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V-Shaped SmC* switching FLC compounds

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V-SHAPED SmC* SWITCHING FLC COMPOUNDS

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Continuing our interest in the ferroelectric liquid crystalline materials for display applications we have synthesized new chiral aryl esters of 4-(6-alkylcyclohex-2-enonoyl-3)benzoic acids and 3,6-diarylcyclohex-2-enones, investigated their mesomorphic properties, physical and electro-optical properties of the FLC compositions on their base.

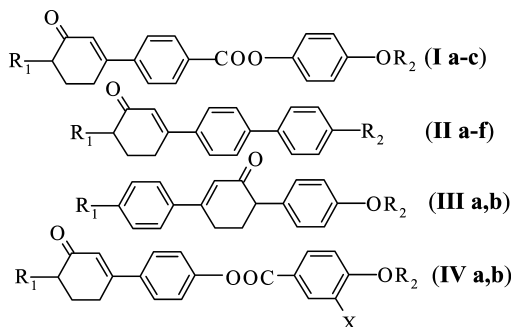
Keywords: 3,6-disubstituted cyclohex-2-enones; ferroelectric liquid crystalline materials

INTRODUCTION

We have shown that chiral aryl esters of 4-alkyl-3-chlorobiphenyl-4-carboxylic acids form smectic C phase at low temperature and over wide temperature ranges [1]. In continuation of these investigations and in an attempt to obtain new promising components of the ferroelectric liquid crystalline materials for display applications we have synthesized chiral aryl esters of 4-(6-alkylcyclohex-2-enonoyl-3) benzoic acids and 3, 6-disubstituted cyclohex-2-enones (**I–IV**), investigated their mesomorphic properties, physical and electro-optical properties of the FLC compositions on their base.

The esters (**Ia–c**, **IVa,b**) were synthesized by the interaction of the corresponding acid with 4-substituted phenols in the presence of dicyclohexylcarbodiimide (DCC) and 4-dimethylaminopyridine as catalyst. 3, 6-Disubstituted cyclohex-2-enones (**IIa–f**, **IIIa,b**) were prepared by Michael condensation of hydrochlorides of 4-substituted 2-dimethylamino-propiofenones with 2-alkylacetoacetic esters or 4-substituted phenylacetones accordingly to our published method [2–4].

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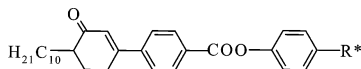
$R_1, R_2 = C_5H_{11}, C_{10}H_{21}, (S)-(-)-CH_2CH(CH_3)C_2H_5, (R)-(-)-CH(CH_3)C_4H_9,$
 $(R)-(-)-CH(CH_3)C_6H_{13}, (R)-(-)-COOCH(CH_3)C_6H_{13}, (S)-(-)-OCH(CH_3)COOCH_3,$
 $(S)-(-)-(CH_2)_2CH(CH_3)(CH_2)_2CH=C(CH_3)_2$

As it can be seen from Tables 1–4 prepared compounds (**I–IV**) are strongly smectogenic compounds forming smectic A and smectic C phases, the latter at low temperature and over wide temperature range. It should be noted that the analogous chloro derivatives either do not form smectic C* phase or so over narrow temperature range [1].

Investigations of the electro-optical properties of compounds (**I–IV**) have shown their main advantages in comparison with well known FLC compounds. The spontaneous polarization of the compounds (**I–IV**) is not high and varies from 20 to 80 nC/cm⁻² dependent upon the chemical structure of the compounds (see Figures 1–4). However, hysteresis free transmission-voltage curves, and V-shaped or thresholdless switching are observed for them and for their FLC mixtures with one another over wide temperature ranges and at different frequencies (see Figures 3 and 6).

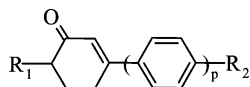
Our additional investigations have shown that V-shaped switching is observed for some the chiral aryl esters of 4-alkyl-3-chlorobiphenyl-4-carboxylic acids [1], which are characterised by a high spontaneous

TABLE 1 Transition Temperatures of the Esters (**Ia–c**)



		Transition temperatures/°C						
N	R*	Cr		SmC*		SmA		I
a	OCH(CH ₃)COOCH ₃	●	44	●	69	●	120	●
b	OCH(CH ₃)C ₆ H ₁₃	●	46	●	61	●	83	●
c	COOCH(CH ₃)C ₆ H ₁₃	●	57	●	121.5	●	122.5	●

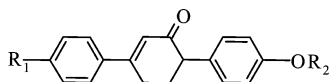
TABLE 2 Transition Temperatures of the Cyclohex-2-enones (**IIa-f**)



N	R ₁	p	R ₂	Transition temperatures/°C						
				Cr	SmC*		SmA		I	
a	H ₂₁ C ₁₀	1	OCH ₂ CH(CH ₃)C ₂ H ₅	●	34	●	(20)	●	70	●
b	H ₂₁ C ₁₀	1	OCH(CH ₃)C ₆ H ₁₃	●		—		—	47	●
c	H ₁₇ C ₈	1	Cit*	●	46	—		●	59.6	●
d	H ₂₁ C ₁₀	2	OCH(CH ₃)C ₄ H ₉	●	49	—		●	146	●
e	H ₂₁ C ₁₀	2	OCH(CH ₃)C ₆ H ₁₃	●	64	●	78	●	134	●
f	Cit*	2	C ₅ H ₁₁	●	<20	●	87	●	155	●

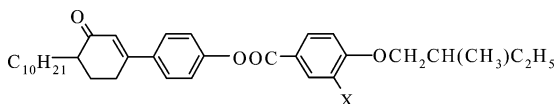
Cit* – (CH₂)₂CH(CH₃)(CH₂)₂CH = C(CH₃)₂

TABLE 3 Transition Temperatures of the Cyclohex-2-enones (**IIIa,b**)



N	R ₁	R ₂	Transition temperatures/°C						
			Cr	SmC*		SmA		I	
a	C ₅ H ₁₁	CH(CH ₃)C ₄ H ₉	●	38	—		●	120	●
b	H ₂₁ C ₁₀	CH(CH ₃)C ₆ H ₁₃	●	37	●	61	●	83	●

TABLE 4 Transition Temperatures of the Esters (**IVa,b**)



Transition temperatures/°C								
N	X	Cr		SmC*		SmA		I
a	H	●	56	●	104	●	176	●
b	F	●	38	●	98	●	171	●

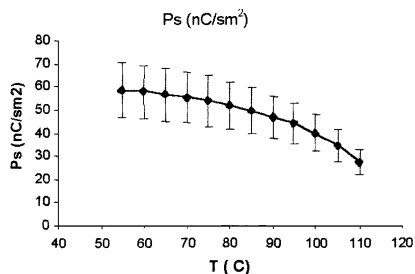


FIGURE 1 Spontaneous polarization of ester (**I c**).

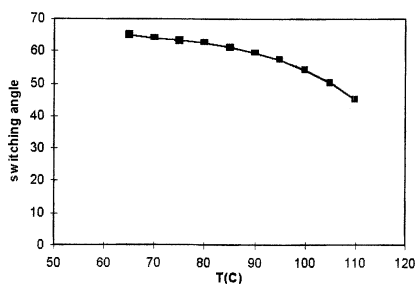


FIGURE 2 Switching angle of ester (**I c**).

polarization (120 nC/cm^{-2}) and a wide switching angle (88°). However, unlike the cyclohex-2-enones derivatives (**I–IV**), these compounds and mixtures based on them, similarly to other FLC compounds [5] form V-shaped and hysteresis free transmission-voltage curves over a wide temperature range, but only at low frequencies of applied electric field. The results presented have shown that not only antiferroelectric, but also ferroelectric LCs

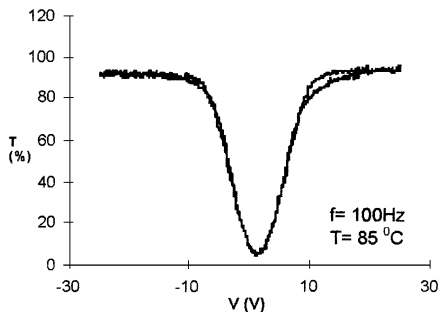


FIGURE 3 Electro-optical response of ester (**I c**).

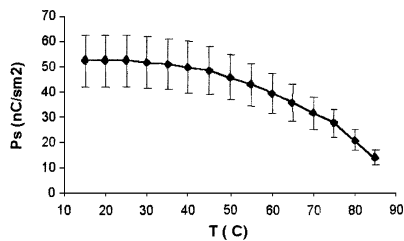


FIGURE 4 Spontaneous polarization of cyclohex-2-enone (**II f**).

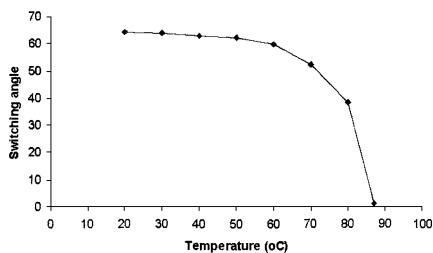


FIGURE 5 Switching angle of cyclohex-2-enone (**II f**).

with low spontaneous polarization can form hysteresis free transmission-voltage curves and give V-shaped or thresholdless switching.

EXPERIMENTAL

The structures of the prepared compounds were confirmed by ^1H -NMR and mass spectroscopy. Phase transition temperatures were measured using a

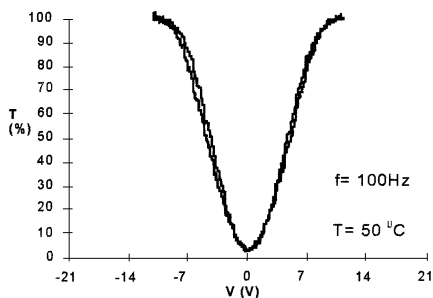


FIGURE 6 Electro-optical response of cyclohex-2-enone(**II f**).

Linkam heating stage having a polarizing PZO microscope and also using a Setaram DSC 92.

Electro-optical studies were performed in the glass cells supplied with ITO electrodes ($\Omega = 150 \text{ Ohm/cm}^2$) and SiO_2 insulating layers 170 nm thick. Aligning layers (nylon 6, 130 nm) were spinned and unidirectionally rubbed. The thickness of the cells was 1.9 mkm and measured in each case interferometrically. During electro-optical measurements the temperature of the cells was controlled with the accuracy 0.3°C and the gradients across the sample did not exceed 1° .

The intermediates, the chiral aryl esters 4-(6-alkylcyclohex-2-enonoyl-3) benzoic acids and 3,6-disubstituted cyclohex-2-enones (**I–IV**) were prepared according to published methods [2–4].

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