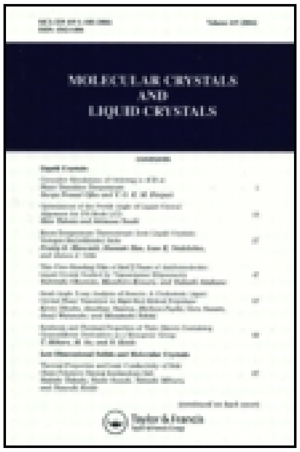


Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

Some Observations on the Sense and Magnitude of Spontaneous Polarization and Twisting Power of a Number of Ferroelectric Liquid Crystal Types

K. Terashima [a] , M. Ichihashi [a] , M. Kikuchi [a] , K. Furukawa [a] & T. Inukai [a]
[a] Fine Chemicals Division, chisso Corporation, 2 Kamariya, Kanazawa-ku, Yokohama, 236, JAPAN

Version of record first published: 20 Apr 2011.

To cite this article: K. Terashima , M. Ichihashi , M. Kikuchi , K. Furukawa & T. Inukai (1986): Some Observations on the Sense and Magnitude of Spontaneous Polarization and Twisting Power of a Number of Ferroelectric Liquid Crystal Types, Molecular Crystals and Liquid Crystals, 141:3-4, 237-249

To link to this article: http://dx.doi.org/10.1080/00268948608079612

Mol. Cryst. Liq. Cryst., 1986, Vol. 141, pp. 237–249
0026-8941/86/1414-0237/$20.00/0

Some Observations on the Sense and Magnitude of Spontaneous Polarization and Twisting Power of a Number of Ferroelectric Liquid Crystal Types

K. TERASHIMA, M. ICHIHASHI, M. KIKUCHI, K. FURUKAWA
and T. INUKAI

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

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

The sense and magnitude of spontaneous polarization of a number of ferroelectric liquid crystal types were measured. Compounds with a polar group close to the chiral center showed large Ps values, amounting to 150 nC/cm^2 in the highest case. The alteration of signs of Ps as the chiral center is moved stepwise from the central core in the series of compounds having an alkyl or alkoxy wing chain was examined. Compounds in which the chiral center is connected to the core by an ether linkage showed singularity. The well-known SED-ROD and SOL-REL rule for cholesterics applied to almost all the diverse types of compounds of the present study also in the S_C^* phase.

Keywords: ferroelectric liquid crystal, spontaneous polarization, chirality, cholesteric phase

I. INTRODUCTION

A chiral smectic C (S_C^*) liquid crystal composition having a large spontaneous polarization (Ps) and a long S_C^* helical pitch is required in order to attain sufficiently quick response, uniform material alignment and bistability of the surface stabilized ferroelectric liquid crystal (SSFLC) mode proposed by Clark and Lagerwall.[1]

To obtain such an S_C^* composition the knowledge of the sense of Ps, i.e., Ps(+) or Ps(−),[2,3] and the twist sense of S_C^* helix, in correlation with chemical structures of candidate components very much helps. With limited Ps values of the components we don't like to partially cancel the spontaneous polarization (Ps) by mixing opposing components. The helical pitch is usually required to be elongated by counteraction of right and left twisting power of the components. These two sometime conflicting requirements must be fulfilled, not separately but concurrently.

We report here the sense and magnitude of Ps and the twist sense and power of a variety of liquid crystal structural types, and present some relevant empirical rules.

II. EXPERIMENTAL

The transition temperatures were measured with a differential scanning calorimeter, Rigaku DSC-8230, and phases were identified by the microscopic observation of textures with a polarizing microscope, Nikon XTP-11, in conjunction with a Mettler hot stage FP52 and control unit FP80.

The values of Ps were measured with the Sawyer-Tower method. The sense of spontaneous polarization was determined by the field reversal method by optical observation of the director motion.[2] When Z, $\hat{n}$ and Ps make a right-handed system, see Figure 1, the sense of Ps is defined as positive, Ps(+), and otherwise defined as negative, Ps(−). This definition is the same as that by Lagerwall et al.[2] The experimental procedures are as follows. First, negative voltage is applied on the upper side electrode, and positive voltage on the lower side electrode, of a homogeneously aligned cell, and the cell is rotated to an extinction position under crossed nicoles state of a polarizing microscope. Next the polarity of applied voltage is reversed and the cell is rotated to a new extinction position counterclockwise for Ps(+) or clockwise for Ps(−) material.

The helical pitch was determined by directly measuring, with a polarizing microscope, the distance between the dechiralization lines corresponding to the full pitch, by using a homogeneously aligned cell of about 200μm cell gap. The twist sense of the helix was determined by observation of textures of a contact preparation using a specimen of known sense of twist as a component of the binary system. When the dechiralization line disappears at the contact region the two components have opposite twist sense, and when this is not the case the two components must have the same twist sense. S-DOBAMBC was usually used as the authentic reference of right-handed

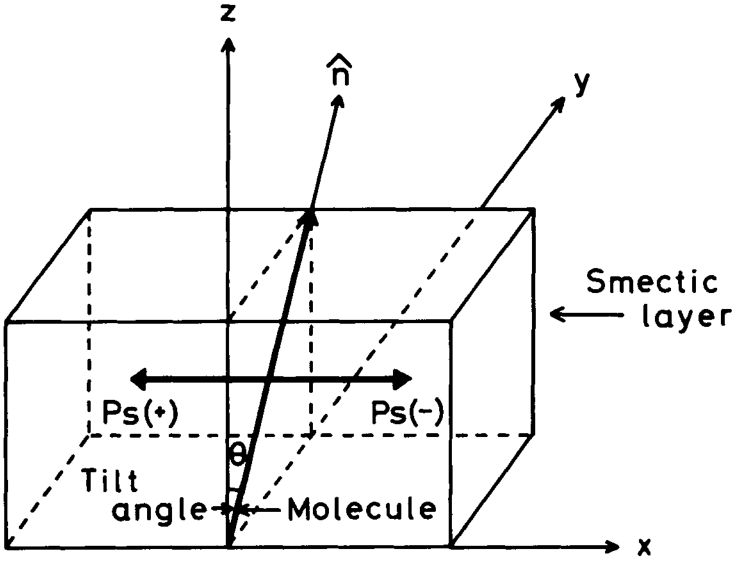


FIGURE 1 The spontaneous polarization direction Ps(+) or Ps(−) in smectic liquid crystals.

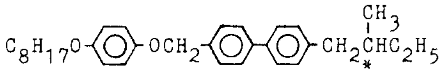
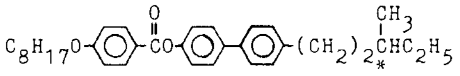
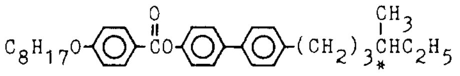
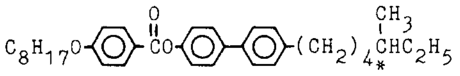
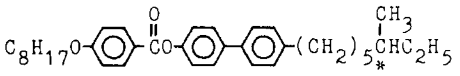
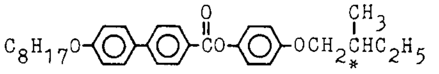
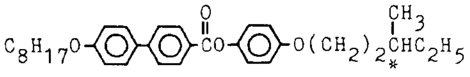
twist. We also determined the twist sense of some of the components directly by the observation of the displacement versus the rotation of the analyser of the isochromatic lines.[4] The experimental procedures are as follows. A homeotropically aligned cell is placed in a linearly polarized light beam which passes vertically through the cell, parallelly to the helical axis, and the analyzer is rotated to a new extinction position. When the rotation required is clockwise, facing to the beam, the sample is dextrorotatory and twist sense is decided to be right-handed. The sense of optical rotation given by DOBAMBC of S structure was found to be dextrorotatory, and therefore the helix right-handed, in conformity with the conclusion of previous works.[3,4,5]

III. RESULTS AND DISCUSSION

The chemical structures of the compounds studied are shown in Table I. The sense and magnitude of Ps, twist sense and S_C^* helical pitch, are shown for the optical isomers, i.e. antipode, of S absolute configuration; some of the compounds actually used were of R absolute configuration and the signs of Ps and twisting sense are shown re-

TABLE I

Chemical structure, sense and magnitude of spontaneous polarization (Ps) and twisting power, and specific rotation of antipodes of S absolute configuration

No.	Chemical structure	Ps (nC/cm^2) sense$^{a)}$	Ps (nC/cm^2) magnitude$^{b)}$	S_C^* pitch (μm) sense$^{c)}$	S_C^* pitch (μm) magnitude$^{d)}$	$[\alpha]_D^{25}$ (°)
1		(+)	0.9	(+)	1.0	+6.3 (c=9.9)
2		(-)	very small	(-)	2.2	+6.8 (c=10)
3		(+)	very small	(+)	very short	
4		(-)	very small	(-)	2.1	+3.5 (c=4.0)
5		(+)	very small	(+)	1.2	
6		(-)	very small	(-)	9.0	+4.4 (c=10.4)
7		(-)	very small	(+)	6.4	+2.5 (c=10.3)

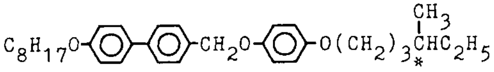
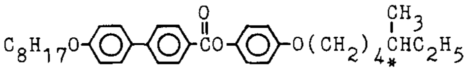
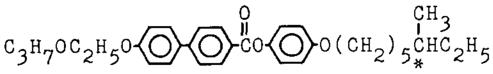
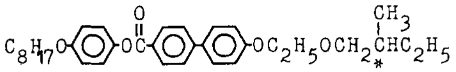
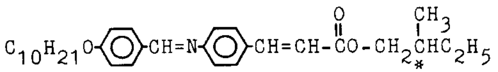
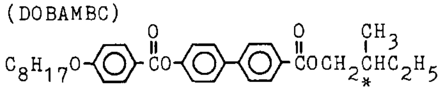
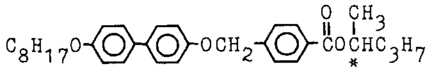
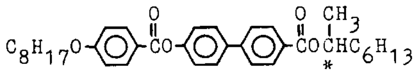
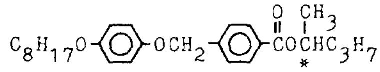
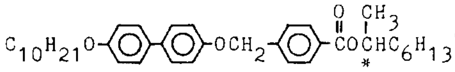
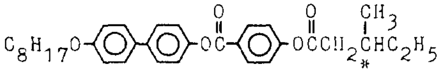
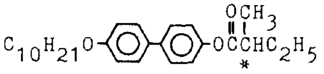
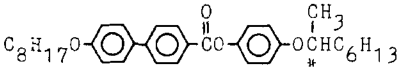
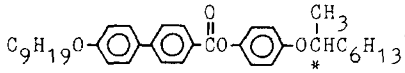
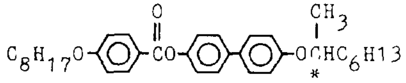
No.	Chemical structure	Ps (nC/cm^2) sense[a)]	Ps (nC/cm^2) magnitude[b)]	S_C^* pitch (µm) sense[c)]	S_C^* pitch (µm) magnitude[d)]	$[\alpha]_D^{25}$ (°)
8		(-)	very small	(-)	5.7	
9		(+)	very small	(+)	5.4	+1.4 (c=10)
10		(-)	very small	(-)	7.6	
11		(+)	very small	(+)	4.6	
12	 (DOBAMBC)	(-)	3	(+)	2	+3.6 (c=10)
13		(-)	4	(+)	6	+2.5 (c=10.3)
14		(+)	99	(-)	very short	+16.0 (c=10.1)
15		(+)	50	(-)	1.3	+27.5 (c=5.0)

TABLE I (*continued*)

No.	Chemical structure	Ps (nC/cm^2) sense[a]	Ps (nC/cm^2) magnitude[b]	S_C^* pitch (μm) sense[c]	S_C^* pitch (μm) magnitude[d]	$[\alpha]_D^{25}$ (°)
16	 e)	(+)	99	(-)	very short	+16.3 (c=2.1)
17	 e)	(+)	145	(-)	very short	+19 (c=10)
18		(+)	15	(+)	very short	
19		(-)	9[g]	(-)	11[g]	-24.8 (c=1.1)
20		(-)	40	(+)	3	+2.0 (c=10.1)
21	 e)	(-)	48	(+)	1.5	+2.5 (c=10.2)
22		(-)	41	(+)	9.6	-1.2 (c=5.1)

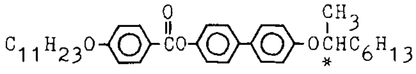
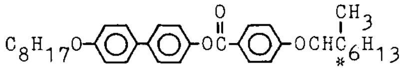
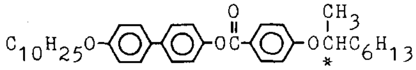
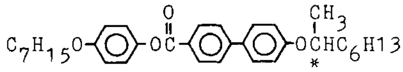
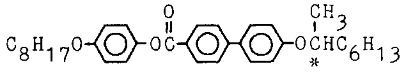
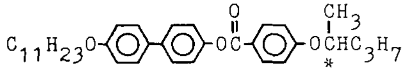
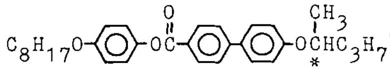
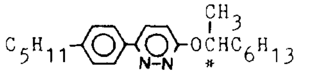
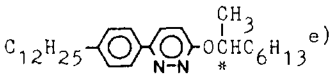
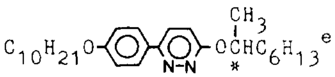
No.	Chemical structure	Ps (nC/cm^2)		S_C^* pitch (μm)		$[\alpha]_D^{25}$ (°)
		sense$^{a)}$	magnitude$^{b)}$	sense$^{c)}$	magnitude$^{d)}$	
23	 $^{e)}$	(-)	47	(+)	11.0	-1.4 (c=5.1)
24		(-)	45	(-)	very short	+2.2 (c=10.2)
25	 $^{e)}$	(-)	42	(-)	very short	
26	 $^{e)}$	(-)	85	(-)	7.5	-3.0 (c=10)
27		(-)	76	(-)	7.5	-2.5 (c=10.2)
28	 $^{e)}$	(-)	26	(-)	very short	
29	 $^{e)}$	(-)	57	(-)	very short	+5.7 (c=10.2)

TABLE I (*continued*)

No.	Chemical structure	Ps (nC/cm^2) sense[a]	Ps (nC/cm^2) magnitude[b]	S_C^* pitch (μm) sense[c]	S_C^* pitch (μm) magnitude[d]	$[\alpha]_D^{25}$ (°)
30		(+)	47[f]	(+)	0.8[f]	-4.3 (c=3.0)
31	 e)	(+)	66[f]	(+)	0.5[f]	-3.8 (c=3.4)
32	 e)	(+)	65[f]	(+)	0.3[f]	-4.3 (c=10)

[a] See text for definition of sign.

[b] Measured at $T - Tc = -10°C$.

[c] Right-handed helix is shown with +; left-handed helix with − sign.

[d] Measured at $T - Tc = -5°C$.

[e] Actually studied material is of R structure and the observed signs were reverted to give those for the S antipodes.

[f] Values for S_C^* phase extrapolated from measurements on 20wt% solutions in a racemic compound.

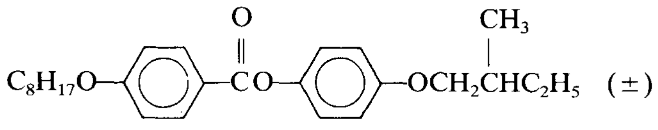
[g] Measured at $T - Tc = -4°C$. Very small; We couldn't obtain exact magnitude of Ps; it was less than 0.5 nC/cm^2.

Very short; We couldn't obtain exact value of S_C^* pitch; it was less than 1 μm.

verted, for the symmetry reason, as specifically indicated in the Table. Specific optical rotations in (isotropic) solution are also shown in Table I.

The absolute stereochemistry of compound 1–13, 18, and 19 is S, because these were prepared starting from S-2-methylbutanol via synthetic steps which are known to proceed without touching the optically active center. The compounds 14–17 were prepared by usual esterification reaction which is known to proceed with retention of configuration of the starting alcohol. The synthetic routes to compounds 20 to 29 involve a step which is believed to proceed with Walden inversion: We assume that the reaction of a potassium aryloxide with R(−) p-toluensulfonate of an R(−) 2-alkanol proceeds with inversion of configuration to give S structure, in analogy with the original work with phenoxide anion by J. Kenyon et al.[6] In the synthesis of compounds 30 to 32, however, the configuration of optically active 2-alkanol is retained, because these were prepared by attack of 2-alkoxide anion on 3-chloro-6-arylpyridazines.

Table II shows the phase transition temperatures. When S_C^* phase appears only in monotropic transition the physical measurements were made on supercooled state. The compound 30, 31 or 32, which does not give S_C^* phase by itself was studied in its 20 wt% solution in achiral smectic C phase of the following racemic compound.



Cr 47.1°C (S_C 44.1°C) S_A 59.4°C Iso

From the results listed in Table I we may deduce the relationship between the sense of Ps and twist sense of S_C^* helix on one hand and the part-structure of the molecules on the other hand, in somewhat extended form, which is shown in Table III.

The main purpose of this paper is to present the experimental results of various types of S_C^* compounds, showing how vast is the problem. It is admitted that further, systematic studies are desirable, but we shall briefly discuss the results so far obtained.

In the following we are referring to the compounds of S-absolute configuration, when mentioning the signs of Ps and twist, to avoid confusion, although some of the materials used were of R-type.

TABLE II

Phase transition temperatures

No.[a]	Phase transition temperatures[b]
1	Cr 106 (S_4 97.5) S_3^* 107.5 S_C^* 122.5 S_A 124.7 Iso
2	Cr 75.3 S_C^* 126.8 Ch 160.6 Iso
3	Cr 79.5 S_C^* 121.5 Ch 154.2 Iso
4	Cr 95 S_C^* 138.7 Ch 159.1 Iso
5	Cr 78.5 S_C^* 135.9 Ch 154.7 Iso
6	Cr 100.2 S_B 105.8 S_C^* 144.9 S_A 189.3 Iso
7	Cr 77.5 S_B 101.5 S_C^* 154.2 S_A 186.8 Ch 187.4 Iso
8	Cr 53.5 S_3^* 91.0 S_2^* 135.2 S_C^* 157.5 Iso
9	Cr 110.5 S_C^* 125.7 S_A 176.6 Iso
10	Cr 115.5 S_C^* 141.6 S_A 168.6 Ch 169.6 Iso
11	Cr 67.2 S_C^* 144.4 Ch 158.5 Iso
12	Cr 76 (S_I^* 63) S_C^* 95 S_A 116 Iso
13	Cr 83.4 S_C^* 121.3 S_A 159.3 Ch 170.5 Iso
14	Cr 71.5 S_3^* 121.2 S_2^* 130 S_C^* 149.1 Iso
15	Cr 92.5 (S_C^* 85) S_A 130.8 Iso
16	Cr 33.5 (S_C^* 18.3 S_A 20.3) Iso
17	Cr 75.5 S_3 91.5 S_2^* 107 S_C^* 129 Iso
18	Cr 110 S_C^* 148.3 Ch 189.9 Iso
19	Cr 77.1 (S_3^* 75.6) S_C^* 79.8 S_A 84.3 Iso
20	Cr 65.7 S_3^* 84.3 S_C^* 107.2 S_A 151.8 Iso
21	Cr 71.1 S_3^* 72.2 S_C^* 121.5 S_A 144.3 Iso
22	Cr 69.8 (S_B 67.4) S_C^* 100.8 Ch 125.3 Iso
23	Cr 66.9 S_C^* 109.1 Ch 118.3 Iso
24	Cr 78.2 S_C^* 99 Ch 122.3 Iso
25	Cr 72.4 S_C^* 104.8 Ch 130.5 Iso
26	Cr 72 S_C^* 100.2 Ch 123.5 Iso
27	Cr 78.7 S_C^* 103.3 Ch 120.8 Iso
28	Cr 78 S_C^* 96.8 Ch 122.7 Iso
29	Cr 71.8 S_C^* 89.8 Ch 137.4 Iso

TABLE II (*continued*)

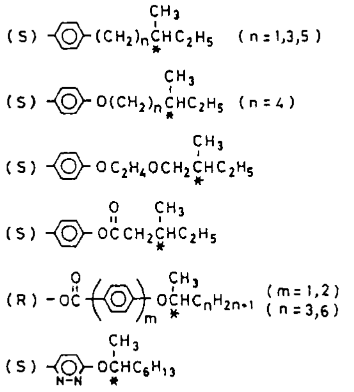
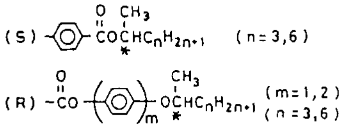
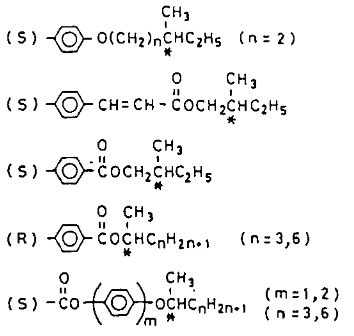
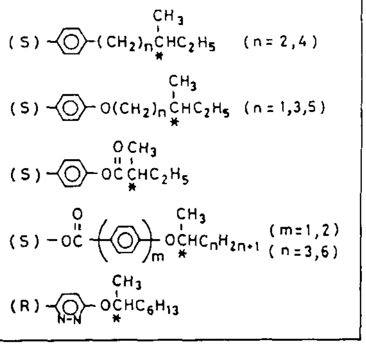
No.[a]	Phase transition temperatures[b]
30	Cr 54.8 Iso
31	Cr 56.3 Iso
32	Cr 87 Iso

[a] Compound numbers correspond to those of Table I.

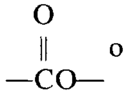
[b] Subindexed S means a smectic modification of undefined nature.

TABLE III

Relationship between the sense of Ps and twist and the chiral structural type

		Twist Sense of S_C^* Helix	
		Right	Left
Sense of Spontaneous Polarization	+		
	−		

1. Magnitude of Ps

Compounds 14 to 17, 20 to 32 show by far larger Ps values than others as evident from Table I. A rough generalization is that a polar group, i.e.  $\overset{\displaystyle O}{\overset{\|}{-CO-}}$ or —O—, located itself close to the chiral center certainly enhances the Ps, a view that has already been presented.[7,8] If we look into details there may be some ununderstandable cases; compound 19 in particular seems to show too low Ps for the structure in which the chiral center is directly connected to carbonyl group.

2. Sense of Ps

The alteration of signs of Ps from Ps(+) to Ps(−) in the series of compound 1 to 5, as the chiral center shifts stepwise from the 2nd through 6th position in the alkyl chain from the central core, is interesting to note. The regularity holds also for the alkoxy wing chain, if we disregard the difference of the methylene group and oxygen atom, in the case of compounds 6, 8, 9, 10, but not for compound 7 (see Table III also). Compound 11 which has five main chain atoms (three carbon and two oxygen atoms) shows Ps(+), a behavior in harmony with the regularity. Compounds 20 to 29 in which the chiral center is connected to the core by ether linkage (but not compound 30 to 32) show positive Ps in disagreement with the above rule.

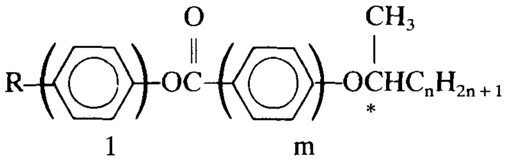
3. Helical pitch in S_C^* phase

Comparison of compounds 1 to 5 show a zig-zag. The series of compounds 6 to 10, however, does not show a clear-cut trend. The dependency of the helical pitch on how far the chiral center is from the central core is not like in the case of cholesteric pitch, where it was shown by Gray et al.[9,10] that the far the chiral center is from the core the larger is the pitch.

4. Sense of twist in S_C^* phase

Goodby and Leslie[11] presented a view that as the chiral center is moved stepwise from the core there appears to be an odd-even effect, i.e. the helical twist sense of S_C^* phase alternates from left to right. The well-known SED-ROD (for right-handed helix) and SOL-REL (for left-handed helix) rule for cholesterics[10] was thereby proposed for S_C^* phase too.

It is almost surprising that this proposed rule applies correctly to all the diverse types of compounds of the present study, except the following type which shows SEL (RED) relationship.



(1 = 2,m = 1; compound 24, 25, 28)

(1 = 1,m = 2; compound 26, 27, 29)

It is interesting to note that the closely related compounds (20 to 23) in which direction of the ester group is inverted, i.e. to $\overset{\displaystyle O}{\overset{\|}{-CO-}}$, come to follow the rule.

Finally it should be mentioned that all the compounds of the present study (No. 1 through 32) follow the SED-SOL rule of Gray et al.[10] without exception in the cholesteric or induced cholesteric phase.

References

1. N. A. Clark and S. T. Lagerwall, *Appl. Phys. Lett.*, **36**, 899 (1980).
2. S. T. Lagerwall and I. Dahl, *Mol. Cryst. Liq. Cryst.*, **114**, 151 (1984).
3. Ph. Martinot-Lagarde, R. Duke and G. Durand, *Mol. Cryst. Liq. Cryst.*, **75**, 249 (1981).
4. J. Billard, A. Dahlgren, K. Flatischler, S. T. Lagerwall and B. Otterholm, *J. Physique*, **46**, 1241 (1985).
5. L. A. Beresnev, V. A. Balknov, L. M. Blinov, E. P. Pozhidaev and G. V. Purvanetskas, *JETP Lett.*, **33**, 536 (1981).
6. J. Kenyon, H. Phillips and V. P. Pittman, *J. Chem. Soc.*, **1935**, 1072.
7. K. Yoshino, M. Ozaki, T. Sakurai, K. Sakamoto and M. Honma, *Jpn. J. Appl. Phys.*, **23**, L175 (1984).
8. J. Wahl and S. C. Jain, the 13th Freiburger Arbeitstagung Flussigkristalle, Abstract No. 21 (1983).
9. G. W. Gray and D. G. McDonnell, *Mol. Cryst. Liq. Cryst.*, **37**, 189 (1976).
10. G. W. Gray and D. G. McDonnell, *Mol. Cryst. Liq. Cryst. Lett.*, **34**, 211 (1977).
11. J. W. Goodby and T. M. Leslie, *Mol. Cryst. Liq. Cryst.*, **110**, 175 (1984).