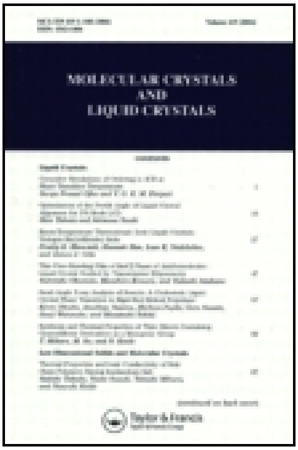

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STUDY OF FERROELECTRIC LIQUID CRYSTALS WITH 2-ALKOXYPROPIONATE CHIRAL GROUP BY X-RAY MEASUREMENTS

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We present the X-ray study of three series of ferroelectric liquid crystalline materials with a 2-alkoxypropionate chiral group in order to establish the connection of physical properties and the number of carbon atoms in the non-chiral chain. All materials have the ferroelectric SmC phase in a broad temperature range. Using X-ray diffraction of non-oriented samples we have identified low temperature non-tilted SmX phase as the SmB phase. The thickness of smectic layers and value of the average distance between the long axes of neighbouring molecules were determined. The temperature dependence of the layer spacing was studied in all phases.*

Keywords: 2-alkoxypropionate group; ferroelectric liquid crystals; layer spacing; molecular parameters; X-ray diffraction

1. INTRODUCTION

In this work, we present the X-ray study of several homologues series of ferroelectric liquid crystals with 2-alkoxypropionate chiral group. General formulae of the studied materials are:

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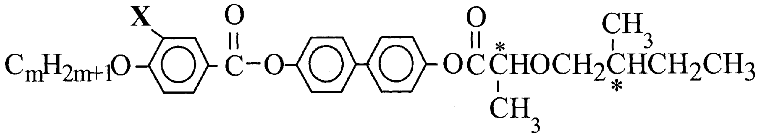
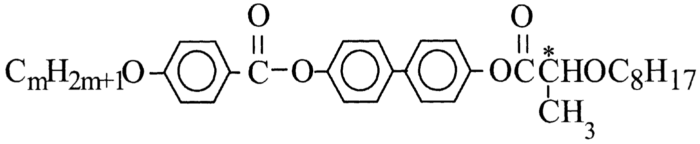


denoted as: **H m**/* where X = H; **M m**/* where X = CH_3 (**m** = 10); **MO m**/* where X = CH_3O (**m** = 10); **Cl m**/* where X = Cl (**m** = 10). Both chiral centres are in configuration (S).



denoted as **H m**/8. The chiral centre is in configuration (S)

Studied materials can be divided into three groups: (i) with two chiral centres denoted as **H m**/*, **M m**/*, **MO m**/* and **Cl m**/* (**m** = 10) differing in lateral groups on the phenyl ring far from the chiral centre; (ii) with two chiral centres denoted as **H m**/* differing in the length of non-chiral alkyl chain and without lateral groups and (iii) denoted as **H m**/8 differing, similarly as (ii), in the length of non-chiral alkyl chain and having only one chiral centre.

Some physical and chemical investigations of the compounds: synthesis, optical measurements (the phase diagrams and the textures), and differential scanning calorimetry (DSC) were performed previously [1,2]. Sequence of phases and phase transition temperatures obtained by optical method and DSC are presented in Table 1.

Now we focused on more detailed structural investigation of non-oriented samples by X-ray diffraction method [3]. The layer spacing, **d**, and the average repeat distance between the long axes of neighbouring parallel molecules, **D**, were determined using the Bragg law: $n\lambda = 2\mathbf{d} \sin\theta$. The values of **d** and **D** were calculated from the position of the small angle and large angle diffraction peak, respectively. In the hexatic SmB phase, the intermolecular distance, **b**, between the long axes of neighbouring parallel molecules can be calculated as $\mathbf{b} = 2\mathbf{D} / 3^{1/2}$ [4].

2. EXPERIMENTAL

An optical study was performed using polarizing microscope Amplival pol-U with a Boetius heating-state. The heating/cooling rate was 3°C/min.

Non-oriented samples were investigated by the X-ray diffraction in a transmission geometry using conventional powder diffractometer, Seifert

TABLE 1 Sequence of Phases, Phase Transition Temperatures [°C] and Values of Spontaneous Polarisation P_s [nCcm^{-2}] at 20 K Below the Transition to the SmC* Phase. All these Data were Obtained on Cooling. (● the Phase Exists; – the Phase does not Exist; # Denotes the SmX Phase)

	Cr		SmC*		SmA		N*		BP		Iso	$\mathbf{P_s}$
MO 10/*	●	55	●	71	●	77	–		–		●	96
CI 10/*	●	52	●	95	–		–		–		●	206
M 10/*	●	– 10	●	82	–		●	89	●	94	●	195
H 6/*	#	47	●	121	–		●	144	●	154	●	137
H 9/*	#	66	●	128	–		●	131	●	137	●	131
H 10/*	#	63	●	126	–		●	132	●	134	●	118
H 11/*	#	65	●	125	–		●	127	●	130	●	127
H 12/*	#	81	●	143	–		●	158	–		●	45
H 6/8	●	67	●	122	–		●	138	●	139	●	103
H 8/8	#	58	●	128	–		●	134	–		●	105
H 9/8	#	57	●	129	–		●	130	●	133	●	95
H 10/8	#	68	●	134	–		–		–		●	88
H 12/8	#	72	●	141	–		–		–		●	75

V-14, CuK_α radiation at 0.15 nm, with an automated high temperature kit Parr HTK-10.

The values of spontaneous polarisation ($\mathbf{P_s}$) have been evaluated from P(E) hysteresis loop detected during $\mathbf{P_s}$ switching in a.c. electric field E of frequency 60 Hz on 25 μm thick planar samples. The $\mathbf{P_s}$ measurements were done on cooling.

3. RESULTS AND DISCUSSION

X-ray diffraction studies were carried out on all the investigated compounds. Figure 1a, b shows the examples of the X-ray diagrams of non-oriented sample as function of the temperature.

In the case of **H 8/8** (see Fig. 1b), we have identified the smectic (SmC*) and the chiral nematic (N*) phase. The analysis of X-ray diagrams obtained at the SmC* phase transition shows the presence of the reflections at small angles ($2\theta \sim 6.1,6,6^\circ$), indicating the layer structure, besides the diffuse outer scattering ($2\theta \sim 22.2^\circ$) corresponding to average repeat distance **D**. The calculation of effective layer thickness **d** and the average repeat distance **D** at 115°C, gives the value of 16.87 Å and 4,66 Å, respectively. If the temperature decreases, the intensity of the small angle peak increases and the effective layer thickness decreases (see Fig. 1a).

In the case of the blue phase (BP) and the nematic (N*) phase one can notice some hardly visible low angle peaks ($2\theta \sim 3$–6°, depending on the

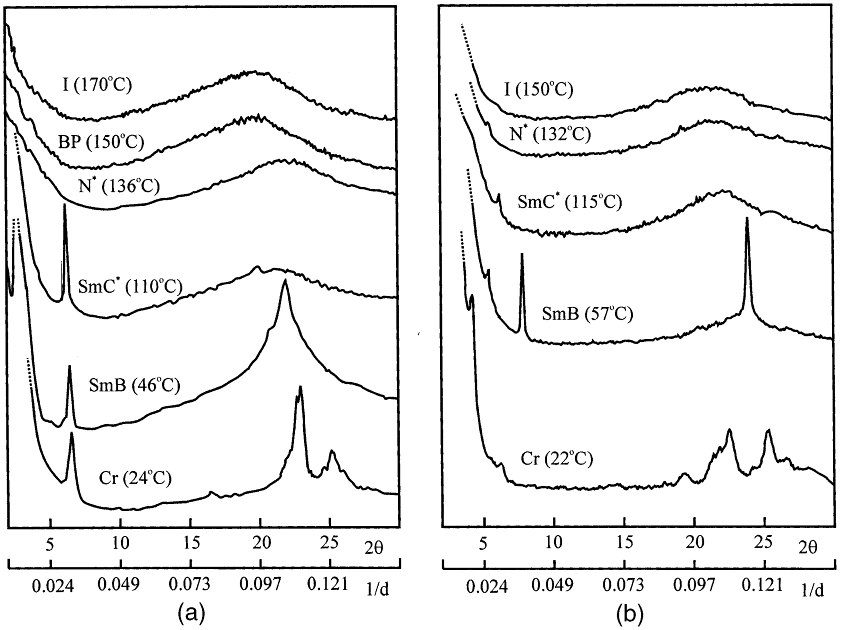


FIGURE 1 X-ray diffraction profiles for **H 6**/* (a) and **H 8/8** (b).

compounds), corresponding to long spacing distance approximately equal to the length of the molecule, which decrease with temperature increase (see Tables 2–4 or Fig. 1a for **H 6**/*).

On the smC* → SmX phase transition temperature (58°C) of **H 8/8**, at the position of the small angle reflection, two peaks appear ($2\theta \sim 4.8^\circ$ and 7.2°) corresponding to long spacing distance, and an additional strong peak ($2\theta \sim 23.2^\circ$) arises (see Fig. 1b). That strong peak corresponds to the hexagonal molecular packing of the centres of mass of the molecules along smectic layers and characterises the SmB phase. Hence, we identified the SmX phase like the SmB Phase. The SmB phase in these compound appears in the temperature range 58–50°C when the first sings of crystallisation appear (see Fig. 1b). In the case of **H 6**/* (see Fig. 1a), this peak (at about 20–25°) is not so sharp. Moreover, it looks like superposition of two peaks, which means that this phase could be the SmG, the SmJ, or the SmB phase. The calculation of average repeat distance between long axes of the neighbouring parallel molecules for the isotropic (I), nematic (N*) and SmC* phases indicate increased packing density of molecules, of mean lateral intermolecular spacing, giving the value $\mathbf{D} = 4.98\,\text{Å}$, 4.88 Å and 4.66 Å, respectively.

On the basis of similar considerations for all components, we have concluded that the SmX phase could be identified as the SmB phase in all studied compounds except for **H 10/8**. The X-ray diagrams of **H 10/8** compound which were recorded in cooling (degree per degree) show only crystallisation effect. The SmC* → SmB phase transition is also connected with a jump up in the layer thickness in all investigated compounds (see Tables 2–4).

Optical investigations show that all the phase transition temperatures for all substituted compounds are significantly lower compared to non-substituted series (see Table 1). For non-substituted compounds, the value

TABLE 2 Molecular Parameters Substituted Compounds for all Observed Phases at a Fixed Temperature T [°C]: Angles Corresponding to the Reflection Peaks **2Θ** [degrees], Effective Layer Thickness **d** [Å] (Error of Measurements $\delta_{\mathbf{d}}$ was about ± 0.05 Å), Average Repeat Distance **D** [Å] (Error of Measurements $\delta_{\mathbf{D}}$ was about ± 0.002 Å), Intermolecular Distance **b** [Å] are Presented. In the BP and N* Phase, **d** Equals Approximately to the Length of the Molecule

	Phase	T	**2Θ**	**d**	**D**	**b**
MO 10/*	**I**	85	21.0	–	4.911	–
	SmA	74	3.05	33.63		
			3.45	29.73		
			21.0		4.911	–
	SmC*	63	3.1	33.09		
			19.8		5.206	–
Cl 10/*	**I**	111	21.0	–	4.925	
	SmC*	85	6.1	17.01		
			23.1		4.483	–
M 10/*	**I**	120	21.2		4.870	–
	BP	92	6.65	15.44		
			22.0		4.694	–
	N*	84	6.65	18.02		
			21.0		4.915	–
	SmC*	79	7.5	13.70		
			22.2		4.653	–
H 10/*	**I**	155	19.2	–	5.371	–
	BP	133	5.1	20.13		
			19.7		5.236	–
	N*	129	5.1	20.13		
			21.0		4.915	–
	SmC*	121	5.4	19.02		
			6.5	15.80		
			21.5		4.802	–
	SmB	50	4.6	22.319		
			22.3		4.632	5.349

TABLE 3 Molecular Parameters of **H m**/* Compounds for all Observed Phases at a Fixed Temperature T [°C]: Angles Corresponding to the Reflection Peaks **2Θ** [Degrees], Effective Layer Thickness **d** [Å] (Error of Measurements $\delta_{\mathbf{d}}$ was about ± 0.05 Å), Average Repeat Distance **D** [Å] (Error Measurements $\delta_{\mathbf{D}}$ was about ± 0.002Å), Intermolecular Distance **b** [Å] are Presented. In the BP and N* Phase, **d** Equals Approximately to the Length of the Molecule

	Phase	T	**2Θ**	**d**	**D**	**b**
H 6/*	**I**	170	19.0	–	5.438	–
	BP	150	3.8	27.07		
			19.6		5.273	–
	N*	136	3.8	27.07		
			20.09		4.949	–
	SmC*	115	6.15	16.73		
	SmB	60.5	6.5	15.83		
			21.9		4.704	5.432
H 9/*	**I**	150	5.2	19.74		
			20.1		5.143	–
	BP	135	5.1	20.13		
			20.8		4.972	–
	N*	129	6.6	15.59		
			20.0		5.169	–
	SmC*	127	5.2	19.60		
			20.6		5.020	–
	SmB	63	5.0	20.58		
			5.2	19.60		
			7.6	13.54		
			23.4		4.426	5.111
H 11/*	**I**	150	21.3	–	4.857	–
	BP	129	5.3	19.41		
			20.9		4.949	–
	N*	126	5.9	17.44		
			22.0		4.704	–
	SmC*	110	6.6	15.59		
			21.0		4.925	–
	SmB	64	4.9	20.99		
			6.6	15.71		
			7.4	13.91		
			23.3		4.445	5.133
H 12/*	**I**	170	20.0	–	5.169	–
	N*	148	3.2	32.08		
			20.0		5.169	–
	SmC*	130	3.5	29.39		
			4.6	22.37		
			21.4		4.843	–
	SmB	57	2.6	39.56		
			3.7	27.80		
			6.2	16.73		
			22.6		4.581	5.290

TABLE 4 Molecular Parameters of **H m/8** Compounds for all Observed Phases at a Fixed Temperature T [°C]: Angle Corresponding to the Reflection Peaks **2Θ** [Degrees], Effective Layer Thickness **d** [Å] (Error of Measurements $\delta_{\mathbf{d}}$ was about ± 0.05 Å), Average Repeat Distance **D** [Å] (Error of Measurements $\delta_{\mathbf{D}}$ was about ± 0.002 Å), Intermolecular Distance **b** [Å] are presented. In the BP and N* Phase, **d** Equals Approximately to the Length of the Molecule

	Phase	T	**2Θ**	**d**	**D**	**b**
H 6/8	**I**	160	20.0	–	5.169	–
	BP	138.5	3.3	31.21		
			21.0		4.925	–
	N*	130	21.5	–	4.805	–
	SmC*	102	6.3	16.30		
			21.9		4.716	–
H 8/8	**I**	150	20.8	–	4.984	–
	N*	132	5.3	19.41		
			21.8		4.879	–
	SmC*	115	6.1	16.87		
			22.2		4.662	–
	SmB	57	4.8	21.66		
			7.2	14.29		
			23.2		4.464	5.155
H 9/8	**I**	150	21.2	–	4.869	–
	BP	131	5.6	18.50		
			21.8		4.791	–
	N*	129	5.7	18.17		
			21.8		4.737	–
	SmC*	120	6.3	19.42		
			20.5		5.034	–
	SmB	54	4.7	21.85		
			7.1	14.47		
			23.3		4.436	5.122
H 10/8	**I**	151	28.0	–	3.703	–
	SmC*	100	5.0	20.54		
			6.3	16.30		
			21.3		4.847	–
H 12/8	**I**	–	–	–	–	
	SmC*	110	3.0	34.19		
			22.6		4.568	–
	SmB	64	3.0	34.19		
			4.5	22.80		
			6.8	15.20		
			23.3		4.432	5.118

of spontaneous polarisation in the SmC* phase increases with decreasing number of carbon atoms in aliphatic chain **m**, and they are significantly higher for compound with two chiral centres. A comparison of the $\mathbf{P_s}$ values

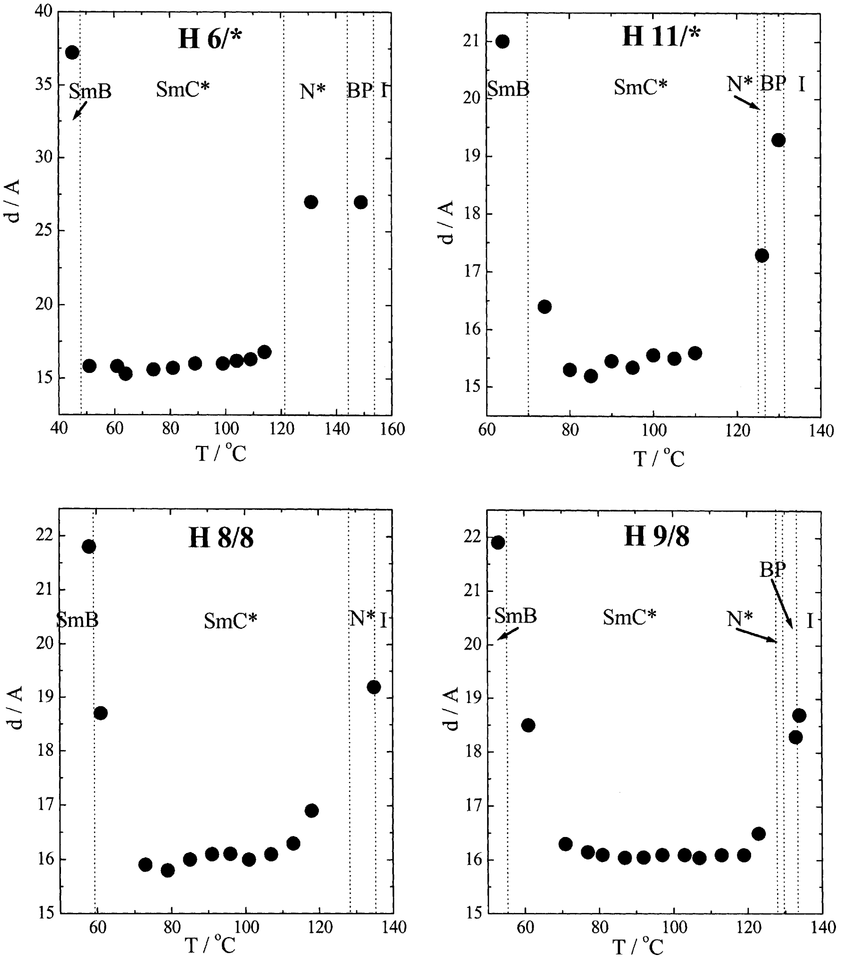


FIGURE 2 Temperature dependences of the layer spacing for indicated compounds.

of the methoxy substituted **MO m**/* (**m** = 10) and non-substituted **H m**/* (**m** = 10) substances shows that the methoxy group does not influence the spontaneous polarisation value, but the methyl and chlorine group in the same position result in strong increase of spontaneous polarisation.

Effective layer thickness **d**, calculated on the basis of 2θ values by the small angle value are significantly higher for compound **MO m**/* (**m** = 10) with lateral methoxy group compare to similar compounds with -**Cl**, -**CH$_3$**, and -**H** lateral substituents placed in the same position (see Table 2). The lowest value of **d** was found for methyl substituted

M m/* (**m** = 10) compound. If the number of carbon atoms in the hydrocarbon chain, **m**, increases, we identified increased **d** value in both **H m**/* and **H m/8** series. Moreover, the lowest value of effective layer thickness is for **M m**/* (**m** = 10), probably due to the steric influence of the methyl group on the molecular packing.

Temperature dependences of the layer spacing, **d**, for some compounds of **H m/8** and **H m**/* series are shown in Figure 2. In the SmC* phase, **d** value decreases on cooling. At the temperature of the SmC* → SmB phase transition, the stretching of the aliphatic molecular chains and zero tilt angle are the causes of the increasing d value.

4. CONCLUSIONS

The results of the study on the three homologous series of ferroelectric liquid crystals with 2-alkoxypropionate chiral group have been shown. On the basis of X-ray diffraction data on the crystalline powder of non-oriented samples we have identified the SmX phase as the SmB phase. The intermolecular distance (**b**) was calculated for all compounds showing the hexatic phase. In the case of **H 6**/*, it is not possible to determine the low temperature non-tilted phase precisely. Due to the broad shape of the respective peak, it could be either SmB phase, the SmJ phase, or SmG phase. We determined the molecular parameters of the studied materials, namely, the average repeat distance, **D**, and along spacing distance, **d**, approximately equal to the length of the molecule in the BP and the N* phase, or the interlayer spacing, in the SmC* and the SmB phases.

For **H 10/8** compound the lower temperature SmX phase was detected by observations in polarising microscope and was not found by the X-ray study probably due to the rather high used cooling rate.

The calculated data of effective layer thickness **d** are significantly lower for the chlorine and methyl substituted materials compared to non-substituted ones with two and one chiral centre. The highest value of the effective layer thickness was found for methoxy substituted compound **MO m**/* (**m** = 10). In the SmC* phase, the increase of **d** value with increasing number of carbon atoms in the hydrocarbon chain, **m**, is observed also for **H m**/* and **H m/8** series. Among the substituted materials, the lowest value of the effective layer thickness is for **M m**/* (**m** = 10), probably due to the steric influence of the methyl group on the molecular packing.

At the temperature of the SmC* → SmB phase transition, the zero molecule tilt, the stretching of the aliphatic molecular chains and increased orientational order of the molecular long axes are the causes of the increased **d** value.

As expected, the increase of the average repeat distance **D** with temperature increasing was established.

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