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Electric field effect on the nematic–isotropic phase transition

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Pulsed electric fields are used to study the influence of a strong field on the nematic–isotropic phase transition for cyanobiphenyl and stilbene-type liquid crystals. Deviation of the electric field-induced optical anisotropy from the Kerr law is observed and it is shown that such electric fields can shift the transition temperature substantially. The induced birefringence and the shift of the transition temperature are measured as a function of the electric field strength. The results are explained qualitatively in the context of the Landau–De Gennes theory with two order parameters. The coefficients of the phenomenological theory are calculated using the simple density functional theory of polar nematics developed in this paper and the results for the shift of the transition temperature are compared with experiment results.

1. Introduction

It is well known that the nematic–isotropic phase transition is accompanied by strong orientational fluctuations which can interact with relatively weak external fields. This property of nematics opens up a possibility of using these materials for the study of external field effects on first order phase transitions. The influence of electric and magnetic fields has been investigated extensively by many authors, both theoretically and experimentally (for a review, see for example [1, 2]), and measurements of the electric and magnetic birefringence and of the light scattering have confirmed the results of the Landau–De Gennes theory for the nematic–isotropic transition. In these experiments, however, relatively weak external fields have been used and the parameters of the phase transition have not been effected (since the corresponding electromagnetic energy appears to be much smaller than the energy of thermal fluctuations).

On the other hand, the case of very strong external fields has been studied theoretically in the framework of the molecular-statistical theory [3, 4]. In these papers, the main attention has been paid to the critical fields which can transform the first-order transition into the continuous one. In this case, the dependence of the nematic order parameter on the external electric field can be calculated only numerically. The corresponding results have been obtained [4] in the context of a mean-field theory and in the two-particle cluster approximation [3]. It should be noted, however, that the corresponding electric fields are too strong to be used in any experiment with real liquid crystals.

In this paper, we are going to show that there is a possibility of using 'intermediate' electric fields which, on the one hand, are sufficiently weak and can be applied to real nematic cells without electrical breakdown and, on the other hand, are strong enough to induce shift of the transition temperature and noticeable orientational order in the isotropic phase. The corresponding electric field can be roughly estimated as $dE \ll kT_{NI}$ where d is the permanent molecular dipole. At the same time the critical electric field corresponds to the estimate $dE \geq kT_{NI}$.

The influence of relatively weak external fields on the nematic–isotropic phase transition can be a subject of separate theoretical study since, in this case, one can take advantage of the fact that the induced polarization is also small. In this paper we use the simple Landau–De Gennes expansion of the free energy, in terms of the nematic order parameter and the induced polarization, and show that our experimental data can be explained qualitatively with the help of this general approach. The influence of the external electric field is considered also in the context of the density functional approach, and the simple model is used to calculate the coefficients of the phenomenological

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theory and to make more quantitative comparison with experiment.

This paper is organized as follows. In § 2 we discuss the use of the pulsed fields in the measurements of the Kerr effect and present the results of the measurements of the transition temperature shift and of the non-linear electric birefringence. In § 3.1 we develop the simple phenomenological theory of the electric field effect on the nematic–isotropic phase transition and in § 3.2 we present the corresponding statistical theory and discuss the relation between the theory and experiment. Finally, in § 4 we present our conclusions and discuss the limitations of the present approach.

2. Experimental results

2.1. *Method of pulsed fields*

Experiments on the effect of strong external fields on liquid crystals run into definite difficulties. The reason is that it is necessary to use magnetic fields strong enough to make the energy of the interaction of the liquid crystal with the external field comparable to the energy of the intermolecular interactions which are responsible for the long-range orientational order in a mesomorphic substance. This condition cannot be met by using magnetic fields which are actually attainable experimentally [5]. Electric fields are far more promising [6, 7]. In the case of a static or alternating (sinusoidal) field, however, fundamental difficulties arise because of the electrical conductivity of liquid crystals, the influence of hydrodynamic flows [8], dielectric heating [9] and the possibility of electrical breakdown in strong fields.

In this section we report the use of pulsed fields to study the influence of strong electric fields on the nematic–isotropic phase transition. The pulsed fields have made it possible to eliminate the influence of the parasitic factors listed above on the corresponding effects. The first experimental results have been reported earlier [10]. The experimental method was based on the Kerr effect (electric birefringence) which made it possible to study both (a) the behaviour of the birefringence as a function of the electric field at temperatures just before the transition region in which there are strong orientational fluctuations in the isotropic state [11, 12] and (b) the effect of the external field on the nematic–isotropic transition temperature.

Single electric pulses with a length of 0·2 ms and a field strength E up to $3 \times 10^7 \, \text{V m}^{-1}$ were applied to the Kerr cell. Two Kerr cells with the optical path length $l = 3 \times 10^{-3} \, \text{m}$ and $5 \times 10^{-3} \, \text{m}$ and the gap between electrodes $5 \times 10^{-4} \, \text{m}$ were used. The cell temperature was held constant within 0·05°C.

For measurements of the phase difference δ which arises in the Kerr cell during the application of the electric field (this difference reaches several tens of wavelength at the field strengths used), we used an electrical pulse with a special shape: an exponentially rising front edge and a short end edge (see figure 1 (a)). The voltage rise at the front edge of the pulse was accompanied by the appearance of maxima and minima in the light flux, corresponding to a change of 2π in the phase difference between the interfering ordinary and extraordinary rays (see figure 1 (b)). The number of observed minima, m, determines the magnitude (Δn) of the birefringence which arises in the substance under study: $\Delta n = m\lambda/l(m = 1, 2, ...)$ at various electric fields. Here $\lambda = 628 \, \text{nm}$ is the wavelength of the light source.

We used homologues of the series of 4-alkyl-4'-cyanobiphenyls (nCB) which have a large positive dielectric anisotropy in the nematic phase $(\Delta\epsilon > 10)$ and differ significantly in the heat of transition (q) from the nematic to isotropic phase: $q = 0.094 \, \text{kcal mol}^{-1}$ (5CB), $q = 0.16 \, \text{kcal mol}^{-1}$ (6CB), $q = 0.64 \, \text{kcal mol}^{-1}$ (10CB) [13].
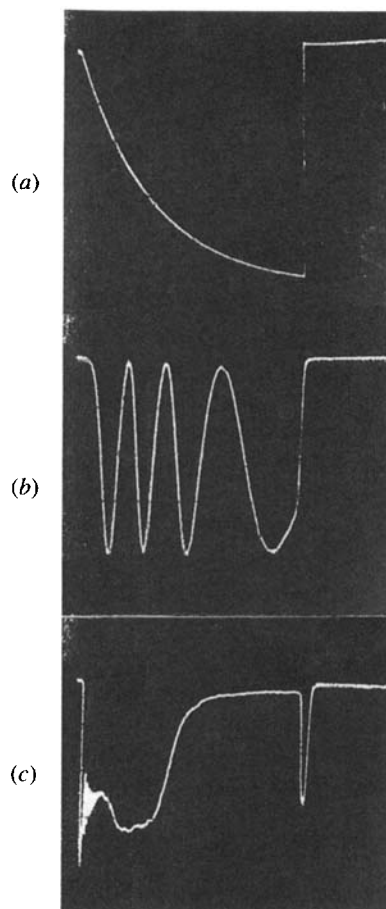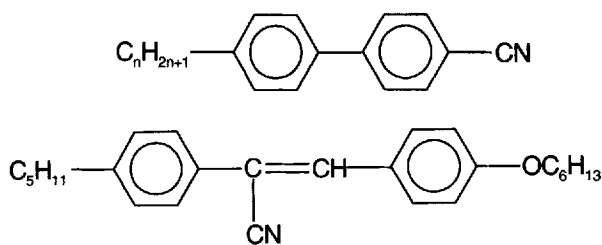

Figure 1. (a) The electrical pulse; (b), (c) oscilloscope traces of the light beam transmitted through a Kerr cell holding 6CB for $\Delta T = 0.4°C$ and for various electric field strengths; (b) $E = 2 \times 10^6 \, \text{V m}^{-1}$; (c) $E = 5.9 \times 10^6 \, \text{V m}^{-1}$.

We used also the nematic material 4-pentyl-4'-hexyloxy-α-cyanostilbene which has a large negative dielectric anisotropy $\Delta\epsilon < -5$ and $q = 0.28 \, \text{kcal mol}^{-1}$ [14, 15].

2.2. Results

Figure 2 shows the measured birefringence versus E^2 for various temperatures $\Delta T = T - T_0$ for 5CB and the cyanostilbene (CS). In accordance with the sign of the dielectric anisotropy, the birefringence is positive for 5CB and negative for CS. At weak fields one observes a linear dependence of Δn on E^2, while at strong fields we found a deviation from the Kerr law, in the direction of an increase in the measured anisotropy for the cyanobiphenyls with positive dielectric anisotropy. By contrast, for the cyanostilbene, the deviation is in the direction of a decrease in the absolute value of the measured anisotropy. The deviations observed correspond to a phase difference δ of several wavelengths. A further increase in the field revealed the value of E at which the
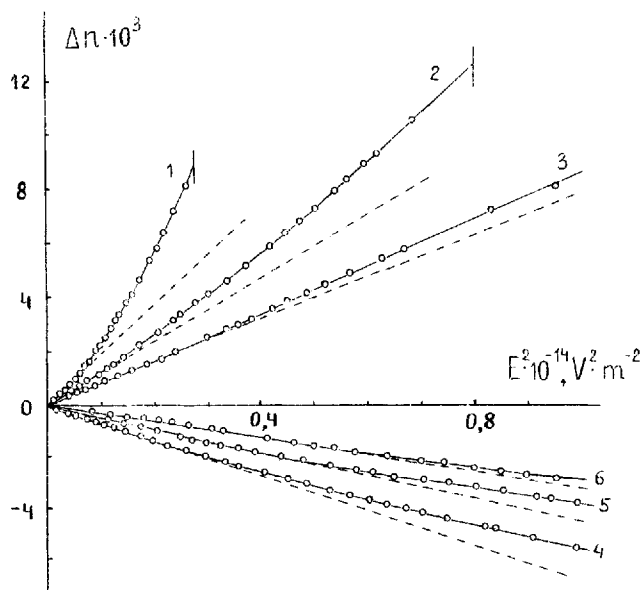

Figure 2. Magnitude of birefringence, Δn, versus the square of the electric field, E^2, in the isotropic phase of 5CB (1)–(3) and CS (4)–(6) at various temperatures $\Delta T = T - T_0$: (1) 0·1°C; (2) 0·5°C; (3) 1·08°C; (4) 0·1°C; (5) 0·45°C; (6) 1·15°C. Vertical lines correspond to the values of the electric field E at which the transition to the nematic phase is induced.

cell holding the substance became opaque in the transmitted beam (see figure 1 (c)). We attribute the disappearance of the light flux to the transition of the substance from the isotropic to the nematic phase caused by the electric field. The field which causes the transition of the samples to the nematic phase is shown as a function of the change in transition temperature ΔT in figure 3. The slope of the straight lines is equal to 2; this slope corresponds to a proportionality between the change in the phase transition temperature and E^2. It can be concluded from the experimental data that the value of E required for the phase transition depends on the transition heat q. At a fixed temperature ΔT, a progressively greater field strength E will bring about a phase transition as the transition heat of the sample is raised (see figure 3). In the case of 10CB (which has the largest heat of transition from the isotropic to the smectic state) and of CS, we were not able to reach a phase transition even at the strongest fields E used in the present experiment.

It has been mentioned already [8, 9] that application of large electric fields to a liquid crystal can cause some parasitic effects which could influence the results of this investigation. In particular, there is some concern over the possibility of thermal heating of the liquid crystal by the electric field pulses. There exists also the possibility of changes in the sample thickness with increasing field strength due to capacitance effects. In addition, some polarization effects could reduce the effective electric field in the liquid crystal media and the nematic ordering could be favoured also by hydrodynamic fluxes determined by the electrical conductivity of the liquid crystal. The influence of these effects is discussed in more detail below.

The change in temperature of the nematic liquid crystal caused by the electric field can be estimated by taking into account the values of the length and the amplitude of the electric pulses used in the experiment. Taking the length of the pulse $\sim 0.2 \, \text{ms}$ and the amplitude $\sim 10^7 \, \text{V m}^{-1}$ and using values of the electrical
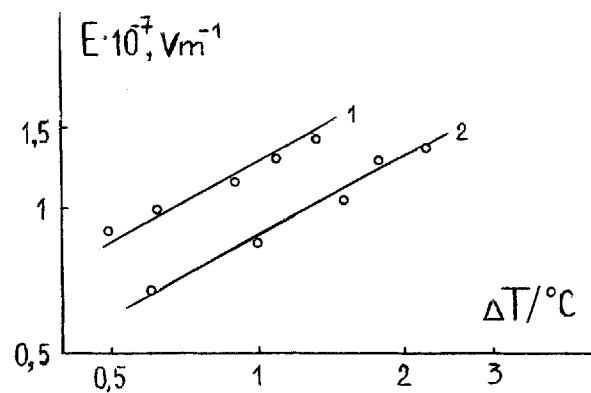

Figure 3. Change in the transition temperature versus the electric field, in logarithmic scale. (1) 5CB, (2) 6CB.

conductivity $\sigma = 10^{-8} (\Omega m)^{-1}$ and the heat capacity $\lambda \sim (2-6) \mathrm{J g}^{-1} \mathrm{grad}$, we arrive at the conclusion that in the present experiment the temperature change is less than 2×10^{-4}.

We note also that the additional heating of the nematic (as well as the decrease in the effective field in the media due to polarization effects) can only diminish the observed deviations from the Kerr law.

One expects also that, in the present case, possible changes in the distance between the electrodes (the sample thickness) have the same effect on the observed phenomena for all temperatures used in the experiment. However, one can readily see from figure 2 that the deviation of the curves from the usual Kerr law depends on temperature. Except for vicinity of the phase transition point (i.e. for $T - T_c > 3°C$), deviations from the linear law are observed for all values of the field strength used in this study.

It should also be noted here that sufficiently thick nematic layers have been used in this experiment (the optical path length was $\sim 5 \times 10^{-3} \mathrm{m}$ and the gap between the electrodes was $\sim 5 \times 10^{-4} \mathrm{m}$). In this case the changes in the layer thickness due to thermal expansion of the electrodes must be several orders of magnitude smaller than the initial cell thickness. Such weak effects cannot cause any noticeable changes in the electric field applied to the material.

Finally we note that the intensity of hydrodynamic fluxes (which can occur in a conductive cell) is expected to depend on the length of the electric pulses. However, we do not see any influence of pulse length on the results of our measurements in the interval 0·1–1·0 ms. This fact, probably, can be considered as an indication that weak hydrodynamic fluxes do not influence practically the results of the present study.

3. Influence of the external electric field on a nematic phase composed of strongly polar molecules

3.1. *Phenomenological theory*

The external electric field induces a macroscopic polarization **P** and, therefore, the free energy of the polar nematic phase is a function of two independent internal thermodynamical variables: the orientational order parameter $Q_{\alpha\beta}$ and the polarization **P**. Taking into account the relatively small value of the induced polarization, one can expand the free energy in powers of $Q_{\alpha\beta}$ and **P**, neglecting the higher order terms in **P**

$$F = \tfrac{1}{2}a(T - T_c^*)Q^2 - \tfrac{1}{3}bQ^3 + \tfrac{1}{4}cQ^4 + \tfrac{1}{2}\chi_0^{-1}P^2$$
$$+ \sigma P_\alpha Q_{\alpha\beta} P_\beta + \kappa_0 Q^2 P^2 + \kappa_1 Q_{\alpha\gamma} Q_{\gamma\beta} P_\beta - P_\alpha E_\alpha, \quad (1)$$

with $b > 0$ and $c > 0$.

Equation (1) can be simplified if one assumes that the polarization is aligned along the nematic director **n**.

In this case

$$F = \tfrac{1}{2}a(T - T_c^*)S^2 - \tfrac{1}{3}bS^3 + \tfrac{1}{4}cS^4$$
$$+ \tfrac{1}{2}\chi_0^{-1}P^2 + \sigma P^2 S + \tfrac{1}{2}\kappa P^2 S^2 - PE, \quad (2)$$

with $\kappa = 2(\kappa_0 + \kappa_1)$.

It should be noted that χ_0 is the polarizability of the isotropic phase, while the parameters σ and κ represent the anisotropy of the polarizability in the nematic phase. Indeed, one can expand the free energy first in powers of the polarization P

$$F = F_0(S) + \tfrac{1}{2}\chi_\parallel^{-1}P^2 - PE, \quad (3)$$

where F_0 is the free energy of the nematic without an external field. Note that the longitudinal polarizability $\chi_\parallel$ is a function of the nematic order parameter S. Expanding the polarizability $\chi_\parallel$ in powers of S one obtains the terms $\sigma P^2 S^2$ and $\kappa P^2 S^2$ which are present in equation (2).

Let us minimize the free energy (2) with respect to P at fixed E. Then the equilibrium polarization P is expressed in terms of the order parameter S and the electric field E

$$P = (1 + 2\sigma\chi_0 S + \kappa\chi_0 S^2)^{-1}\chi_0 E. \quad (4)$$

Substitution of equation (4) into equation (2) and expansion in powers of S yields the new expression for the free energy with the coefficients depending on the external electric field E

$$F \approx \tfrac{1}{2}a(T - T_c^*)S^2 - \tfrac{1}{3}bS^3 + \tfrac{1}{4}cS^4$$
$$+ \sigma\chi_0^2 SE^2 + \chi_0^2(\tfrac{1}{2}\kappa - 2\chi_0\sigma^2)S^2E^2 - \tfrac{1}{2}\chi_0 E^2. \quad (5)$$

The analysis of equation (5) shows the influence of the external electric field on the nematic liquid crystal results in two main effects. First, the external field produces a shift of the transition temperature T_c^* which is proportional to the square of the electric field

$$\Delta T_c^* = \chi_0^2 a^{-1}(4\sigma^2\chi_0 - \kappa)E^2. \quad (6)$$

This result is in qualitative agreement with the experimental data presented in figure 3. Secondly, the external field induces weak orientational ordering in the isotropic phase. This effects is determined by the fourth term in equation (5). Indeed, the value of the order parameter S is determined by minimization of the free energy (5)

$$a(T - T_c - \alpha E^2)S - bS^2 + cS^3 = \lambda E^2, \quad (7)$$

with

$$\alpha = a^{-1}\chi_0^2(4\sigma^2\chi_0 - \kappa) \quad (8)$$

and

$$\lambda = \sigma\chi_0^2. \quad (9)$$

The orientational order parameter, induced by a weak external field, also appears to be small and can be expanded in powers of E^2

$$S = \beta E^2 + \gamma E^4 + \ldots, \quad (10)$$

with

$$\beta = \frac{\sigma\chi_0^2}{a(T - T_c)^2}\left(\alpha + \frac{b\sigma\chi_0^2}{a(T - T_c)}\right), \qquad (11)$$

where the coefficient α is determined by equation (8).

Note that in the first approximation, $S \approx \beta E^2$. This conclusion corresponds to the well-known result in the theory of the Kerr for liquids composed of non-polarizable molecules (see, for example, [1], § 2.4.2).

In the case of a weak nematic ordering, induced by the external field, the birefringence Δn is proportional to the order parameter S

$$\Delta n \approx n_0 S. \qquad (12)$$

Thus the dependence of the birefringence on the amplitude of the external field is determined also by the expansion (10)

$$\Delta n = n_0\beta E^2 + n_0\gamma E^4 + \dots. \qquad (13)$$

One can readily see that the simple expansion (13), supplemented by equations (11), (12) and (8) for the coefficients β and γ, enables us to explain qualitatively the experimental behaviour of Δn as a function of E^2, as presented in figure 2. Indeed, at weak electric fields, the birefringence Δn is proportional to E^2 and, according to equation (11), the corresponding coupling constant grows when one approaches the transition point (since $\beta \propto (T - T_c^*)^{-1}$). At larger fields one observes a positive deviation from the simple Kerr law. This deviation can be described by the second term in the expansion (10).

It should be noted that in the general case, the coefficient σ in equations (5) and (11) can be both positive and negative. However, the external electric field induces the ordering of long molecular axes only in the case of $\sigma > 0$. From the microscopic point of view, the positive values of σ corresponds to the case when the angle between the molecular dipole and the long axis is less than 45°. In the cyanobiphenyls investigated experimentally in the present work, the dipole moment is approximately parallel to the molecular long axis and therefore $\sigma > 0$.

Thus, for $\sigma > 0$ the external electric field induces the ordering of long molecular axes and shifts the phase transition temperature. The value of the shift is determined by equation (6). Note that the experimental values of ΔT_c^* are positive and therefore the coefficient $\alpha > 0$. Then the coefficient γ in equation (13) is also positive and the birefringence Δn grows faster than E^2 in accordance with the experiment.

It is interesting to discuss also the case of $\sigma < 0$, which corresponds to a nematic composed of molecules with transverse dipoles. In such systems, the external electric field induces a negative orientational order parameter (see equations (10) and (11)), since now the short molecular axes are ordered along the field. Note that at small electric fields, the birefringence is still proportional to E^2, but has the negative sign. At the same time, the non-linear correction to S or Δn in equations (10) and (13) is positive, because it is proportional to σ^2. Thus, in this case the birefringence must grow more slowly than E^2, contrary to the case of $\sigma > 0$.

The experimental data, obtained for the nematic stilbene with a negative dielectric anisotropy, confirm these theoretical predictions. Indeed, the birefringence Δn appears to be negative (see figure 2) and its absolute value is less than the extrapolated value, calculated according to the Kerr law. This behaviour is in striking contrast with the properties of the cyanobiphenyls discussed in detail in § 2.

3.2. *Density functional approach*

Let us consider now the influence of the external electric field on the nematic–isotropic phase transition from the microscopic point of view. The energy of the single molecule 'i' in the external electric field $\mathbf{E}$ can be written in the form

$$U_E(i) = -\alpha_{\alpha\beta}E_\alpha E_\beta - d_\alpha E_\alpha, \qquad (14)$$

where $\alpha_{\alpha\beta}$ is the molecular polarizability tensor and $\mathbf{d}$ is the permanent molecular dipole.

It is interesting to consider the orders of magnitude of the first and second terms in equation (14) for typical values of the field used in the experiment. Indeed, for the nematic cyanobiphenyls, the polarizability $\alpha < 10^2 \times 10^{40}\,\text{F m}^{-2}$ and $d \approx 5\,\text{D}$ [2].

Substituting the amplitude of the electric field $E \sim 10^5\,\text{V cm}^{-2}$, one obtains $dE/\alpha E^2 \sim 10^2 \gg 1$, i.e. the predominant contribution arises from the interaction between the external field and the permanent molecular dipole. In this case, in the first approximation, one can neglect the effects of molecular polarizability. Note that this conclusion corresponds to the existing understanding of the static polarizability of strongly polar nematics, which is determined mainly by the ordering of permanent dipoles [2].

Thus, in the first approximation, we can neglect the molecular polarizability and consider the influence of the external electric field in the framework of the simple model of rigid molecules with longitudinal dipoles. It should be noted that the statistical theory of such nematic liquid crystals in strong external fields has been considered by several authors [3, 4]. In this section we consider in more detail the influence of the relatively weak electric field (i.e. $dE \ll kT$) and derive the Landau–De Gennes expansion of the free energy in powers of two order parameters. The coefficients of this expansion will be expressed in terms of the minimal number of model parameters.

The most general statistical theory of nematic liquid crystals can be developed with the help of the Density

Functional Approach [16]. In this approach the free energy is represented as a sum of two terms

$$F = \Phi + H, \tag{15}$$

where Φ is the free energy of the system without intermolecular interactions

$$\Phi = \rho_0 kT \int dx_1 f_1(x_1)(\ln f_1(x_1)\Lambda + 1 - (d_1 E)/kT), \tag{16}$$

where ρ_0 is the number density, $f_1(x_1)$ is the one-particle distribution function and the variable $x = (r; \omega)$ stands for position and orientation.

The functional H is determined by intermolecular interactions and depends on the one particle distribution function $f_1(x)$. The functional derivatives of H are proportional to the direct correlation functions of the system. These properties of the functional H enable one to expand the free energy of the nematic phase around its value in the isotropic phase

$$F = F_0 + \rho_0 kT \int dx_1 f_1(x_1)(\ln f_1(x_1)\Lambda + 1 - (d)1E)/kT),$$

$$- \tfrac{1}{2}\rho_0^2 kT \int dx_1 dx_2 C_2(x_1, x_2)\Delta f_1(x_1)\Delta f_1(x_2) + \ldots, \tag{17}$$

where F_0 is the free energy of the isotropic phase, $C_2(x_1, x_2)$ is the direct pair correlation function of the isotropic phase and $\Delta f_1(x) = f_1(x) - \tfrac{1}{4}\pi$ is the difference between the one-particle distributions in the nematic and isotropic phases. Note that the equation (17), we have neglected the higher order terms in Δf_1. At the same time, one has to take into account that the external electric field induces the relatively weak orientational order in the isotropic phase, except in the close vicinity of the transition point. Thus, far from the transition point, equation (17) appears to be very accurate.

Equation (17) can be simplified in the case of uniaxial molecules with permanent dipoles $(d)_i$ parallel to the molecular long axes a_i

$$F = F_0 + \rho_0 kT \int d^2 a_1 f_1(a_1 n)(\ln f_1(a_1 n)\Lambda + 1 - d_{\parallel}(a_1 E)$$

$$- \tfrac{1}{2}\rho_0^2 kT \int d^2 a_1 d^2 a_2 \tilde{C}_2(a_1, a_2)\Delta f_1(a_1 n)\Delta f_1(a_2 n), \tag{18}$$

with

$$\tilde{C}_2(a_1, a_2) = \int d^3 r_{12} C_2(r_{12}, a_1, a_2) \tag{19}$$

where n is the nematic director.

The one-particle distribution function $f_1(an)$ corresponds to the minimum of the free energy (18) with fixed external field E

$$f_1(a_1 n) = Z^{-1} \exp\left[\int d^2 \tilde{C}_2(a_1, a_2) + \frac{d_{\parallel}(a_1 E)}{kT}\right] \tag{20}$$

with

$$Z = \int d^2 a_1 \exp\left[\int d^2 a_2 \tilde{C}_2(a_1, a_2) + \frac{d_{\parallel}(a_1 E)}{kT}\right]. \tag{21}$$

In principle, equation (20) enables one to calculate the main thermodynamic properties of nematics in the external electric field, provided that the direct correlation function $C_2(1, 2)$ is known. At the same time, it is possible to obtain many qualitative results even without detailed information about the correlation function. Indeed, the function $\tilde{C}_2(a_1, a_2)$ (see equation (19)) depends on the scalar product $(a_1 a_2)$ only and can be expanded in Legendre polynomials $P_n(a_1 a_2)$:

$$\tilde{C}_2(a_1, a_2) = \sum_n J_n P_n(a_1 a_2). \tag{22}$$

In the case of polar nematics the main contribution to the effective potential comes from the first two terms in the expansion (22) which determine the polar and non-polar ordering of molecular long axes. This ordering is characterized by two independent order parameters p and S

$$p = \langle(a_1 n)\rangle, \tag{23}$$

$$S = \langle P_2(a_1 n)\rangle, \tag{24}$$

where $\langle \ldots \rangle$ is the statistical averaging. Note that the macroscopic polarization $P = \rho_0 d_{\parallel} p$.

In this paper we develop a simple qualitative theory which is sufficient to describe our experimental data. Then, for simplicity, we shall not take into account the higher order terms in the expansion of the direct correlation function. As a result we arrive at the following simple model expression for the function $\tilde{C}_2(a_1 a_2)$

$$\tilde{C}_2(a_1 a_2) \approx \text{const.} + \frac{J_1}{kT}(a_1 a_2) + \frac{J_2}{kT}(\tfrac{3}{2}(a_1 a_2) - \tfrac{1}{2}). \tag{25}$$

Substitution of equation (25) into (18) yields the following simple expression for the free energy of the nematic in the external electric field

$$F = F_0 + \rho_0 kT \int d\cos\Theta f_1(\cos\Theta)[\ln f_1(\cos\Theta)\Lambda + 1]$$

$$- \rho_0 d_{\parallel} E p - \tfrac{1}{2}\rho_0^2 J_1 p^2 - \tfrac{1}{2}\rho_0^2 J_2 S^2, \tag{26}$$

where the order parameters p and S are determined by equation (23) and (24) and $\cos\Theta = (an)$.

It should be noted that in the context of this model the influence of the external electric field is determined by the two parameters J_1 and J_2 only.

3.3. Derivation of the Landau–De Gennes expansion for polar nematics

In § 3.1 we have used the phenomenological expansion of the free energy in terms of the polarization P and the nematic order parameter S. This expansion can also be

derived from equation (26). In this way one also obtains simple expressions for the coefficients of the phenomenological theory.

The general method of derivation of the Landau–De Gennes expansion, starting from a molecular model for nematics, has been proposed by Katriel, Kventsel *et al.* [17]. In the present paper we use this method in the description of the polar nematic phase with two independent internal parameters S and p.

The equilibrium free energy density of the nematic phase with fixed external parameters (i.e. the temperature T, electric field E and the number density ρ_0) can be obtained after minimization of the free energy with respect to the one-particle distribution function. On the other hand, this procedure can be performed in two steps [17]. At the first stage, the free energy is minimized at the fixed values of the two order parameters S and p. After this partial minimization, one obtains the free energy (i.e. the enthalpy) as a function of two order parameters. The expansion of this free energy in powers of S and p is equivalent to the Landau–De Gennes expansion discussed in § 3.1.

One can readily see from equation (26) that the minimization of the free energy F at fixed S and p is equivalent to the maximization of the entropy determined by the second term in equation (26). Therefore, one has to find a minimum of the following functional:

$$\Delta H = kT \int d\cos \Theta f_1(\cos \Theta) \ln f_1(\cos \Theta)$$

$$- \lambda_1 \int d\cos \Theta f_1(\cos \Theta) \cos \Theta$$

$$- \lambda_2 \int d\cos \Theta f_1(\cos \Theta) P_2(\cos \Theta) \qquad (27)$$

where λ_1 and λ_2 are the corresponding Lagrange multipliers. The minimum of the functional (27) corresponds to the one-particle distribution function which depends on the parameters λ_1, λ_2

$$f_1(\cos \Theta) = Z_0^{-1} \exp\left[\frac{\lambda_1}{kT} \cos \Theta + \frac{\lambda_2}{kT} P_2(\cos \Theta)\right] \qquad (28)$$

and

$$Z_0 = \int d\cos \Theta \exp\left[\frac{\lambda_1}{kT} \cos \Theta + \frac{\lambda_2}{kT} P_2(\cos \Theta)\right]. \qquad (29)$$

The Lagrange multipliers λ_1 and λ_2 can be expressed in terms of the order parameters S and p using the definitions (23) and (24). Indeed, by definition

$$S = \int P_2(x) f_1(x) dx = Z_0^{-1} \int P_2(x) \exp[\lambda_1 x + \lambda_2 P_2(x)] dx \qquad (30)$$

and

$$p = \int x f_1(x) dx = Z_0^{-1} \int x \exp[\lambda_1 x + \lambda_2 P_2(x)] dx \qquad (31)$$

where Z_0 is determined by equation (29).

Note that the parameters λ_1, λ_2 are determined completely by equations (30) and (31). Substituting equations (28) and (29) into (26), we obtain an expression for the free energy as a function of the parameters λ_1, λ_2

$$F = F_0 + \rho_0 kT \lambda_1 p + \rho_0 kT \lambda_2 S$$

$$- \rho_0 kT \ln Z_0 - \tfrac{1}{2}\rho_0^2 J_1 p^2 - \tfrac{1}{2}\rho_0^2 J_2 S^2 - d_\parallel \rho_0 pE. \qquad (32)$$

Note, however, that we need an expression for the free energy as a function of the order parameters S and p. Then one has to express the parameters λ_1 and λ_2 in terms of S and p using equations (30) and (31). Let us expand the right-hand sides of equations (30) and (31) in powers of λ_1, λ_2 and represent the order parameters S and p in the form of a power series

$$S = \tfrac{1}{5}\lambda_1 + \tfrac{1}{35}\lambda_1^2 + \tfrac{1}{15}\lambda_2^2 - \tfrac{1}{175}\lambda_1^3 + \tfrac{2}{105}\lambda_1\lambda_2^2 + \dots \qquad (33)$$

and

$$p = \tfrac{1}{3}\lambda_2 + \tfrac{2}{15}\lambda_1\lambda_2 - \tfrac{1}{45}\lambda_2^3 + \tfrac{2}{105}\lambda_1^2\lambda_2 + \dots . \qquad (34)$$

The function $\ln Z_0$ can also be expanded in powers of λ_1, λ_2

$$\ln Z_0 = \tfrac{1}{10}\lambda_1^2 + \tfrac{1}{6}\lambda_2^2 + \tfrac{1}{105}\lambda_1^3 + \tfrac{1}{15}\lambda_1\lambda_2^2$$

$$+ \tfrac{1}{4}\lambda_1^4 + \tfrac{1}{24}\lambda_2^4 + \tfrac{1}{105}\lambda_1^2\lambda_2^2 + \dots . \qquad (35)$$

Now it is possible to invert equations (33) and (34) (see [16] for a similar procedure in the case of one order parameter) and to get the expansion of λ_1, λ_2 in powers of the order parameters S and p:

$$\lambda_1 = 5S - \tfrac{25}{7}s^2 - 3p^2 + \tfrac{17 \cdot 25}{49}S^3 + 4Sp^2 + \dots \qquad (36)$$

and

$$\lambda_2 = 3p - 6Sp - \tfrac{9}{5}p^3 + 12S^2 p + \dots . \qquad (37)$$

Substitution of equations (36) and (37) into equation (32) finally yields an expansion of the free energy of the polar nematic in terms of the order parameter S and polarization P

$$F = F_0 + \tfrac{1}{2}a(T - T_c^*)S^2 - \tfrac{1}{3}bS^3 + \tfrac{1}{4}cS^4$$

$$+ \tfrac{1}{2}\chi_0^{-1}P^2 - \sigma P^2 S + \tfrac{1}{2}\kappa P^2 S^2 - PE, \qquad (38)$$

with

$$a = 5\rho_0 kT, \qquad (39)$$

$$kT^* = \frac{\rho_0 J_2}{5}, \qquad (40)$$

$$b = \tfrac{25}{21}\rho_0 kT, \qquad (41)$$

$$c = \tfrac{425}{196}\rho_0 kT, \qquad (42)$$

$$\chi_0^{-1} = 3\left(\rho_0^{-1}kT - \frac{J_1}{3}\right)d_\parallel^{-2}, \qquad (43)$$

$$\sigma = 3kTd_\parallel^{-2}\rho_0^{-1}, \qquad (44)$$

and

$$\kappa = 12kTd_\parallel^{-2}\rho_0^{-1}. \qquad (45)$$

One can readily see that the expansion (38) is equivalent to equation (2) which has been obtained in the framework of the phenomenological theory. However, the coefficients of this expansion are expressed now in terms of the polar (J_1) and non-polar (J_2) orientational interaction coupling constants.

Note that the coefficient σ is negative. This result corresponds to the fact that in nematics with positive dielectric anisotropy, the external electric field induces a positive orientational order parameter (see equations (8), (9)). The shift of the transition temperature ΔT_c^*, given by equation (6), is also positive since $4\sigma^2\chi_0 > \kappa$ for $\chi_0 > \frac{1}{3}$. Indeed, for cyanobiphenyl liquid crystals the dielectric susceptibility $\epsilon \approx 10$ and thus $\chi_0 \approx 0.75$.

In principle, we cannot exclude the situation when the polarizability χ_0 is small and the external field diminishes the transition temperature even in nematics with positive dielectric anisotropy. However, from the experimental point of view, this is hardly possible, since nematics with low dielectric susceptibility are composed of weakly polar molecules and thus it would be necessary to apply too high fields to observe the effect.

Note that the expression for the shift of the transition temperature ΔT_c^* (see equations (6), (42) and (43)) does not contain any unknown model parameters and therefore we can directly estimate the value of the shift and compare it with the experimental data. Indeed, for cyanobiphenyl liquid crystals the dipole moment $d = 15 \times 10^{-7}$ C m, the number density $\rho_0 \approx 2 \times 10^{-15}$ m^{-3} and the typical value of χ_0 is 0.8. Substituting these values into equations (6), (42) and (43), we arrive at the estimate $\Delta T_c^*/E^2 \approx 0.45 \times 10^{-14}$ (grad m^2 V^{-2}) for the maximum value of the electric field $E = 1.5 \times 10^3$ V m^{-1} which we could use in our experiment. This is very close to the experimental values of this relation for 5CB which are changed from 0.35 to 0.62×10^{-14} (grad m^2 V^{-2}). It should be stressed here that the molecules of 5CB possess relatively short alkyl tails and therefore they are closer to the simple model of rigid molecules which we use in the present paper.

4. Conclusions

The experimental data, presented in § 2, indicate that the method of pulsed fields appears to be very effective for a study of the influence of strong electric fields on the parameters of the nematic–isotropic phase transition. It is

important to note that pulsed fields can be made sufficiently strong to produce noticeable shifts of the transition temperature and to observe the deviation of the induced anisotropy from the Kerr law. It should be noted also that the influence of the electric field strongly depends on the dielectric anisotropy of the nematic phase. The sign of the induced birefringence always coincides with that of the dielectric anisotropy, while the non-linear correction to the Kerr law is not sensitive to the sign of $\Delta\epsilon$.

The main experimental results of the present study have been explained qualitatively in § 3.1 using the Landau–De Gennes expansion of the free energy of a polar nematic phase. In this case, there are two independent internal parameters: the orientational order parameter S and the polarization P induced by the external field. The coefficients of this expansion have been calculated within the simple molecular-statistical theory which enabled us also to obtain an expression for the shift of the transition temperature which does not depend upon any model parameters. As shown in § 3.2, the qualitative agreement between the theoretical and experimental values of ΔT_{NI} appears to be surprisingly good in spite of some rather crude approximations made in the development of the present model. It should be noted, however, that it is difficult to distinguish between the members of the nCB homologous series within the present model and thus one obtains approximately the same values of ΔT_{NI} for different cyanobiphenyls (since the values of the parameters ρ_0, $d_\parallel$ and χ_0 do not differ much for the 5CB, 6CB and 10CB used in the present study). By contrast, the experimental values of ΔT_{NI} are different and correlate with the transition heat, growing significantly when one goes from 5CB to 10CB. For example, in the case of 10CB, which has the largest transition heat, the available electric fields have not been strong enough to produce an observable shift of the transition temperature.

This contradiction is related to the oversimplified model of rigid molecules used in the present theory. It is well known that, within this model, one cannot account for the rapid growth of the transition heat in homologous series of nematic liquid crystals [18]. In the same spirit, the influence of the electric field on different members of the nCB series can be explained only in the context of a more advanced statistical theory which takes into consideration the molecular flexibility.

References

[1] CHANDRASEKHAR, S., 1992, *Liquid Crystals*, second edition (Cambridge University Press), Chap. 2.

[2] DE JEU, W. H., 1980, *Physical Properties of Liquid Crystalline Materials* (Gordon & Breach).

[3] SAVITRAMA, K. L., and MADHUSUDANA, N. V., 1983, *Molec. Crystals liq. Crystals*, **103**, 99.

[4] DUNMUR, D. A., and TOMES, A. E., 1981, *Molec. Crystals liq. Crystals*, **76**, 231.

[5] ROSENBLATT, C., 1983, *Phys. Rev.* A, **27**, 1234.

[6] NICASTRO, A. J., and KEYES, P. H., 1984, *Phys. Rev.* A, **30**, 3156.

[7] HELFRICH, W., 1970, *Phys. Rev. Lett.*, **24**, 201.

[8] NICASTRO, A. J., and INMAN, X. G., 1982, *Molec. Crystals liq. Crystals*, **90**, 111.

[9] SHADT, M., 1982, *Physics Lett.* A, **81**, 355.

[10] ROTINJAN, T. A., RJUMTSEV, E. I., and YASIKOV, S. B., 1987, *Soviet Phys. JETP Lett.*, **46**, 331.

[11] TSVETKOV, V. N., 1939, *Zh. eksp. teor. Fiz.*, **9**, 290.

[12] TSVETKOV, V. N., and RJUMTSEV, E. I., 1968, *Kristallogr.*, **13**, 290.

[13] COLES, H. J., 1978, *Molec. Crystals liq. Crystals*, **49**, 67.

[14] AGAFONOV, M. A., POLUSHIN, S. G., and RJUMTSEV, E. I., 1987, *Optica Spectrosk.*, **62**, 784.

[15] RJUMTSEV, E. I., KOVSHIK, A. P., POLUSHIN, S. G., and TSVETKOV, V. N., 1984, *Dokl. Akad. Nauk USSR*, **274**, 313.

[16] SLUCKIN, T. J., and SHUKLA, P., 1983, *J. Phys.* A, **16**, 1539.

[17] KATRIEL, J., KVENTSEL, G. F., LUCKHURST, G. R., and SLUCKIN, T. J., 1986, *Liq. Crystals*, **1**, 337.

[18] LUCKHURST, G. R., 1985, *Nuclear Magnetic Resonance of Liquid Crystals*, edited by J. W. Emsley (Reed Publishing Company).