Manifestation of chiral asymmetry of ferroelectric liquid crystals induced by optically active dipole dopants in a linear electrooptic effect

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Manifestation of chiral asymmetry of ferroelectric liquid crystals induced by optically active dipole dopants in a linear electrooptic effect

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The existence of eight combinations of absolute spatial configuration, helix handedness and handedness of director tilt has been shown for ferroelectric liquid crystals induced by optically active dipole dopants (optically active diesters of 4,4″-terphenyl dicarboxylic acid). As in the case of individual ferroelectrics alternation of the helix handedness is observed depending on absolute configuration of the C*-atom and its position relative to the rigid core of the molecule. However for these induced ferroelectric liquid crystals the helix handedness does not depend on the inductive effect of the substituent adjacent to the C* atom, e.g. the helix handedness of all the (S)-2-chlorine substituted materials coincides with that of the (S)-2-methyl-butyl derivative. Substitution of a chlorine atom by a cyano group followed by conversion of absolute spatial configuration of the C* atom results in the opposite helical sense. Thus asymmetric parameters of the induced ferroelectric liquid crystals helix handedness and the handedness of director tilt (or the sign of P_s) do not depend directly on the absolute configuration of C* atom and its position in a molecule. For the substances investigated within all of the temperature range of the induced smetic C* phase no reversal of the tilt direction handedness was observed.

1. Introduction

The discovery of ferroelectricity in the tilted smectic phases of chiral liquid crystals [1, 2] has revealed a new field in the physics of the mesomorphic state and recently it has made it possible to create a new generation of electrooptic devices whose response is two or three orders higher than that of conventional nematic devices [3]. The intrinsic property of ferroelectric liquid crystals, namely spontaneous polarization, is due to the mirror asymmetry of the constituent chiral molecules or the mirror asymmetry of optically active dipole dopant molecules dissolved in the smectic C phase [4, 5]. The natural effect of the molecular chirality, of at least one of the components of the ferroelectric material, is the helical ordering of the director on passing from layer to layer about an axis normal to the layer plane.
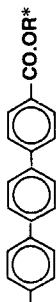
It has been shown that individual ferroelectric liquid crystals [6, 7] incorporating a lateral methyl substituent at the chiral centre follow the rules given by Gray and McDonnel [8] for the helical twist sense of the cholesteric phase, When the methyl substituent is replaced by a chlorine atom which has a negative inductive effect, the opposite twist sense is observed for the equivalently substituted materials [6]. Thus the twist of the helical ordering is likely to depend on the following set of conditions: the absolute configuration of the chiral centre (R or S), its position relative to the rigid core of a molecule (e even or o odd number of atoms between the core and C*-atom) and the inductive effect of the substituents (+J effect or −J effect) adjacent to the

Table 1. Asymmetry parameters of ferroelectric liquid crystals induced by symmetrically substituted optically active dopants.

RO.OC-⬡-⬡-⬡-CO.OR

	R* =	Absolute configuration	Odd or even	Helix	J-effect	Tilt handedness	Sign of P_s	Tilt indices	P_s-indices
1	CH_3 / C_2H_5 \ C^*H-CH_2-	S	e	RH	+	Left	–	SLl	SL–
2	CH_3 / C_6H_{13} \ C^*H-	S	o	LH	+	Right	+	SDr	SD+
3	CH_3 / C_6H_{13} \ C^*H-	R	o	RH	+	Left	–	RLl	RL–
4	CH_3-$\overset{*}{C}H$-(phenyl)	S	o	LH	+	Right	+	SDr	SD+
5	CH_3 / $CH_2\overset{*}{C}H$-(phenyl)	S	o	LH	+	Left	–	SDl	SD–
6	$CH(CH_3)_2$ / cyclohexyl $(CH_3)_2$	R 1R, 3R, 4S	o	LH	+	Left	–	RDl	RD–
7	CH_3 / Cl \ C^*H-CH_2-	S	e	RH	–	Right	+	SLr	SL+
8	CH_3 / CN \ C^*H-CH_2-	R	e	RH	–	Right	+	RLr	RL+

No.	R^*								
9	$R^* = CH_3-CH_2-C^*H-CH_2-$, Cl	S	e	RH	−	Right	+	SLr	SL+
10	$R^* = CH_3-CH_2-C^*H-CH_2-$, CN	R	e	LH	−	Right	+	RDr	RD+
11	$R^* = CH_3-CH_2-CH_2-CH_2-C^*H-CH_2-$, Cl	S	e	RH	−	Right	+	SLr	SL+
12	$R^* = CH_3-CH_2-CH_2-CH_2-C^*H-CH_2-$, CN	R	e	LH	−	Right	+	RDr	RD+
13	$R^* = CH_3-CH(CH_3)-C^*H-CH_2-$, Cl	S	e	RH	−	Right	+	SLr	SL+
14	$R^* = CH_3-CH(CH_3)-C^*H-CH_2-$, CN	R	e	LH	−	Right	+	RDr	RD+
15	$R^* = CH_3-C^*H(C_2H_5)-C^*H-CH_2-$, Cl	$2S, 3S$	e	RH	−	Right	+	SLr	SL+
16	$R^* = CH_3-C^*H(C_2H_5)-C^*H-CH_2-$, CN	$2R, 3S$	e	LH	−	Right	+	RDr	RD+
17	$R^* = CH_3-CH_2-CH_2-C^*H-CH_2-$, Cl	S	e	RH	−	Right	+	SLr	SL+

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Table 1 (*continued*).

RO.OC-◯-◯-◯-CO.OR	Absolute configuration	Odd or even	Helix	J-effect	Tilt handedness	Sign of P_s	Tilt indices	P_s-indices
18 R^* = $CH_3-CH_2-CH_2$ CN C^*H-CH_2-	R	e	LH	−	Right	+	RDr	RD+
19 R^* = $CH_3-CH-CH_2$ CH_3 ... Cl C^*H-CH_2-	R	e	LH	−	Left	−	RDl	RD−
20 R^* = $CH_3-CH-CH_2$ CH_3 ... CN C^*H-CH_2-	S	e	RH	−	Left	−	SLl	SL−

C* atom. It has been shown experimentally [9] that for R and S absolute configurations of the chiral centre right and left handed directions of the helix both are possible. In other words, there can be a total of four combinations of the absolute asymmetric centre configuration and helical handedness: RD, RL, SD, SL (here D and L indices correspond to a dextro and levo rotation of plane polarized light when the observer is looking along the oncoming beam).

This paper deals with ferroelectric liquid crystal materials induced by optically active dopants. Table 1 lists a number of compounds synthesized with known absolute spatial configurations which have been used as dopants to form chiral smectic C materials. It can be seen that for the investigated ferroelectrics four combinations of absolute configuration and helical handedness are also possible. As in the case of individual ferroelectric liquid crystals, alternation of the sign of optical rotation of plane polarized light (handedness of the helix) is observed depending on the absolute configuration of the C* atom and its position relative to the rigid core of the molecule. It should be noted that for the induced ferroelectrics, the handedness of the helix does not depend on the inductive effect of the substituent adjacent to the C*-atom, i.e. the helix handedness of all the (S)-2-chlorine-substituted materials coincides with that of the (S)-2-methyl-butyl derivative. Substitution of the chlorine atom by a cyano group followed by conversion of the absolute spatial configuration of the C*-atom results in the opposite helical sense.

The most important feature of ferroelectric liquid crystals is their linear electrooptic effect, i.e. a reorientation of the director, ñ, relative to z by the applied electric field [2, 10]. The most probable model of the director reorientation in a chiral smectic C phase is thought to be the motion on a conical surface with the cone angle of 2θ (θ is the tilt angle) see the figure. When a DC voltage of known polarity is applied, the director, **n**, can lie either to the right or to the left of the layer normal, z (see figures (*a*) and (*b*), respectively). Thus, the intrinsic ferroelectric asymmetry manifests itself in the orientational linear electrooptic effect as a right or lefthand director tilt caused by the electric field of known polarity. We shall call a ferroelectric liquid crystal right when the director of a planar oriented sample (the smectic layers are perpendicular to the cell surfaces) moves to the right with respect to the layer normal, z, when a positive potential is applied to the electrode nearest to the observer. This case is in accord with the convention [11] where the sign of the P_s vector coinciding with the E vector is positive ($P_s(+)$, see figure (*a*)). The alternative situation is shown in the figure (*b*) (left ferroelectric, or $P_s(-)$). Note that for each of these combinations of chircal centre configurations and helical handedness both right and left director tilts with respect to z are possible. Thus basically we have eight possible combinations of absolute configuration, helical handedness and a director tilt, denoted by a combination of three indices (see table 3).

The absence of direct relationship between the absolute configuration of the C*-atom, the helix handedness and the tilt direction handedness (P_s sign) was first noted for individual ferroelectric liquid crystals when studying (S)-*p*-decyloxybenzylidene-*p'*-amino-2-methylbutyl-cinnamate and (S)-*p*-decyloxybenzylidene-*p'*-amino-2-methylbutyl-α-cyano-cinnamate [12]. For these compounds the inversion of the tilt direction handedness was not due to changes of the chiral centre parameters. Moreover, some compounds are known for which reversal of the tilt angle sign, indicating the reversal of the sign of the spontaneous polarization, is observed at a certain temperature. This anomaly is not accompanied by a reversal of helix handedness [13].
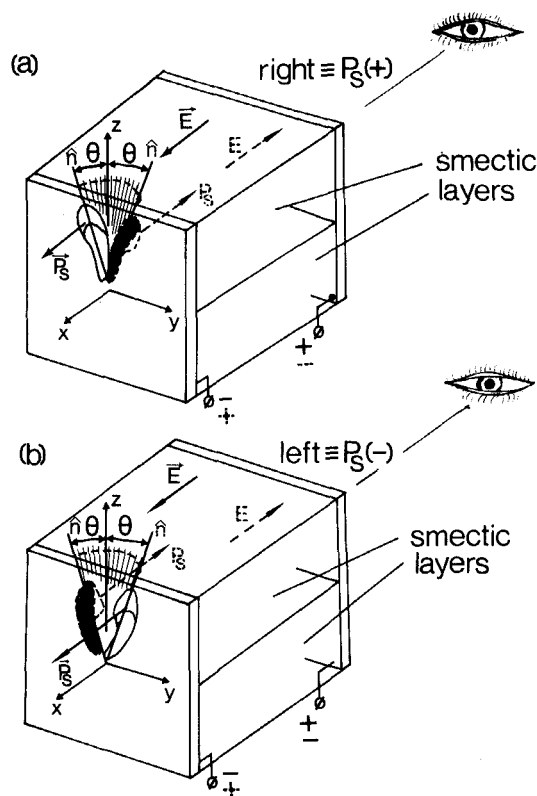
Determination of the spontaneous polarization in relation to the molecular tilt orientation in an electrooptic experiment. The solid lines represent the situation for a positive charged electrode nearest to the observer, and the dashed lines that for a negative one. (*a*) 'right' (P_s +) ferroelectric liquid crystal, (*b*) 'left' (P_s −).

The studies carried out on ferroelectrics induced by optically active dopants revealed the existence of eight combinations of absolute spatial configuration, helix handedness and tilt direction (see table 1). The data obtained show an obvious independence of two manifestations of chiral asymmetry in achiral smectic C phase optically active dopant systems—helix handedness and tilt direction handedness. For example, the same helix handedness and the opposite signs of the tilt direction handedness were observed for compounds 4 and 5 (see table 1), although the C*-atoms of these materials have identical absolute spatial configurations, the same parity and electronic environments of the asymmetric centre. On the other hand, the retention of the tilt direction handedness and the reversal of the helix handedness always occur on C*–Cl → C*–CN substitution followed by conversion of the C*-atom absolute configuration (see table 1, compounds 7, 9, 11, 13, 15, 17, 19 and 8, 10, 12, 14, 16, 18, 20, respectively).

Table 2 lists the asymmetry parameters of ferroelectric liquid crystals induced by optically active dopants containing a single terminal substituent with an asymmetric carbon atom. Comparison of the data for mono and di equivalently substituted compounds reveals a coincidence of twist sense and handedness of the tilt direction for induced ferroelectric systems, irrespective of the number of terminal chains with an asymmetric carbon atom. It should be noted that the asymmetry parameters of

Table 2. Asymmetry parameters of ferroelectric liquid crystals induced by optically active dopants with one chiral tail.
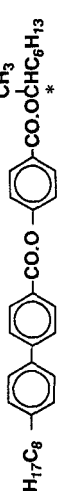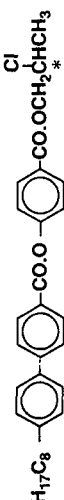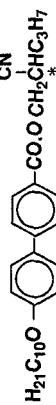
Compound	Absolute configuration	Odd or even	Helix	J-effect	Tilt handedness	Sign of P_s	Tilt indices	P_s-indices
$H_{17}C_8$—◯—◯—CO.O—◯—CO.OCHC$_6$H$_{13}$ (CH$_3$, *)	S	o	LH	+	Right	+	SDr	SD+
$H_{17}C_8$—◯—◯—CO.O—◯—CO.OCH$_2$CHCH$_2$CH(CH$_2$)$_3$ (Cl, *)	R	e	LH	−	Left	−	RDl	RD−
$H_{17}C_8$—◯—◯—CO.O—◯—CO.OCH$_2$CHCH$_3$ (Cl, *)	S	e	RH	−	Right	+	SLr	SL+
$H_{17}C_8$—◯—◯—◯—CO.OCH$_2$CHCH$_3$ (CN, *)	R	e	RH	−	Right	+	RLr	RL+
$H_{17}C_8$—◯—◯—◯—CO.OCH$_2$CHC$_2$H$_5$ (CH$_3$, *)	S	e	RH	+	Left	−	SLl	SL−
$H_{17}C_8$—◯—◯—◯—CO.OCH—◯ (CH$_3$, *)	S	o	LH	+	Right	+	SDr	SD+
$H_{21}C_{10}O$—◯—◯—CO.OCH$_2$CHC$_3$H$_7$ (CN, *)	R	e	RH	−	Right	+	RDr	RD+

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Table 3. Eight combinations of the absolute spatial configuration of the chiral centre, the helical handedness and the tilt handedness (or the sign of the spontaneous polarization)

Absolute configuration

	R Twist sense					S Twist sense		
	Right-handed helix (ccw) – L		Left-handed helix (cw) – D		Right-handed helix (ccw) – L		Left-handed helix (cw) – D	
	Tilt handedness		Tilt handedness		Tilt handedness		Tilt handedness	
	Right P_s +	Left P_s –	Right P_s +	Left P_s –	Right P_s +	Left P_s –	Right P_s +	Left P_s –
	RLr	RLl	RDr	RDl	SLr	SLl	SDr	SDl
	RL+	RL–	RD+	RD–	SL+	SL–	SD+	SD–

induced ferroelectric are independent of the rigid core structure of dopant molecules, provided that the latter do not contain a strong withdrawing substituent or a bulky substituent in the o-position to the chiral tail.

Thus, considering only the molecular structure (particularly, a new one) it is impossible to predict the combination of ferroelectric liquid crystal indices and the sign of the electrooptic effect. Nevertheless, the indexing of ferroelectric and dopant is necessary, especially in the design of multi-component mixtures. Thus combination of ferroelectrics or dopant having opposite twist sense for the helix results in a mixture with elongated or infinite pitch. For mixtures containing two optically active components with opposite handedness of tilt direction, the value of the spontaneous polarization is cancelled. The latter circumstance makes the method of asymmetry indexation of ferroelectrics by the sign of P_s quite reasonable. Exactly in the same ferroelectric experiments the sign of P_s is proposed to be positive or negative depending upon the sign of the applied field that caused a definite (according to [11] right) tilt direction of **n** with respect to z (see table 3). Such indexing is convenient for determining whether the P_s values of various components are added or cancelled (because the long molecular axes of all components are aligned in the same direction).

When using the sign indexing of P_s (absolutely equivalent to the indexing by the tilt direction), misunderstanding due to the different approaches to the definition of the P_s sign, i.e. by the sign of the transverse projection of the total dipole moment (typical of chemists) or by the sign of the electric induction vector coinciding with the sign of the electric field (typical of physicists) [6, 11], should be eliminated by achieving some conventional agreement.

Our failure to predict what set of indices for ferroelectric liquid crystals (individual chiral smectic C, induced by an optically active dopant or multicomponent ferro-electric mixture) we should expect, is most probably due to the lack of our present knowledge of the mechanism of chiral molecular ordering in a chiral smectic C phase. We suppose that future investigations of a wide range of ferroelectric liquid crystals with a wide range of optically active tails will throw light on this problem.

2. Experimental section
2.1. *Synthesis and classification of materials*
Optically active diesters of *p*-terphenyl-4,4″-dicarboxylic acid have been prepared by acylation of the corresponding optically active alcohols with *p*-terphenyl-4,4″-dicarboxylic acid chloride in anhydrous pyridine. The absolute configurations of compounds 1–20 (see table 1) were predetermined by known absolute configurations of the starting alcohols. (*S′*)-2-methylbutane-1-ol, (*R*)- and (*S*)-octane-2-ols are commercially available products with about 99 per cent optical purity; α-phenyl-ethyl- and α-benzylethyl alcohols have been prepared by division of racemic mixtures into optical isomers, $\alpha_D^{20} = -43.5°$ (neat) and $\alpha_D^{20} = +27.3°$ (neat), respectively. 2-chlorosubstituted alchols were synthesized according to [14] by diazotization of L- or D-α-aminoacids with the following reduction of prepared *S*- or *R*-2-chlorosub-stituted acids with $LiAlH_4$ in absolute ether. No inversion of a chiral centre can occur in these reaction pathways. (*S*)-2-chloropropanol-1, $\alpha_D^{20} = +19.85°$ (neat); (*S*)-2-chlorobutanol-1, $\alpha_D^{20} = -32.48°$ (neat); (*S*)-2-chloro-3-methylbutanol-1, $\alpha_D^{20} = +3.86°$ (neat); (*R*)-2-chloro-4-methylpentanol-1, $\alpha_D^{20} = +44.48°$ (neat); (*S*)-2-chlorohexanol-1, $\alpha_D^{20} = -35.56°$ (neat) were prepared starting from L-alanine, L-2-aminobutyric acid, L-norvaline, L-valine, D-leucine, L-isoleucine and 4-norleucine.

Optically active 2-cyanosubstituted alcohols were obtained from the corresponding 2-chlorosubstituted alcohols by interaction of the latter with KCN in DMF: (*R*)-2-cyanopropanol-1, $\alpha_D^{20} = -1.43°$ (neat); (*R*)-2-cyanobutanol-1, $\alpha_D^{20} = +5.08°$ (neat); (*R*)-2-cyanopentanol-1, $\alpha_D^{20} = +10.3°$ (neat); (*R*)-2-cyano-3-methylbutanol-1, $\alpha_D^{20} = -1.29°$ (neat); (*S*)-2-cyano-4-methylpentanol-1, $\alpha_D^{20} = -11.52°$ (neat); (2*R*, 3*S*)-2-cyano-3-methylpentanol-1, $\alpha_D^{20} = -10.79°$ (neat); (*R*)-2-cyano-hexanol-1, $\alpha_D^{20} = -10.79°$ (neat); (*R*)-2-cyano-hexanol-1, $\alpha_D^{20} = +2.67°$ (neat).

2.2. *Determination of the tilt direction handedness (P_s sign)*

Tilt direction handedness was determined from the electrooptic response (see figure). The temperature dependence of θ and P_s were measured simultaneously in the same cells by two methods: the polarization-reversal method [15] according to [16] and the pyroelectric method [17]. These methods allow us to achieve high accuracy in the measurement of $P_s(T)$ over the whole temperature range of the S_C^* phase, since the pyroelectric method provides a high accuracy near T_c, while the polarization-reversal technique is accurate far from T_c. High P_s values (at the level of DOBAMBC and higher) were found for a 5 per cent solution of the optically active dopants (compounds 1–20, table 1) in an achiral smectic C phase such as 4-*n*-hexyloxyphenyl-4'-*n*-octyloxybenzoate and 5-*n*-octyl-2-(4'-*n*-octyloxyphenyl)-pyridine. Within the temperature range of the induced S_C^* phase the reversal of the tilt direction handedness was not observed.

2.3. *Determination of the sign of the optical rotation of the optically active dopant*

The sign of the optical rotation of compounds 1–20 was determined by the modified Kano–Grandjean method [18] for a 1 per cent solution of the dopant in a nematic phase (of E7 type). We did not succeed in determining the sign of the optical rotation in an achiral S_C matrix for each of the compounds 1–20. However, the introduction of two compounds (out of 1–20) with the opposite helix handedness determined in a nematic phase leads to a complete or partial compensation of the helix. Thus, there can be two possibilities: either the helix has the same handedness both in S_C and nematic phases or on passing from the nematic to the smectic C phase the helix reverses its sign. Anyhow, we believe the latter circumstance does not touch upon the essence of the problem discussed.

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