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## Liquid Crystals

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# The effect of a lateral substituent on the mesomorphic properties in a series of ferroelectric liquid crystals with a 2-alkoxypropionate unit

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A new series of ferroelectric liquid crystal materials containing a lateral methyl group on the aromatic ring of the alkoxybenzoate unit has been synthesized and investigated. These materials exhibit a wide temperature range of ferroelectric SmC\* phase on cooling (including supercooling) with a very high spontaneous polarization. All phase transition temperatures are lower when compared with those of similar non-substituted materials. In comparison with the compounds containing the lateral methoxy group, only the SmC\*–Cr transition changed significantly. The values of spontaneous polarization are mostly increased compared with both non-substituted and methoxy substituted compounds.

## 1. Introduction

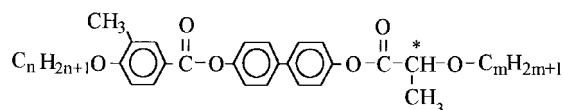
In previous papers we have described the synthesis and physical properties of FLC series containing the chiral 2-alkoxypropionate unit in the molecule. The first series was that with relatively simple molecular structure without any lateral substituent [1]. The next series had a lateral methoxy substituent in the *meta*-position to the carboxylic group of the 4-alkoxybenzoate unit [2]. This substitution resulted in a decrease of the phase transition temperatures from the isotropic phase to the N\*, SmA or SmC\* phases by about 50 K compared with the non-substituted analogues. However, the melting temperatures as well as the values of the spontaneous polarization  $P_s$  were not significantly affected [2].

A theoretical explanation of this phenomenon is complicated because the methoxy group causes several effects: firstly, as a bulky substituent, it prevents close packing of molecules and, as a result, decreases the intermolecular interactions; secondly, due to a mesomeric effect (sharing of non-bonding orbitals), the  $\pi$ -electron density of the substituted aromatic ring increases, which can result in an increase of the interactions among the molecules in the SmC\* phase and formation of charge transfer complexes; thirdly, the methoxy substituent raises the transverse dipole moment.

In this study we have chosen the methyl group as a

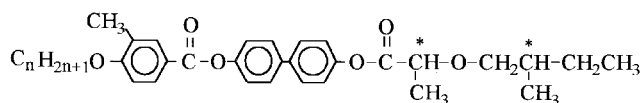
bulky substituent in the mesogenic core with negligible dipole moment and mesomeric effect with the aim of studying its effect on the phase transition temperatures. Similar substitution by the methyl group on the biphenol core [3] and on the cyclohexane ring [4] gives substantial lowering of the transition temperatures to the isotropic state (up to 60–70 K). The same effect has been reported when a methyl group [5], chlorine [6] as well as a hydroxy group [7, 8] are laterally substituted on an ester bonded aromatic ring.

The general formula of the FLCs studied in this contribution is



abbreviated as **Mn/m** where  $n$  and  $m$  are the numbers of carbon atoms in the hydrocarbon chain of the alkoxybenzoate and alkoxypropionate units, respectively.

In addition, we have prepared and studied substances having the branched chain carrying another chiral group (the (*S*)-2-methylbutoxy group as a terminal substituent) of general formula:



abbreviated as **Mn/m\*\***.

\* Author for correspondence.

Both of these series exhibit a monotropic SmC\* phase with a rather high spontaneous polarization.

## 2. Experimental

The methyl substituted compounds were synthesized similarly to the non-substituted compounds [1]. The basic synthon, 4-alkoxy-3-methylbenzoic acid, was prepared from the appropriate *o*-cresyl ether by bromination followed by formation of the Grignard reagent. Reaction with solid CO<sub>2</sub> yielded, after acidifying the reaction mixture, 4-alkoxy-3-methylbenzoic acid (see scheme 1).

The final esters were carefully purified by column chromatography on silica gel (Kieselgel 60, Merck Darmstadt) using a mixture of chloroform and acetonitrile (97:3) as eluent and recrystallized from ethanol.

The purity of the intermediates and final products was checked by thin layer chromatography (TLC). The TLC plates used were Silufol 254 and Kieselgel 60 F<sub>254</sub>; a mixture of chloroform and acetonitrile was used as the solvent. The product purity was determined by high pressure liquid chromatography using an HPLC chromatograph Ecom and a silica gel column (Separon 7 μm, 3 × 150, Tessek) with a mixture of 99.9% toluene and 0.1% methanol as eluent; eluting products were detected by a UV-VIS detector (λ = 290 nm).

The results of HPLC and elemental analyses for the final compounds are listed below.

**M6/9:** HPLC purity 98%; elem. anal. (%), found C, 75.70; H, 8.41; calc. C, 75.71; H, 8.36. **M8/\*\*:** HPLC purity 99%; elem. anal. (%), found C, 75.16; H, 8.09; calc. C, 75.26; H, 8.01. **M8/5:** HPLC purity 99%; elem. anal. (%), found C, 74.96; H, 8.17; calc. C, 75.23; H, 8.07. **M8/6:** HPLC purity 98%; elem. anal. (%), found C, 75.00; H, 8.30, calc. C, 74.97; H, 8.39. **M8/10:** HPLC purity 98%; elem. anal. (%), found C, 76.65; H, 8.79, calc. C, 76.36; H, 8.75. **M10/\*\*:** HPLC purity 98%; elem. anal. (%), found C, 75.66; H, 8.49; calc. C, 75.71, H, 8.36; **M10/10:** HPLC purity >99%; elem. anal. (%), found C, 76.74; H, 9.12; calc. C, 76.75; H, 8.99. **M12/6:** HPLC purity 98%; elem. anal. (%), found C, 76.45; H, 8.95; calc. C, 76.41, H, 8.70. **M12/10:** HPLC purity 99%; elem. anal. (%), found C, 76.94; H, 9.21; calc. C, 77.15, H, 9.14.

The structures of the intermediates and the final products were checked by <sup>1</sup>H NMR spectroscopy using a 300 MHz Varian spectrometer and solutions in CDCl<sub>3</sub> with tetramethylsilane as internal standard.

<sup>1</sup>H NMR data for 4-*n*-hexyloxy-3-methylbenzoic acid are (given in the order: chemical shift/δ, ppm/, multipli-

city, number of protons and identification): 7.95 d (1H, HAr *para* to CH<sub>3</sub>), 7.90 d (1H, HAr *ortho* to CH<sub>3</sub>), 6.85 d (1H, HAr *meta* to CH<sub>3</sub>), 4.05 t (2H, -CH<sub>2</sub>-O-Ar), 2.26 s (3H, CH<sub>3</sub>Ar), 1.83 *quint* (2H, -CH<sub>2</sub>-CH<sub>2</sub>-O-Ar), 1.3–1.6 m (6H, -CH<sub>2</sub>-), 0.92 t (3H, CH<sub>3</sub>-).

<sup>1</sup>H NMR spectral data for **M6/9** are 8.01 dd (1H, HAr *para* to CH<sub>3</sub>), 8.00 d (1H, HAr *ortho* to CH<sub>3</sub>), 7.60 dd (4H, HAr *meta* to biphenol oxygens), 7.28 d (2H, HAr *ortho* to -OCOAr), 7.20 d (2H, HAr *ortho* to -OCOR\*), 6.90 d (1H, HAr *meta* to CH<sub>3</sub>), 4.22 q (1H, -C\*H-), 4.06 t (2H, -CH<sub>2</sub>-O-Ar), 3.3 m and 3.7 m (1H, 1H, -C\*H-O-CH<sub>2</sub>-), 2.30 s (3H, CH<sub>3</sub>-Ar), 1.85 *quint* (2H, -CH<sub>2</sub>-CH<sub>2</sub>-OAr), 1.60 d (3H, CH<sub>3</sub>-C\*H-), 1.2–1.7 m (20H, -CH<sub>2</sub>-), 0.90 m (6H, CH<sub>3</sub>-). The other homologues in **M*n*/*m*** series had similar <sup>1</sup>H NMR spectra, differing only in the number of methylene protons (integral value) in the range of 1.2–1.7 ppm.

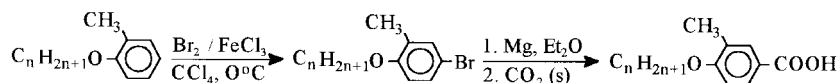
<sup>1</sup>H NMR spectral data for **M10/\*\*** are 8.04 dd (1H, HAr *para* to CH<sub>3</sub>), 8.00 d (1H, HAr *ortho* to CH<sub>3</sub>), 7.60 dd (4H, HAr *meta* to biphenol oxygens), 7.28 d (2H, HAr *ortho* to -OCOAr), 7.19 d (2H, HAr *ortho* to -OCOR\*), 6.90 d (1H, HAr *meta* to CH<sub>3</sub>), 4.20 q (1H, -C\*H-), 4.06 t (2H, -CH<sub>2</sub>-O-Ar), 3.60 m and 3.27 m (1H, 1H, -C\*H-O-CH<sub>2</sub>-), 2.3 s (3H, CH<sub>3</sub>-Ar), 1.85 *quint* (2H, -CH<sub>2</sub>-CH<sub>2</sub>-OAr), 1.72 m (1H, >C\*H-), 1.60 d (3H, CH<sub>3</sub>-C\*H-), 1.2–1.6 m (16H, -CH<sub>2</sub>-), 0.85–1.0 m (9H, CH<sub>3</sub>-). The ester **M8/\*\*** gave the same <sup>1</sup>H NMR data as **M10/\*\*** differing only in the integral value in the range 1.2–1.6 ppm.

Optical rotations were measured using an Optical Activity AA-5 polarimeter. All the new compounds (table 1) had the same values of [α]<sub>D</sub><sup>25</sup> = -28.0 (c = 0.1; CHCl<sub>3</sub>).

The sequences of phases were determined from texture observations made by polarizing light microscopy, and the phase transition temperatures by DSC. The spontaneous polarization values were determined from P(E) dependences in the form of a hysteresis loop detected during ferroelectric switching in an a.c. electric field of frequency 60 Hz, by the procedure used in refs. [1, 2, 10].

## 3. Results and discussion

The phase sequences on cooling, the melting temperatures, phase transition temperatures and enthalpies, and the spontaneous polarization values for the new compounds are summarized in table 1. All the compounds exhibit a wide temperature range ferroelectric SmC\* phase on cooling (including supercooling). The observed phase transitions are of 1st order with the temperature range of coexistence of phases rather narrow



Scheme 1:

Table 1. Transition temperatures ( $^{\circ}\text{C}$ ) from DSC, measured *on cooling* ( $5\text{ K min}^{-1}$ ), spontaneous polarizations  $P_s$  ( $\text{nC cm}^{-2}$ ) measured at temperatures 5 K below the transition to the  $\text{SmC}^*$  phase, melting points m.p. ( $^{\circ}\text{C}$ ) and transition enthalpies [ $\Delta H$  ( $\text{kJ mol}^{-1}$ )] for homologous series  $\text{M}n/m$  and  $\text{M}l/^{**}$ . • the phase exists, — the phase does not exist.

$\text{M}n/m$	m.p.	Cr	$\text{SmC}^*$	$\text{N}^*$	BP	Iso	$P_s$				
<b>M6/9</b>	63 [28·5]	•	6	•	77 [2·4]	•	105 [0·7]	—	•	120	
<b>M8/^{**}</b>	46 [15·4]	•	10	•	80 [3·5]	•	87	•	94 [0·8]	•	192
<b>M8/5</b>	50 [8·3]	•	10	•	89 [25·8]	•	—	—	104 [1·0]	•	121
<b>M8/6</b>	65 [23·0]	•	25	•	80 [3·2]	•	—	—	107 [1·0]	•	180
<b>M8/10</b>	76 [55·0]	•	34	•	—	•	76 [3·6]	—	—	•	—
<b>M10/^{**}</b>	57 [37·4]	•	-10	•	82 [3·2]	•	89	•	94 [1·0]	•	153
<b>M10/10</b>	75 [38·3]	•	25	•	89 [4·3]	•	90	•	91 [1·1]	•	83
<b>M12/6</b>	44 [21·9]	•	25	•	91 [4·1]	•	—	—	96 [1·1]	•	81
<b>M12/10</b>	50 [29·5]	•	24	•	—	—	—	—	87 [6·1]	•	74

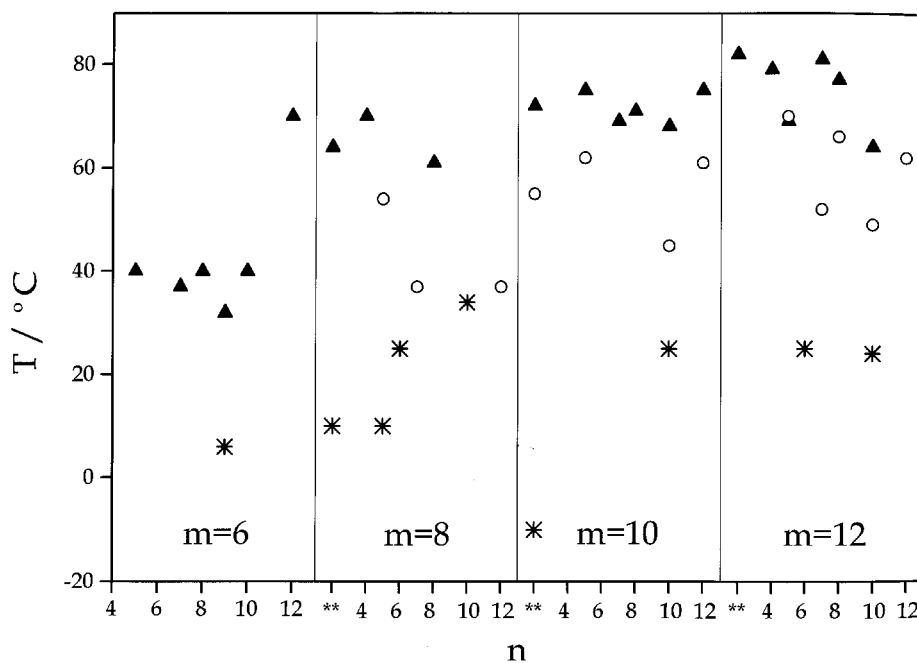


Figure 1. Temperatures of transitions from  $\text{SmC}^*$  phase to Cr or as yet unassigned Sm phase for  $\blacktriangle$  non-substituted compounds ( $\text{H}n/m$ ,  $\text{H}n/^{**}$ ),  $\circ$  methoxy substituted compounds ( $\text{MO}n/m$ ,  $\text{MO}n/^{**}$ ) and  $*$  methyl substituted compounds ( $\text{M}n/m$ ,  $\text{M}n/^{**}$ ).

(<1 K), except for **M8/10**. In this compound, at  $76^{\circ}\text{C}$  islands of both  $\text{N}^*$  and  $\text{SmC}^*$  phases appear in the isotropic phase on cooling. The coexistence of the phases persists on cooling until crystallization, the amount of the isotropic phase gradually decreasing. For this reason the value of the spontaneous polarization could not be determined. This compound has been purified by the same procedure as others, recrystallized from ethanol and methanol, and it exhibited the same purity. A similar anomaly of coexistence of phases was observed with the

compound **MO12/7** [2]; the other homologues of that series again behaved in the usual way.

The blue phase, which exists in **M10/10**, **M8/^{\*\*}**, and **M10/^{\*\*}**, could not be detected by DSC but was clearly seen using the polarizing microscope; thus the temperature range of each BP has been determined by microscopy. Also the crystallization of **M6/9**, **M8/^{\*\*}**, **M10/^{\*\*}** and **M8/6** from the  $\text{SmC}^*$  phases could not be detected by DSC, probably due to supercooling and the slow kinetics of crystallization of the relatively thick ( $\approx 1\text{ mm}$ )

DSC samples. It is also possible that a glassy state is formed at low temperatures on cooling, and this needs a long time for crystallization. A similar phenomenon was noted in ref. [9]. With the thin planar cells used for microscopy, crystallization on cooling occurs easily. Therefore the crystallization temperatures determined by microscopic observation are given in table 1 for these compounds.

The values of the spontaneous polarization ( $P_s$ ) measured 5 K below the phase transition to the SmC\* phase seem to increase with decreasing number of carbon atoms in the aliphatic chain  $m$ , and they are significantly higher for compounds with two chiral centres  $Mn/m$ \*\* (see table 1). To estimate the effects of the substitution on the properties of the compounds we will compare the phase transition temperatures and  $P_s$  values of the methyl substituted ( $Mn/m$ ), methoxy substituted ( $MOm/m$  [2]) and the non-substituted ( $Hn/m$  [1, 10])

compounds. Data for comparison are presented in table 1, table 2 and in the figure. The phase transition temperatures for  $Hn/m$  reported in refs. [1, 10] were determined from texture observation. For the purpose of comparison the phase transition temperatures of these compounds have been redetermined by DSC under the same conditions as for  $Mn/m$  and  $MOm/m$ . The phase transition temperatures determined by the two methods differ slightly. Some of the non-substituted substances ( $H10/m$ \*\*,  $H10/5$  and  $H10/7$ ) are here reported for the first time.

As shown in tables 1 and 2, all phase transition temperatures for the methyl substituted compounds are significantly lower compared with the non-substituted series [1]. This effect is well known and can be explained in terms of the steric influence of the methyl group on molecular packing.

When we compare the properties of the methyl

Table 2. Transition temperatures ( $^{\circ}\text{C}$ ) from DSC, measured *on cooling* ( $5\text{ K min}^{-1}$ ) and values of spontaneous polarization  $P_s$  ( $\text{nC cm}^{-2}$ ) measured by the same procedure as for  $Mn/m$  at temperatures 5 K below the transitions to the SmC\* phase for the non-substituted compounds ( $Hn/m$ ) [1, 10] and the methoxy substituted compounds ( $MOm/m$ ) [2]. • the phase exists, — the phase does not exist.

Compound		SmC*		SmA		N*		BP		Iso	$P_s$	
H6/5	Cr	40	•	127	—	•	150	—		•	64	
H6/7	Cr	37	•	124	—	•	143	—		•	57	
H6/8	Cr	40	•	122	—	•	138	•	139	•	62	
H6/9	Cr	32	•	120	•	126	•	134	•	135	•	57
H6/10	Cr	40	•	119	•	128	•	132	•	133	•	45
H6/12	Cr	70	•	119	•	129	•	131	•	133	•	43
H8/**	Sm <sup>†</sup>	64	•	122	—	•	153	—		•	59	
H8/4	Sm <sup>†</sup>	70	•	138	—	•	163	—		•	62	
H8/8	Sm <sup>†</sup>	61	•	128	—	•	134	—		•	60	
H10/**	Sm <sup>†</sup>	72	•	126	—	•	112	•	114	•	77	
H10/5	Sm <sup>†</sup>	75	•	135	—	•	139	—		•	86	
H10/7	Sm <sup>†</sup>	69	•	130	—	•	139	—		•	67	
H10/8	Sm <sup>†</sup>	71	•	133	—	—	—	—		•	66	
H10/10	Sm <sup>†</sup>	68	•	128	—	—	—	—		•	61	
H10/12	Sm <sup>†</sup>	75	•	132	—	—	—	—		•	50	
H12/**	Sm <sup>†</sup>	82	•	142	—	•	157	—		•	32	
H12/4	Sm <sup>†</sup>	79	•	142	—	•	143	—		•	55	
H12/5	Sm <sup>†</sup>	69	•	136	—	—	—	—		•	59	
H12/7	Sm <sup>†</sup>	81	•	144	—	•	149	—		•	43	
H12/8	Sm <sup>†</sup>	77	•	136	—	—	—	—		•	59	
H12/10	Sm <sup>†</sup>	64	•	127	—	—	—	—		•	63	
MO8/5	Cr	54	•	69	•	79	•	80	—	•	66	
MO8/7	Cr	37	•	82	—	•	103	—		•	50	
MO8/12	Cr	37	•	65	—	•	85	—		•	24	
MO10/**	Cr	55	•	71	•	77	—	—		•	66	
MO10/5	Cr	62	•	81	—	—	—	—		•	57	
MO10/10	Cr	45	•	89	—	—	—	—		•	57	
MO10/12	Cr	61	•	80	—	—	—	—		•	35	
MO12/5	Cr	70	•	82	•	85	—	—		•	27	
MO12/7	Cr	52	•	86	—	—	—	—		•	61	
MO12/8	Cr	66	•	80	•	85	•	87	—	•	47	
MO12/10	Cr	49	•	85	—	—	—	—		•	76	
MO12/12	Cr	62	•	82	—	—	—	—		•	66	

<sup>†</sup> Here and below, Sm signifies a smectic phase of higher order, as yet unassigned.

substituted compounds **Mn/m** and their methoxy substituted analogues (**MO<sub>n</sub>/m**) [2], a significant difference can be observed: for the series **Mn/m** the SmC\*–Cr phase transitions are substantially lowered and the transitions to the isotropic state are shifted slightly to higher temperatures (see tables 1 and 2 and the figure). The narrow blue phase, which appears for **Mn/m** series was not observed for the methoxy substituted **MO<sub>n</sub>/m** series.

Since lowering of the SmC\*–Cr transition temperatures is smaller for the **MO<sub>n</sub>/m** than for the **Mn/m** compounds, it is obvious that the methoxy group favours the packing of the molecules into the crystalline structure. This can be understood as an increase of the intermolecular interactions in the **MO<sub>n</sub>/m** series due to the mesomeric effect, which can compensate for the disordering steric effect of a bulky lateral group. However, the influence of the mesomeric effect of the methoxy group on the transition temperatures close to the isotropic state is much weaker.

A comparison of the  $P_s$  values for **MO<sub>n</sub>/m** and **H<sub>n</sub>/m** (see table 2 and more detail in [1, 2]) shows that the methoxy group does not influence the spontaneous polarization value. On the other hand, the introduction of the methyl group results in a strong increase of the spontaneous polarization. Similarly, an increase of  $P_s$  has been observed when a chlorine is substituted in the same position [10]. In that case, the  $P_s$  increase has been ascribed to the increase of the transverse molecular dipole-moment and to the increase of the material density due to the mesomeric effect, which strengthens the intermolecular interactions. Similar behaviour could be expected with the methoxy substituent because of its polar properties, but not with the methyl substituent,

which is non-polar. Why the increase of  $P_s$  occurs for the methyl substituent, but not for the methoxy substituent, is not understood. As all the substituents are far from the chiral centre, a direct influence upon the chiral centre is not probable.

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