# **Quasicritical behavior of dielectric permittivity in the isotropic phase of smectogenic** *n***-cyanobiphenyls**

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Results are presented of temperature and pressure studies of static dielectric permittivity  $(\varepsilon)$  and the nonlinear dielectric effect (NDE) in the isotropic phase of smectogenic *n*-cyanobiphenyls: 9CB, 10CB, and 12CB  $(4-cyano-4'-n-alkylbipheny, n=9, 10, and 12)$ . For the mentioned properties, pretransitional effects can be well portrayed by applying the relations used for the isotropic phase of nematogens, where evidence of the quasicritical, fluidlike behavior with exponents  $\alpha \approx 0.5$  and  $\gamma = 1$  exists. This kind of behavior one can also observe on approaching the isotropic–smectic A transition. NDE studies in 10CB and 12CB made it possible to determine the pressure evolution of the discontinuity  $(\Delta T)$  of the *I*-Sm *A* transition. It was found that pressure first decreases the discontinuity of the transition, and that next a gradual rise appears. This behavior is unlike the one observed for the isotropic-nematic transition, where only an increase of  $\Delta T$  with rising pressure was observed.

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# **INTRODUCTION**

Pretransitional behavior in the isotropic phase of smectogenic compounds is still an almost unknown area. In monographs this item was simply omitted, unlike the pretransitional effects in the isotropic phase  $(I)$  of nematogens  $\lceil 1-5 \rceil$ . The latter can be associated with the success of the meanfield (MF) Landau–de Gennes (LdG) model  $|1|$  in describing pretransitional anomalies of susceptibility-related properties, e.g., light scattering  $(I_L)$ , the Kerr effect (KE), the Cotton-Mouton effect (CME), and turbidity  $(\tau_L)$  [1–7]:

$$
\mathcal{E}_{\text{KE}}^{-1}, \mathcal{E}_{\text{CME}}^{-1}, \mathcal{E}_{\tau_L}^{-1}, \mathcal{E}_{\tau_L}^{-1} \propto \chi^{-1} = A_{\varepsilon}^{-1} (T - T^*)^{\gamma},
$$
  
with  $\gamma = 1$ , for  $T > T_{I-N} = T^* + \Delta T$ , (1)

where  $\mathcal{E}_{KE}$ ,  $\mathcal{E}_{I_L}$ ,  $\mathcal{E}_{CME}$ , and  $\mathcal{E}_{\tau_L}$  are experimental measures of KE,  $I_L$ , CME, and  $\tau_L$ , respectively.  $A_{\varepsilon}$  denotes the pretransitional amplitude, appropriate for a given physical property.  $T_{I-N}$  is the nematic (*N*) clearing temperature,  $T^*$  is the extrapolated temperature of a hypothetical (virtual) continuous phase transition, and  $\Delta T$  is the measure of the discontinuity of the transition.

Relation  $(1)$  made it possible to estimate experimentally the value of parameter  $\Delta T$ =0.7–2 K [1–17]. Such a small value of  $\Delta T$  is the result of the weakly discontinuous character of the *I*-*N* transition. This constituted the main point of disagreement with the theoretical, MF based models which gave a much higher value  $\Delta T = 27-7$  K [1,18–20]. Recently Mukherjee and co-workers  $[21–23]$  obtained an agreement with experiment, assuming fluidlike, critical description of the *I*-*N* transition. In this model the nematic clearing point is located on the branch of a hypothetical binodal curve.

In smectogens the linear temperature dependence predicted by relation  $(1)$  is observed only remotely from the clearing point, whereas in its fairly broad vicinity  $\mathcal{E}_{KE}^{-1}$ ,  $\mathcal{E}_{CME}^{-1}$ ,  $\mathcal{E}_{I_L}^{-1}$ , etc bend strongly up or down, or remain constant [6,8– 12,24]. This behavior was observed both for the isotropic– smectic *A*(*I*-Sm *A*) transition and for the *I*-*N* transition in smectogens with a narrow nematic "gap" between the isotropic and smectic phase. However, recently application of the low-frequency (static) nonlinear dielectric effect (LF NDE) showed that  $[25–28]$ :

$$
\mathcal{E}_{\text{NDE}}^{-1} \propto A_{\text{NDE}}^{-1} (T - T^*)^{\gamma} = \frac{2}{3a} \varepsilon_0 \frac{(\Delta \varepsilon^0)^2}{T - T^*}
$$
  
for  $f^{-1} \gg \tau$ ,  $T > T_C$  and  $\gamma = 1$ , (2)

where  $\mathcal{E}_{NDE} = (\varepsilon^{E} - \varepsilon)/E^{2}$  is the measure of the NDE,  $\varepsilon$  and  $\varepsilon^E$  are dielectric permittivities in a weak and strong electric field  $E$ , respectively, and  $A_{NDE}$  is the pretransitional amplitude,  $\Delta \varepsilon^0$  is the molecular anisotropy of dielectric permittivity in the zero-frequency limit, and *a* is the amplitude of the second rank term in the LdG series which may be associated with the amplitude of susceptibility.  $T_c$  is the clearing temperature, *f* is the frequency of the weak measuring field, and  $\tau$  is the relaxation time of collective pretransitional processes.

Particularly noteworthy is the fact that Eq.  $(2)$  remains valid up to about  $T_C + 40$  K both for the *I*-*N* and *I*-Sm *A* transitions, with no distortions in the immediate vicinity of  $T_c$  and without an additional, "nonpretransitional" background term. In a series of smectogenic *n*-cyanobiphenyls, a systematic increase from  $\Delta T \approx 1.7$  K (8CB) to 6.5 K (12CB) was observed  $[25]$ . These results are in a good agreement with a recent preliminary considerations on a fluidlike description applied to the LdG model for the *I*-Sm *A* transition in Ref. [29]. These authors obtained a single term singularity, with the exponent  $\gamma=1$ , and theoretically estimated the discontinuity of the transition in 12CB:  $\Delta T \approx 6.78$  K, in good agreement with the experimental value given above.

In earlier considerations for smectogenic compounds, the application of the perturbation theory to the LdG model by

taking into account the coupling between the orientational (nematic) and positional (smectic) ordering in pretransitional fluctuations gave  $[6,30,31]$ 

$$
\chi^{-1} = C^{-1}t - \frac{B_1^2}{(t - \Delta_0)^{3/2}} + \frac{B_2}{(t + \Delta_0)^{1/2}},
$$
 (3)

where  $t=(T-T_{I-N}^*)/T_{I-N}^*$ ,  $\Delta_0=(T_{IN}^*-T_{I-SmA}^*)/T_{I-SmA}^*$ ,  $T_{I-N}^*$ , and  $T_{I-SmA}^*$  are the bare temperatures, i.e., in the absence of orientational or translational ordering, of hypothetical continuous phase transitions.  $C$ ,  $B_1$ , and  $B_2$  denote amplitudes. In nematogens only the first term should be present.

Both in nematogens and smectogens an additional, nonsingular background term is expected. Relation  $(3)$  was successfully applied only in  $I_L$  studies where distortions from relation  $(1)$  are relatively small and similar to those observed in nematogens where  $\mathcal{E}_{I_L}^{-1}$  slightly bends down from the linear dependence on approaching  $T_{I-N}$ [6].

Another way of empirical quantitative analysis in smectogens is the application of relation  $(1)$  but with the adjustable exponent  $\gamma$ . For the *I*-Sm *A* transition,  $\gamma = 0.8 - 0.4$  was obtained  $[6,32]$ . It is noteworthy that the MF approximation gives  $\gamma=1$  [relation (1)], and predicts no pretransitional anomaly in the high temperature phase for properties such as density  $(\rho)$  or specific heat  $(c_p)$  [6]. However, in nematogens pretransitional anomalies of  $\rho(T)$  [33,34] and  $c_p(T)$  [6,35] were observed. For the latter,

$$
c_p(T) = A(T - T^*)^{-\alpha} + A_1 + A_2(T - T^*) + A_3(T - T^*)^2,
$$
\n(4)

where  $A$  is the critical amplitude,  $A_i$  are amplitudes of the "background" term, and  $\alpha$  is the exponent of the specific heat.

Despite the minute scale of the anomaly and the limited range of its appearance  $(T - T_{I-N} < 4 K)$  the estimate of  $\alpha$  $= 0.5-0.3$  was found to be reliable [35]. The eventual validity of  $\alpha=0.5$  may point to the tricritical or Gaussian [6,36] nature of the *I*-*N* transition. In the case of the lower value it was treated as the result of the effective exponent caused by the crossover between  $\alpha$ =0.5 and  $\alpha \approx 0.11$ . The latter value appears in the three-dimensional Ising universality class, to which critical solutions belong  $[6,36]$ . For smectogens the perturbation theory predicts an additional term  $[6,37]$ 

$$
\delta c_p \propto (t + \Delta_0)^{-3/2}.\tag{5}
$$

There are reference data of the appearance of the pretransitional anomaly for properties associated with exponent  $\alpha$  in smectogens  $\vert 6 \vert$ . However, the experimentally observed divergence on approaching the smectic clearing point is much lower than in nematogens. Hence it seems impossible to reach a conclusive fitting of experimental data  $[6]$ . This can be related to the greater discontinuity of the *I*-Sm *A* than of *I*-*N* transition. Regarding the parametrization of pretransitional anomalies in smectogens, there is a clear trend to increase the number of fitted parameters in comparison with nematogens. This feature additionally increases the uncertainty of the eventual fitting of experimental data in smectogens.

Almost two decades ago Bradshaw and Raynes [38] and Thoen and Menu [39] suggested that a strong bending down of the static dielectric permittivity on approaching the nematic clearing point may be associated with the pretransitional, critical-like effect. However, this method of analysis has hardly been explored since then (see Refs.  $[3]$ ,  $[4]$ ,  $[40]$  and references therein). Only recently it was shown that in nematogenic *n*-cyabiphenyls (*n* CB), relations analogous to those applied in the homogeneous phase of critical solutions  $[41-44]$  made it possible to parametrize the behavior of dielectric permittivity even remote from the clearing point  $[26-28]$ :

$$
\varepsilon = \varepsilon^* + b^T (T - T^*) + B^T (T - T^*)^{1 - \alpha}, \quad P = \text{const}, \tag{6a}
$$

$$
\varepsilon = \varepsilon^* + b^p \times (P^* - P) + B^P \times (P^* - P)^{1 - \alpha}, \quad T = \text{const},\tag{6b}
$$

where  $(T^*, P^*)$  and  $(P_C, T_C)$  are the coordinates of the virtual continuous phase transition point, and the coordinates of the discontinuous transition at the nematic clearing point,  $b<sup>T</sup>$ , *bP*, *BT*, and *BP*, denote amplitudes.

It was shown that relation  $(6a)$  can portray well the experimental data even up to  $T_{I-N}$ +100 K with the exponent  $\alpha$ =0.5±0.02. In one of the first attempts at a quantitative analysis of the anomaly of the static dielectric permittivity in critical, binary Mistura  $[45]$  pointed out that the derivative of the permittivity should be directly proportional to the anomaly of the specific heat. To the best of the authors knowledge, there is no experimental test of this possibility in critical mixtures. However, its validity was clearly shown in the isotropic phase of nematogenic *n*-cyanobiphenyls  $[28]$ . The obtained parameters are in a good agreement with results of analysis by means of relations  $(6)$ . It is noteworthy here that also relation  $(2)$ , describing the pretransitional NDE anomaly, can be derived basing on the model of the pretransitional behavior in the homogeneous phase of critical solutions  $[27, 46]$ .

Measurements of NDE, the dielectric permittivity  $[26 28,47,48$  and the turbidity  $[7]$  for nematogens were also conducted as functions of pressure. They pointed to the validity of the postulate of isomorphism of critical phenomena [6] for the *I*-*N* transition [27,28]. However, investigations of the influence of pressure on properties characterizing the isotropic liquid-crystalline mesophase phase transitions are scarce  $[40]$ . This is undoubtedly due to experimental difficulties encountered when the physical properties mentioned above are adopted to high-pressure conditions. For the *I*-*N* transition, apart from results mentioned above, a systematic increase of  $\Delta T$  was obtained [7,26–28,48,47]. Such a behavior is in good agreement with theoretical predictions  $[49]$ . A recent paper indicated the possibility of a decrease in the discontinuity of the  $\Delta T$  with rise of pressure in 12CB [47].

This paper presents results of ''linear'' and ''nonlinear'' dielectric permittivity studies in smectogens with the *I*-Sm *A* transition: 4-cyano-4'-decyl-alkylbiphenyl  $(10CB, T_{I-SmA})$  $=$  323.8 K) and 4-cyano-4'-dodecyl-alkylbiphenyl (12CB,  $T_{I-SmA}$ =331.2 K), and with a narrow nematic gap between isotropic and smectic phases  $(T_{I-N}-T_{N-SmA}\approx 1.5 \text{ K})$ : 4-cyano-4'-nonyl-alkylbiphenyl (9CB,  $T_{I-N}$ =323.05 K). Results obtained made possible investigations of the influence of pressure on the discontinuity of the *I*-Sm *A* transitions  $(\Delta T)$ ,  $T_{I\text{-Sm }A}$ , and  $T^*$ . They also show the pretransitional behavior of nonlinear and linear static dielectric permittivity in tested compounds. These gave estimations of the exponents  $\alpha$  and  $\gamma$ , for pressure and temperature paths of studies, in smectogenic compounds.

## **EXPERIMENT**

The measurement setup for NDE studies was described in detail in Ref. [50]. The frequency of the weak measuring field was  $f = 200 \text{ kHz}$  and the voltage (peak-peak)  $U_m$  $=1.5$  V. A strong electric field was applied in the form of rectangular pulses of duration  $\Delta t_D = 8$  ms and voltage *U* = 300–1200 V, so the condition  $U \ge U_m$  was well fulfilled. The registered changes in capacitance were from 1 fF to 5 fF. At each measurement point the validity of the condition  $\varepsilon^{E}$  $-\epsilon \propto E^2$  was tested. The time scale introduced by the frequency of the weak measuring field,  $f^{-1} \gg \tau$ , made it possible to avoid the influence of relaxation processes on results. In pressure studies, to reduce the possible error associated with the gradient of temperature along the pressure chamber, measurements were conducted isothermally as a function of pressure. Measurements of the static dielectric permittivity were made using a Solartron 1260A impedance analyzer. The averaging over 1000 periods made it possible to obtain a five digit precision. The applied measurement frequencies  $(f=1-10$  kHz) i.e., within the static permittivity region for *n*-cyanobiphenyls. For temperature measurements the Invar capacitor with  $C_0$ =7.6 pF and gap  $d$ =0.5 mm was used. For pressure measurements a specially designed chamber with  $C_0$ =5.94 pF and gap  $d$ =0.3, which needed only 0.3 cm<sup>3</sup> of the sample, was used. In both cases quartz rings were used as spacers. In these studies pressure was transmitted into the sample via the deformation of a  $50-\mu m$ -thick Teflon film. Hence there was no influence of the pressurized liquid (silicone oil) on the samples. The capacitor for temperature studies under atmospheric pressure was placed in a special jacket, fed from a Julabo FP 45HD thermostat with an external circulation. In the same way the temperature of the pressure chamber was stabilized. The temperature was measured by means of a miniature platinum resistor  $(DIN 43 260)$ placed in one of the capacitor's covers by a Keithley 195A multimeter. In pressure studies, temperature was measured by means of the platinum resistor placed in the jacket of the pressure chamber and by a copper-constantan thermocouple placed inside the same chamber. An additional thermocouple scanned the temperature gradient along the pressure chamber–it was smaller than 0.02 K. Pressure was measured using a Nova Swiss tensometric pressure meter placed in a special valve, 10 cm from the pressure chamber. This made it possible to avoid the influence of temperature changes on the pressure sensor.

The tested compounds, carefully degassed prior to measurements, were obtained thanks to Roman D'browski and Krzysztof Czupryñski from the Military Academy of Technology (WAT), Warsaw, Poland. Clearing temperatures and pressures were determined with accuracies of  $\pm 0.05$  MPa and  $\pm 0.01$  K due to the strong change in dielectric permittivity on passing the clearing point. Experimental data were analyzed using ORIGIN 5.0 software.



FIG. 1. Dielectric permittivity behavior in the isotropic phase of 9CB. The dashed arrow shows the clearing temperature. The solid lines parameterize Eq. (6a):  $\varepsilon = 10.16_{\pm 0.07} - 0.044_{\pm 0.004}(T - T^*)$  $1+0.29_{\pm 0.005}(T-T^*)^{0.46(\pm 0.06)}$ , with  $T^*=320.3\pm 0.5$  K. The inset shows results of the differential analysis of the experimental data. In this case the solid line is parametrized by relation  $(7)$ , with the value of the exponent given in the inset and the amplitude  $A_T$  $=0.14\pm0.02$ . The error for the exponent is equal to  $\pm 0.1$ .

#### **RESULTS AND DISCUSSION**

Figures 1 and 2 show results of dielectric permittivity studies in the isotropic phase of 9CB and 12CB. In both cases equation (6a) portrays the experimental well. The obtained values of discontinuity of the transition,  $\Delta T \approx 4.0 \text{ K}$ (9CB) and  $\Delta T \approx 6.7$  K (12CB), agree with those obtained by the LF NDE method  $[25]$ . It should be noted that the error for  $\varepsilon(T)$  fit of experimental data is much larger than for LF NDE results. For the latter only a simple linear regression fit is needed. The inset of Fig. 2 shows the behavior of dielectric permittivity for the isothermic pressure path on approaching the smectic clearing point in 12CB. In this case



FIG. 2. The behavior of static dielectric permittivity in the isotropic phase of 12CB, for the temperature (main part) and the pressure (the inset) paths approaching the smectic clearing point. The star shows the position of the virtual critical point. The dashed arrows denote clearing points. Solid curves parametrize equations  $\varepsilon(T) = 9.55_{\pm 0.07} - 0.035_{\pm 0.005}(T - T^*) + 0.2_{\pm 0.01}(T - T^*)^{0.48(\pm 0.06)},$  $T^* = 327.2 \pm 0.8 \text{ K},$   $\varepsilon(P) = 9.31_{\pm 0.06} - 0.011_{\pm 0.004}(P^* - P)$ +  $0.14_{\pm 0.01}(P^* - P)^{0.5(\pm 0.06)}$ , and  $P^* = 101.8 \pm 1$  MPa.



FIG. 3. Results of differential analysis of experimental data from Fig. 2 (the isotropic phase of  $12CB$ ). Solid lines are parametrized by relation  $(7)$  with values of critical exponents given in the figure (the errors  $\pm$  0.05) and amplitudes:  $A_T = 0.1 \pm 0.02$  K, and  $A_P = 0.8 \pm 0.02$  MPa.

experimental data are well parametrized by Eq.  $(6b)$ , which is the pressure analog of Eq.  $(6a)$ . For all data presented in Figs. 1 and 2, the same value of exponent  $\phi \approx 1 - \alpha \approx 0.5$ was obtained. A straightforward estimation of the critical exponent  $\alpha$  can be obtained by applying the differential analysis to experimental data in Figs. 2 and 3. These results are shown in Fig.  $3~(12CB)$  and the inset to Fig. 1  $(9CB)$ . Solid lines parametrize the following relations:

$$
\frac{d\varepsilon}{dT} = \frac{A_T}{(T - T^*)^{-\alpha}} + \text{const} \quad \text{and}
$$
\n
$$
\frac{d\varepsilon}{dP} = \frac{A_P}{(P^* - P)^{-\alpha}} + \text{const.}
$$
\n(7)

The application of the differential analysis made it possible to reduce the number of fitted parameters. The validity of relations  $(6)$  and  $(7)$  also supports the existence of the fluidlike behavior  $[21–23,26–28]$  in the isotropic phase of smectogens. Noteworthy is the fact that analysis by means of relation  $(7)$  was possible in the whole tested range of temperatures and pressures:  $(T - T_c \approx 40 \text{ K})$ , and  $(P_c - P$  $\approx$ 90 MPa).

The pretransitional behavior of nonlinear changes of dielectric permittivity on approaching the smectic clearing point are shown in Fig. 4 for 10CB. Tests were conducted for a series of isothermal pressure paths. The obtained pretransitional behavior suggests that it can be portrayed by the pressure analog of relation  $(2)$ :

$$
\mathcal{E}_{\text{NDE}}^{-1} \propto A_P^{-1} (P^* - P) \quad \text{for}
$$
  

$$
P < P_C, \quad P^* = P_C + \Delta P, \quad \text{and} \quad \gamma = 1,
$$
 (8)

where  $A<sub>P</sub>$  is the isothermal pretransitional amplitude of NDE, *P*\* is the pressure coordinate of the virtual point of a continuous phase transition,  $P<sub>C</sub>$  is the clearing pressure, and  $\Delta P$  is the isothermal pressure discontinuity of the transition.

The validity of Eq.  $(8)$  in the whole range of tested pressures, without any additional "background term"  $[8-12]$ , made it possible to estimate the value of  $P^*$  and consequently the value of  $\Delta P$ . Reciprocals of slopes of solid lines



FIG. 4. Reciprocals of the experimental NDE values for tested isotherms in the isotropic phase of 10CB. The dashed lines show clearing pressures. Intersections of the solid lines with abscissa determine the parameters of virtual critical points ( $\mathcal{E}_{NDE}\rightarrow\infty$ ). The left-hand inset gives values of the temperatures:  $\Delta T_{\text{exp}} = T_C(P)$  $-T<sub>C</sub>(0.1 MPa)$  (K). The right-hand inset shows the evolution of NDE pretransitional amplitudes for 10 CB and 12 CB.

in Fig. 4 determined the pretransitional amplitudes  $A_p$ . The inset in Fig. 4 presents the experimental behavior of  $A<sub>p</sub>$  in 10CB and 12CB. The latter was plotted based on data from Ref. [47]. It also contains results of measurements which made it possible to extend the range of pressures up to 300 MPa. The obtained evolution of the amplitude is similar in both compounds.

Figures 5 and 6 show the obtained dependencies of  $T^*(P)$  and  $T_C(P)$  for 10CB and 12CB, respectively. For both compounds these parameters rise with the increase in pressure as in the  $I-N$  transition  $[7,26-28,47]$ . They can be parametrized by equations given below. For 10CB,



FIG. 5. Temperature dependence of  $T_C(P)$  (full circles) and  $T^*(P)$  (open circles) for 10CB. The solid line and the dashed curve are parametrized by means of relation  $(3)$ . The inset shows the experimental dependence of discontinuity of the transition (lefthand and bottom axes). The solid line parametrizes the equation  $\Delta P(\Delta T_{\text{expt}})$ =9.9-0.16 $\Delta T_{\text{expt}}$  (MPa). The dashed curve shows the dependence of the temperature discontinuity:  $\Delta T(P) = T_C(P)$  $-T^*(P)$ , calculated from Eq. (9a) (upper and right-hand axes). The minimum of the dashed curve is equal to  $\Delta T_{\text{min}}$  (54 MPa)  $=2$  K $\pm$ 0.2.



FIG. 6. Temperature dependence of  $T_C(P)$  (full circles) and  $T^*(P)$  (open circles) in 12CB. The solid and the dashed curves are parametrized from relation (9b). The inset shows the experimental dependence of discontinuity of the transition (left-hand and bottom axes). The solid line parameterizes the equation  $\Delta P(\Delta T_{\text{exp}})=20$  $-0.25\Delta T_{\rm exp}$  (MPa). The dashed curve shows the dependence of the temperature discontinuity calculated from Eq.  $(9b)$ :  $\Delta T(P)$  $T_{C}(P) - T^{*}(P)$  (upper and right-hand axes). The minimum of the dashed curve is equal to  $\Delta T_{\text{min}}(125 \text{ MPa}) = 3.2 \text{ K} \pm 0.2$ .

$$
T_C(P) = 323.8 + 0.315P,
$$
  
\n
$$
T^*(P) = 319.8 + 0.39P + 0.00071P^2,
$$
\n(9a)

and, for 12CB,

$$
T_C(P) = 330.9 + 0.276P + 0.0001P^2,
$$
  
\n
$$
T^*(P) = 324.5 + 0.327P + 0.00031P^2,
$$
\n(9b)

where  $T(K)$  and  $P(MPa)$ .

The insets of Figs. 5 and 6 present the evolution of the discontinuity of the *I*-Sm*A* transition in the tested compounds. It should be stressed that experimental values of  $\Delta P(T)$  were determined. However, owing to the equations above, it was also possible to plot  $\Delta T(P)$  dependencies. Such a transformation enabled us to compare the results obtained in the studies with results of LF NDE investigations under atmospheric pressure  $[25]$ . It is evident that the discontinuity decreases from  $\Delta T(0.1 \text{ MPa}) \approx 4.2 \text{ K}$  to  $\Delta T_{\text{min}}(54 \text{ MPa}) \approx 2 \text{ K}$  in 10CB, and from  $\Delta T(0.1 \text{ MPa})$  $\approx$  6.4 K to  $\Delta T_{\text{min}}(125) \approx$  3.2 K in 12CB. Hence one may conclude that higher pressure is required for 12CB than for

10CB to minimize  $\Delta T$  and  $\Delta T$ (0.1 MPa)/ $\Delta T$ <sub>min</sub>(*P*) $\approx \frac{1}{2}$  for both compounds. It should be noted that the transformation to  $\Delta T(P)$  scale destroys the possible linear dependencies of  $\Delta P(T)$  (the solid lines in the insets in Figs. 5 and 6). Ranges of eventual linearity for  $\Delta P(T)$  seem to be approximately the same as for  $A_p(T)$ .

Concluding, the reason for such different pressure behaviors of the discontinuities of *I*-*N* and *I*-Sm*A* transitions still remains unsolved. One may expect that in nematogens the increase of pressure reduces the free volume, and consequently causes a rise of the uniaxial, orientational ordering. Hence the distance between symmetries of the isotropic liquid and the nematic phase, and consequently the discontinuity of the *I*-*N* transition, may increase. For the *I*-Sm*A* transition, the distance between symmetries of the isotropic and smectic phases is larger than for nematogens. Hence, values of  $\Delta T$  [25] and of the latent heat [6] for the *I*-Sm*A* transition are higher than for the *I*-*N* transition. For smectogens the increase of pressure will probably shift rodlike molecules along the direction of the preferred orientational ordering. This may destroy the Sm*A* structure and cause the appearance of a similar structure to that known as the high pressure re-entrant nematic phase [4]. Such an evolution will narrow the distance between symmetries of the mesophase and isotropic liquids, and should lead to a decrease of the discontinuity transition up to the appearance of the pressure-induced nematic phase. Next, in the nematic phase, the degree of orientational ordering will increase with the rise of pressure, which may result in a rise of  $\Delta T$ .

Results presented above also show that pretransitional effects of the static ''linear'' and ''nonlinear'' dielectric permittivity exhibit similar pretransitional behaviors in smectogens and nematogens. In both types of compounds critical exponents  $\alpha \approx 0.5$  and  $\gamma = 1$ . The application of Josephson's scaling law [6,36] gives  $d=3$ , i.e., the same dimensionality as in critical, binary solutions. This fact, as well as the obtained isomorphism of the pressure and temperature paths of study, point to the critical fluidlike behavior  $[21–23,26–28]$ of the *I*-Sm*A* transition at least as far as orientational ordering is concerned.

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