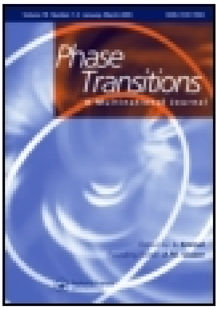

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Unique chiral compounds as part of mixtures with optimized properties for different types of FLCDs

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Unique chiral compounds as part of mixtures with optimized properties for different types of FLCDs†

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The effect of the molecular structure of liquid crystals on their mesomorphic and physico-chemical properties is studied. The unique compounds described in this work contain three or four phenyl rings. Modifications of the molecules via bridge fragments or via lateral substituents allowed the preparation and optimization of specific mixtures for different purposes. The formation of defect-free layers in ferroelectric liquid crystals (FLCs) stable against various mechanical or temperature deformations is studied. The impact of viscous-elastic and chiral properties on the formation of smectic C* layers were established. A new electro-optic effect based on chiral-nematic mixtures for creating high-speed devices with switching time less than 1 ms was developed. All the boundary conditions necessary for the realization of this effect were experimentally investigated.

Keywords: chiral compounds; helical pitch; V-shaped switching; shock-free; fast-switching chiral-nematic

1. Introduction

The ability to use liquid crystal materials for display applications lead to increased scientific and technological interest aiming to develop new materials for low-viscous liquid crystal (LC) mixtures allowing new high-speed effects with short switching time for stable and high-contrast images. In order to introduce such new materials and effects, a purposeful improvement of physico-chemical and electro-optical properties of LC materials based on the quantitative relationships between micro- and macroscopic characteristics is needed. Based on the study of intermolecular interactions and the influence of external parameters, new high-speed effects leading to stable orientation of the layers was developed. LC mixtures with optimal parameters and design based on these new high-speed effects lead to promising and advanced display applications.

A modern liquid crystal material is a specially selected multi-component mixture consisting of compounds of different chemical classes. The selection of the components of the mixture is important for the creation and optimization of some physico-chemical parameters such as phase transition temperature, viscosity, dielectric and optical

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anisotropy, etc., which determine the electro-optical characteristics of liquid crystal displays (LCDs) [1–9]. At present, the establishment of LCDs with high-performance is limited because of the low speed re-orientation of the nematic liquid crystal materials under the influence of the electric field (reorientation time is not less than 7 ms). Yet, for fast switchable ferroelectric liquid crystals (FLCs), the lack of a stable orientation is limiting. In comparison, FLC materials for LCD application allow a switching time of less than 300 μs, but the orientation can break under mechanical deformation [7,8].

A comprehensive study of the physico-chemical and electro-optical properties of chiral- nematic and of FLCs, especially the study of the intermolecular interactions in the mesophase and the interaction with alignment materials, the consideration of optical properties of the chiral-nematic media with different helical twisting power and viscous-elastic properties, have been strongly considered in our work.

A series of new chiral compounds have been synthesized [9–12]. The relevant relationships between the mesomorphic properties, the physico-chemical properties and the molecular structure of ferroelectric liquid crystalline compounds containing three or four phenyl rings with different lateral substituents and with bridge fragments between the phenyl rings has been investigated. This allowed creating LC compositions with a broad temperature range usable for different well-known effects.

Recently, a new approach for the creation of defect-free FLC materials has been reported [13–16]. This approach originated on the evaluation of the boundary conditions between the viscous-elastic properties of non-chiral and chiral dopant at certain anchoring energy of alignment materials. A model for the formation of highly ordered layers has been reported [13–16].

The electro-optic effect based on the chiral-nematic mixtures for creating high-speed devices with a switching time of less than 1 ms was developed. All the boundary conditions necessary for the realization of this effect were experimental investigated.

2. Experimental

The phase transition temperatures of the single compounds and mixtures were determined using the optical polarizing microscope MEIJI ML9400 connected with the heating stage LINKAM TNMS 600. The heating/cooling rate was 1.0 K min^{-1}.

Solution of the alignment materials with low pretilt angle were spin coated on a glass substrate with indium–tin oxide (ITO) layer (resistance is about 10–20 Ω cm^{-2}) at 3000 rpm and then baked at 200°C for 1 h. Aligning layers were unidirectional rubbed under a velvet-covered cylinder. Planar cells with an effective area of 1 cm^2 have been fabricated. The thickness of the cells was about 2–5 μm, measured in each case interferometrically. The quality of alignment was controlled using polarizing microscopy.

The helical pitch (p) was determined via light transmission measurements with the help of a spectrometer in the range of 300–900 nm. Using the formula $p = \lambda_{\max}/n$, the pitch was calculated, where $\lambda_{\max}$ is the wavelength at the maximum of the selective reflection and n is the average refractive index. For such materials, the average refractive index is about 1.5.

Spontaneous polarization (P_s) was measured using the reversal current method [17] with a triangular wave at 10 Hz obtained from function generator HP 34401A. The amplitude of the applied voltage was 20 V$_{pp}$.

The tilt angle was estimated from the measurements of light transmission through the cells in crossed polarizer under applied electric field. The transmission was fitted as a function of the cell orientation to the sinusoidal curve; the doubled molecular tilt angle was derived.

The electro-optical properties of the test cells were measured between crossed polarizer using a He–Ne laser. The light transmittance was detected by a photomultiplier and recorded by the digital oscilloscope HP 500 MHz Infinium. A control signal of desired voltage was obtained from the function generator HP 34401A. The rise and decay times were defined as the transmittance changes from 10% to 90% and vice versa. The temperature of the cells during the electro-optic measurements was with an accuracy of 0.3 K.

3. Results and discussion

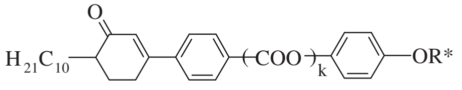
3.1. *Mesomorphic properties of chiral compounds*

The optically active LC derivatives of biphenyl and terphenyl compounds are widely used as components for creating ferroelectric and antiferroelectric LC mixtures [1,3,6,18,19]. However, unfortunately, many of such compounds do not form a mesophase, therefore it is impossible to develop ferroelectric LC mixtures with a wide SmC*-phase range. The goal of our investigation over the last 10 years was to develop and synthesize LC derivatives of aryl esters with three or four phenyl rings and of quaterphenyls with different lateral substituents leading to a broad temperature range of the SmC*-phase and importantly to low melting points. Those compounds can be used for the preparation of FLC mixtures for different types of LCDs.

To demonstrate the development of different kinds of LC materials for practical application on the base of only few compounds we selected twelve of the synthesized and examined compounds (see Tables 1 and 2). A low temperature melting point and the presence of the SmC*-phase characterizes these compound. Such compounds in a larger amount can added to non-chiral matrixes because of the good solubility and miscibility with other chemical classes.

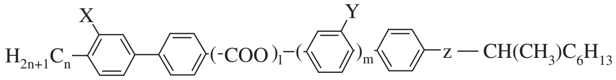
The most promising quaterphenyl compounds for wider temperature range of the SmC*-phase are those with 6 and up to 10 carbon atoms in the alkyl chain, further oxygen group close to the chiral centre, and Cl atom or CH_3-group in the third position of the third benzene ring. Introduction of the carboxylate COO-group before the chiral center and change of the position of lateral substitutes lead to a strong increase of the melting point or the absence of the SmC*-phase. Therefore the solubility of these compounds in other classes of liquid crystals degrades. The most promising chiral aryl esters for wider

Table 1. Phase transition temperatures of chiral aryl esters (**1**)



			Transition temperatures (°C)						
No.	K	R*	Cr		SmC*		SmA*		I
1a	1	$CH(CH_3)COOCH_3$	●	44	●	69	●	120	●
1b	1	$CH(CH_3)C_6H_{13}$	●	57	●	120	●	122	●
1c	0	$CH(CH_3)C_6H_{13}$	●	64	●	78	●	134	●

Table 2. Phase transition temperatures of chiral compounds (**2**)



							Transition temperatures (°C)						
No.	*n*	X	l	m	Y	Z	Cr		SmC*		SmA*		I
2a	10	Cl	1	0	–	O	●	40	●	47	●	85	●
2b	10	Cl	1	0	–	OCH_2	●	42	●	43	●	88	●
2c	5	CH_3	1	0	–	OCH_2	●	27	●	66	●	88	●
2d	10	CH_3	1	1	H	COO	●	44	●	107	●	140	●
2e	10	Cl	1	1	H	COO	●	52	●	138	●	156	●
2f	8	H	0	1	Cl	O	●	29	●	99	●	140	●
2g	10	H	0	1	Cl	O	●	39	●	129	●	146	●
2h	10	H	0	1	CH_3	O	●	47	●	119	●	145	●

Table 3. Spontaneous polarization (P_s), tilt angle and pitch (p) of compounds presented in Table 1 and Table 2 at +25°C.

No	P_s (nC cm^{-2})	Tilt angle (°)	P (μm)
1a	60	33	0.84
1b	48	31	>1.0
1c	42	30	>1.0
2a	80	32	0.42
2b	112	39	0.28
2c	92	32	0.34
2d	140	36	0.27
2e	165	44	0.22
2f	47	29	>1.0
2g	52	33	>1.0
2h	50	29	>1.0

temperature range of the SmC*-phase are those with 10 carbon atom in the alkyl chain, further COO- or OCH_2-group close to the chiral centre, and Cl atom or CH_3-group in the second position of the first benzene ring.

The main physical parameters (see Table 3) have shown that such compounds are promising components for the preparation of FLC mixtures with needed value of P_s, switching angle and helical pitch.

3.2. *FLC mixtures for different types of displays*

For the development of LC mixtures down to low temperature, the chiral dopants were added to a non-chiral matrix. In this case, the key physical parameters are difficult to calculate because of the strong differences in the structures of the chiral and non-chiral molecules, apart from the unpredictable influences of components on each other. On one hand the chiral compounds were characterized by the presence of the SmC*-phase at high temperatures and on the other hand by a low melting point without a SmC*-phase. As an important step the chiral compounds **1a**–**1c**, **2a**–**2h** (Tables 1 and 2) allowed us to

Table 4. Mixing ratio of some LC mixtures.

Mixture No	V-1 wt%	SP-1 wt%	SP-2 wt%	SP-3 wt%	SF-1 wt%	SF-2 wt%	SF-3 wt%
1a	20	–	–	–	–	–	–
1b	42	–	–	–	–	–	–
2a	38	18	–	32	–		–
2b	–	28	22	–	–	–	–
2c	–	–	–	30	30	–	–
2d	–	–	26	–	–	30	–
2e	–	54	52	38	–	–	–
2h	–	–	–	–	–	–	30
BM-1	–	–	–	–	70	70	70

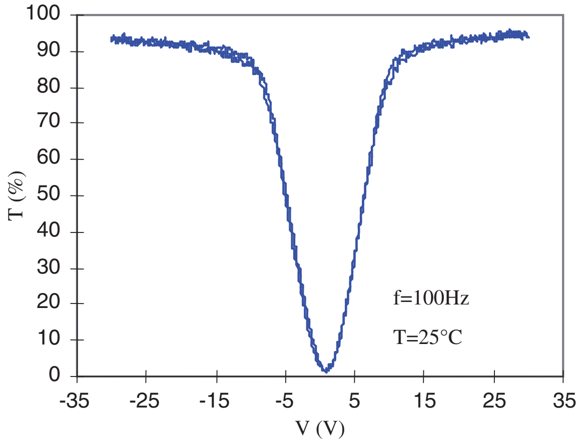


Figure 1. Electro-optical response of mixture V-1.

develop ferroelectric LC mixtures based on only two up to four components of a single homologous series, different only in the lateral substituent or the alkyl chain.

For chiral aryl esters hysteresis free transmission-voltage curves and V-shaped or thresholdless switching at different temperatures and at different frequencies are observable [11]. In order to optimize mixtures for this purpose we selected compounds **1a**–**1c**, **2a**–**2e**. As a result, the mixture (V-1) was prepared (see Table 4) and developed. The V-shaped switching in the temperature range +10°C to +60°C at a fixed frequency of 100 Hz (see Figure 1) was been described. The presented results envisage that not only antiferroelectric [20–23], but also ferroelectric LCs can form hysteresis free transmission-voltage curves at wide operating temperature range.

Considering three and four ring esters (**2a**–**e**) with various values of spontaneous polarization, high tilt angle and low helical pitch, we could develop FLC mixtures for the deformed helical ferroelectric (DHF) mode [11]. The data in Table 5 showed mixing of three of such chiral compounds in different percentages leading to short-pitch DHF-FLC mixtures (**SP-1**, **SP-2**, and **SP-3**) (see Tables 4 and 5) with a broad temperature range of the SmC* phase 0°C to +100°C and different physical properties.

The spontaneous polarization P_s is in the range of 50 and 120 $\mathrm{nC\,cm^{-2}}$, the tilt angle 35° to 43° and the helical pitch 0.2 to 0.7 µm. This example showed using only 2 or 3 of such components the main material parameters for specific tasks can be easily adjusted.

Table 5. Physical parameters of some FLC mixtures at +25°C.

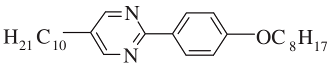
Mixtures	SmC* range (°C)	P_s (nC cm^{-2})	Tilt angle(°)	p (μm)
SP-1	+10–+100	120	43	0.28
SP-2	+10–+105	127	39	0.24
SP-3	0–+74	92	35	0.38

For the compensation of the helical pitch we used sometimes compounds with a different sign of the optical rotation but with the same sign of P_s. The dependence of the helical pitch on the temperature for such mixtures is weak. These results reveal that the parameters of the mixtures strongly depend on the chemical structures and the amount of their components. The chiral aryl esters with COO- or OCH_2-group close to the chiral centre and Cl atom or CH_3-group at second position of first benzene ring are favorable for the preparation of FLC mixtures for such practical application.

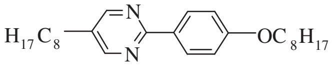
3.3. *Viscous chiral quaterphenyls for fast-switching LCDs*

Based on previous results, we assumed that the viscous flexural rigid rod-like chiral molecules with a defined length, a large helical pitch, low melting point and a broad temperature range of the SmC* phase could play a key role in the formation of defect-free SmC* layers and elimination of the ‘‘back-flow’’ effect in nematic liquid crystals.

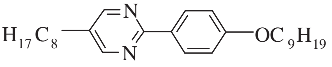
Previously, we established the optimal concentration of the chiral additive (30%) in the substituted phenylpyrimidine matrix in order to maintain stability against mechanical deformations [14]. The stability of smectic layers against mechanical deformation for the same base mixture (**BM-1**) [14] with chiral additives of various lengths lead to mixtures **SF-1**, **SF-2**, **SF-3** (see Table 4) in cells with different thicknesses of alignment layers were investigated. The mixture **BM-1** is with the following compounds and their percentage:



- 43.3%



- 23.4%



- 33.3%

Cr -7°C SmC 57.8°C SmA 67.2°C N 68.1 I

Figure 2 shows the recovery of the contrast, if the thickness of alignment layer is about 45–65 nm, hence there is no irreversible destruction of the smectic layers. The best results was achieved for the mixtures based on long and viscous additive without bridge fragments (**2h**); in contrast the worst result was for a short additive (**2c**) and an additive with a bridge fragment (**2d**).

Based on these results, we can assume that the resistance against deformation depends on the viscosity and the length of chiral molecules, as well as the anchoring energy between the LC molecules and the substrate. To explain this extraordinary behavior the following aspect should taken into consideration in a very basic and qualitative approximation, and

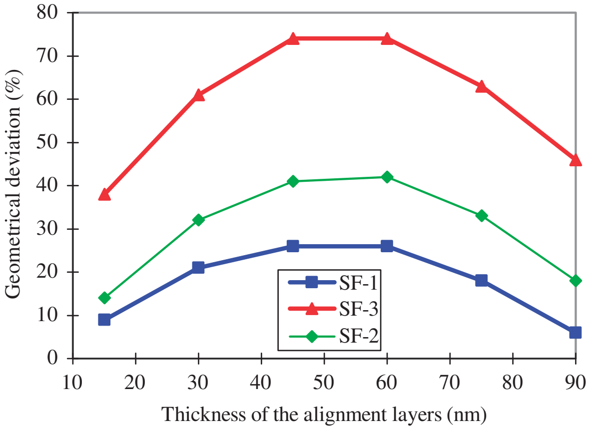


Figure 2. Dependence of the maximum of the defect-free deformation for mixtures SF-1, SF-2, and SF-3 on the alignment layer thickness.

Table 6. Electrooptical parameters of our chiral-nematic mixtures at +25°C.

Mixtures	V_{10} (V)	V_{90} (V)	τ_{on} (ms)	τ_{off} (ms)
LB-1	1.6	2.1	0.5	1.1
LB-2	2.1	2.3	0.3	1.0
LB-3	1.8	2.0	0.2	0.7

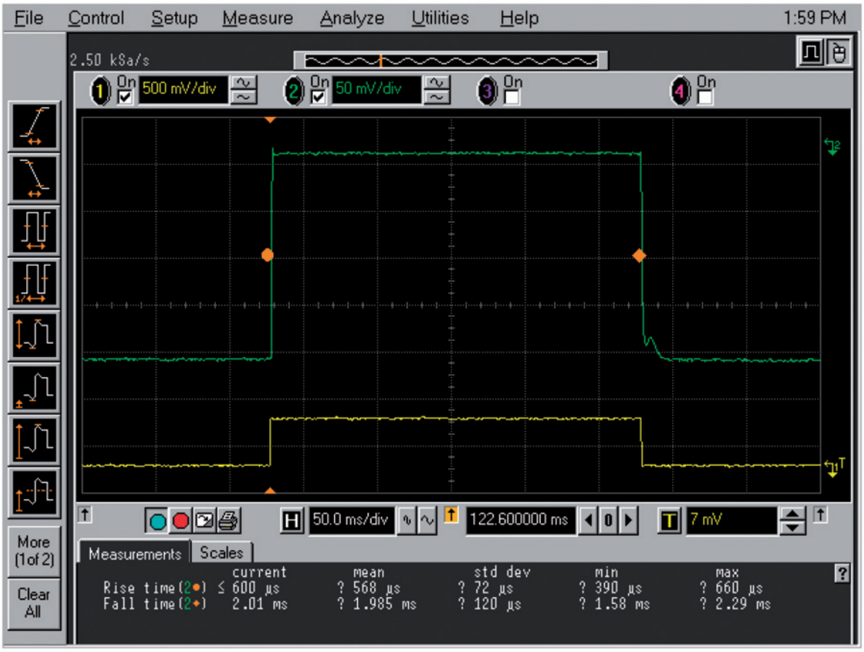
Table 7. Electrooptical parameters of some Merck-mixtures without and with our chiral dopants at +25°C.

Mixtures	V_{10} (V)	V_{90} (V)	τ_{on} (ms)	τ_{off} (ms)
M-1	1.8	2.7	3.1	13.6
LM-1	2.2	2.5	0.5	0.6
M-2	2.1	3.0	5.8	19.7
LM-2	2.7	3.1	0.9	1.3

hence we assume that under mechanical stress more viscous and longer chiral molecules fix the smectic layers, preventing them from breakage.

Further, we assume that the chiral molecules of formula (**2**) (Table 2) can solve the back-flow problem in the middle part of cells containing chiral nematic mixtures because of the reduced switching off time; the time delay in switching off will be equal to zero. The chiral nematic mixtures were prepared by mixing compounds of formula (**2**) (Table 2) with different nematic LC compounds or with well-known Merck-mixtures.

Data for the switching time presented in Tables 6 and 7 confirm our approaches. After optimization of the pretilt angle of the alignment materials, the helical twisting power, the viscosity of chiral compounds and twist angle Ψ, we achieved the desired result for our mixtures (**LB-1**, **LB-2**, **LB-3**) and for Merck-mixtures with our chiral dopant (**LM-1**, **LM-2**). **M-1** and **M-2** are MLC-6657-100 and ZLI-3201-100, respectively.



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                 current       mean         std dev      min          max
Rise time(2●) ≤ 600 µs      ? 568 µs     ? 72 µs      ? 390 µs     ? 660 µs
Fall time(2◆)   2.01 ms     ? 1.985 ms   ? 120 µs     ? 1.58 ms    ? 2.29 ms
```

Figure 3. Example of the switching time curve for a chiral-nematic mixture.

Figure 4. Example of fast-switching chiral-nematic display.

Figure 3 shows, after switching the electric field on and then off, that the molecules in the mid-layer region start to move back to the original state without back-flow, while the time delay is zero.

Figure 4 shows as example a small display with response time (on + off) less than 1.0 ms after optimization of all boundary conditions.

4. Conclusions

The uniqueness of the presented classes of liquid crystal compounds stems from the fact that they mix well with each other. While mixing only three or up to five of such compounds one can develop diverse ferroelectric liquid crystal compositions with any specified parameters. Mixtures developed on the basis of such compounds are characterized by weak temperature dependence of the key parameters and as a consequence of this by a broad interval of the operating temperature. Furthermore, for such FLC mixtures, in principle, there is no need for an often used non-chiral matrix. Due to this the optimization of parameters such as spontaneous polarization, switching angle and helical pitch became much more easier.

Based on the analysis of the experimental data a model of the formation of highly ordered smectic layers was suggested. On the basis of the presented experimental data we could establish a picture of the reorientation of molecules inside the cell, depending on the nature of chiral molecules and their helical twisting power, their anchoring energy and the pretilt angle of the alignment materials. It should be noted that the response time for our effect does not depend very strongly on the cell gap in contradiction to well-known modes.

Acknowledgements

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