Phase transitions from the isotropic liquid to liquid crystalline mesophases studied by linear and nonlinear static dielectric permittivity

Aleksandra Drozd-Rzoska and Sylwester J. Rzoska

Institute of Physics, Silesian University, ulica Uniwersytecka 4, 40-007 Katowice, Poland

Krzysztof Czupryñski

Military Technical Academy, ulica S. Kaliskiego, 01-489 Warsaw, Poland

(Received 2 September 1999)

Results of studies of static dielectric permittivity (ε) and nonlinear dielectric effect (NDE) in the isotropic phase of 4-n-4′-isothiocyanatobiphenyl (nBT) homologous series from $n=2$ to $n=10$ exhibiting the isotropic-smectic E (I-SmE) transition, are presented. They are compared with results of similar studies in 4-cyano-4-n-alkylbiphenyls (nCB) from $n=4$ to $n=12$. In this homologous series isotropic-nematic (I-N) and isotropic-smectic-A (I–Sm-A) transitions take place. Despite significant differences between N, Sm-A, and Sm-E phases the same pretransitional behavior of ε and NDE in the isotropic phase, described by critical exponents $\gamma=1$ and $\alpha=0.5$, was found. It has been shown that when the length of the alkyl chain of a compound increases the discontinuity of the transition drops in nBT and rises in nCB. The influence of pressure on the discontinuity is also discussed.

PACS number(s): 64.70.Md, 64.30.+t, 77.22.Ch

INTRODUCTION

Despite several decades of studies there is still a limited knowledge concerning properties of phase transitions from the isotropic liquid to liquid crystalline mesophases [1–9]. Liquid crystalline phases are an intermediate state of matter between the liquid and the solid crystal and hence the weakly discontinuous character of this transition is not surprising. The phenomenological, mean field Landau–de Gennes (LdG) model made a quantitative estimation of this discontinuity possible [1–3]. It enabled the parameterization of strong pretransitional anomalies of susceptibility related properties as the Kerr effect (KE), the Cotton-Mouton effect (CME) and the intensity of the scattered light (I_L) on approaching the isotropic-nematic (I-N) transition [1–22]:

$$\mathcal{E}_{\mathrm{KE}}^{-1}, \mathcal{E}_{\mathrm{CME}}^{-1}, \mathcal{E}_{I_L}^{-1} \propto T - T^*, \quad T > T_C = T^* + \Delta T, \qquad (1)$$

where $\mathcal{E}_{\mathrm{KE}}, \mathcal{E}_{\mathrm{CME}}, \mathcal{E}_{I_L}$ are experimental measures of KE, CME, and I_L respectively. T^* denotes the extrapolated, temperature of hypothetical continuous phase transition, T_C is the clearing temperature.

The obtained values of discontinuity of the I-N transition range from 0.7–2 K [1–3,9–22] whereas mean-field based models point to a much stronger discontinuity with $\Delta T = 7.6$–26 K [3,9,23–25]. The mean-field approximation [6] does not predict pretransitional anomalies of a specific heat and density which are weak but detectable in experiments [6,26–28]. Only recently, an essential breakthrough in this long-standing puzzle due to the introduction of the fluidlike critical description was possible. Assuming that the nematic clearing point lies on a branch of a hypothetical coexistence curve and applying the fluidlike scaling equation of state Mukherjee *et al.* obtained $\Delta T = 1$–3 K [9,29–31].

Significant insight into properties of the complex structure of the isotropic liquid phase strongly penetrated by nematic fluctuations was possible due to recent studies of 5CB and MBBA by the transient grating Kerr effect [32–34], isothermal nonlinear dielectric effect studies in 7CB-benzene solution [35], and the NDE and dielectric permittivity fluidlike analysis in several nematogenic and smectogenic (nCB) [36–42]. For the latter it was shown that for the ''static'' measurement frequency [37,39]

$$\varepsilon(T) = \varepsilon^* + b(T - T^*) + B(T - T^*)^{1-a}, \qquad (2)$$

$$\mathcal{E}_{\mathrm{NDE}} = \frac{A_{\mathrm{NDE}}^T}{T - T^*} = \frac{2\varepsilon_0}{3a} \frac{(\Delta\varepsilon^0)^2}{(T - T^*)^\gamma} \propto \langle \Delta M^2 \rangle_v \chi, \qquad (3)$$

where $\mathcal{E}_{\mathrm{NDE}}$ is the measure of NDE, A_{NDE}^T, b, B are amplitudes, a is the constant amplitude of the second rank term in the LdG expansion of the free energy, $\Delta\varepsilon^0$ is the molecular anisotropy of dielectric permittivity in the zero frequency limit, $\langle \Delta M^2 \rangle_v$ is the mean of the square of the order parameter fluctuations, $\chi \propto (T - T^*)^{-1}$ denotes the susceptibility, α is the critical exponent of the specific heat: in this case $\alpha \approx 0.5$ was found. Relations (2) and (3) are valid for the ''static'' conditions: $f\tau \ll 1$ and $f\tau_m \ll 1$ where f is the NDE measurement frequency, τ is the relaxation time of pretransitional processes and τ_m is the molecular relaxation time of rodlike molecules.

These equations are similar to those applied in the isotropic phase of critical solutions [37,39,43]. The reciprocal of $\mathcal{E}_{\mathrm{NDE}}^I(T)$ was found to be linear up to $T_x \approx T_C + 38$ K, with no distortions in the immediate vicinity of T_C [39]. The value of T_x agrees with the temperature at which prenematic fluctuations cease to exist [32–34]. Concerning dielectric permittivity equation (2) was found to be valid even 100 K from T_C [39]. It is worth noticing that in KE, CME, or I_L studies, experimental data describing relation (1) are valid in the range 5–10 K from T_C only, with small distortions in its immediate vicinity [1–20]. Furthermore additional, empirical

background terms had to be introduced into the analysis. Studies of KE, I_L, and CME in smectogenic materials yielded more ambiguous results [6,12,14–17]. The simple behavior given by Eq. (1) was found here to be valid only remote from the smectic clearing point. In its vicinity pretransitional effects exhibit small distortions strongly bend down, bend up or remain constant. To the best of the authors knowledge there is no sucsessfull theoretical description of pretransitional effect beyond the I-N transition. For the I-SmA some attempts were made by applying the perturbation theory to the Landau–de Gennes model [6]. However, the obtained relation only portrayed $\mathcal{E}_{I_L}^{-1}(T)$ experimental results where the mentioned discrepancies from relation (1) are relatively small [6]. It should be noted that such an analysis significantly increases the number of fitted parameters. Recently, Mukherjee *et al.* [44] showed that basic features of the I–Sm-A transition, particularly relatively large value of discontinuity can be obtained within a simple LdG model. When phase transitions from the isotropic liquid to more complex mesophases are considered worth mentioning is also recent analysis of the topology of the I-N transitions in biaxial nematics [45]. Particularly noteworthy is recent reanalyses of the LdG model by Nandi *et al.* [46]. Paying attention to the identification of the order parameter for the I–Sm-A transition and to the proper renormalization of terms in the LdG series they obtained a simple Curie-Weiss type relation dependence:

$$\chi = \frac{a}{T-T^*}, \qquad (4)$$

where a is the constant coefficient of the second rank term in the renormalized free energy expansion.

Particularly interesting in Ref. [46] is the possibility of calculating the value of ΔT for the I–Sm-A transition. For 12CB $\Delta T = 6.78$ K was obtained which is in a very good agreement with $\Delta T \approx 6.4$ K obtained from static (low frequency) NDE tests [36]. The models mentioned above did not predict an anomaly of the specific heat related properties in the isotropic phase of smectogenic compounds. The anomaly of the specific heat was observed experimentally but it was too weak for a numerical analysis [6].

This paper shows results of studies of ''linear'' (ε) and ''nonlinear'' (NDE) static dielectric permittivity in the homologous series of 4-n-4′-isothiocyanatobiphenyl (nBT) [47] for $n = 2 - 10$. For all compounds only the transition from the isotropic liquid to the ''soft crystal'' smectic E phase takes place [8]. Apart from the pretransitional behavior in the isotropic phase the dependencies of $T^*(n)$, $\Delta T(n)$ in the homologous series are discussed. In 5BT the influence of pressure on mentioned parameters was tested. The obtained results are compared with those for the I-N and I–Sm-A transitions in 4-cyano-4-n-alkylbiphenyls (nCB) homologous series, for $n = 4$ to $n = 12$, including recent results on pressure studies [36–42,48].

EXPERIMENT

The measurement set up applied in these studies is the same as in the author's previous works [36–42]. The detailed description of the NDE apparatus is given in Ref. [49]. NDE
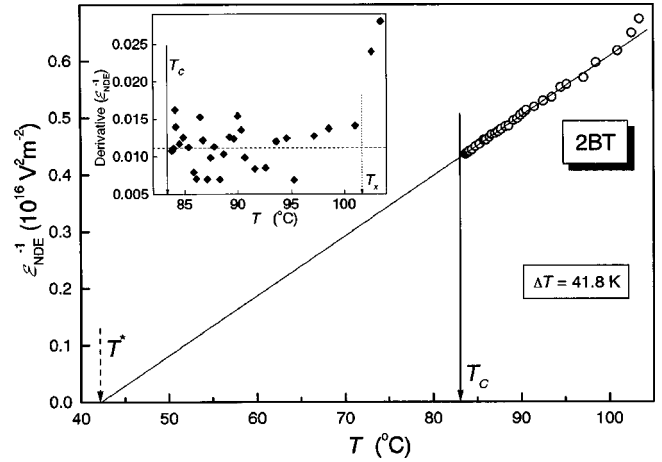

FIG. 1. Reciprocals of measured static NDE values in the isotropic phase of 2BT. The inset shows the derivative of experimental data from the main part of the figure. The solid arrows point to the discontinuous I–Sm-E phase transition. The dashed arrow shows the extrapolated temperature of a hypothetical continuous phase transition. The value of the discontinuity is given in the figure.

measurement involves application of two electric fields: the weak, measuring field ($f = 400$ kHz and $U_{\text{peak-peak}} = 1.5$ V) and a strong steady field in the form of pulses of duration $\Delta t_D = 8$ ms with voltage from 200 to 1200 V. At each measurement point the condition $\Delta \varepsilon^E \propto E^2$ was fulfilled. For the chosen frequency of the measuring field the mentioned above ''static'' condition was always satisfied, manifested in the lack of discrepancies from relation (3) in the vicinity of T_C [36–42]. The strong electric field changed the capacitance of the measurement capacitor of the sample by (1–10 fF). These changes were registered with three-digit resolution. Dielectric permittivity was measured using SOLARTRON 1260 impedance analyzer with 1000 periods averaging giving a five-digit accuracy. The measurement frequencies $f = 1 - 10$ kHz was placed on the out of dispersion ''static plateau'' [5] frequency increase the dispersion processes were detectable for $f > 300$ kHz. On the other hand low frequency ionic polarization was significant below 200 Hz. The sample was placed in specially designed capacitors, with gap $d = 0.3$ mm and $C_0 = 6.6$ pF, made from Invar. The capacitor contained 0.3 cm^3 of the sample. In pressure studies the pressure was transmitted to the sample by deformation of 50 mm Teflon film, so the sample was always isolated from the medium exerting pressure (silicon oil). The pressure chamber and the capacitor for tests under atmospheric pressure was surrounded by a special jacket fed from FP 45 HD Julabo thermostat with external circulation. It made the stabilization and changes in temperature $\pm$ 0.01 K in a wide range of temperatures possible. Temperature was measured by a means a miniature platinum resistor (DIN 43 260) using Keithley 195 multimeter. Data were analyzed by means of 5.0 ORIGIN software.

RESULTS AND DISCUSSION

Figure 1 and 2 show inverses of measured NDE values for two ''boundary'' compounds in the tested nBT homologous series: 2BT and 10BT. It can be seen that dependencies (2) and (3) portray the NDE behavior in the large range of tem-
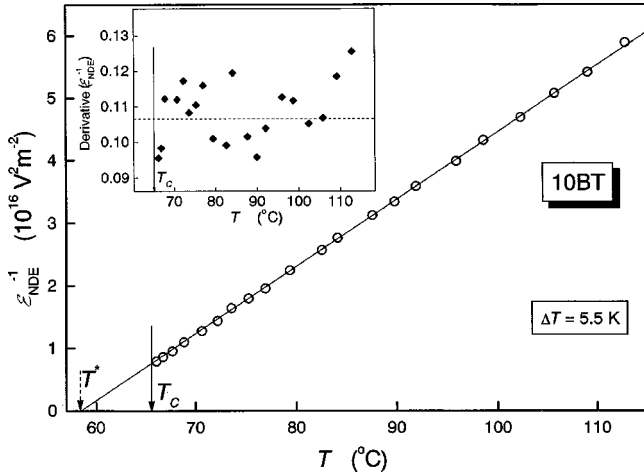
FIG. 2. Reciprocals of measured static NDE values on approaching SmE phase in the isotropic phase of 10BT. The inset shows the derivative of experimental data from the main part of the figure.

peratures from $T_C = T_{I-Sm-E}$ to $T_x \approx T^* + 60$ K. The latter temperature, which may be identified as the limit of existence of pretransitional fluctuations, is clearly visible for the differential analysis shown on insets. The value of T_x in nBT is approximately the same for all tested nBT. It is noteworthy that in the nCB series $T^* - T_x \approx 38$ K [39].

In 10 BT the discontinuity is equal to about $\Delta T \approx 5.4$ K whereas in 2BT $\Delta T \approx 41$ K. To the best of the authors knowledge the latter value is the largest value of ΔT ever detected in studies of liquid crystalline materials. Values of $\Delta T(n)$ for all tested nBT compounds determined from NDE studies are shown in Fig. 3. A systematic decrease of this parameter with the rise of the number of carbon atoms in the alkyl chain can be approximated by an almost linear function:
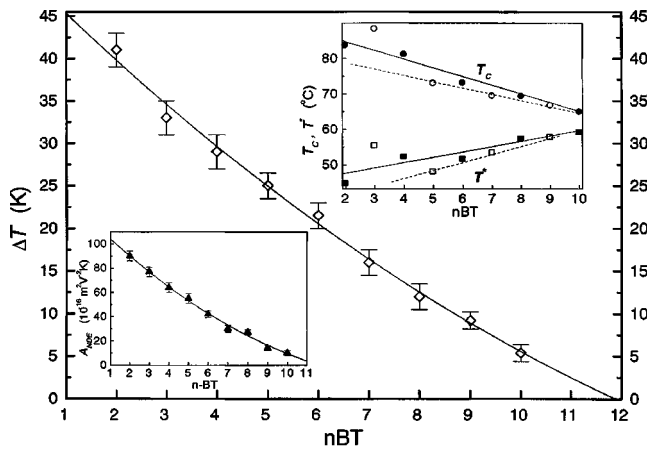

FIG. 3. Values of discontinuities of $I - $Sm-$E$ transition in the nBT homologous series obtained from the NDE studies. The bottom inset shows the experimental dependence of the NDE amplitude in the nBT series. Solid line portrays relations (5) and (6). The upper inset presents the evolution of clearing temperatures (T_c, circles) and temperatures of hypothetical continuous phase transitions (T^*, squares). Solid points and open point are for even and odd nBT compounds, respectively. Solid and dotted lines are only a guide for the eyes.

TABLE I. Values of parameters determined in NDE measurements in the isotropic phase of compounds from nBT homologous series. The temperature of the hypothetical continuous transition is equal to $T^* = T_c - \Delta T$.

n	ΔT (K)	T_c (°C)	A_{NDE}^T (10^{-16} m^2 V^{-2})
2	41	83.8	90
3	33	88.5	77
4	29	81.3	64
5	25	73.1	55
6	21.5	73.2	42
7	16	69.5	30
8	12	69.5	27
9	9.2	66.8	14
10	5.5	65.0	10

$$\Delta T(n) = 51.1 - 5.91n(1 - 0.023n) \, °C \qquad (5)$$

The bottom inset shows that the NDE amplitude changes in a similar way as $\Delta T(n)$:

$$A_{NDE}^T(n) = 119 - 15.5n(1 - 0.03n) \times 10^{-16} \, \text{m}^2 \, \text{V}^2 \qquad (6)$$

Taking relation (3) into account one may suppose that A_{NDE}^T reflects the change of the susceptibility amplitude. The upper inset shows the experimental dependence of $T_C(n)$ and $T^*(n)$. The Sm-E clearing temperature exhibits a well-known odd-even effect [3,5,7,8]. It is also clearly visible for $T^*(n)$ estimated in NDE studies. This effect definitely does not appear for ΔT. Result of fitting for data from Fig. 3 are collected in Table I.

Figure 4 shows that the static dielectric permittivity exhibits a pretransitional behavior analogous to that discussed in the introduction [relation (2)]:

$$\varepsilon(T) = 6.565_{\pm 0.03} - 0.018_{\pm 0.0015}(T - 60.16_{\pm 0.1})$$
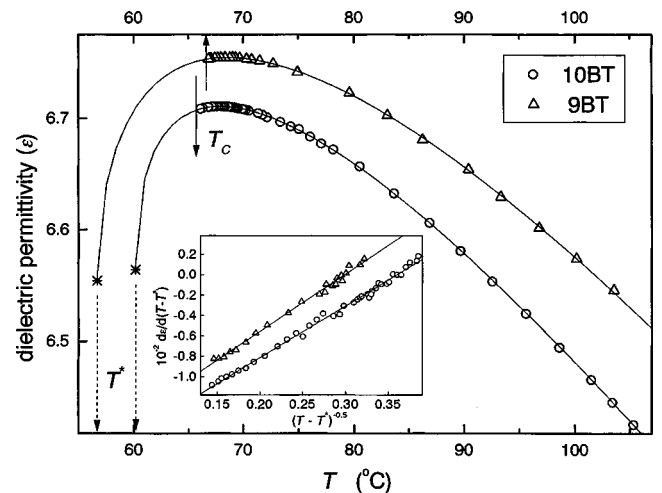$$+ 0.11_{\pm 0.03}(T - 60.16)^{0.49(\pm 0.03)} \quad \text{for} \ 10 \, \text{BT,} \quad (7)$$

FIG. 4. The temperature dependence of dielectric permittivity in the isotropic phase of 10BT ($\Delta T \approx 5.5$ K) and 9BT ($\Delta T \approx 9.2$ K). The inset shows results of differential of experimental data from the main part of the figure.
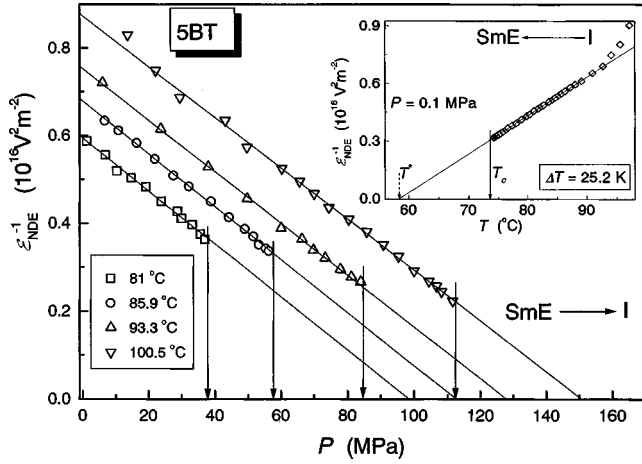
FIG. 5. Isothermal, pressure behavior of the inverse of measured NDE values in the isotropic phase of 5BT. The inset shows the pretransitional behavior for temperature studies under atmospheric pressure. The solid arrows show positions of SmE clearing points (T_c, P_c). The intersection of solid lines with the abscissa determine the parameters of (P^*, T^*).

$$\varepsilon(T) = 6.53_{\pm 0.08} - 0.018_{\pm 0.002}(T - 56.6) + 0.12_{\pm 0.1}$$
$$\times (T - 56.6)^{0.48(\pm 0.1)} \quad \text{for } 9\,BT, \quad (8)$$

For the nBT compounds with smaller number of carbon atoms of the alkyl chain (n) this anomaly disappears due to the increase of the discontinuity of the transition. Even for 9BT the fit was possible only if the value of T^* was taken from the fit of the NDE measurements. Noteworthy is the fact that experimental data are portrayed by relation (2) in the whole tested range of temperatures. The inset in Fig. 4 presents results of differential analysis of $\varepsilon(T)$ experimental data, which do not reveal any distortions from relations (8) and (9). The result of this analysis is plotted in the inset in the form which clearly confirms the validity of these equations with exponent $\alpha \approx 0.5$. It should be noted that the dependence of $d\varepsilon/dT \propto c_P \propto (T - T^*)^{-a}$, where c_p is the specific heat, was first proposed by Mistura for the anomaly of dielectric permittivity in the homogeneous phase of critical, binary solutions [50]. As mentioned before the same behavior of dielectric permittivity was found for the static dielectric permittivity in the isotropic phase on approaching the nematic phase. It can be related to the cancellation of permanent dipole moments, positioned along rodlike molecules, which are contained in prenematic fluctuations. The fact that the same pretransitional behavior was obtained on approaching the nematic [36–41,48] and the Sm-A phase [43] and now the Sm-E phase may mean that the same mechanism may be valid in all these cases.

When discussing the properties of the discontinuity of the transition the influence of pressure is worth noticing. For the I-N transition an increase of $\Delta T(P)$ with rising pressure was found [39,41], in agreement with theoretical predictions [51]. Only recently first studies of this type were conducted for the I–Sm-A transition [41,42]. It has been found that $\Delta T(P)$ first decreases from $\Delta T(0.1\,\text{MPa}) = 6.4\,\text{MPa}$ to $\Delta T(125\,\text{MPa}) = 3.2\,\text{K}$ in 12 CB and from $\Delta T(0.1\,\text{MPa}) = 4.2\,\text{K}$ to $\Delta T(54\,\text{MPa}) = 2\,\text{K}$ in 10 CB [42]. Next a strong increase of $\Delta T(P)$ with rising pressure was found. This be-

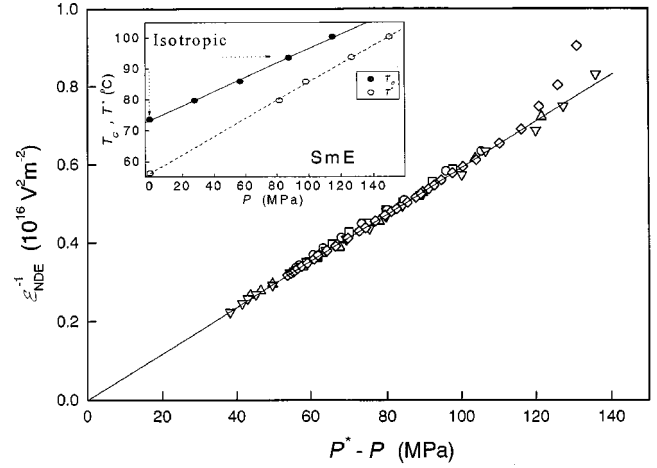
FIG. 6. The scaling behavior of NDE pretransitional effect for pressure and temperature paths of approaching the line of virtual critical points (T^*, P^*) in 5BT for data from Fig. 5. The inset shows the behavior $T_c(P)$ and $T^*(P)$ obtained in NDE studies. Solid lines parametrize equations $T_c(P) = (73.25_{\pm 1} + 0.232_{\pm 0.015})P$ and $T^*(P) = (56.1_{\pm 1.2} + 0.295_{\pm 0.02})P$.

havior may be related to the fact that the increase of pressure will mainly shift molecules along the direction of the local director, showing the preferred orientational ordering of rod-like molecule. This may finally destroy the SmA structure and cause the appearance of a "well packed" and strongly ordered nematic structure. Such an evolution narrows the distance between symmetries of the mesophase and the isotropic liquid which should initially decrease the discontinuity of the transition. The resulting appearance of the pressure-induced nematic phase and the isotropic–nematic–smectic-A triple point has been yet reporting for smectogenic compounds [52].

Figure 5 show inverses of measured NDE for isothermic, pressure studies in the isotropic phase of 5BT. The temperature behavior under atmospheric pressure is presented in the inset in Fig. 6. It is clearly visible that pressure studies the pressure analogue of relation (3) is valid:

$$\mathcal{E}_{\text{NDE}}(P) = \frac{A_{\text{NDE}}^B}{P^* - P}, \quad P < P_C + \Delta P. \quad (9)$$

The inset in Fig. 7 shows that on approaching the SmE clearing point in 5BT pressure initially reduces the discontinuity of the transition as in the case of the I–Sm-A transition [41,42]. Similarly to the case of I-N and I–Sm-A transitions T_C and T^* increases with rising pressure. The main part of Fig. 7 shows that temperature and pressure NDE pretransitional effects can be superposed into a one scaling curve due to the transformation of temperature scale into the pressure scale via

$$T - T^* \rightarrow P^* - P = \left(\frac{dT^*}{dP}\right)^{-1}(T - T^*). \quad (10)$$

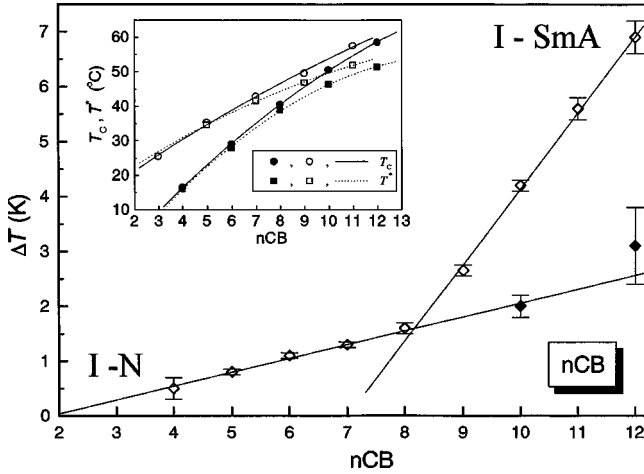The appearance of the single, scaling line may be treated as the consequence of the Ehrenfest-type relation

FIG. 7. The evolution of the discontinuity of the *I*-*N* and *I*–Sm-*A* transitions in *n*CB homologous series obtained in static, low-frequency, NDE studies. Open points are for temperature studies under atmospheric pressure [36–41,48] and solid points denote the smallest ΔT values obtained in pressure studies of 10CB and 12CB [42].

$$\frac{A_{\mathrm{NDE}}^{P}}{A_{\mathrm{NDE}}^{T}} = \frac{\chi_0^T}{\chi_0^P} = \frac{(dV/dP)_{T \to T^*}}{(dV/dT)_{P \to P^*}} = \frac{dT^*}{dP^*} = \frac{dT^*}{dP}. \quad (11)$$

Its validity was previously shown for the *I*-*N* transition [39].

In the opinion of the authors it would be interesting to compare the above results with similar results for other homologous series. This is possible for *n*CB homologous series basing on static NDE studies. Figure 7 shows the $\Delta T(n)$ dependence for all compounds from $n=4$ to $n=12$, collecting results from refs. [36–42], [48]. For $n=4$ there is a monotropic *I*-*N* transition and the sample crystallized before reaching T_C [48] and its value was taken from catalog data [53]. The discontinuity of isotropic-mesophase transitions (ΔT) increases with the rise of parameter *n*. This dependence follows two different straight lines for smectogenic and nematogenic *n*CB. Noteworthy is the decrease of ΔT whose extrapolated value reaches approximately zero for 2CB. Unfortunately, in 2CB the sample crystallizes 60 K above hypothetical $T_C (\approx T^*)$. For 10CB and 12CB there are two values for each ΔT. The smaller values are the minimum ones obtained in pressure studies mentioned above [42]. Within the limit of experimental error they are located on the extrapolated line describing the nematogenic compounds. This behavior supports the mentioned hypothesis formulated in Ref. [42] that pressure destroys the Sm-*A* phase and the transition from the isotropic liquid to well packed, high pressure nematic appears. The inset in Fig. 7 shows the well-known odd-even dependence for $T_C(n)$ and the similar evolution of $T^*(n)$ from NDE studies. The odd-even effect does not appear for $\Delta T(n)$ dependence. All data shown in Fig. 7 are collected in Table II. The table also contains values of the NDE pretransitional amplitudes. Its evolution is similar to that found in *n*BT, i.e., A_{NDE}^T decreases with the rise of the parameter *n*:

$$A_{\mathrm{NDE}}^T = 315_{x4} - 39.6_{x1} n (1 + 0.037\, n)(10^{-16}\,\mathrm{m^2\,V^{-2}}). \quad (12)$$

TABLE II. Values of parameters determined in NDE measurements in the isotropic phase of compounds from *n*CB homologous series. The temperature of the hypothetical continuous transition is equal to $T^* = T_c - \Delta T$. For 10CB and 12CB the upper value of ΔT is for temperature studies under atmospheric pressure. The lower value of ΔT is the minimum one found in pressure studies.

n	ΔT (K)	T_C (°C)	A_{NDE}^T ($10^{-16}\,\mathrm{m^2\,V^{-2}}$)
4	0.5	16.5	180
5	0.8	35.3	150
6	1.1	29.0	130
7	1.3	42.8	113
8	1.6	40.5	92
9	2.7	49.5	81
10	4.2	50.5	69
	2		
11	5.6	57.5	60
12	6.4	58.5	52
	3.1		

CONCLUSIONS

The main difference between results obtained for *n*BT and *n*CB series is the behavior of the discontinuity of the transition in the homologous series. It seems that in the *n*CB series the orientational ordering of the nematic phase increases with the rise of the total length of the rodlike molecule. Hence, the distance between symmetries of the isotropic liquid and the following mesophase also increases giving the $\Delta T(n)$ dependence presented in Fig. 7.

The Sm-*E* phase, appearing in *n*BT, is often called ''soft smectic crystal'' and is located between the solid crystal state and the ''ordinary'' liquid crystalline mesophases [8]. Apart from the smectic layer structure, the Sm-*E* phase additionally exhibits a strong herringbone array [8]. The well-packed structure may cause that the only flexible part of the molecule is the alkyl chain. Hence, the increase of the length of this chain may decrease the level of the Sm-*E* arrangement. Consequently, the distance between symmetries of Sm-*E* and *I* phases increases giving the obtained evolution of $\Delta T(n)$. It is interesting that despite the different dependence of $\Delta T(n)$ in *n*CB and *n*BT series the hydrostatic pressure seems to influence this parameter in a similar way. Experimental results presented above and that of Refs. [36–42], [48] show that the pretransitional behavior of ''linear'' and ''nonlinear'' dielectric permittivity is analogous to the *I*-*N*, *I*–Sm-*A*, and *I*–Sm-*E* transitions. Particularly noteworthy is the evidence for exponent $\gamma=1$ and $\alpha=\frac{1}{2}$ for the *I*–Sm-*E* transition. It poses the question concerning the range of validity of the mentioned critical, fluidlike description [9,29–31,37,39] also for phase transitions from the isotropic to smectic mesophases.

[1] P. G. de Gennes, Phys. Lett. **30A**, 454 (1969).

[2] P. G. de Gennes, Mol. Cryst. Liq. Cryst. **12**, 193 (1971).

[3] P. G. de Gennes, *The Physics of Liquid Crystals* (Oxford University Press, Oxford, 1974); P. G. de Gennes and J. Prost, *The Physics of Liquid Crystals* (Oxford University Press, Oxford, 1994).

[4] F. H. Gramsbergen, L. Longa, and W. H. de Jeu, Phys. Rep. **135**, 195 (1986).

[5] G. Vertogen and W. H. de Jeu, *Thermotropic Liquid Crystals-Fundamentals*, Vol. 45 of *Springer Series in Chemical Physics* (Springer, Berlin, 1988).

[6] M. A. Anisimov, *Critical Phenomena in Liquids and Liquid Crystals* (Gordon and Breach, Philadelphia, 1991).

[7] S. Chandrasekhar, *Liquid Crystals* (Cambridge University Press, Cambridge, 1994).

[8] *Fundamentals*, Vol. 1 of Handbook of Liquid Crystals, edited by D. Demus, J. Goodby, G. W. Gray, H.-W. Spiess, and V. Vill (Wiley-VCH, Weinheim, 1998).

[9] P. K. Mukherjee, J. Phys.: Condens. Matter **10**, 9191 (1998).

[10] Stinson and Litster, Phys. Rev. Lett. **25**, 503 (1970).

[11] R. Yamamoto, S. Isihara, S. Hayakawa, and K. Morimoto, Phys. Lett. **69A**, 276 (1978).

[12] K.-I. Muta, H. Takezoe, A. Fukuda, and E. Kuze, Jpn. J. Appl. Phys. **8**, 2073 (1979).

[13] P. V. Kolynski and B. R. Jennings, Mol. Phys. **40**, 979 (1980).

[14] D. A. Dunmurr and E. A. Thomes, Mol. Cryst. Liq. Cryst. **76**, 231 (1981).

[15] Z. Shu-Lin, P. Zheng-Yu, and W. Jin, Mol. Cryst. Liq. Cryst. **91**, 295 (1983).

[16] B. Pouligny, J. Marceau, J. R. Lalanne, and H. J. Coles, Mol. Phys. **4**, 583 (1983).

[17] H. Zink and W. H. de Jeu, Mol. Cryst. Liq. Cryst. **124**, 287 (1985).

[18] W. Pyzuk, I. Słomka, J. Charapeć, S. J. Rzoska, and J. Zioło, Chem. Phys. **121**,

[19] J. Fuchs and W. Burchard, J. Phys. II **4**, 1451 (1994).

[20] L. K. Schneider, Ph.D. thesis, Philips Universitaet, Marburg, 1996.

[21] L. K. Schneider and J. H. Weindorff, Liq. Cryst. **22**, 29 (1997).

[22] D. Kang, M. P. Mahajan, S. Zhang, R. G. Petschek, C. Rosenblatt, Ch. He, P. Liu, and A. C. Griffin, Phys. Rev. E **60**, 4980 (1999).

[23] W. Maier and Z. Sauper, Z. Naturforsch. **14**, 882 (1959).

[24] Yu Mingh Shis, H. M. Huang, and Chia-Wei Woo, Mol. Cryst. Liq. Cryst. **34**, 7 (1976).

[25] R. G. Priest, Mol. Cryst. Liq. Cryst. **42**, 223 (1976).

[26] J. Thoen, H. Marynissen, and W. van Dael, Phys. Rev. A **26**, 2886 (1982).

[27] G. Koren, Phys. Rev. A **13**, 1177 (1976).

[28] E. Gulari and B. Chu, J. Chem. Phys. **62**, 795 (1975).

[29] P. K. Mukherjee and M. Saha, Phys. Rev. E **51**, 5745 (1995).

[30] P. K. Mukherjee and T. B. Mukherjee, Phys. Rev. B **52**, 9964 (1995).

[31] P. K. Mukherjee, T. R. Bose, D. Ghose, and M. Saha, Phys. Rev. E **51**, 4570 (1995).

[32] A. Sengupta and M. D. Fayer, J. Chem. Phys. **102**, 4193 (1995).

[33] R. Torre and S. Califano, J. Chim. Phys. Phys.-Chim. Biol. **93**, 1843 (1996).

[34] R. Torre, F. Tempestini, P. Bartolini, and R. Righini, Philos. Mag. **77**, 645 (1997).

[35] J. Małecki and J. Nowak, J. Mol. Struct. **71**, 11 (1997).

[36] A. Drozd-Rzoska, S. J. Rzoska, and J. Zioło, Liq. Cryst. **21**, 273 (1996).

[37] A. Drozd-Rzoska, S. J. Rzoska, and J. Zioło, Phys. Rev. E **54**, 6452 (1996).

[38] A. Drozd-Rzoska, Liq. Cryst. **24**, 835 (1998).

[39] A. Drozd-Rzoska, Phys. Rev. E **59**, 5556 (1999).

[40] A. Drozd-Rzoska and S. J. Rzoska, Mol. Cryst. Liq. Cryst. **330**, 29 (1999).

[41] A. Drozd-Rzoska, S. J. Rzoska, and J. Zioło, Mol. Cryst. Liq. Cryst. **330**, 7 (1999).

[42] A. Drozd-Rzoska, S. J. Rzoska, and J. Zioło, Phys. Rev. E (to be published).

[43] S. J. Rzoska, Phys. Rev. E **48**, 1136 (1993).

[44] P. K. Mukherjee, H. Pleiner, H. D. Brand, Europhys. Lett. (to be published).

[45] P. K. Mukherjee and H. Brand, Phys. Rev. Lett. (to be published).

[46] B. Nandi, M. Saha, and P. K. Mukherjee, Int. J. Mod. Phys. B **11**, 2424 (1997).

[47] R. Dabrowski, J. Dziaduszek, and T. Szczuciñski, Mol. Cryst. Liq. Cryst. **102**, 155 (1984).

[48] A. Drozd-Rzoska, S. J. Rzoska, and J. Zioło, Proc. SPIE **3318**, 218 (1997).

[49] M. Górny, J. Zioło, and S. J. Rzoska, Rev. Sci. Instrum. **67**, 4290 (1996).

[50] L. Mistura, J. Chem. Phys. **59**, 4563 (1973).

[51] V. K. Piershin, Zh. Fiz. Khim. **LX**, 2540 (1986).

[52] J. L. Walker and P. J. Collings, Liq. Cryst. **9**, 751 (1991).

[53] *Licristal Catalogue* (BDH-Merck, Darmstadt, 1987).