

V-Shaped SmC* switching FLC compounds

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ABSTRACT

Chiral aryl esters of 4-alkyl-3-chlorobiphenyl-4'-carboxylic and 4-(6-alkylcyclohex-2-enonyl-3)benzoic acids have been synthesized. The phase transition temperatures and V-shaped SmC* switching of the prepared compounds are discussed.

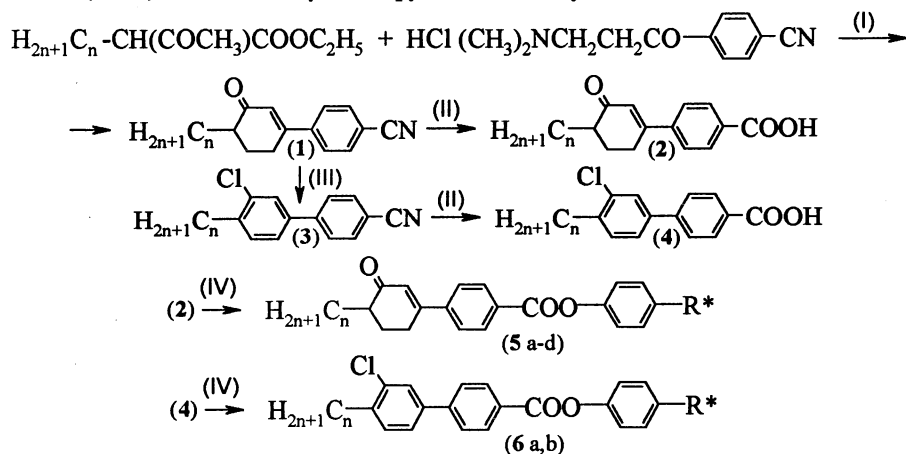
Keywords: liquid crystals, synthesis, biphenyls, phenylcyclohex-2-enones

1. INTRODUCTION

In the previous publication¹ we have shown that chiral aryl esters of 4-alkyl-3-chlorobiphenyl-4-carboxylic acids form smectic C phase at low temperature and in a wide temperature range. 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 the new chiral aryl esters of 4-alkyl-3-chlorobiphenyl-4'-carboxylic and 4-(6-alkylcyclohex-2-enonyl-3)benzoic acids and investigated the mesomorphic, physical and electrooptical properties of the FLC compositions on their base

2. RESULTS AND DISCUSSION

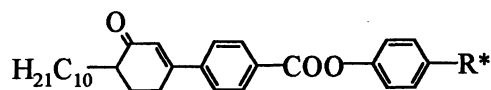
4-Alkyl-3-chlorobiphenyl-4'-carboxylic and 4-(6-alkylcyclohex-2-enonyl-3)benzoic acids (**2**, **4**) were prepared by the hydrolysis of 4-(6-alkylcyclohex-2-enonyl-3)benzoyltriles (**1**) and 4-alkyl-3-chloro-4'-cyanobiphenyls (**3**) in boiling ethylene glycol in the presence of potassium hydroxide. 4-(6-Alkylcyclohex-2-enonyl-3)benzoyltriles (**1**) we synthesized with a yield 50-70 % by Michael condensation of hydrochloride of 4-(2-dimethylaminopropionyl)-benzoyltrile with 2-alkylacetoacetic esters accordingly to our published method^{2,3}. The esters (**5 a-d**) and (**6 a,b**) (tables 1 and 2) were synthesized by the interaction of the acids (**2**) or (**4**) with chiral 4-substituted phenols in the presence of dicyclohexylcarbodiimide (DCC) and 4-dimethylaminopyridine as catalyst.



$n = 8, 10$; $\text{R}^* = \text{OCH}_2\text{CH}(\text{CH}_3)\text{OC}_2\text{H}_5, \text{O}(\text{CH}_2)_3\text{CH}(\text{CH}_3)\text{C}_2\text{H}_5, \text{COOCH}(\text{CH}_3)\text{C}_6\text{H}_{13},$
 $\text{OCH}(\text{CH}_3)\text{COOCH}_3, \text{C}_6\text{H}_4\text{COOCH}(\text{CH}_3)\text{C}_6\text{H}_{13}.$

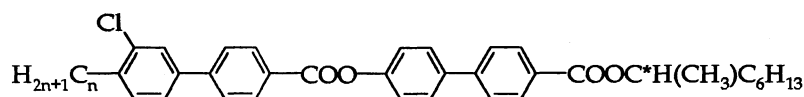
I. KOH, dioxan; II. KOH, ethylene glykol; III. PCl₅, IV HOPhR, DCC, DMAP.*

Table 1. Transition temperatures of the esters (5 a-d)



N	R*	Transition temperatures/ °C						
		Cr	Sm C	Sm A	I			
a	OCH ₂ CH(CH ₃)OC ₂ H ₅	•	52	•	98	•	165	•
b	O(CH ₂) ₃ CH(CH ₃)C ₂ H ₅	•	62	•	138	•	190	•
c	OCH(CH ₃)COOCH ₃	•	44	•	69	•	120	•
d	COOCH(CH ₃)C ₆ H ₁₃	•	57	•	121.5	•	122.5	•

Table 2. Transition temperatures of the esters (6 a,b)



n	Transition temperatures/ °C							
	Cr	Sm A _f	Sm C	Sm A	I			
a 5	• (34)	•	98	•	117	•	184	•
b 10	•	-	72	•	138	•	156	•

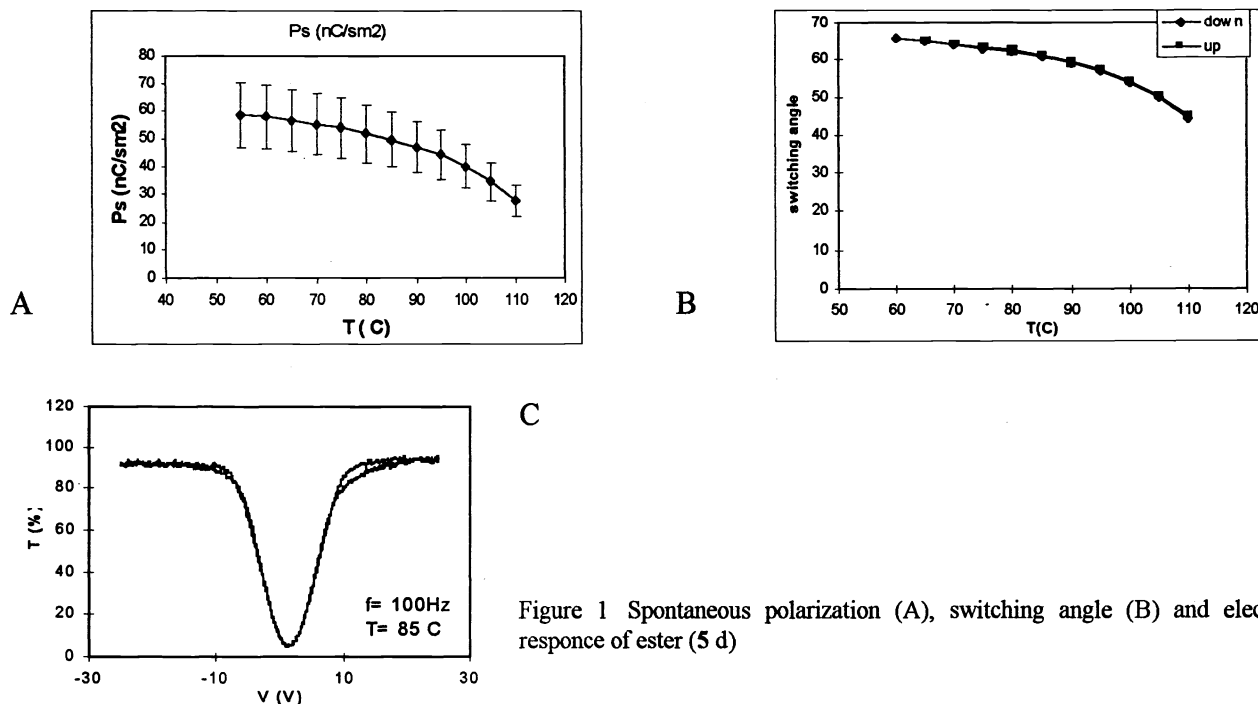


Figure 1 Spontaneous polarization (A), switching angle (B) and electro-optic response of ester (5 d)

As it can be seen from tables 1 and 2 prepared esters (5 a-d; 6 a,b) are strongly smectogenic compounds forming smectic A and smectic C* phases at low temperature and in a wide temperature range.

Our investigations have shown that the spontaneous polarization of the esters (5 a-d) is not high and varied from 20 till 80 nC/cm² in dependence from the chemical structure of the compounds (figures 1A and 1B). Anyway, hysteresis free

transmission voltage curves, V-shaped or thresholdless switching are observed for them and for FLC mixtures on their base in a wide temperature range and at different frequencies (figures 1C and 2). Detail investigations have shown that these materials are really ferroelectric and not antiferroelectric and such behaviour can be explained by specific geometry of the molecules of the esters (5 a-d) (fig 3) and strong lateral polar interactions of cyclohex-2-enone fragment with the surface.

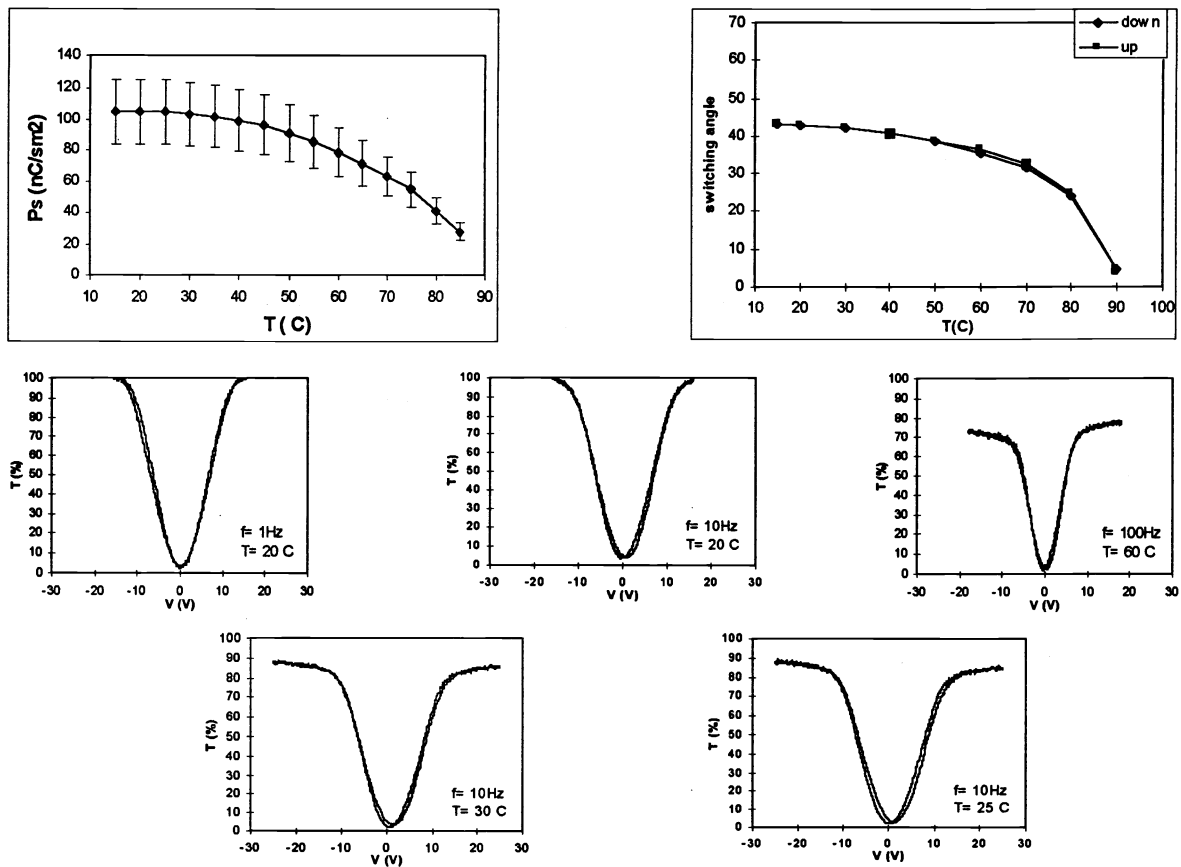


Figure 2 Spontaneous polarization, switching angle and electro-optic response of FLC mixture of esters (5 a, b and d)

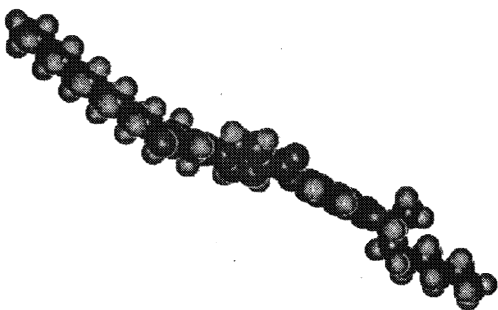


Figure 3 Molecular model of the ester (5d)

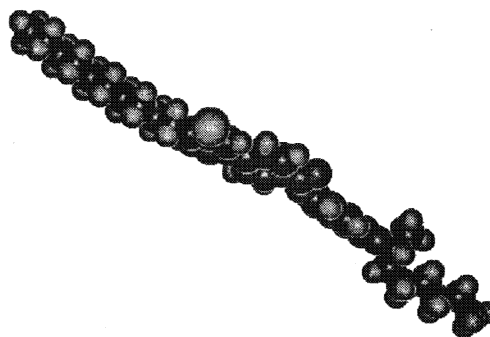


Figure 4 Molecular model of the ester (6a)

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 (6 a,b) (fig 4)¹. But, unlike the cyclohex-2-enones derivatives (5a-d), these compounds and the FLC compositions on their base similar to other FLC compounds⁴ form V-shaped and hysteresis free transmission voltage curves in a wide temperature range, but only at low frequencies of applied electric field (figure 5).

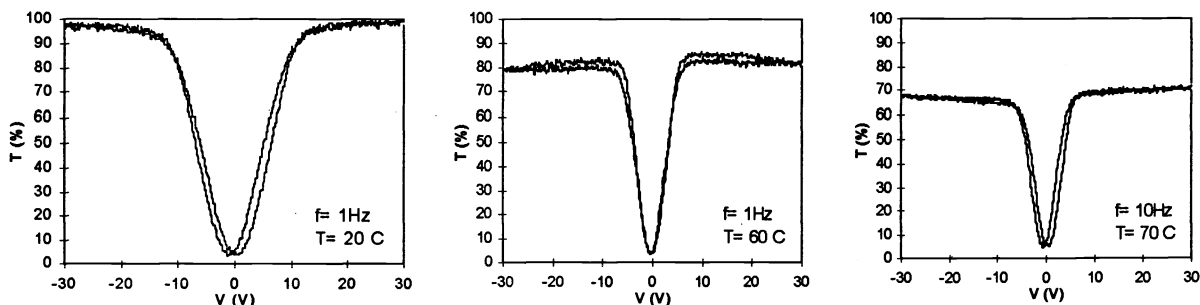


Figure 5 Electro-optic response of FLC mixture of 4-(2-octyloxycarbonyl)-4-biphenyl ester of 4-decyl-3-chlorobiphenyl-4-carboxylic acid, 4-(2-octyloxycarbonyl)phenyl ester of 4-decyl-3-chlorobiphenyl-4-carboxylic acid, 4-(2-methylbutyloxycarbonyl)phenyl ester of 4-hexyl-3-chlorobiphenyl-4-carboxylic acid (ratio – 2 : 2 : 1).

3. EXPERIMENTAL

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

4-(6-Decylcyclohex-2-enonoyl-3)benzoytrile (1)

A mixture of (0.30 mol) of corresponding Mannich salt, 0.31 mol of ethyl 2-decyloacetate and 0.91 mol potassium hydroxide in 350 ml of dioxane was refluxed during 5 h under stirring (evolution of dimethylamine!). After cooling to room temperature 600 ml of 10% sulphuric acid solution was added carefully (evolution of carbon dioxide!) and the product was extracted with 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 the solvent had been recrystallized from isopropanol. The yield 72 per cent.

4-(6-Decylcyclohex-2-enonoyl-3)benzoic acid (2)

The mixture of 0.02 mol of 4-(6-decylcyclohex-2-enonoyl-3)benzoytrile (3), 0.08 mol KOH in 100 ml ethylene glycol was refluxed with energetic stirring during 10 h. After cooling, the reaction mixture was acidified with 10% hydrochloric acid, the product was filtered and used, after drying on the air, in the next stage. The yield was 78%.

3.3. The esters (5 a-d) and (6a,b) were synthesised accordingly¹.

4. CONCLUSION

Prepared results have shown that the ferroelectric LC with low spontaneous polarization can form hysteresis free transmission voltage curves and V-shaped or thresholdless switching

5. REFERENCES

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