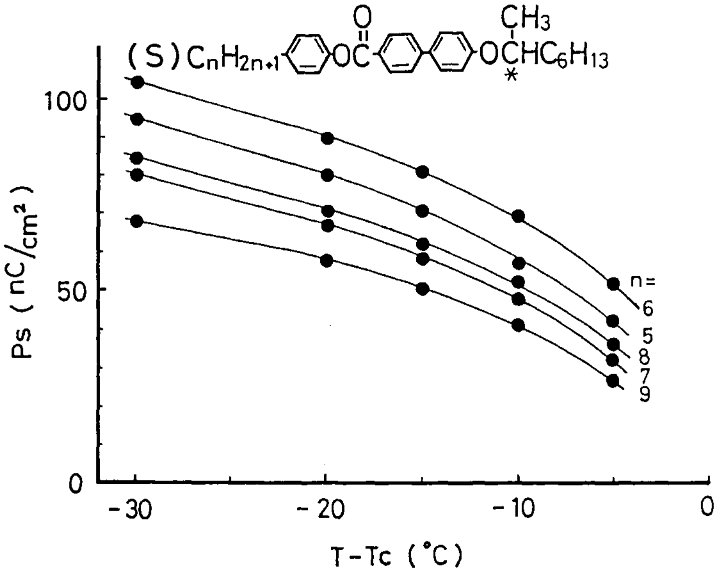


FIGURE 3 Plots of values of the spontaneous polarization against temperature (T − Tc) of compounds IA (m = 6).

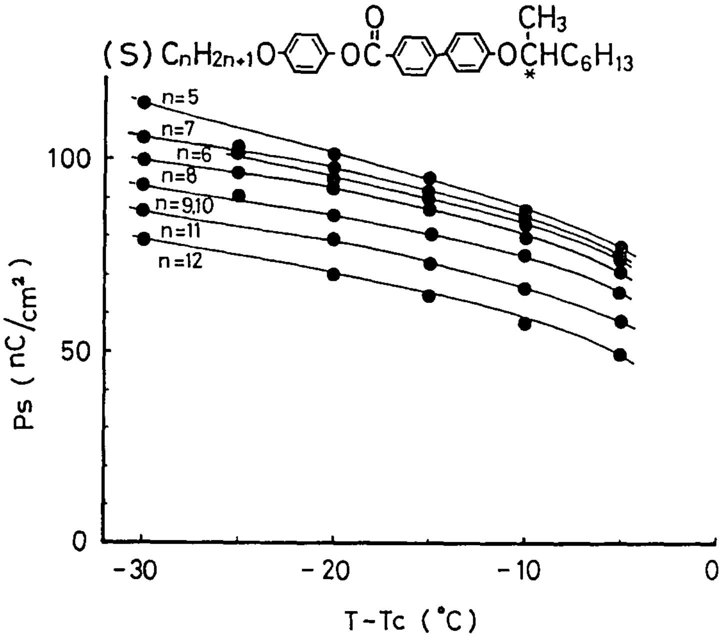


FIGURE 4 Plots of values of the spontaneous polarization against temperature (T − Tc) of compounds IB (m = 6).

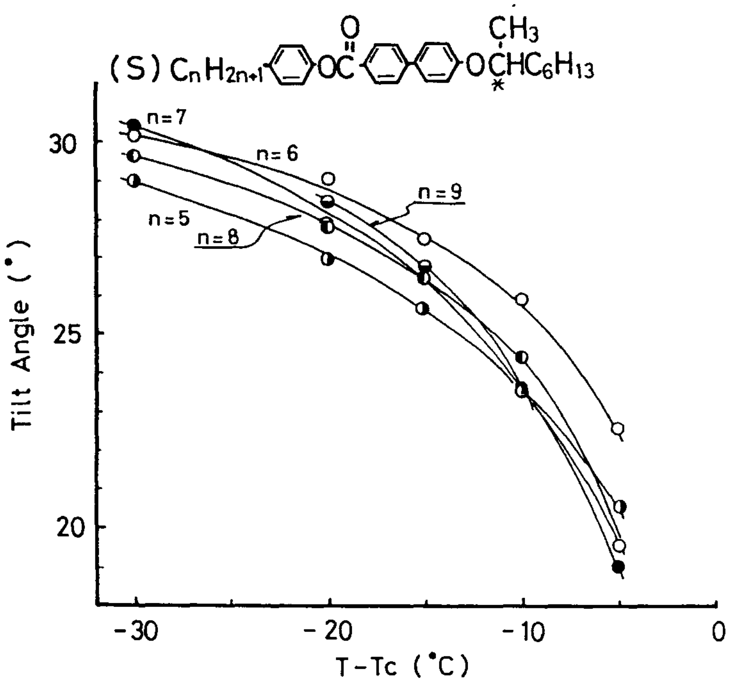


FIGURE 5 Plots of tilt angles against temperature ($T - Tc$) of compounds IA (m = 6).

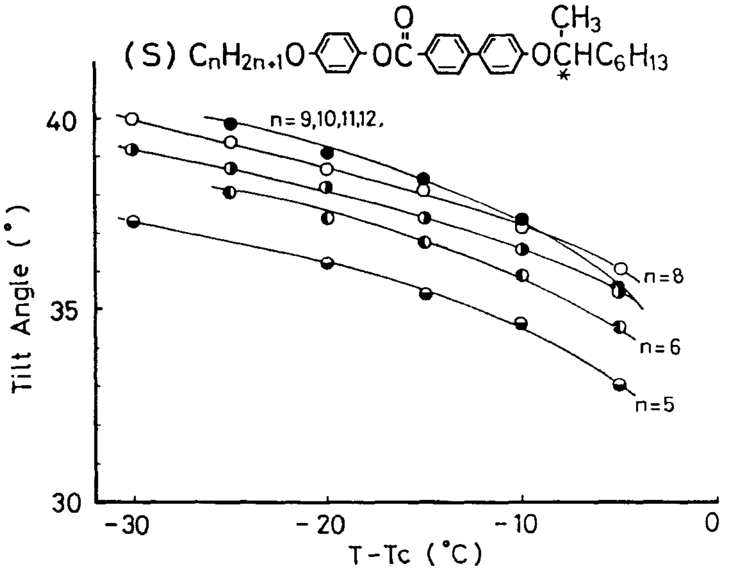
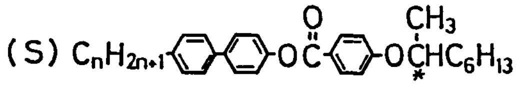


FIGURE 6 Plots of tilt angles against temperature ($T - Tc$) of compounds IB (m = 6).

TABLE I

The phase transition temperatures, values of spontaneous polarization and tilt angles of compounds IIA (m = 6)



	Transition Temperature (°C)							Ps (nC/cm²)	Tilt Angle (°)
n	Cr.		S_c^*		N*		I	T−Tc = −30°C	
7	*	53.1	*	58.9	*	106.2	*	14[1]	42[1]
8	*	50.0	*	62.5	*	87.2	*	43	42

[1] T−Tc = −5°C

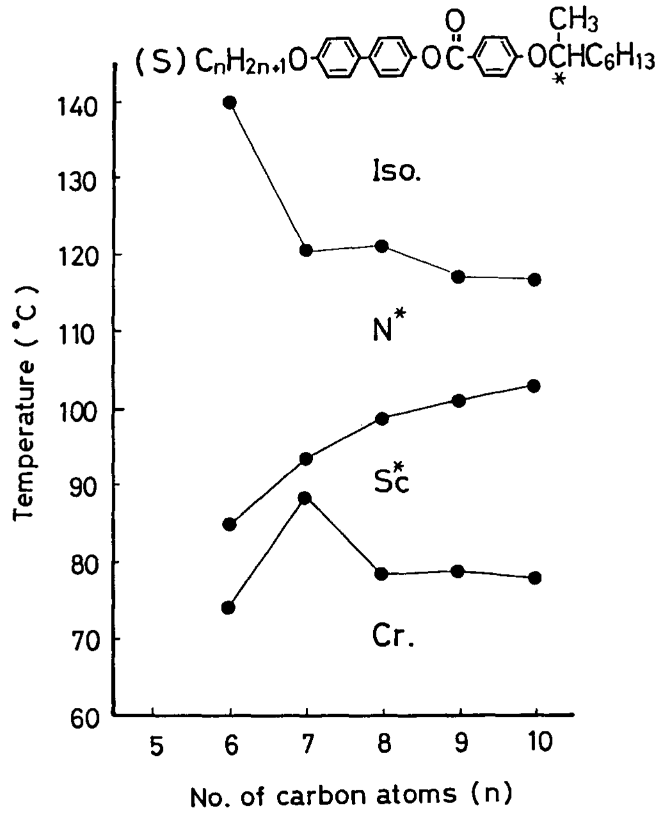


FIGURE 7 Plots of transition temperatures against the number of carbon atoms (n) of compounds IIB (m = 6).

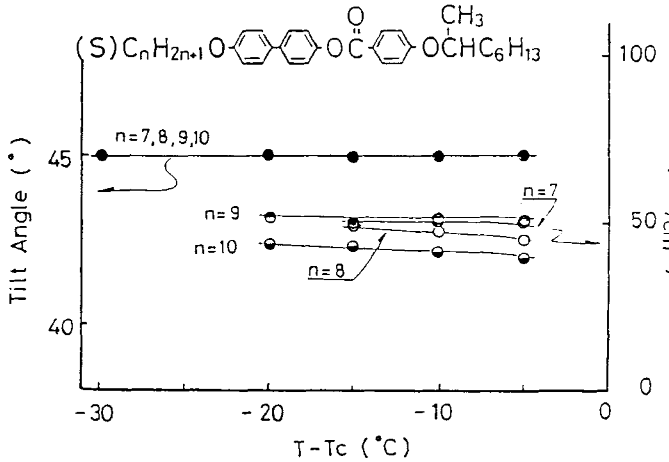
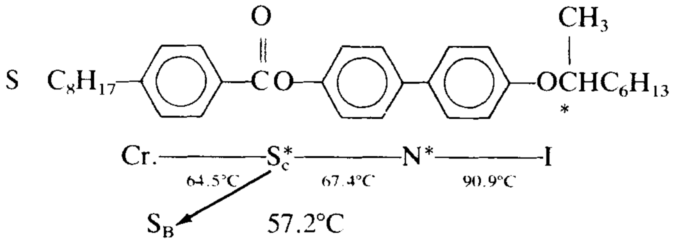


FIGURE 8 Plots of values of the spontaneous polarization and tilt angles against temperature ($T - Tc$) of compounds IIB (m = 6).

3. 4′-(1-Methyl-alkoxy)-4-biphenylyl esters of *p*-alkyl- and *p*-alkoxybenzoic acids. (IIIA, IIIB)

Compound IIIA (R = n—C_8H_{17}—, n = 6) shows the following phase transition.



Ps of 52 nC/cm^2 and tilt angle of 35° were observed at 62.4°C. ($T - Tc = -5$°C).

Table III shows the results of compounds IIIB, m = 6.

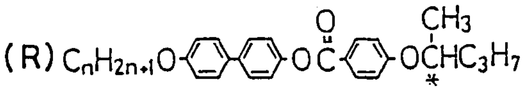
It is interesting to note that the Ps values are only about a half of compounds IB, in which direction of ester group is reversed.

4. *p*-(1-Methyl-alkoxy)-phenyl esters of 4′-alkyl- and 4′-alkoxy-4-biphenylcarboxylic acids. (IVA, IVB)

Compound IVA (R = n—C_8H_{17}—, m = 6) failed to show the S_C^* phase, and was not studied further.

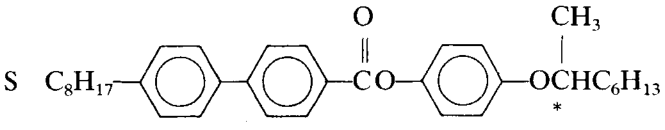
TABLE II

The phase transition temperatures, values of spontaneous polarization and tilt angles of compounds IIB (m = 3)



	Transition Temperature (°C)				Ps (nC/cm²)	Tilt Angle (°)
n	Cr.	S_C^*	N^*	I	T-Tc = -15°C	
6	* 99.0	(* 84.3)	* 143.2	*	$19^{1)}$	—
8	* 91.4	* 95.4	* 136.7	*	34	45
9	* 90.0	* 96.5	* 130.0	*	36	44
11	* 78.0	* 96.8	* 122.7	*	28	44

1) T-Tc = -2°C

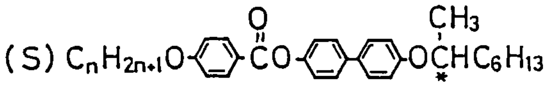


$$\text{Cr.}\underset{61.5^\circ\text{C}}{\text{———}}S_B\underset{74.7^\circ\text{C}}{\text{———}}S_A\underset{112.6^\circ\text{C}}{\text{———}}\text{I}$$

Figures 9 to 11 show the phase transitions, Ps, and tilt angle of compounds IVB (m = 6). The magnitude of Ps is similar to IIB which has reversed direction of ester group.

TABLE III

The phase transition temperatures, values of spontaneous polarization and tilt angles of compounds IIIB (m = 6)



	Transition Temperature (°C)				Ps (nC/cm²)	Tilt Angle (°)
n	Cr.	S_C^*	N^*	I	T-Tc = -30°C	
7	* 76.0	* 91.5	* 124.6	*	57	38
8	* 69.8	* 100.8	* 125.3	*	48	34
11	* 66.9	* 109.1	* 118.3	*	58	37

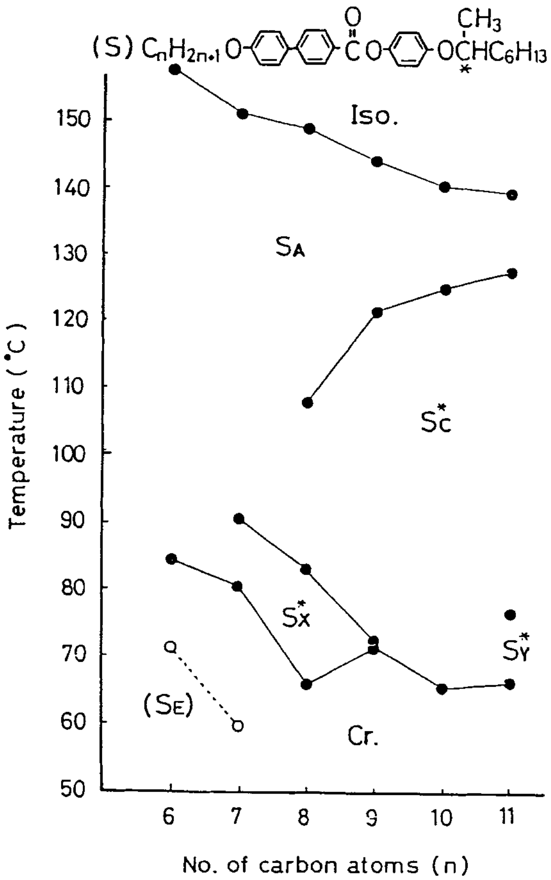
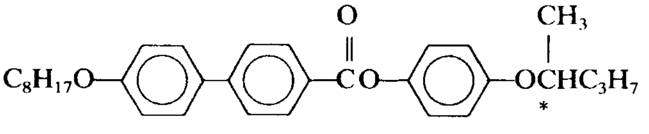


FIGURE 9 Plots of transition temperatures against the number of carbon atoms (n) of compounds IVB (m = 6).

R *p*-(1-Methyl-butoxy)-phenyl 4′-octyloxy-4-biphenyl-carboxylate (IVB, R = n—$C_8H_{17}O$—, m = 3)

R



$$C_8H_{17}O-C_6H_4-C_6H_4-\overset{O}{\overset{\|}{C}}O-C_6H_4-O\overset{CH_3}{\overset{|}{\underset{*}{C}}}HC_3H_7$$

$$\mathrm{Cr.}\xrightarrow[66.5^\circ C]{}S_X^*\xrightarrow[80.5^\circ C]{}S_C^*\xrightarrow[122.5^\circ C]{}S_A\xrightarrow[162.5^\circ C]{}\mathrm{I}$$

shows Ps of 43 nC/cm² and tilt angle of 25° at $T - Tc = -30°C$.

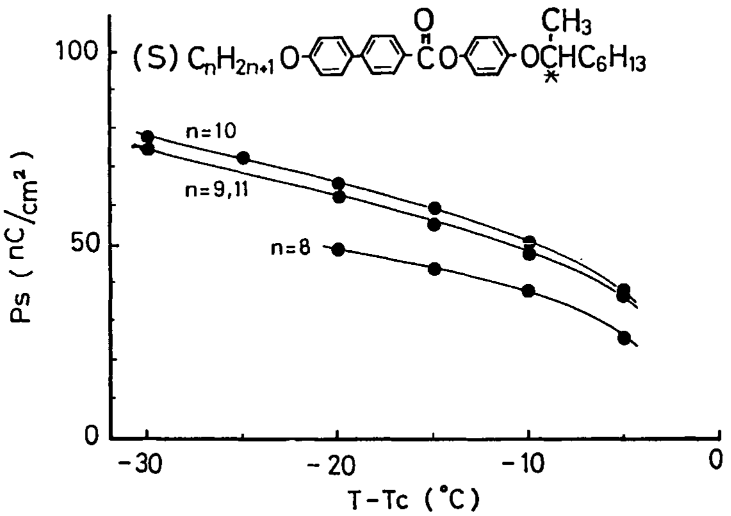


FIGURE 10 Plots of values of the spontaneous polarization against temperature ($T - Tc$) of compounds IVB (m = 6).

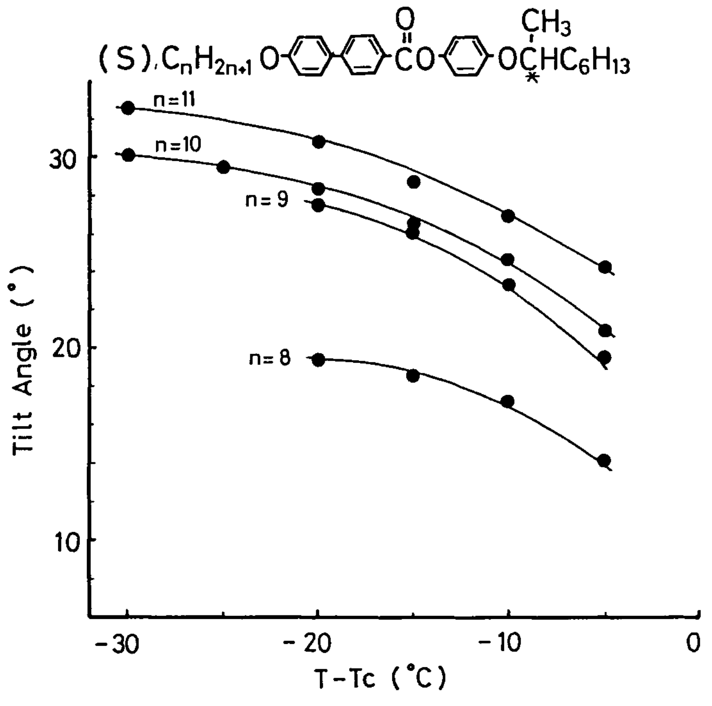


FIGURE 11 Plots of tilt angles against temperature ($T - Tc$) of compounds IVB (m = 6).

5. The sign of spontaneous polarization

All the compounds of S-absolute stereochemical structure of present study, except for IVA type in which experiment was impossible because of lack of S_C^* phase, give negative Ps (see preceding paper[1] for the definition of sign of Ps). Those of R-absolute structure as far as available for experiments show positive Ps, which results obviously conform to the expectation from symmetry reason. The sign of Ps in relation to the absolute configuration of several chiral alkyl and alkoxy groups, including 1-methyl-alkyl group, has been already described in the preceding paper.[1]

6. The sense of twist

The sense of twist in the S_C^* phase is listed in Table IV. This was determined with either, or both, of i) the contact method or ii) direct observation of rotation of plane of polarization. The results are here dealt with in terms of the relation of twist sense and the absolute stereochemical configuration of the compounds proposed by Goodby and Leslie[2], i.e. the rule of SED, ROD and so on. Since 1-methylalkoxy group has a chiral center at the second position in the wing chain, we have *E* (even) for the second label. Now we have, from the results of Table IV, SED and REL for compounds type III and IV, in harmony with the proposed rule. Compound types I and II, however, give SEL and RED relationship in disagreement with it, as shown in the preceding paper. It is interesting that seemingly subtle change of chemical structure, that is just reversing the direction of ester group in remote site from the chiral center brings about such a drastic change in the twist sense. We should not be involved in premature attempts of rationalization, but simply note that the rule that may work in the twist sense of cholesteric helix need not apply to that of S_C^* helix, since the spatial relation between the helical axis and the molecular axis distinctly differs in the two phases. The twist sense of cholesteric phase exhibited by compounds I-IV, shown also in Table IV, obeys the rule of SED, ROD and so on by Gray and McDonnell[3] without exception.

EXPERIMENTAL

The physical measurements were carried out in the same way as described in the preceding paper.[1] The compounds were synthesized by the usual esterification reaction, and purified by recrystallization to constant phase transition temperatures. The purity was checked by HPLC (Shimadzu: LC-5A). Structural checks were carried out using NMR (JEOL Ltd.: JNM-PMX60). Examples of the preparation of the compounds are described below.

Preparation of S 4'-n-Octyloxy-4-biphenylyl p-(1-Methyl-heptyloxy)-benzoate (*IIB*, $R = n\text{-}C_8H_{17}O\text{-}, m = 6$)

To a solution of methyl *p*-hydroxybenzoate 285g (1.87 mol) in methanol (1.2 1) containing 101 g (1.87 mol) of potassium hydroxide was added 586 g (2.06 mol) of R(−) 2-octyl *p*-toluenesulfonate, prepared from R(−) 2-octanol (Fluka) and *p*-toluenesulfonyl chloride in pyridine, and the mixture refluxed for 5 hrs. The crude product (142 g), S methyl *p*-(1-methyl-heptyloxy)-benzoate, was isolated in the usual way, and was hydrolyzed by heating with 250 ml of 20% aqueous ethanol containing 32 g of potassium hydroxide for 2 hrs under reflux. The benzoic acid obtained was purified by recrystallization from ethanol to obtain 81 g of S(+) *p*-(1-methyl-heptyloxy)-benzoic acid, m.p. 62–63°C, $[\alpha]_D^{25°} = +8.8°$ (C = 10.4 in $CHCl_3$). This was converted to the acid chloride, with thionyl chloride, which was used without purification in the next step. 4'-n-Octyloxy-4-hydroxybiphenyl, 12 g, was dissolved in 200 ml of dry pyridine and 11.5 g of the above benzoyl chloride in 50 ml of dry toluene was added dropwise at room temperature, and the mixture heated at 80°C for 2 hrs. The crude product, isolated in the conventional way, passed through an alumina column in dry toluene solution, and was purified by recrystallization from ethanol-ethyl acetate solvent. Its phase transition was Cr, 78.2°C, Sc, 99.0°C, Ch, 122.3°C, Iso., $[\alpha]_D^{25°} = +2.2°$ (C = 10.2 in $CHCl_3$).

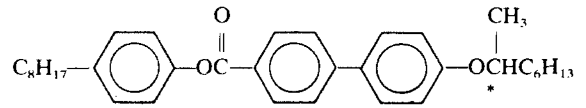
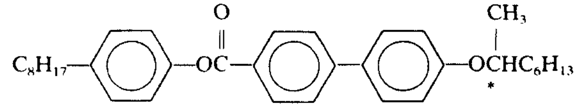
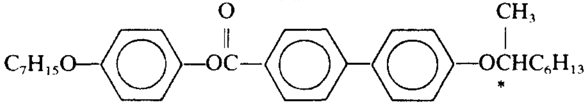
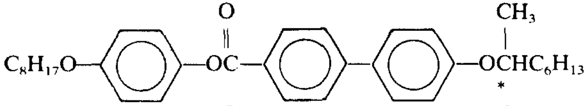
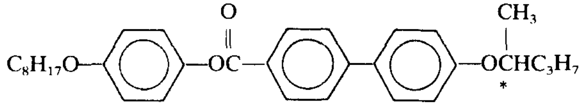
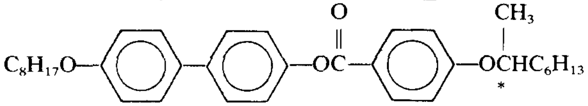
Preparation of S p-(1-Methyl-heptyloxy)-phenyl 4'-Octyloxy-4-biphenylcarboxylate (*IVB*, $R = n\text{-}C_8H_{17}O\text{-}$, $m = 6$)

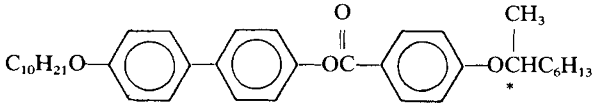
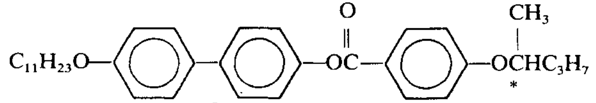
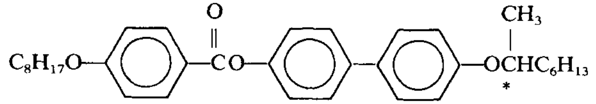
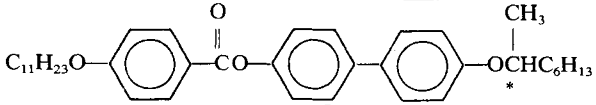
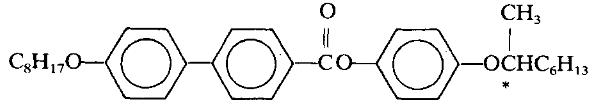
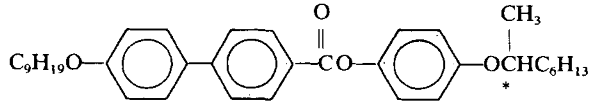
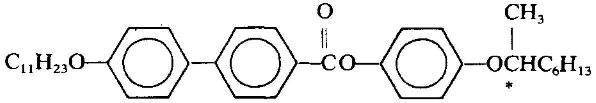
To a solution of 50 g (0.27 mol) of *p*-benzyloxyphenol in 175 ml of 90% aqueous ethanol containing 25 g of potassium hydroxide was added 83 g (0.29 mol) of R(−) 2-octyl *p*-toluenesulfonate, and the mixture refluxed for 5 hrs. The crude product (69 g), S *p*-benzyloxy-(1-methyl-heptyloxy)-benzene, was isolated in the usual way, and debenzylated by Pd/C catalyzed hydrogenation at normal temperature and pressure. The product, S(+) *p*-(1-methyl-heptyloxy)-phenol, b.p. 129–130.5°C (0.5 mm Hg), was obtained in 30.7 g yield. $[\alpha]_D^{25°} = +11.4°$ (C = 10.1 in $CHCl_3$).

This phenol, 3.0 g, was dissolved in 10 ml of dry pyridine and to this was added dropwise 4.0 g of 4'-octyloxybiphenyl-4-carbonylchloride in 15 ml of dry toluene at room temperature, and the mixture was heated at 80°C for 2 hrs. The crude product, isolated in the

TABLE IV

Chemical structure, and twist senses of S_c^* and N* phase

Type	Chemical structure	Absolute configuration	S_c^* phase Twist sense	S_c^* phase Measurement method	N* phase Twist sense	N* phase Measurement method
IA		S	(−)	A[a], B[b]	R	B, C[c]
IA		R	(+)	A, B	L	B
IB		R	(+)	B	L	B
IB		S	(−)	B	R	B
IB		R	(+)	B	L	B
IIB		S	(−)	B	R	B

IIB		R	(+)	B	L	B
IIB		R	(+)	B	L	B
IIIB		S	(+)	B	R	B
IIIB		R	(−)	A, B	L	B
IVB		S	(+)	A, B	(R)[d]	C
IVB		R	(−)	B	−	
IVB		R	(−)	A, B	−	

---

[a]A: Direct method.

[b]B: Contact method.

[c]C: By the contact method in which one cholesteric phase is the induced cholesteric phase from the sample in ZLI-1132 and a left handed cholesteric phase of S 4′-(2-methyl-butyloxycarbonyl)-4-biphenylyl *p*-n-heptyloxybenzoate.

[d]Sense of induced cholesteric phase.

conventional way, passed through an alumina column in dry toluene solution, and was purified by recrystallization from ethanol-ethyl acetate solvent. Its phase transition was Cr, 65.7°C, Sx, 84.3°C, S_c^*, 107.2°C, SA, 151.8°C, Iso. $[\alpha]_D^{25°} = +2.0°$ (C = 10.1 in $CHCl_3$).

References

1. In this issue (Proceeding of 11th International Liquid Crystal Conference, 1986).
2. J. W. Goodby and T. M. Leslie, *Mol. Cryst. Liq. Cryst.*, **110**, 175 (1984).
3. G. W. Gray and D. G. McDonnell, *Mol. Cryst. Liq. Cryst. Lett.*, **34**, 21 (1977).