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The Influence of the Structural Features of Molecules on Spontaneous Polarization Value in Induced Ferroelectric Liquid Crystal Systems

L.S. Bezhanova*, A.K. Atanesyan

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Institute of Applied Problems of Physics of the National Academy of Sciences of the Republic of Armenia
25 Hrachya Nersisyan Str., 0014, Yerevan, Republic of Armenia

*E-mail: libezhanova@mail.ru

Abstract. The experimental and theoretical study of the influence of the molecular structure features and the composition of liquid system (LC) on the value of spontaneous polarization in $_5H_{11}O-(OH)C_6H_3-CH=N-\ _6H_4-\ _5H_{11}$ {A}; $_{10}H_{21}O-\ _6H_4-CH=CH-\ _6H_4-OC_{10}H_{21}$ {B}; $_7H_{15}O-\ _6H_4-\ _6H_4-\ OO-\ H_2\ ^*H(CH_3)C_2H_5$ {C}; $_8H_{17}O-\ _6H_4-\ _6H_4-\ _2H_4\ ^*H(\ H_3)\ _2H_5$ {D} and their mixtures has been carried out. The occurrence of the large value of spontaneous polarization is established in LC system whose composition`s molecular structure does not satisfy the obligatory conditions for the occurrence of spontaneous polarization that are imposed by theory on a molecular structure. The essential role of short range intermolecular forces in the process of ferroelectric phase transition in the studied LC systems is shown. It was found that for {CC}, {DD} and {AD} interactions the most beneficial molecules` packing in terms of energy is the antiparallel one(↑↓). In the case of {AA} and {AC} interactions both parallel (↑↑) and ↑↓ are equally beneficial in terms of energy. The possibility of formation of molecular clusters–dimers is shown. It is concluded that these are stabilized, in particular, by dipole–dipole interaction of molecules. A dimer model for increasing the value of spontaneous polarization is proposed.

Molecular interaction plays a substantial role in liquid crystals (LC) structures` characterization. This interaction determines the physical properties of LC, as well as the type and kinetics of physical and physicochemical processes taking place in these substances. From the practical point of view the large interest represent ferroelectric LC systems, which have much more value of spontaneous polarization (P_s) and wider temperature range of the ferroelectric phase existence than the individual ferroelectric LC component of the system. And from the point of view of the directed synthesis, studies of the effect of molecular structure on the P_s value are of considerable interest, as well.

In the present paper the investigation of the influence of molecular structure and the concentration of the components on the value of induced P_s in LC systems of smectic matrixes with various chiral adding was carried out. As investigated objects the following smectic C (SmC) LC:

$$C_5H_{11}O-(OH)C_6H_3-CH=N-C_6H_4-C_5H_{11} \quad \{A\}$$
$$C_{10}H_{21}O-C_6H_4-CH=CH-C_6H_4-OC_{10}H_{21} \quad \{B\}$$

and ferroelectric smectic C (SmC^*) LC:

$$C_7H_{15}O-C_6H_4-C_6H_4-COO-CH_2C^*H(CH_3)C_2H_5 \quad \{C\}$$
$$C_8H_{17}O-C_6H_4-C_6H_4-C_2H_4C^*H(CH_3)C_2H_5 \quad \{D\}$$

were chosen. Below are given the phase transition temperatures:

$$Cr_1 \xrightarrow{34℃} Cr_2 \xrightarrow{46℃} SmC^* \xrightarrow{55℃} SmA \xrightarrow{60℃} ChN \xrightarrow{65℃} I \qquad \{A\}/\{D\}\,(5,7,20\%)$$

$$Cr \xrightarrow{46℃} SmC^* \xrightarrow{55℃} SmA \xrightarrow{60℃} ChN \xrightarrow{65℃} I \qquad \{A\}/\{C\}\,(5,7,20\%)$$

$$Cr \xrightarrow{49℃} SmC^* \xrightarrow{60℃} SmA \xrightarrow{66℃} ChN \xrightarrow{72℃} I \qquad \{B\}/\{D\}\,(5,7,20\%)$$

$$Cr \xrightarrow{49℃} SmC^* \xrightarrow{60℃} SmA \xrightarrow{66℃} ChN \xrightarrow{72℃} I \qquad \{B\}/\{C\}\,(5,7,20\%)$$

In our experiments the LC test samples were filled in “sandwich” type cells which glass surfaces were preliminarily given a planar orientation. The cell thickness was 20μm. To obtain a homogeneous orientation of the test sample the cell with LC was heated to an isotropic phase in special thermal chamber. After which the cell with LC was placed in a magnetic field:$\sim 1{,}2\ T$. The direction of magnetic field was parallel to the orientation preliminarily given to glass surface. Then, after the slow cooling of the test sample to the temperature of smectic phase, the magnetic field was removed. Only after that the precise measurements of temperature dependences of P_s in the range of phase transitions in the test samples were carried out by the Sawyer–Tower repolarization method [1,2].

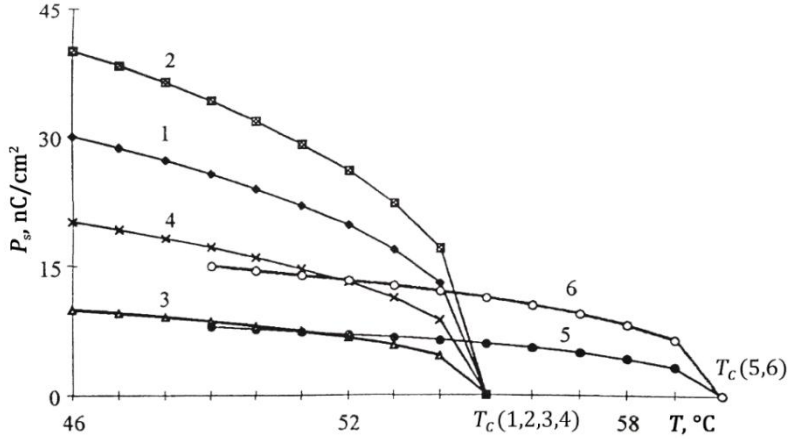

Fig. 1. Dependence of P_s spontaneous polarization on temperature in LC systems: 1– {A}/{D}(5%), 2– {A}/{D}(20%), 3– {A}/{C}(5%), 4– {A}/{C}(20%), 5– {B}/{D}(5%), 6– {B}/{D}(20%).

The measurement results are shown in Fig. 1. Comparing the obtained P_s experimental results with P_s data of ferroelectric LC {C} and {D}, submitted in [3], it becomes clear that the LC systems under study have approximately 10 times greater value of P_s. In LC systems under investigation the temperature range of the ferroelectric phase existence is also much wider. As seen in Fig. 1 in the $SmC^* \leftrightarrow SmA$ phase transition range the value of P_s changes continuously. This indicates that the $SmC^* \leftrightarrow SmA$ phase transition in investigated systems has the features of a second order phase transition. Experimentally, many of these transitions turn out to be first–order phase transitions. However, from the point of view of the Landau rules [4], all of them can be second–order transitions. Although these transitions of the second–order are less common, they are of great interest because they are always accompanied by pre–transitional anomalies. Based on the results presented in Fig. 1, let us note one more feature of the P_s temperature dependence. Not being a parameter of the ferroelectric phase transition, which is typical for improper ferroelectrics, the P_s value in investigated LC systems turns out to be proportional to the true transition parameter. Based on the known relations [5, 6] for temperature changes of the order parameter, we have:

$$|P_s| \approx \chi|\mu_1 - \mu_2 q|\theta \tag{1}$$

$$P_s \sim (T - T_C)^{\beta} \tag{2}$$

$$\theta \sim (T - T_C)^{\gamma} \tag{3}$$

where χ – is dielectric susceptibility; μ_1 and μ_2– are coefficients of piezo– and flex electric effects, respectively; q– is wave vector of the helix pitch; θ – is order parameter, the angle of inclination of the long axes of molecules to the Sm layer; T_C– is $SmC^* \leftrightarrow SmA$ phase transition temperature; β and γ– are critical indices. According to the data shown in Fig.1, $\gamma \approx \beta \approx 0{,}38$. It is noteworthy that $\gamma \neq 0{,}5$, although according to Landau's phase transition theory it should be equal to $\gamma = 0{,}5$. We can conclude that in these LC systems the role of short–range (dispersive, steric) intermolecular forces in the process of ferroelectric phase transition is significant.

The dependence of spontaneous polarization P_s on the concentration of chiral adding at a fixed temperature: $T = 52$℃ is given in Fig. 2. As follows from the presented results the largest value of P_s corresponds to the {A}/{D}20% LC system.

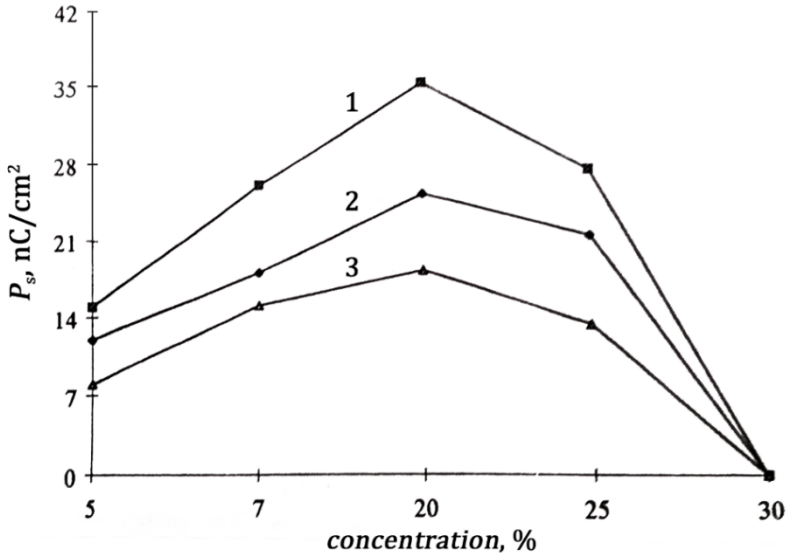

Fig. 2. Dependence P_s spontaneous polarization on a concentration of chiral adding in LC systems at $T = 52$℃. : 1– {A}/{D}, 2– {A}/{C}, 3– {B}/{C}.

This circumstances looks rather unexpected from the viewpoint of the obligatory conditions (● ability of compound with long alkyl tails of molecules to form a Sm phase with a spontaneous tilt of molecules; ●● availably of a chiral fragment; ●●● presence whenever possible the transverse dipole moment ensuring the contribution in P_s through the value of piezoelectric and flex electric coefficients [7]) imposed by the theory on molecular structure of the chiral adding for the P_s occurance. LC {D}, though has weak ferroelectric properties [3], but it has not rigidly connected transverse dipole moment of molecules near the asymmetric carbon atom. In this regard the large value of P_s in {A}/{D}20% LC system it seems possible to explain by the structural features of the {A}, {C}, {D} matrix and their stacking.

For the most complete answer to the question about the influence of the molecules` structural features on the P_s value, the study of the dependence of U_{pair} energy of pair interaction ($U_{pair} = \sum_{i.j=1}^{N} A r_{ij}^{-6} + B e^{-a r_{ij}} + W_{dd}$; where N– is the number of atoms in the molecule, r_{ij} – is the distance from i –th atom of one molecule up to j–th atom of other molecule) on the displacement of molecules from each other along the long X axis, as well as, on θ angle between molecules` long axes has been carried out in the minimum point vicinity (See Table1, Fig. 4 and Fig. 5). As an approximation, for dipole–dipole interaction W_{dd} the expression from [8] was used:

$$W_{dd} = \frac{\mu_1 \mu_2}{d_{12}^3} (2cos\theta_1 - sin\theta_1 sin\theta_2 cos\gamma) \tag{4}$$

where μ_1, μ_2 are the magnitudes of dipole moments of polar groups (see Fig. 3).

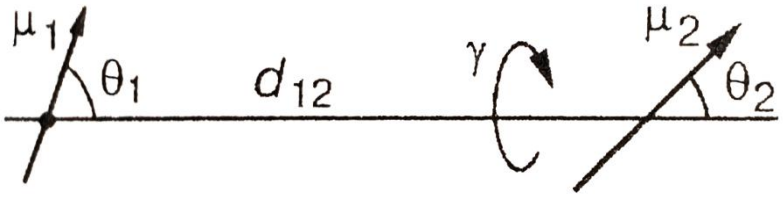

Fig. 3. Dipole–dipole interaction.

The optimal structure of pairs {A}{A}, {B}{B}, {C}{C} and {D}{D}, being adequate to a minimum of the $E_{sum} = U_{pair} + \Phi$ (Φ –is the potential function expressing the intramolecular interaction) function, corresponds to the conformation of molecules, which are sharply distinct from the conformation of appropriate isolated molecules, as the [7] calculations show. The molecules acquire a form like plane under the influence of intermolecular forces. The curves of the dependence of energy of pair interaction U_{pair} on the displacement of molecules from each other on an axis of X (Fig. 5), have a more complicated form with regard to the rotation (Fig. 4). As to the case {A}{D}, the displacement in an interval $3 - 5$Å does not result in a significant modification of the energy of interaction, and the displacement is possible only in a positive direction along the X– axis. Special attention has to be paid to the presence of the several deep extrema on the curve of the U_{pair} dependence on displacement along the X– axis, which reflects the conception about the distribution of "active" centers of interaction along a molecule. The existence of these potential barriers, apparently, will be considered as one of the main reasons of local ordering in the smectic phases.

Table 1. Minimum magnitudes of energy of pair interaction U_{pair} for (↑↑) and (↑↓) arrangements of molecules and the main parameters, specifying their optimum packing [7].

Interaction	**Pack–ing**	U_{pair}, **kcal/mol**	W_{dd}, **kcal/mol**	**Rotation, degr.**			**Shift, Å**		
				X	**Y**	**Z**	**X**	**Y**	**Z**
{A}{A}	↑↑	–20,73	1,84	0,0	0,0	0,0	–1,3	0,49	3,74
	↑↓	–20,85	–1,01	0,0	0,0	170,0	1,02	–0,3	3,7
{B}{B}	↑↑	–29,02	0,96	0,0	0,0	2,0	–1,21	–0,55	3,8
	↑↓	–	–	–	–	–	–	–	–
{C}{C}	↑↑	–11,09	1,03	0,0	0,0	1,0	1,35	–0,59	4,65
	↑↓	–19,45	–0,71	0,0	180,0	–6,0	2,08	–0,09	3,33
	↑↑	–9,96	1,08	0,0	0,0	–4,0	–0,53	–0,23	4,72
{D}{D}	↑↓	–17,09	–1,1	0,0	180,0	–10,0	4,4	–0,72	3,63
	↑↑	–15,71	–0,15	0,0	0,0	17,0	–1,24	0,15	3,36
{A}{C}	↑↓	–16,52	1,25	0,0	0,0	198,0	–1,15	0,86	3,38
	↑↑	–9,37	–0,69	0,0	0,0	0,0	0,97	–0,87	4,65
{A}{D}	↑↓	–17,55	–0,54	0,0	180,0	–2,0	2,54	–0,31	3,52

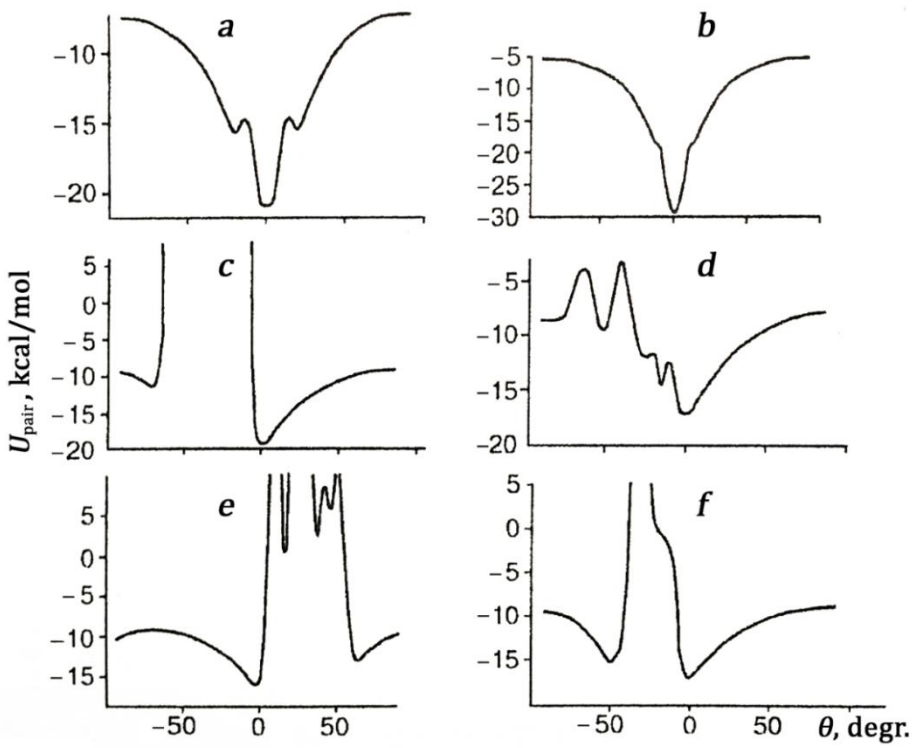

Fig. 4. Dependence of U_{pair} energy of pair interaction on θ angle between molecules` long axes: a–$\{A\}\{A\}(\uparrow\downarrow)$; b– $\{B\}\{B\}(\uparrow\downarrow)$; c– $\{C\}\{C\}(\uparrow\downarrow)$; d– $\{D\}\{D\}(\uparrow\downarrow)$; e– $\{A\}\{C\}(\uparrow\downarrow)$; f– $\{A\}\{D\}(\uparrow\downarrow)$.

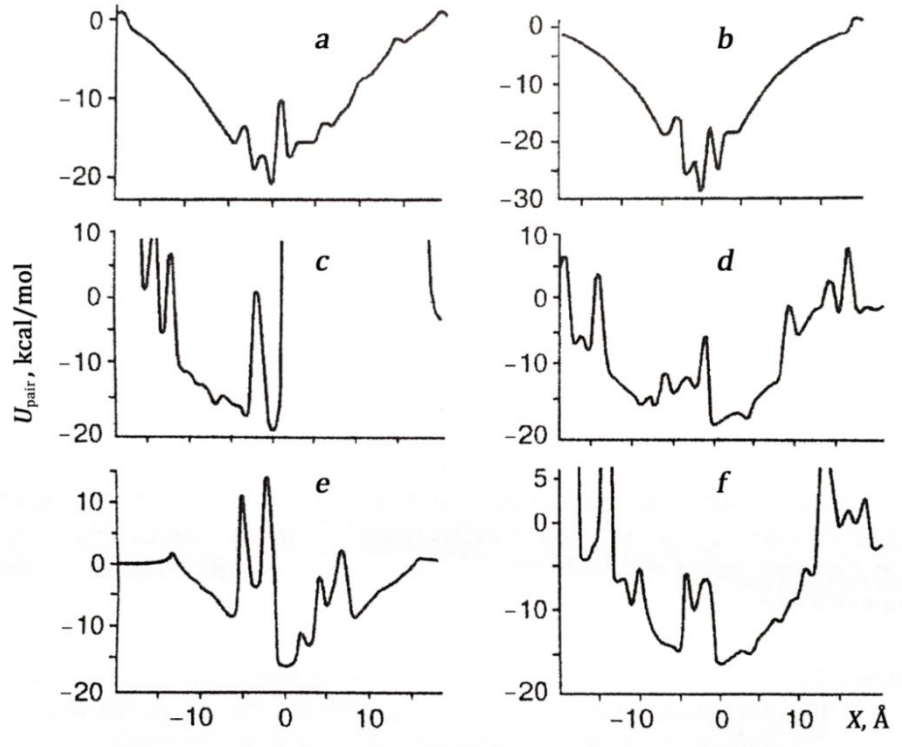

Fig. 5. Dependence of U_{pair} energy of pair interaction on displacement of molecules along the long X axes: a– $\{A\}\{A\}(\uparrow\downarrow)$; b– $\{B\}\{B\}(\uparrow\downarrow)$; c– $\{C\}\{C\}(\uparrow\downarrow)$; d– $\{D\}\{D\}(\uparrow\downarrow)$; e– $\{A\}\{C\}(\uparrow\downarrow)$; f– $\{A\}\{D\}(\uparrow\downarrow)$.

As it is apparent from the Table 1, for the {C}{C}, {D}{D} and {A}{D} the ↑↓ packing of molecules is the most favorable, which corresponds to the experimental data on local arrangement for some Sm LC. As to {A}{A} and {A}{C} interactions, both ↑↑ and ↑↓ arrangement of

molecules similarly are energetically advantageous ($\Delta U_{pair} \approx 0{,}8 kcal/mol$). It is worth mentioning, that for {A}{A**}** and {B}{B**}** interactions, the angle θ between the long axes of molecules is approximately 0°, that is – the molecules in the near order are strictly parallel. As to {C}{C}, {D}{D}, {A}{C} and {A}{D} pairs, especially for (↑↓) packing, angle θ equals $\sim 6 \div 18^{\circ}$, that is – the long axes of molecules are not strictly parallel. As to an equilibrium distance between the long axis of molecules for the cases energetically most favorable arrangement in pairs ({A}{A}, {B}{B}, {C}{C} (↑↓)), {D}{D} (↑↓), {A}{C} and {A}{D} (↑↓) – interaction), the molecules are located closer to each other ($\Delta Z = 3{,}33 \div 3{,}74$ Å), that is – they are packed more closely, than for the remaining cases ({C}{C} (↑↑), {D}{D} (↑↑) and {A}{D} (↑↑) – interaction). Existence of side groups: OH in a molecule **{**A}, and CH_3 in chiral molecules of {C} and {D} – are one of the main causes of ↑↓ stacking, which allows the molecules to come close to each other. Such a packing obviously is enhanced also by the availability of the electric dipoles: $-O-, OH, CH=N, COO$. Dipole correlation of molecules can be brought by dipole–dipole interaction as well, advancing the formation of dimers. It should be noted that dipole–dipole correlations play the essential role in formation of smectic phases mainly of dimers. It seems that this correlation determines various types of local arrangements in smectic phases. As the observations of the system`s instant structures showed, transversal dipole moments of dimers tend to be oriented in the same direction within each layer, which is very specific for ferroelectric LC [9] that leads to the appearance of a large P_s in Sm layers.

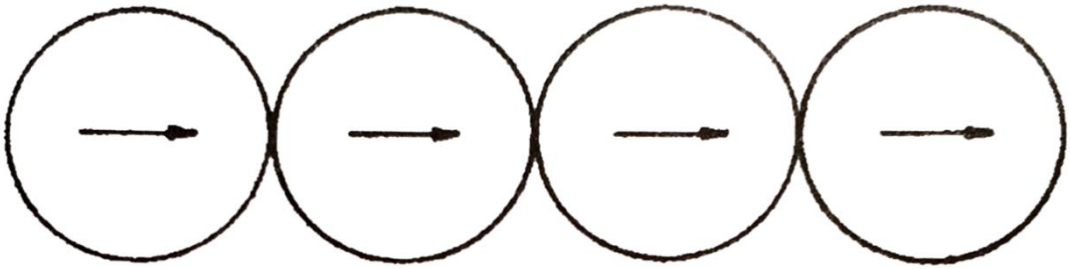

Fig. 6. Ordering of dipoles within one layer. It is shown in the projection orthogonal to the molecule`s long axes.

It is noteworthy that at the same (20%) concentrations of chiral adding {C} and {D} the value of P_s in {A}/{C} is less than the value of P_s in {A}/{D}(Fig. 2). Our calculations (Table 1) show that the presence of the COO group in the backbone of the {C} molecule leads to the fact, that the U_{pair} interaction energy in {A}{C}(↑↓) dimer ($U_{pair} = -16{,}52 kcal/mol$) is less than in {A}{D}(↑↓) dimer ($U_{pair} = -17{,}55 kcal/mol$). Consequently, the relative amount of {A}{D}(↑↑) dimers decreases compared to the amount of {A}{D}(↑↓) dimers in {A}/{D}20% LC system. Also, as already noted, due to the antiparallel stacking of molecules in dimers the anti–ferroelectric short–range order of the molecules` dipoles arises, as a result of which the transverse dipole moments are summed up. The decrease in the value of P_s in LC system with {A} matrix is explained by obtained calculation results when adding {D} is replaced by adding {C}. In LC {A}/{C} both ↑↑ and ↑↓ arrangement of molecules are similarly energetically advantageous ($\Delta U_{pair} \approx 0{,}8 kcal/mol$). This experimental fact, in its turn, leads to the decrease of relative number of mixed dimers by ↑↓ packing of molecules. The greater value of P_s in {A}/{C} LC systems in comparison with the values of P_s in {B}/{C} LC systems and no spontaneous polarization in {B}/{D} LC systems also shows the molecules` structure influence on the value of P_s. In the first case, apparently, proposed model for increasing spontaneous polarization loses its meaning, since the molecular structure of the {B} matrix does not contain a transverse polar group. As for the second case, it can be associated both with the absence of a transverse polar group in the molecule {B} and with the structure of chiral adding {D}, which does not satisfy the

obligatory conditions for the occurrence of spontaneous polarization that are imposed by theory on a molecular structure.

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