Polar order and tilt in achiral smectic phases

Damian Pociecha,[1] Ewa Gorecka,[1] Mojca Čepič,[2,3] Nataša Vaupotič,[2,4] and Wolfgang Weissflog[5]
[1]*Department of Chemistry, Warsaw University, aleya Zwirki i Wigury 101, 02-089 Warsaw, Poland*
[2]*Jozef Stefan Institute, Jamova 39, 1000 Ljubljana, Slovenia*
[3]*Faculty of Education, University of Ljubljana, Kardeljeva pl 16, 1000 Ljubljana, Slovenia*
[4]*Faculty of Education, University of Maribor, Koroška 160, 2000 Maribor, Slovenia*
[5]*Institute of Physical Chemistry, Department of Chemistry, Martin-Luther Universität Halle-Wittenberg, Halle, Germany*
(Received 21 April 2006; published 7 August 2006)

Material with the phase sequence Sm*A*-Sm*AP*-Sm*CP* is studied as an example of a system in which the spontaneous electric polarization and the molecular tilt develop independently at the Sm*A*-Sm*AP* and the Sm*AP*-Sm*CP* phase transition, respectively. The temperature dependence of the spontaneous electric polarization clearly shows a strong coupling between the polarization and tilt. The system exhibits also very strong precritical polarization and tilt fluctuations. Experimental observations are explained within the theoretical model.

DOI: 10.1103/PhysRevE.74.021702 PACS number(s): 61.30.Cz, 64.70.Md, 77.84.Nh, 77.22.Gm

I. INTRODUCTION

In the chiral smectic phases made of rodlike molecules the polarization is an improper order parameter and as such it can appear only if the phase is tilted [1]. On the other hand, in the bent-core molecular systems [2] both the polarization and the tilt are proper order parameters and they can appear in the system independently. The appearance of the spontaneous electric polarization without the molecular tilt, i.e., the phase transition from the paraelectric to the orthogonal polar phase, has already been reported in some materials [3–6]. In general, materials exhibiting such a phase transition are rare since the vast majority of the bent-core liquid crystals tend to form polar tilted phases. In Ref. [6] we reported on the critical freezing of molecular rotation, which led to polar ordering through the second order paraelectric-antiferroelectric phase transition in the achiral liquid crystal formed by the bent-core molecules. The system was studied both experimentally and theoretically.

To study the development of polarization and tilt, a material with the phase sequence: orthogonal paraelectric—orthogonal polar—tilted polar phase is needed. Any material with such a phase sequence can be considered as a model system in which the spontaneous electric polarization and the molecular tilt appear independently at the paraelectric-orthogonal polar and the orthogonal-tilted phase transition, respectively. In the present paper we report on experimental and theoretical studies of a liquid crystal formed by the bent-core molecules exhibiting the phase sequence smectic A(SmA)-smectic AP_A(SmAP_A)-smectic CP_A(SmCP_A).

II. EXPERIMENTAL RESULTS

In order to examine the polarization and tilt development in an achiral smectic phase formed by bent-core molecules, the material named **1g** in Ref. [7] with a phase sequence: Iso (142 °C) SmA (96 °C) SmAP_A (90 °C) SmCP_A has been chosen (Fig. 1). Texture observations revealed the interlayer tilt structure of the SmCP_A phase, which shows a strong memory effect. In the freshly cooled samples the ground state is synclinic, SmC_SP_A. The application of the electric field switches the sample to the ferroelectric state, however the synclinic interlayer tilt structure is preserved. The synclinic ferroelectric state transforms into the anticlinic antiferroelectric structure after the field is switched off, and even several hours later the sample does not relax completely to the initial synclinic state.

The temperature dependence of the tilt (Fig. 2) was deduced from the x-ray measurements of the smectic layer spacing. The measurements were performed with the modified DRON diffractometer (Cu $K\alpha$ line) in the reflection mode using one surface free sample. The temperature stability was controlled with the accuracy 0.1 K. The results show continuous SmAP_A-SmCP_A phase transitions with the tilt temperature dependence as $(T-T_c)^{0.4}$, where T_c is the transition temperature to the tilted phase.

The polar and optical properties of the materials were studied in 3–5 μm thick glass cells, having ITO transparent electrodes and surfactant layers for planar orientation. The cells were placed into Mettler FP82HT hot stage for temperature control with the accuracy 0.1 K.

In both polar phases, SmAP_A and SmCP_A, the switching of the electric polarization upon the reversal of the applied electric field is accompanied by the double current peak. This unambiguously confirms the antiferroelectric nature of the phases. The spontaneous polarization P_s, was determined by integrating the current peaks obtained upon the electric field reversal. It is about ~300 nC cm^{-2} in the SmAP_A phase and

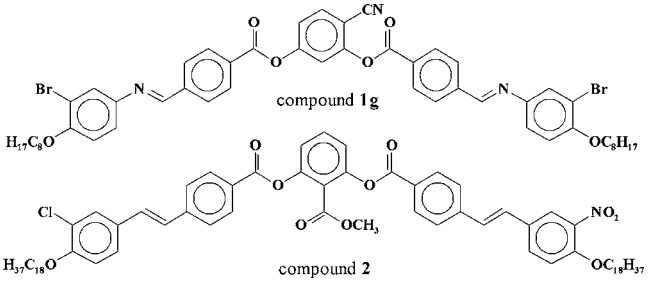

FIG. 1. Chemical formulas for the studied compounds.

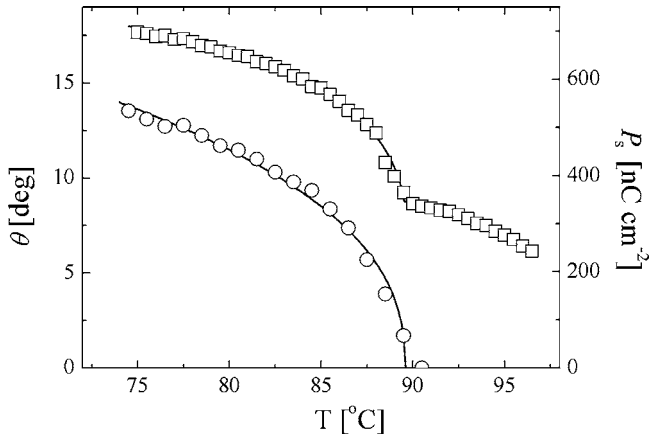

FIG. 2. Temperature dependences of the tilt angle, θ (circles), calculated from the changes of the layer spacing, $\cos(\theta)=d_{SmCP}/d_{SmAP}$ and the spontaneous electric polarization, P_s (squares) in material **1g**. The tilt dependence was fitted to the power law $(T\text{-}T_c)^{0.4}$, where T_c is the transition temperature to the SmCP phase.

it further increases at the phase transition to the tilted SmCP_A phase, following the temperature dependence of the tilt angle (Fig. 2). This shows that the spontaneous polarization and the tilt are coupled. The spontaneous polarization reaches 700 nC cm^{-2} several degrees below the SmAP_A-SmCP_A phase transition.

The dielectric studies, performed with the Solartron Impedance Analyzer SI1260, revealed a single polar relaxation process active in all phases (Fig. 3). In the SmA phase, far from the transition temperature to the SmAP_A phase the relaxation frequency of the mode decreases with decreasing temperature following the Arrhenius law. Close to the SmA -SmAP_A phase transition temperature the relaxation frequency deviates downward from the Arrhenius dependence, while the mode strength strongly increases, indicating the vicinity of the polar phase. At the SmAP_A-SmCP_A phase transition there is a slight increase of the relaxation frequency on cooling, directly below the transition to the tilted SmCP_A phase. Far from the phase transition temperature the frequency decreases again, due to the increasing rotational viscosity.

As dielectric measurements give information on the polarization fluctuations, the tilt fluctuations are studied by optical methods. The birefringence was measured with a setup based on the He-Ne laser, photoelastic modulator PEM-90, lock-in amplifier EG&G 7265 and photodiode FLCE PIN20, for the light propagating along the normal to the cell surface. The birefringence behaves nonmonotonically in the SmA phase (Fig. 4). At first it increases with decreasing temperature, while close to the transition to the polar SmAP_A phase the birefringence decreases. The decrease is even more pronounced within the SmAP_A phase temperature region. In the tilted SmC_SP_A phase the sharp increase of the birefringence on cooling is observed. In order to associate the temperature dependence of the birefringence with the softening of fluctuations of the polarization or the tilt, we measured the birefringence in the material **2** (Fig. 1) exhibiting a simple phase sequence: SmA-SmAP_A with a continuous phase transition

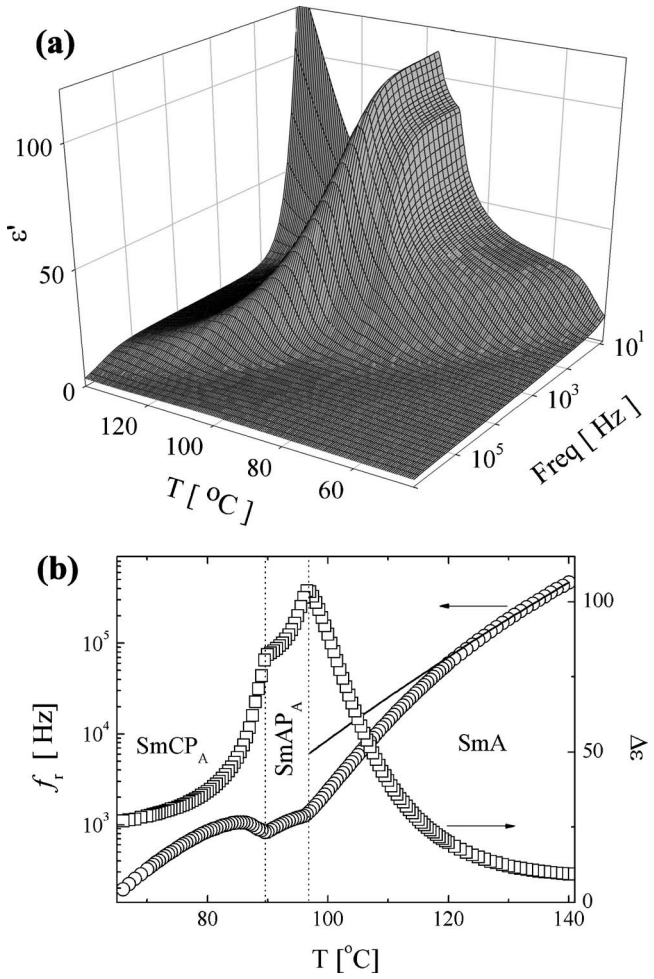

FIG. 3. (a) Three-dimensional temperature-frequency plot of the real part of the dielectric constant for compound **1g**. (b) The relaxation frequency f_r (circles) and the dielectric strength (squares) $\Delta\varepsilon$ of the mode vs temperature obtained by fitting the dielectric dispersion data at each temperature to the Cole-Cole formula. The solid line is the frequency calculated from the Arrhenius dependence, determined from the data taken above 125 °C and extrapolated to lower temperatures.

between the two phases [6]. In such a material critical behavior of the tilt fluctuations is not expected. In the compound **2** the birefringence increases in the SmA phase toward the phase transition to the polar SmAP_A phase and the later stabilizes at $\Delta n \approx 0.08$ (Fig. 4). Therefore the decrease of the birefringence observed for the compound **1g** in the SmA and the SmAP_A phases can be undoubtedly associated with the collective tilt fluctuations which increase toward the transition to the SmC_SP_A phase. The sharp increase of the birefringence in the tilted phase therefore appears due to the suppression of the tilt amplitude fluctuations in the tilted phase, similarly as it is observed in the chiral antiferroelectric liquid crystals [8,9].

III. THEORY AND COMPARISON WITH EXPERIMENTS

It is interesting to look closely at how the order develops at subsequent phase transitions. We expect that

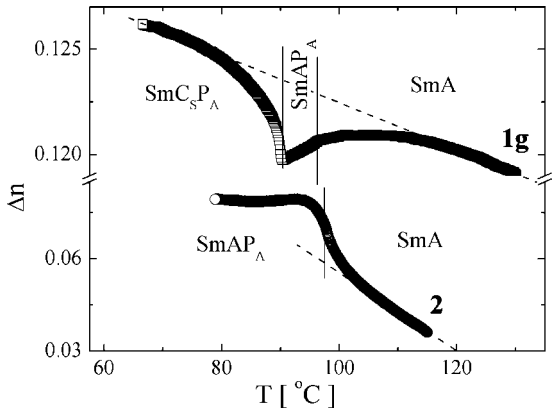

FIG. 4. Temperature dependence of the optical birefringence in compounds **1g** (square) and **2** (circles). The dashed lines show a noncritical background of the birefringence. Solid vertical lines indicate the phase transition temperatures. The birefringence values measured in the SmC_SP_A phase have a systematic error, which depends on the tilt angle as $(1\text{-}\theta^2)$ due to the formation of two types of synclinic domains. The error does not exceed 10% for the tilt angles below 15°, which is the maximum observed for the SmC_SP_A phase.

the condensation of the polar order should be signified by the freezing of molecular rotation around the long axis [6], while the vicinity of the tilted polar phase should be signified by collective tilting of molecules from the layer normal. The theoretical analysis of an achiral system should consider both the polarization and the tilt as proper order parameters, the coupling between them should be included, which is suggested by the experimental finding related to the temperature dependence of the spontaneous polarization. Thus the free energy, which allows for the observed SmA-SmAP_A-SmC_SP_A phase sequence is

$$G = \sum_j \tfrac{1}{2}a_{0P}P_j^2 + \tfrac{1}{4}b_{0P}P_j^4 + \tfrac{1}{2}c_{0P}P_j^6 + \tfrac{1}{2}a_{0t}\xi_j^2 + \tfrac{1}{4}b_{0t}\xi_j^4 + \tfrac{1}{2}\Omega(\vec{\xi}_j \times \vec{P}_j)_z^2 + \tfrac{1}{2}a_{1P}(\vec{P}_j \cdot \vec{P}_{j+1}) + \tfrac{1}{2}a_{1t}(\vec{\xi}_j \cdot \vec{\xi}_{j+1}) - \vec{E} \cdot \vec{P}_j \quad (1)$$

The first three terms describe the steric and van der Waals interactions that lead to the ordering of the molecular dipoles. The next two terms describe the steric and van der Waals interactions expressed in the tilt that lead to a tilted phase. In general, both coefficients $a_{0P}=a_P(T-T_{0P})$ and $a_{0t}=a_t(T-T_{0t})$ are temperature dependent. The parameter T_{0P} is the temperature at which the polarization appears in an isolated nontilted layer and the parameter T_{0t} is the temperature, at which an isolated nonpolar layer becomes tilted. The relation between these two temperatures defines the observed phase sequence, SmA-SmAP-SmCP [7] for $T_{0P}>T_{0t}$ or SmA-SmC-SmCP [7,10,11] for $T_{0P}<T_{0t}$. The system studied here can be modeled by the first condition $T_{0P}>T_{0t}$. The negative parameter Ω in the coupling term describes the favorable perpendicular direction of the tilt with respect to the polarization. The tilt direction is doubly degenerated; the tilt and the polarization cross product can be either negative or positive. The details of the interlayer phase structure, synclinic, or anticlinic tilt order and ferroelectric or antiferroelectric polar order, are described by the appropriate signs of the model coefficients a_{1t} and a_{1P}, respectively. In the studied material the orientation of tilts in the neighboring layers in the ground state is synclinic, so $a_{1t}<0$. The orientation of polarizations in the neighboring layers is antiferroelectric, therefore $a_{1P}>0$.

Using the ansatz for the synclinic and antiferroelectric SmC_SP_A phase

$$\vec{P}_{2j} = P\{1,0,0\}; \quad \vec{P}_{2j+1} = P\{-1,0,0\};$$

$$\vec{\xi}_{2j} = \theta\{0,\pm 1,0\}; \quad \vec{\xi}_{2j+1} = \theta\{0,\pm 1,0\}; \quad (2)$$

where the ± sign stands for the two oppositely tilted synclinic domains; the free energy is minimized with respect to P and θ. The result is a set of two coupled nonlinear equations. At high enough temperature the only solution is $P=0$ and $\theta=0$, which is characteristic of the paraelectric orthogonal SmA phase. At temperatures lower than $T_{0P}+a_{1P}/a_P$ the polar phase is stable and one gets two possible solutions of the coupled set of equations:

$$P^2 = \frac{1}{2}\frac{-b_{0P}+\sqrt{b_{0P}^2-4c_{0P}(a_{0P}-a_{1P})}}{c_{0P}} \quad \text{and} \quad \theta^2 = 0 \quad \text{if} \quad (3a)$$

$$a_{0t}+|a_{1t}|-|\Omega|P^2>0$$

and

$$P^2 = \frac{1}{2}\frac{-b_{0P}+\sqrt{b_{0P}^2-4c_{0P}(a_{0P}-a_{1P}+\Omega\theta^2)}}{c_{0P}} \quad \text{and} \quad (3b)$$

$$\theta^2 = \frac{a_{0t}+|a_{1t}|+\Omega P^2}{b_{0t}} \quad \text{if } a_{0t}+|a_{1t}|-|\Omega|P^2<0.$$

The solution (3a) describes temperature dependence of the polarization in the SmAP_A phase, while the solution (3b) describes the temperature dependence of the polarization and the tilt in the SmC_SP_A phase. It should be noted that the coupling between the tilt and the polarization additionally favors polar order if the tilt is already present, which is consistent with the increase of the polarization below the transition temperature to the tilted SmC_SP_A phase.

One can argue, that the same phase sequence, SmA-SmAP_A-SmC_SP_A can be modeled with the parameter a_{0t} independent of temperature. The tilt order is then driven by the Ω coupling term if the polarization exceeds a critical value. As the majority of banana phases are characterized by a rather high spontaneous electric polarization, which probably in most cases exceeds the critical value, it explains why the orthogonal polar phases are rare. In the case of the studied system the continuous transition from the SmA to the SmAP_A phase ensures the temperature region where the condition given in (3a) is fulfilled.

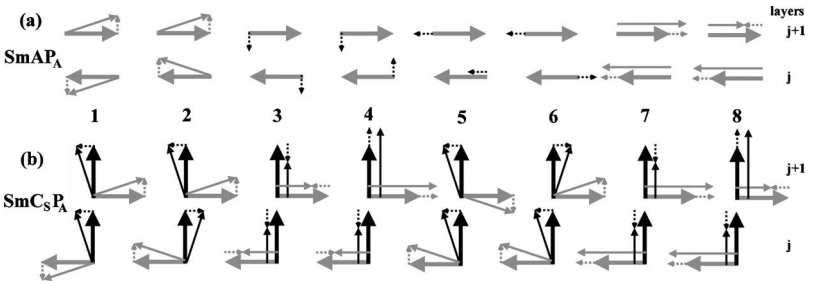

FIG. 5. Schematic drawing of the eigenmodes present in the SmAP_A and SmC_SP_A phases. Gray arrows show the polarization vectors and black arrows—the tilt vectors in the neighboring smectic layers, j and $j+1$. Thick arrows represent the ground state vectors, dotted arrows—the fluctuation vectors while thin arrows—the resulting instantaneous vectors.

From the presented model the dependence of the tilt on the temperature in the SmC_SP_A phase is described by a critical exponent close to 0.25, if the effect of the tilt coupling to the polarization is prevailing. If the tilt appears mostly due to the temperature dependence of the a_{0t} coefficient, the critical exponent should be close to 0.5. The experimental observations show that in the studied system the critical exponent is somewhere in between, indicating that both processes are relevant.

The described system has rather complex dynamics. Symmetry considerations require four collective modes related to the order parameters fluctuations in the SmA phase and eight collective modes in the SmAP_A and SmC_SP_A phases. To account for the mode frequencies and the type of collective fluctuations associated with them, the standard procedure [12] is used. The instantaneous order parameters in the jth smectic layer are expressed as

$$\vec{P}_j = P_{j0}\vec{e}_{jP\parallel} + \delta P_{j\parallel}\vec{e}_{jP\parallel} + \delta P_{j\perp}\vec{e}_{jP\perp},$$

$$\vec{\xi}_j = \xi_{j0}\vec{e}_{j\xi\parallel} + \delta\xi_{j\parallel}\vec{e}_{j\xi\parallel} + \delta\xi_{j\perp}\vec{e}_{j\xi\perp}, \tag{4}$$

where unit vectors $\vec{e}_{jP\parallel}, \vec{e}_{jP\perp}, \vec{e}_{j\xi\parallel}, \vec{e}_{j\xi\perp}$ are oriented parallel or perpendicular to the local order parameters. The $\delta P_{j\parallel}$, $\delta\xi_{j\parallel}$ give the amplitude fluctuations of the polarization and the tilt order parameters, respectively, while the phase fluctuations of both order parameters are given by $\delta P_{j\perp}$, $\delta\xi_{j\perp}$. The fluctuating order parameters given in Eq. (4) are inserted in the free energy [Eq. (1)], which is developed up to the second order terms around the equilibrium values of P and θ. Defining the fluctuation vector η as

$$\eta = \{\delta P_{1\parallel}, \delta P_{2\parallel}, \delta P_{1\perp}, \delta P_{2\perp}, \delta\xi_{1\parallel}, \delta\xi_{2\parallel}, \delta\xi_{1\perp}, \delta\xi_{2\perp}\} \tag{5}$$

in which the two layer periodic structure of the SmC_SP_A system is taken into account, the part of the free energy that appears due to the fluctuations can be written as

$$\partial^2 G = \tfrac{1}{2}\eta \cdot \underline{G_2} \cdot \eta, \tag{6}$$

where

$$G_2 = \begin{bmatrix} A & E & 0 & 0 & G & 0 & 0 & 0 \\ E & A & 0 & 0 & 0 & G & 0 & 0 \\ 0 & 0 & B & E & 0 & 0 & H & 0 \\ 0 & 0 & E & B & 0 & 0 & 0 & H \\ G & 0 & 0 & 0 & C & F & 0 & 0 \\ 0 & G & 0 & 0 & F & C & 0 & 0 \\ 0 & 0 & H & 0 & 0 & 0 & D & F \\ 0 & 0 & 0 & H & 0 & 0 & F & D \end{bmatrix} \tag{7a}$$

with the matrix elements

$$A = a_{0P} + 3b_{0P}P^2 + 5c_{0P}P^4,$$

$$B = a_{0P} + b_{0P}P^2 + c_{0P}P^4,$$

$$C = a_{0t} + 3b_{0t}\theta^2,$$

$$D = a_{0t} + b_{0t}\theta^2,$$

$$E = a_{1P},$$

$$F = a_{1t},$$

$$G = 2\Omega P\theta,$$

$$H = \Omega P\theta. \tag{7b}$$

The eigenvalues of the matrix G_2 give, after rescaling with the appropriate viscosity coefficients, the frequencies of the modes and the corresponding eigenvectors give the information about the type of collective movements and the polarity of the modes.

In the SmA phase two tilt fluctuation modes exist: synclinic (instantaneous tilt direction is the same in the neighboring layers) and anticlinic (instantaneous tilt direction is opposite in the neighboring layers), as well as two polarization fluctuation modes: ferroelectric (instantaneous polarization direction is the same in the neighboring layers) and antiferroelectric (instantaneous polarization direction is opposite in the neighboring layers). Only the ferroelectric polarization fluctuations, i.e., the condensation of the ferroelectric mode, can contribute to the dielectric response. Indeed in the SmA phase the single relaxation process is observed that, on approaching the SmA-SmAP_A phase transition, shows collective behavior, as evidenced by the softening of the dielectric response—the relaxation frequency decreases more rapidly than predicted by the

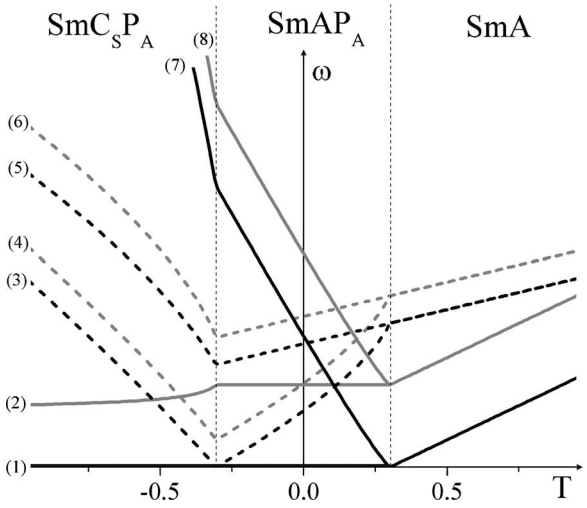

FIG. 6. Theoretical temperature dependence of the eigenmode frequencies. The coefficient values, expressed in units of $a_P=a_t$, used for calculations are $a_{0t}=a_{0P}+1.9$, $b_{0P}=50$, $c_{0P}=600$, $a_{1P}=0.3$, $b_{0P}=100$, $a_{1t}=-0.2$, and $\Omega=-70$. The eigenmode numbers (1)–(8) correspond to the numbers used in Fig. 5.

Arrhenius dependence [13], while the amplitude of the response quickly increases on cooling (Fig. 3). In the SmAP_A phase the degeneracy of the polarization modes is lifted, each of the polarization modes breaks into a phason and an amplitudon. The polarization fluctuation vectors (given by the difference between the instantaneous and the ground state vectors) can be in the opposite direction in the neighboring layers, [phason 1(a) and amplitudon 7(a) in Fig. 5] or in the same direction [phason 2(a) and amplitudon 8(a) in Fig. 5]. The degeneracy is lifted not only for the polarization modes; the fluctuations of the tilt parallel [modes 5(a) and 6(a) in Fig. 5] or perpendicular [modes 3(a) and 4(a) in Fig. 5] to the polarization also have different energies. Thus, four different tilt modes exist in the SmAP_A phase. Out of 8 polarization and tilt modes there are two polar modes, 2a and 8a. In the SmC_SP_A phase all the polarization and the tilt changes become coupled, however, in the considered model modes are still exclusively phasons or amplitudons. Two out of four phason modes preserve the tilt being perpendicular to the polarization direction, as they involve the molecular rotation on the tilt cone only [modes 1(b) and 2(b) in Fig. 5]. The other two involve also the molecular rotation around the long molecular axis, leading to the instantaneous tilt being oblique to the polarization direction [modes 5(b) and 6(b) in Fig. 5]. Amplitudons involve either simultaneous increase (decrease) of the tilt and the polarization magnitude in the layer [modes 3(b) and 4(b) in Fig. 5] or increase (decrease) of the tilt but decrease (increase) of the polarization in the layer [modes 7(b) and 8(b) in Fig. 5]. In the SmC_SP_A there are four polar modes—2(b), 4(b), 6(b) and 8(b).

Temperature dependence of the mode frequencies, for the system showing the SmA-SmAP_A-SmC_SP_A phase sequence, is given in Fig. 6. For such a system, at the SmA-SmAP_A phase transition, the antiferroelectric polarization mode condenses faster than the ferroelectric one, leading to the antiferroelectric structure of the SmAP_A phase. In the SmAP_A phase the system becomes soft with respect to tilt fluctuations. The synclinic tilt mode 3a condenses faster than the anticlinic mode 4a, therefore the synclinic structure of the tilted smectic phase SmC_SP_A develops.

In the SmAP_A phase the main contribution to the dielectric response comes from the phason 2a. The same type of fluctuations governs the dielectric response of the SmC_SP_A phase, however, in this phase the fluctuations of polarization are coupled to the tilt angle fluctuations (mode 2b). Since it is experimentally observed that the strength of this mode in the SmC_SP_A is considerably lower than in the SmAP_A phase, it could thus be concluded that the distortion of the antiparallel orientation of polarizations in the consecutive layers is now more difficult, as a simultaneous change of the azimuthal tilt angle breaks the thermodynamically stable synclinic tilt arrangement. In the SmC_SP_A phase also another polar mode, 6b, having a critical temperature dependence, contributes to the experimental dielectric response close to the SmAP_A-SmC_SP_A phase transition temperature. As a result the relaxation frequency has a minimum at the SmAP_A-SmC_SP_A phase transition temperature that indicates softening of the polar fluctuations at this transition.

While the polar fluctuations can be studied by the dielectric spectroscopy, the tilt fluctuations related to the orientational order of molecules can be observed by optical methods [8,9,14]. The SmA phase is optically uniaxial with the refractive indices in the directions perpendicular to the long molecular axis averaged due to the free molecular rotation. The SmAP_A phase, although biaxial in general, can be considered as pseudouniaxial in the studied sample geometry. This is due to the polarization splay, which appears in the sample [15]: molecules at the glass plates are oriented with the polarization vector perpendicular to the glass plates, while in the bulk the polarization is parallel to the glass plane. The splay causes an averaging between the two refractive indices in the directions perpendicular to the long molecular axis, similarly as in the SmA phase. Thus in the studied samples, the temperature variation of the birefringence at the SmA-SmAP_A phase transition reflects mainly the change in the order of the long molecular axis; the increasing (decreasing) tilt fluctuations would decrease (increase) the refractive index in the direction along the layer normal and increase (decrease) the averaged refractive index in the direction perpendicular to the layer normal. As a result the overall birefringence of the sample decreases if the tilt fluctuations grow. In the SmA phase far from the transition to the tilted phase, the birefringence increases with decreasing temperature as the orientational order of the long molecular axis in the layers increases. In the material **2** where the tilted phase is not observed, the birefringence further steeply increases at the transition to SmAP_A phase. This increase seems to be due to the sharp increase of the orientational order of the long molecular axes induced by the appearance of the polar order (Fig. 4). Contrary, in the studied compound **1g**, which exhibits the tilted SmC_SP_A phase below the orthogonal phases, the nonmonotonic temperature dependence of the birefringence is observed. The reason is in the strong tilt fluctuations. In the SmA phase the instantaneous tilt, $\delta\theta$, may appear in any direction around the layer normal, lowering the birefringence as $\Delta n(T)=\Delta n_0(T)\left(1-\frac{3}{2}\langle(\delta\theta)^2\rangle\right)$, where $\Delta n_0(T)$ is the noncritical background of the birefringence

and could be extrapolated from the data obtained far above the Sm*A*-SmAP_A phase transition temperature. In the SmAP_A phase the tilt fluctuation in the direction perpendicular to the polarization are favorable and thus $\Delta n(T)=\Delta n_0(T)-\frac{3}{2}\Delta n_{\max}\langle(\delta\theta)^2\rangle$, where $\Delta n_{\max}$ is the difference between refractive indices in the direction along the long molecular axis and perpendicular to the banana plane for ideally ordered molecules. The $\Delta n_{\max}$ value can be roughly estimated from the birefringence obtained in the sample subjected to the electric field. The birefringence $\Delta n(T)$ starts to decrease already in the Sm*A* phase—due to the growing tilt fluctuations it deviates downward from the $\Delta n_0(T)$. The decrease in birefringence is even more pronounced in the SmAP_A phase, indicating that the appearance of the polar order further promotes the tilt fluctuations. This is in agreement with the predicted softening of the tilt modes 3a, 4a in the SmAP_A phase. The exact analysis of the fluctuations is difficult, as their calculated magnitudes depend on the chosen background $\Delta n_0(T)$ and the $\Delta n_{\max}$ value, however it could be estimated that the pretransitional fluctuations in the Sm*A* and the SmAP_A phases involve the average change of $\sqrt{\langle(\delta\theta)^2\rangle}$ as high as 6° and 8°, respectively, which is a rather high value compared to the tilt angle observed in the SmC_SP_A phase (up to 15°). The $\Delta n(T)$ has its minimum at the SmAP_A-SmC_SP_A phase transition and sharply increases on cooling in the tilted phase, as the amplitudon tilt fluctuations, responsible for lowering $\Delta n(T)$, are pronounced only close to the orthogonal-tilted phase transition temperature.

IV. SUMMARY

The bent-core molecular system in which the polarization and the tilt, both being proper order parameters, appear at two subsequent phase transitions Sm*A*-SmAP_A and SmAP_A-SmC_SP_A, was studied. Experimental observations were explained within the scope of the discrete phenomenological theoretical model. The theoretical considerations show that the SmAP_A-SmC_SP_A phase transition can result from the temperature dependence of the Landau coefficient a_{0t} or it can be induced solely due to the strong coupling of the tilt and the polarization. In both cases the polarization in the tilted phase increases following the tilt angle temperature dependence, which is consistent with the experimental results. The system exhibits strong critical fluctuations of the polarization and the tilt. In the Sm*A* phase the polar fluctuations show a softening in the vicinity of the SmAP_A phase, that appears due to the critical slowing down of the molecular rotation around the long molecular axis. In the SmAP_A phase the main contribution to the polar mode comes from the collective rotation of polarization vectors in the consecutive layers. In the SmC_SP_A phase the motions of the polarization vectors become coupled to the tilt fluctuations and as a result the dielectric response decreases. The tilt fluctuations were deduced from the pretransitional behavior of the optical birefringence. In materials where the tilted phase is absent the birefringence increases at the Sm*A*-SmAP_A phase transition, as the polar order apparently favors a stronger orientational order of the molecular long axis. In the material with the tilted phase below the orthogonal one, Δn has pronounced pretransitional decrease as the tilt fluctuation disturbs the orientational order of the long molecular axes, which is in agreement with theoretical consideration.

ACKNOWLEDGMENTS

This work was supported by the KBN Grant No. 4T09A 00425. The theoretical part of the work was done within the Program No. P1-0055 financed by the MVZT, Slovenia.

[1] R. Meyer, L. Liebert, and P. Keller, J. Phys. (France) Lett. **36**, L69 (1975).
[2] H. Takezoe and Y. Takanishi, Jpn. J. Appl. Phys., Part 1 **45**, 597 (2006).
[3] A. Eremin, S. Diele, G. Pelzl, H. Nádasi, W. Weissflog, J. Salfetnikova, and H. Kresse, Phys. Rev. E **64**, 051707 (2001).
[4] R. A. Reddy and B. K. Sadashiva, J. Mater. Chem. **14**, 310 (2004).
[5] L. Kovalenko, M. W. Schroder, R. A. Reddy, S. Diele, G. Pelzl, and W. Weissflog, Liq. Cryst. **32**, 857 (2005).
[6] D. Pociecha, E. Gorecka, M. Cepic, N. Vaupotic, K. Gomola, and J. Mieczkowski, Phys. Rev. E **72**, 060701(R) (2005).
[7] U. Dunemann, M. W. Schroder, R. A. Reddy, G. Pelzl, S. Diele, and W. Weissflog, J. Mater. Chem. **15**, 4051 (2005).
[8] M. Skarabot, K. Kocevar, R. Blinc, G. Heppke, and I. Musevic, Phys. Rev. E **59**, R1323 (1999).
[9] M. Skarabot, M. Cepic, B. Zeks, R. Blinc, G. Heppke, A. V. Kityk, and I. Musevic, Phys. Rev. E **58**, 575 (1998).
[10] A. Eremin, H. Nadasi, G. Pelzl, S. Diele, H. Kresse, W. Weissflog, and S. Grande, Phys. Chem. Chem. Phys. **6**, 1290 (2004).
[11] I. Wirth, S. Diele, A. Eremin, G. Pelzl, S. Grande, L. Kovalenko, N. Pancenko, and W. Weissflog, J. Mater. Chem. **11**, 1642 (2001).
[12] I. Muševič, R. Blinc, and B. Žekš, *The Physics of Ferroelectric and Antiferroelectric Liquid Crystals* (World Scientific, Singapore, 2000).
[13] M. E. Line and M. Glass, *Principle and Applications of Ferroelectric and Related Materials* (Oxford University Press, Oxford, 2001).
[14] K. C. Lim and J. T. Ho, Phys. Rev. Lett. **40**, 1576 (1978).
[15] F. Araoka, H. Hoshi, and H. Takezoe, Phys. Rev. E **69**, 051704 (2004).