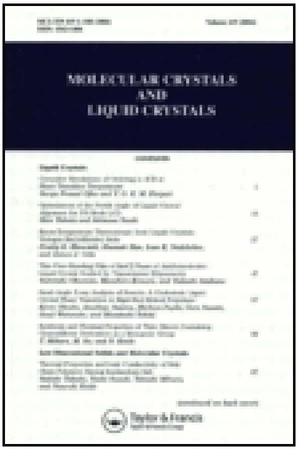

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Temperature and Pressure Studies of the Isotropic – Mesophase Transition Discontinuity by Static Nonlinear Dielectric Effect

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Results of studies of static nonlinear dielectric effect (*NDE*) in the isotropic phase in the homologous series of *n*DBT: (5-*n*-alkyl-2-(4-isothio-cyanatophenyl)-1,3-dioxane) for *n*= 4, 6 and 8 exhibiting the I-SmA transition are presented. The strong pretransitional anomaly in the isotropic phase is similar to the one observed in nematogens. It has been found that the discontinuity of the I-N transition increases from 10.8 K to 18.8 K when moving from 4DBT to 8DBT. It has been also shown that pressure reduces the discontinuity of the I-SmA transitions. Results obtained are compared with similar studies in two other homologous series (*Phys. Rev.* **E61** (2000) 5349 and *Phys. Rev.* **E61** (2000) 5355).

Keywords: discontinuity; isotropic – Smectic A transition; nonlinear dielectric effect; pressure

INTRODUCTION

On approaching the nematic clearing point in the isotropic liquid such properties as the Kerr effect (*KE*), Cotton – Moutton effect (*CME*) and the intensity of the scattered light (I_L) exhibit a simple pretransitional anomaly [1-10]:

$$KE^{-1}, CME^{-1}, I_L^{-1} \propto T - T^*, \qquad T^* = T_{I-N} - \Delta T \text{ and } T > T_{I-N} \qquad (1)$$

where T^* denotes the extrapolated temperature of a hypothetical continuous phase transition, T_{I-N} is the nematic clearing temperature and ΔT is the measure of the discontinuity of the transition.

The small experimental values of $\Delta T = 0.7 - 2$ [1-10] stated the main point of disagreement with mean-field (MF) based theories which predict $\Delta T = 43 - 7K$ [11 and refs. therein]. It is also noteworthy that in the MF approximation there should be no anomaly of properties associated with the exponent α but the appearance of specific or density pretransitional anomalies were reported as far back as the seventies [11-19]. Nevertheless, in leading monographs the I-N transition is presented as an example of the validity of the MF description [4-10]. This statement is most often supported by the successful parameterization of relation (1) within the Landau – de Gennes model (LdG). Yet recently an agreement between the theory and the experiment has been reached due to the concept of *fluidlike*, critical behavior [20-24]. The theoretical model proposed by Mukherjee et al. did not only give reasonable values of ΔT but also predicts a non-zero

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value of the critical exponent $\alpha = 0.5$ in the isotropic phase [11, 23,24] . Recent tests on static dielectric permittivity in nematogenic *n*CB showed that [20-22]:

$$\varepsilon = \varepsilon^{*} + a\left(T - T^{*}\right) + A\left(T - T^{*}\right)^{1-\alpha} \tag{2}$$

$$\text{for } T_{I-N} < T < T_{I-N} + 100K \quad \text{and } \alpha = 0.5 \pm 0.02$$

Taking this value and $\gamma = 1$ from relation (1), the Josephon's scaling relation [7, 21,22] gives the *fluidlike* dimensionality d =3. When discussing relation (1) as the basic tool for determining the value of ΔT some problems should be mentioned. Most often the reciprocals of *KE*, *CME*, I_L are linear functions of temperature only up to 5 - 10 K from T_{I-N}. In the immediate vicinity of the clearing temperature weak distortion from such dependence are noted. Results may strongly influence the additional, empirical, background term. Probably all these are responsible for about 50% scatter of ΔT values for a given nematogen [1-11, 25-27] . In smectogens relation (1) describes experimental only remote from the clearing point. In its broad vicinity pretransitional effects may strongly bend down, bend up or remain constant. This behavior was found for the isotropic – smectic A (I-SmA) transition and for I-N transition in materials with a "narrow" nematic phase between the isotropic and smectic phase [7, 25-27]. The exception is the intensity of the scattered light where the mentioned discrepancies are relatively small [7]. Such behavior makes an unequivocal estimation of ΔT impossible. All these causes that despite several decades of studies there are still limited experimental data concerning the discontinuity of the phase transitions from the isotropic liquid to liquid crystalline mesophases. Significant progress made it possible the application of the static (low frequency) nonlinear dielectric effect. In refs. [20-22, 28,29] the validity of the LdG model based relation was shown:

$$NDE = \frac{A_{NDE}}{T - T^{*}} = \frac{2}{3a}\varepsilon_0 \frac{\left(\Delta\varepsilon^{0}\right)}{T - T^{*}} \tag{3}$$

where A_{NDE} is the amplitude, a is the constant coefficient 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. $NDE = \varepsilon^{E} - \varepsilon / E^{2}$, where ε and ε^{E} are dielectric permittivities in the weak and in the strong electric field E

It is noteworthy that analogous relation can be derived basing on the dependence for the pretransitional effect in binary critical mixture. This relation is valid for the "static" condition $f\tau << 1$, where f is the measurement radio-frequency of the weak measuring field and t is the relaxation time of pretransitional processes. The reciprocal of the *NDE* was found to linear function both in nematogens and smectogens even up to $T_x = T^{C} + 40K$ with no distortions near the clearing point and without any additional background term [22]. This made it possibly to investigate the evolution of ΔT in homologous series of LC compounds and to test the pressure evolution of ΔT. This paper shortly discusses such recent results for 4-cyano-4'-*n*-alkylbiphenyls (*n*CB, *n* = 3 – 12: I –N and I-SmA transitions) and in 4-*n*-4'-isothiocyanatobiphenyls (*n*BT, *n* = 2 to 10: I-SmE transition)[29]. It also shows new temperature and pressure results for 4DBT and 8DBT (*n*DBT: 5-n-alkyl-2-(4-isothio-cyanatophenyl)-1,3-dioxane, I-SmA transitions)[30].

RESULTS AND DISCUSSION

The *NDE* measurements involved the application of two electric field: the weak, measuring (f = 300 kHz and $U_{peak-peak} = 1.5V$ and a strong steady field in the form of pulses of duration $\Delta t_D = 4ms$ and U = 500 – 1300 V. The gap of the capacitor was d = 0.5 mm. The detailed description of measurement set – ups are given in refs. [20-22, 28, 29]. In the applied experimental solution registered are straightforwardly nonlinear changes of dielectric permittivity. For a typical measured capacitance 100 pF the strong electric field induced change are 10 fF – 0.1 fF, registered with 3-digit resolution. Always the condition: $\Delta\varepsilon^E \propto E^2$ was fulfilled.

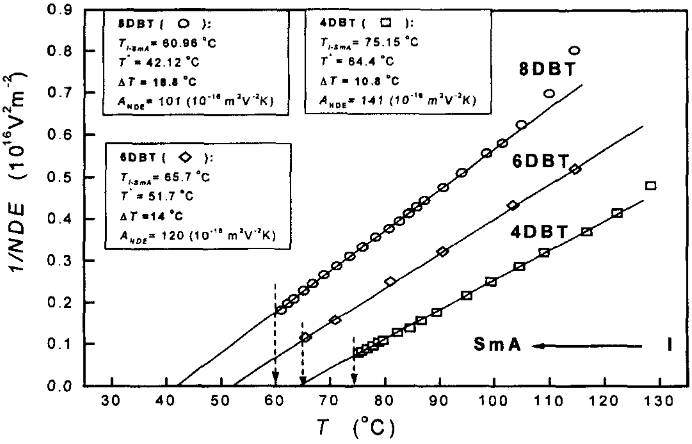

Figure 1 Results of measurements the static *ND*E in the isotropic phase of 4 DBT, 6DBT and 8DBT. Arrows indicate smectic clearing points.

The obtained results show all favorite feature of the static *NDE* mentioned above. The clearing temperature was determined with the precision $\pm 0.01\,\mathrm{K}$ due to the significant change in the *NDE* output signal. The obtained value of discontinuities significantly smaller for 4DBT (10.8 K) than for 8DBT (18.8 K). Similar behavior was found in nCB homologous series. Data from ref. [29] shows following dependencies: $\Delta T = -0.534 + 0.266n$ from 3CB to 8 CB and $\Delta T = -8.4 + 1.26n$ from 8CB to 12CB. The preliminary test in nDBT compounds gave $\Delta T = -2.7 + 2n$. In both series of compounds the discontinuity increases with the rise of the parameter n. However, the discontinuity of the I-SmA transition for nDBT is significantly larger than in nCB. For the mention in the introduction nBT series with the I-SmE transition following dependence was found (n = 2 – 10): $\Delta T = 51.1 - 5.9n(1 - 0.023n)$. In this case the discontinuity decreases with length of the alkyl chain [29].

The difference in the behavior of $\Delta T(n)$ may be associated with the structure of the mesophase. In *n*CB and *n*DBT the orientational ordering increases with the rise of the total length of the rodlike molecule. Hence, the value of ΔT characterizing the distance between symmetries of the isotropic liquid and the mesophase also increases. The well packed structure of SmE phase in *n*BT causes that the alkyl chain may remain the only flexible part of the molecule. Hence, its increase may lower the SmE ordering and consequently the distance between isotropic phase and the mesophase and the value of ΔT[29].

Figure 2 shows the pressure evolution of ΔT in 8DBT. The validity of the pressure analogue of relation (1) is clearly visible:

$$NDE = \frac{A^P_{NDE}}{P^* - P} \quad \text{for} \quad P^* = P_{I-SmA} + \Delta P \text{ and } P < P^* \tag{4}$$

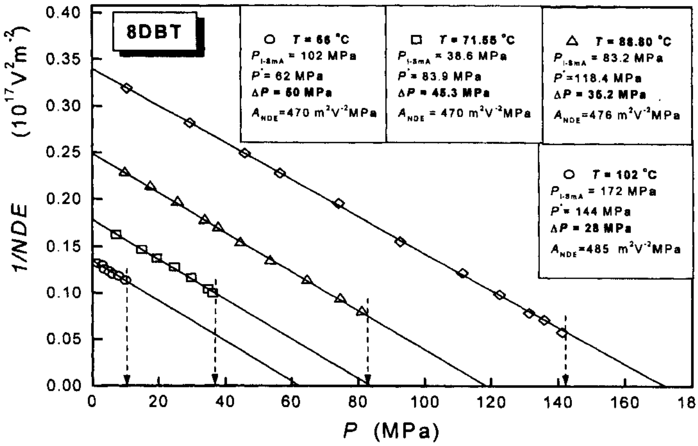

Fig. 2 Isothermic, pressure dependencies of the static *NDE* in the isotropic phase of 8DBT.

For the I-N transition the rise of pressure increases the value of ΔT. This may be related to the fact that pressure first reduces the free volume. For the nematic phase the inscrease of pressure causes the rise of the orientational ordering and hence the distance between symmetries of the isotropic liquid and the nematic phase increase. In smectogens the rise of pressure will probably first shift molecules along the direction of the preferred orientational ordering. This may narrow between symmetries of the isotropic liquid and the smectic phase giving the decreases of ΔT with rising pressure. Results of this paper (8DBT, I-SmA) and that of refs. ([28]: I-SmA in 10CB, 12CB; [29]: I-SmE in 5BT) show such evolution of $\Delta T(P)$. When discussing properties of the parameter ΔT noteworthy is also the lack of the odd – even effect, strongly manifested for the clearing temperature and for the virtual critical temperature T^*[29].

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