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The effect of a lateral methoxy group on the mesomorphic properties of ferroelectric liquid crystals

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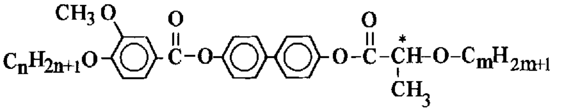
A new series of ferroelectric liquid crystal materials having the methoxy group substituted in an aromatic ring of the mesogenic core has been synthetized and characterized. This electron–donor methoxy group makes the ferroelectric S_C^* phase narrower in range and monotropic when compared to the series with the unsubstituted molecules, the values of the spontaneous polarization remaining unaffected.

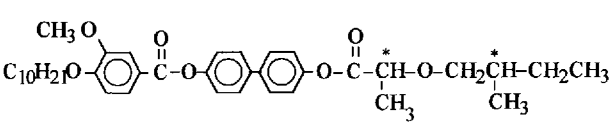
1. Introduction

Recently we have reported on ferroelectric liquid crystal (FLC) materials containing a 2-alkoxypropionate chiral unit in the molecule [1]. In this contribution, the change in the mesomorphic properties is studied when a hydrogen atom on the first aromatic ring is substituted by the methoxy group.

A common formula for the 11 substances presented in this contribution is


I

One substance contains two chiral centres


II

All these compounds exhibit monotropic smectic C* phases, for which the basic characteristics, the spontaneous polarization P_S and the tilt angle Θ_S of the molecules from the smectic layer normal, have been determined. The results are compared with those for the substances without the ring-OCH_3 group.

2. Experimental

The compounds have been prepared by the method reported in [1] from the ethyl ester of vanillic acid, which was alkylated with the corresponding bromoalkane in a mixture of ethanol and sodium ethoxide. Reaction of the 3-methoxy-4-alkoxybenzoic acid obtained with thionyl chloride and subsequent esterification in pyridine with 4,4′-biphenol yielded the mesogenic phenol. Esterification of the phenol with an (*S*)-(-)-alkyl-lactic acid in the presence of dicyclohexylcarbodiimide in dichloromethane yielded the final products.

The *O*-alkyl-lactic acid was prepared using the method described in [2]. The substance of formula **II** was synthetized from 2-(*S*)-[2-(*S*)-methylbutoxy]propanoic acid [1].

The purification of the materials was carried out using column chromatography on silica gel (Kieselgel 60, Merck, Darmstadt), a mixture of chloroform and acetonitrile (97:3) being used as eluent; products were then recrystallized from ethanol and dried in vacuum. Purities of the final products were checked by high performance liquid chromatography using a silica gel column (Separon 7 μm, Tessek) and toluene with 0·1 per cent methanol as the eluent. Detection of the eluting products was made spectroscopically at $\lambda = 290$ nm.

The structures of the final products were confirmed by ^{1}H NMR spectroscopy. ^{1}H NMR spectral data for the substance *n*/*m* = 12/12 measured in $CDCl_3$ are presented as an example (the data for protons are given in the following order: chemical shift, multiplicity, number of protons, *J*(Hz) and identification): 7·86, dd (1 H, J_1 = 8·43; J_2 = 1·95; HAr *para* to CH_3O): 7·69, d (1 H, *J* = 2·01; HAr *ortho* to CH_3O); 7·61, m (4 H, HAr *meta* to biphenyl oxygens); 7·28, d (2 H, *J* = 9·80; HAr *ortho* to –OCOAr); 7·19, d (2 H, *J* = 8·61; HAr *ortho* to –OCOR*); 6·96, d (1 H, *J* = 8·61, HAr *ortho* to $C_{12}H_{25}O$–); 4·22, q (1 H, *J* = 6·9; –C*H–); 4·12, t (2 H, *J* = 6·87; –CH_2–OAr); 3·96,

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Table 1. Transition temperatures (°C) measured on cooling, transition enthalpies [ΔH] (kJ mol^{-1}), values of the spontaneous polarization P_S (nC cm^{-2}) at a temperature $T_C - 5$ K, and melting points, m.p. (°C) obtained on heating for the homologues *n*/*m* of series **I** and for the substance 10/** (**II**). ● the phase exists; — the phase does not exist.

n/*m*	m.p.	Cr		S_C^*		S_A		N*		I	P_S
12/5	86·9 [42·8]	●	69·8 [32·2]	●	82·3 [0·1]	●	85·1 [4·1]	—		●	26·5
12/7	87·7 [55·0]	●	51·6 [9·1]	●	85·6 [5·1]	—		—		●	61
12/8	87·5 [48·8]	●	66·3 [34·3]	●	79·6 [0·2]	●	84·6 [0·2]	●	86·5 [3·9]	●	46·5
12/10	66·6 [46·0]	●	49·2 [16·9]	●	84·7 [6·2]	—		—		●	75·5
12/12	79·3 [62·8]	●	61·8 [51·0]	●	81·5 [4·9]	—		—		●	65·5
10/5	92·7 [48·3]	●	62·3 [27·6]	●	80·6 [3·3]	—		—		●	64·5
10/10	78·4 [49·3]	●	44·8 [13·0]	●	88·6 [5·2]	—		—		●	56·7
10/12	86·6 [55·0]	●	60·8 [50·8]	●	79·8 [3·6]	—		—		●	34·9
8/5	77·1 [30·8]	●	54·4 [19·6]	●	69·4 [0·5]	●	79·5 [0·5]	●	79·9 [2·5]	●	65·9
8/7	64·3 [13·2]	●	37·4 [12·4]	●	82·2 [0·2]	—		●	103·2 [1·2]	●	50·2
8/12	76·2 [29·5]	●	37·1 [17·9]	●	64·7 [0·2]	●	87·4 [3·5]			●	23·9
10/**	75·8 [36·3]	●	54·9 [22·5]	●	71·4 [0·3]	●	77·1 [4·1]	—		●	65·9

s (3 H, CH_3–OAr); 3·7, m and 3·5, m (1 H, 1 H, –CH*–O–C$\underline{H}_2$–); 1·59, d (3 H, $J = 6{\cdot}44$; C*H–C$\underline{H}_3$); 1·2–1·9, m (40 H, –CH_2–); 0·9, m (6 H, CH_3–).

The sequences of phases and the phase transition temperatures have been determined from texture observations using a polarizing microscope. DSC (Perkin–Elmer DSC 7) confirmed the phase transition temperatures and yielded transition enthalpies. For the ferroelectric S_C^* phases, the P_S and Θ_S values have been measured. The values of P_S were determined from the $P(E)$ dependence in the form of a hysteresis loop detected during P_S switching under an a.c. electric field of frequency 60 Hz. The values of Θ_S were determined optically from the difference between the extinction positions of the sample between crossed polarizers under opposite d.c. electric fields of ±40 kV cm^{-1}.

3. Results and discussion

The phases, phase transition temperatures and enthalpies are given in table 1. Compounds of series **I** are distinguished by the number of carbon atoms in the terminal chain *n* and by the number of carbon atoms in the alkoxypropionate chain *m*. The substance of formula **II** is denoted as 10/**. The phase transition temperatures shown in table 1 are those detected by DSC on cooling at a rate of 5 K min^{-1}, except for the N*–S_A transition which was distinguishable only a lower scanning rates for example, 1 K min^{-1}. A typical example of a DSC curve is shown in the figure.

Similar data for the unsubstituted compounds of the same chain lengths are given in table 2 for comparison.

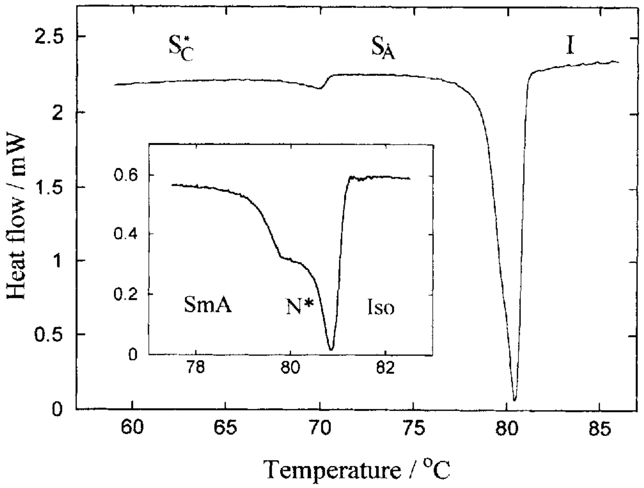


Figure 1. DSC curve for the substance 8/5 at a cooling rate of 5 K min^{-1}. The inset shows DSC curve at a cooling rate of 1 K min^{-1}.

Table 2. Transition temperatures (°C) measured on cooling, transition enthalpies [ΔH] (kJ mol^{-1}), values of the spontaneous polarization P_S (nC cm^{-2}) at a temperature $T_C - 5$ K, and melting points, m.p. (°C) obtained on heating for the unsubstituted compounds [1]. ● the phase exists; — the phase does not exist. For a definition of S_N, see [1].

n/m	m.p.	S_N		S_C^*		N*		I	P_S
12/5	73·1 [41·4]	●	69·4 [9·7]	●	135·7 [7·3]	—		●	66·0
12/7	79·9 [54·4]	●	81·3 [13·8]	●	144·3 [5·7]	●	148·9 [4·9]	●	44·0
12/8	71·1 [36·3]	●	77·2 [15·2]	●	135·7 [8·3]	—		●	59·0
12/10	69·6 [30·5]	●	64·1 [5·6]	●	126·7 [4·5]	—		●	62·0
10/10	62·1 [35·8]	●	68·3 [8·1]	●	128·0 [6·9]	—		●	61·0
10/12	70·1 [42·6]	●	75·1 [10·6]	●	132·2 [8·0]	—		●	50·0

These data have been extracted from [1], except for the enthalpy values that were measured for this work.

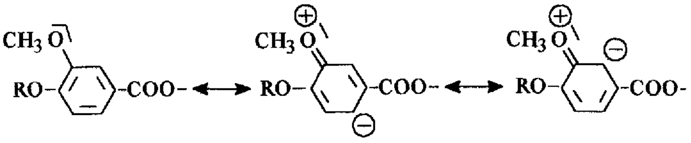
All the compounds studied exhibit monotropic ferroelectric phases which are much narrower in range when compared to the unsubstituted materials. This effect is caused by the remarkable lowering in the phase transition temperature to the S_C^* phase, the crystallization temperature remaining unaffected (see table 2). In contrast to the unsubstituted systems, in some homologues the S_A phase has been observed, which is also monotropic. The occurrence of the S_A phase in substances 12/5 and 12/8 has been confirmed by both DSC and texture observation. In 12/7, no corresponding peak has been found in the DSC curve, and we observed the coexistence of the isotropic and the S_C^* phase on cooling. This fact, together with the low enthalpy value of the observed S_A–S_C^* transitions, emphasizes the low stability of the S_A phase in this series. Similarly, the chiral nematic phase is rare, and it has been detected only in three homologues out of the twelve.

All the phase transitions observed are strongly of the first order except those between the S_A and S_C^* phases which may be either of the second or weakly of the first order.

The P_S values of both the substituted and unsubstituted materials are comparable (cf. tables 1 and 2), showing that the methoxy group (see formulae **I** and **II**) does not influence the spontaneous polarization. The spontaneous tilt angle values are of about 33°. They are temperature independent within the S_C^* phase for all the substances except those exhibiting the S_A–S_C^* transition. With these substances, the spontaneous tilt angle increases gradually on moving from the phase transition temperature T_C, following roughly the dependence $\Theta_S \approx (T_C - T)^{1/2}$.

In the homologue 10/10 of the unsubstituted compounds, a helix inversion has been detected [3]. This property has not been found with the compounds of formulae **I** and **II**.

The variation in mesomorphic properties occasioned by introduction of the lateral substituent into the molecule could have its origin in both mesomeric and steric effects. The electron donating substituent increases the π-electron density in the aromatic ring owing to mesomeric effects, according to the scheme:



Due to this effect, an increase of the intermolecular repulsion of negatively charged aromatic rings in a smectic layer may occur and result in the observed decrease in the phase transition temperatures, specifically the considerable decrease in the transition temperature to the isotropic phase. On the other hand, the steric effect of the bulky methoxy substituent prevents a close molecular packing, and thus the liquid crystalline order is more easily destroyed by thermal fluctuations. This effect has been observed frequently with lateral substitution, in particular by bulky alkyl groups. A strong lowering of the S_C–I transition temperature has been observed with the ethyl group [4] and with the methyl group [5, 6]. In those substances, the mesomeric effects are excluded as the polar C–O bond of the methoxy group in not present.

At present we are preparing a series of substances with a methyl substituent instead of the methoxy group. A comparison of the mesomorphic properties of these two series will elucidate the role of the oxygen atom in the substituent on the transition temperature decrease.

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