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Preliminary communication
New SmC* V-shaped switching FLC compounds

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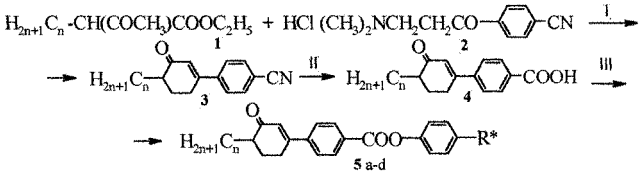
In a previous publication [1] we showed that chiral aryl esters of 4-alkyl-3-chlorobiphenyl-4-carboxylic acids form smectic C phases at low temperatures and over wide temperature ranges. Continuing our interest in ferroelectric liquid crystalline compounds we have synthesized new aryl esters of 4-(6-alkylcyclohex-2-enon-3-yl)benzoic acids and investigated their properties.

Polycyclic carboxylic acids can be synthesized from the corresponding cyano derivatives [2]. Taking this into account, we synthesized 4-(6-alkylcyclohex-2-enon-3-yl)-benzonitriles **3** in yields of 50–70% by Michael condensation of the hydrochloride of 4-(2-*N*,*N*-dimethylaminopropanoyl)benzonitrile **2** with 2-alkylacetoacetic esters **1** [3] and used them for the preparation of the corresponding benzoic acids **4** and the new liquid crystalline chiral esters **5a–d** (see the table).



$n = 10$; R^* = $OCH_2CH(CH_3)OC_2H_5$, $O(CH_2)_3CH(CH_3)C_2H_5$, $COOCH(CH_3)C_6H_{13}$, $OCH(CH_3)COOCH_3$.

I. KOH, dioxan; II. KOH, ethylene glycol; III, HOPh*R**, DCC, DMAP.

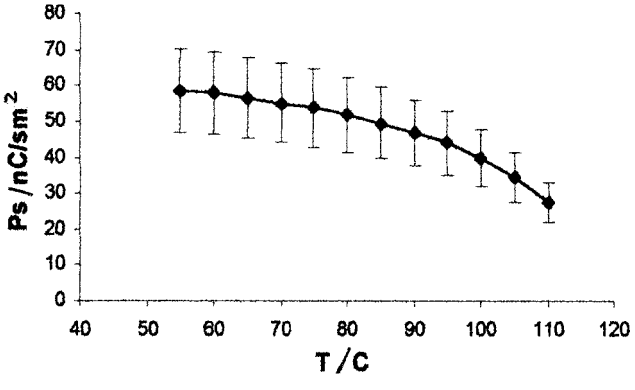


Figure 1. Spontaneous polarization of the ester **5d**.

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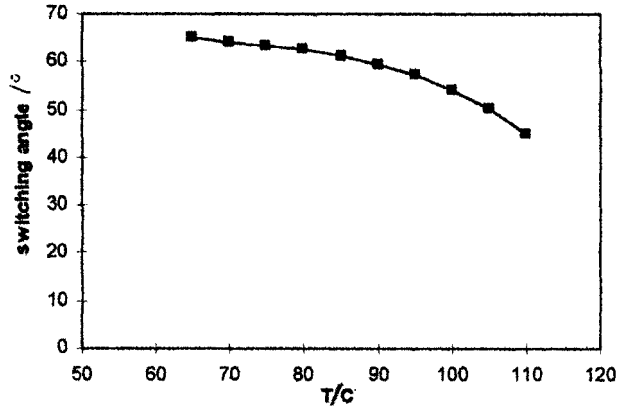

Figure 2. Switching angle of the ester **5d**.

The structures of the prepared compounds were confirmed by ^{1}H NMR and mass spectroscopy. Phase transition temperatures were measured using a Linkam heating stage in conjunction with a PZO polarizing microscope and also using a Setaram DSC 92.

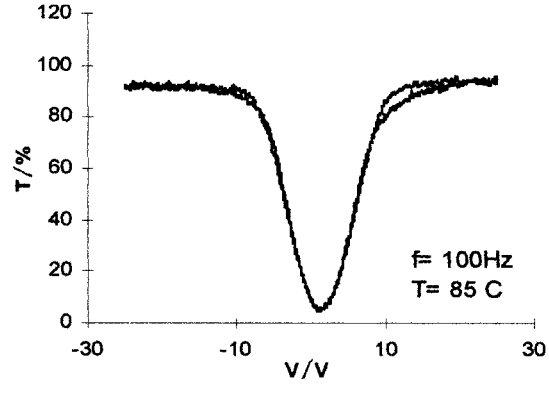

Figure 3. Electro-optic response of the ester **5d**.

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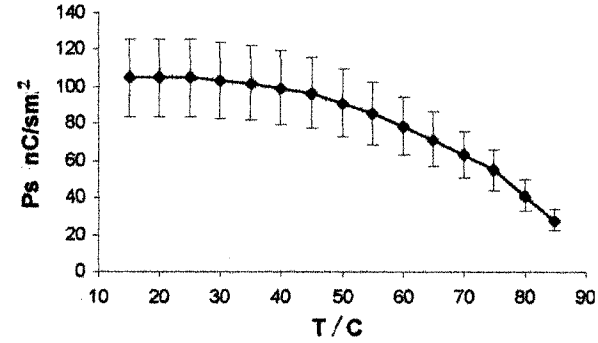
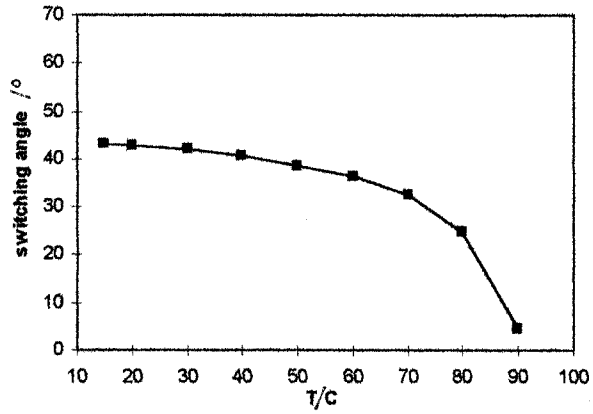
For the synthesis of 4-(6-decylcyclohex-2-enon-3-yl)-benzonitrile **3**, a mixture of (0.30 mol) of the appropriate Mannich salt, 0.31 mol of ethyl 2-decylacetoacetate and 0.91 mol of potassium hydroxide in 350 ml of dioxan was heated under reflux for 5 h with stirring. After cooling the reaction mixture to room temperature, 600 ml of 10% aqueous sulphuric acid were added carefully (evolution of carbon dioxide) and the product was





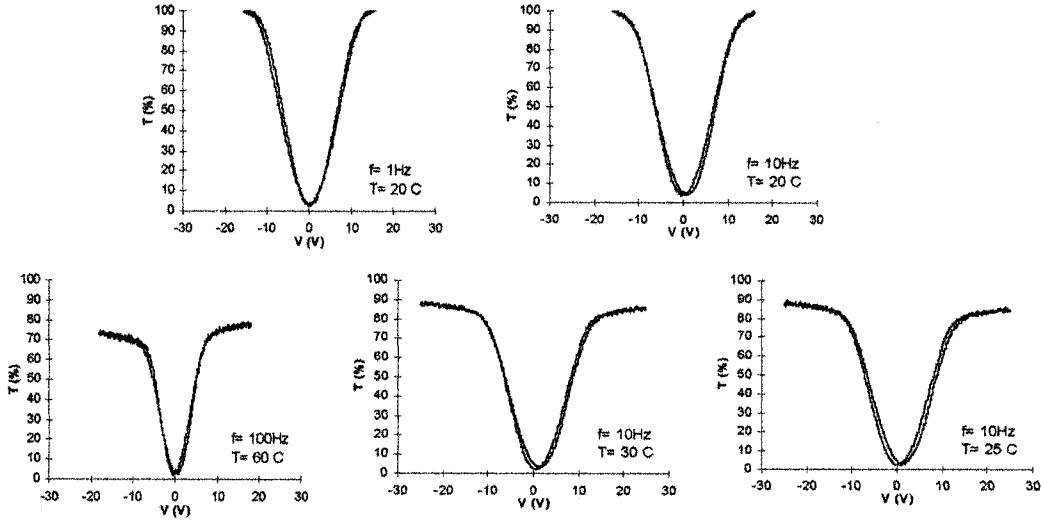


Figure 4. Spontaneous polarization, switching angle and electro-optic responses of an FLC mixture of the esters **5a**, **5b** and **5d**.

Table. Transition temperatures of the esters **5a–d**.

Ester	*R**	Transition temperatures/°C							
		Cr		SmC		SmA		I	
5a	$OCH_2CH(CH_3)OC_2H_5$	•	52	•	98	•	165	•	
5b	$O(CH_2)_3CH(CH_3)C_2H_5$	•	62	•	138	•	190	•	
5c	$OCH(CH_3)COOCH_3$	•	44	•	69	•	120	•	
5d	$COOCH(CH_3)C_6H_{13}$	•	57	•	121.5	•	122.5	•	

extracted into benzene. The organic layer was washed with water, dried over anhydrous magnesium sulphate and filtered through a layer of aluminium oxide. The residue obtained after removing the solvent was crystallized from isopropanol; yield 72%.

For the synthesis of 4-(6-decylcyclohex-2-enon-3-yl)-benzoic acid **4**, a mixture of 0.02 mol of 4-(6-decyl-cyclohex-2-enon-3-yl)benzonitrile **3**, and 0.08 mol of KOH in 100 ml of ethylene glycol was heated under reflux with energetic stirring for 10 h. The reaction mixture, after cooling, was acidified with 10% aqueous hydrocloric acid and the product was filtered off and used, after drying in air, in the next stage; yield 78%.

The esters **5a–d** (see the table) were synthesized by the interaction of the acid **4** with chiral 4-substituted phenols in the presence of dicyclohexylcarbodiimide (DCC) and 4-*N*,*N*-dimethylaminopyridine as catalyst [1].

As can be seen from the table, the esters **5a–d** are strongly smectogenic compounds forming smectic A and smectic C phases, the latter at low temperatures and over wide temperature ranges. It should be noted that the analogous esters of 4-alkyl-3-chlorobiphenyl-4′-carboxylic acids either do not form smectic C* phases or do so over narrow temperature ranges [1].

Investigations of the electro-optical properties of compounds **5a–d** have shown their main advantages in comparison with well known FLC compounds. The spontaneous polarization of the esters **5a–d** is not high and varies from 20 to 80 nC cm^{-2} dependent upon the chemical structures of the compounds (see figures 1 and 2). 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 figure 3 and 4). Detailed investigations have shown that these materials are truly ferroelectric and not antiferroelectric, and this behaviour can be explained by the specific geometry of the ester molecules **5a–d** (see figure 5) and the strong lateral polar interactions of the cyclohex-2-enone fragment with the surface.

Additional investigations have shown that V-shaped switching is observed for some chiral aryl esters of laterally substituted 4-alkylbiphenyl-4′-carboxylic acids, such as chiral aryl esters of 4-alkyl-3-chlorobiphenyl-4′-carboxylic acids (see figure 6) [1]. However, unlike the cylcohex-2-enone derivatives **5a–d**, these compounds and mixtures based on them, similarly to other FLC compounds [4], form V-shaped and hysteresis-free transmission–voltage curves over a wide temperature range, but only at low frequencies of the applied electric field (see figure 7).

The results presented have shown that not only antiferroelectric, but also ferroelectric LCs with low spontaneous polarization can form hysteresis-free transmission/

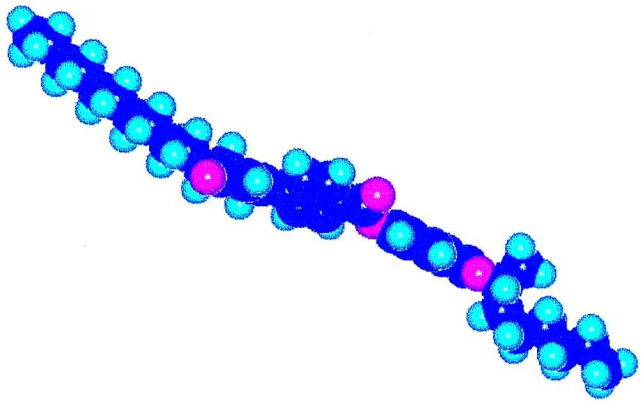


Figure 5. Molecular model of the ester **5d.**

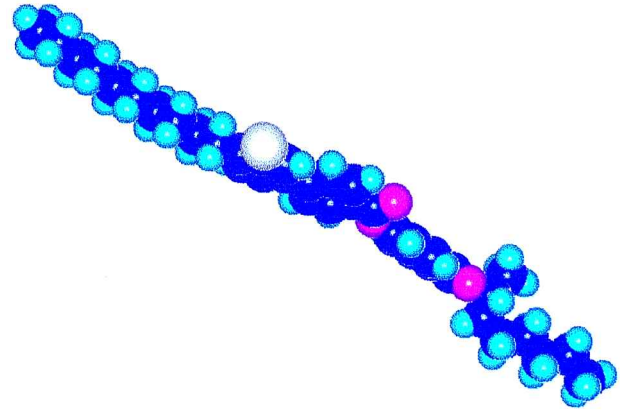


Figure 6. Molecular model of 4-(2-octyloxycarbonyl)-4-phenyl ester of 4-decyl-3-chlorobiphenyl-4′-carboxylic acid [1].

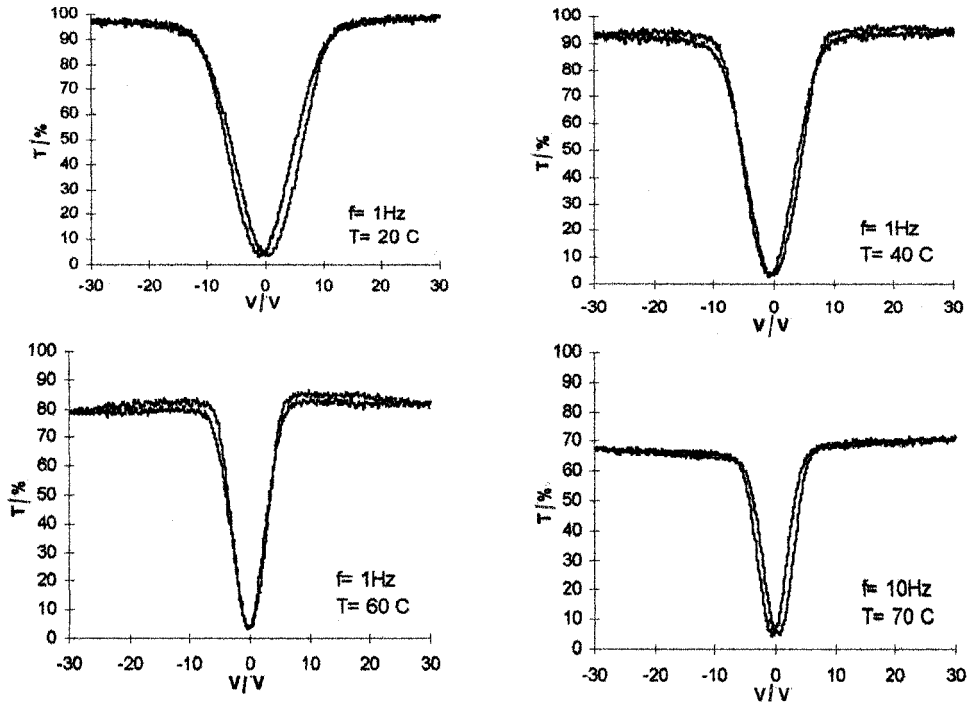


Figure 7. Electro-optic responses of an FLC mixture of 4-(2-octyloxycarbonyl)biphenyl-4′-yl 4-decyl-3-chlorobiphenyl-4′-carboxylate, 4-(2-octyloxycarbonyl)phenyl 4-decyl-3-chlorobiphenyl-4′-carboxylate, and 4-(2-methylbutyloxycarbonyl)phenyl 4-hexyl-3-chlorobiphenyl-4′-carboxylate (ratio 2:2:1).

voltage curves and give V-shaped or thresholdless switching.

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