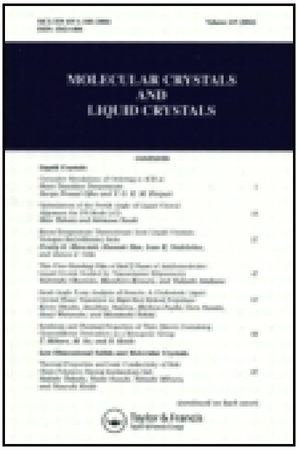

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The Pretransitional Kerr Effect in 4-*n*-Pentyl-4′-Cyanobiphenyl

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New experimental results are presented for the Kerr constant of 4-*n*-pentyl-4′-cyanobiphenyl in the isotropic phase close to the isotropic to nematic transition temperature, and a divergence from the Landau-de Gennes theory is noted. Previously neglected contributions in the Landau-de Gennes theory are calculated and can account for some discrepancies between experimental results obtained by different groups. However the behavior of the Kerr constant within 1K of the transition remains unexplained.

INTRODUCTION

The transition from the isotropic liquid phase to the partially ordered nematic liquid crystal phase is often described as being weakly first order, since discontinuities in the first derivatives of the Gibbs free energy at the transition are small in comparison with the corresponding quantities for the liquid to crystal phase transition. Low values for the enthalpy[1] and volume[2] changes at the nematic to isotropic transition have been measured, and are related to the discontinuity in the orientational order parameter at the transition. The possibility of a second order phase transition between nematic and isotropic phases has been discussed theoretically,[3] but such a transition has not been observed experimentally. However some of the features of second order phase transitions are observed at the weak first order transition between the nematic and isotropic liquid phases.[4,5]

A characteristic of second order phase transitions is that there are strong fluctuations in certain thermodynamic properties close to the transition, which may manifest themselves as a variety of pretransitional effects. Close to the transition from the isotropic liquid to the nematic phase, strong fluctuations about zero of the orientational order parameter lead to an anomalously high turbidity.[6] In the pretransitional region (i.e. in the isotropic phase, but close to the isotropic to nematic transition temperature) the fluctuations in order parameter may be partially quenched by electric or magnetic fields, and the consequent field-induced order can result in strongly optically anisotropic liquids. Such effects have been studied by a number of groups, and pretransitional divergence of the magnetic birefringence[6] (Cotton-Mouton effect) and the electric birefringence[7] (Kerr effect) has been observed.

This paper is concerned with the low frequency Kerr effect measured for the isotropic phase of liquid crystalline materials close to the isotropic to nematic transition temperature T_{NI}. De Gennes has applied Landau's theory of second order phase transitions to the nematic/isotropic transition,[4] and predicted that the magnetic field-induced birefringence should be proportional to $(T - T^*)^{-\gamma}$. T^* is a critical temperature less than T_{NI} which is characteristic of the hypothetical second order transition, and γ is a critical exponent which mean field theories predict to be 1. A simple extension of the Landau-de Gennes theory to the description of electric birefringence produces a similar result.[8] Many authors[9–11] have confirmed the predictions of the Landau-de Gennes theory with $\gamma = 1$ for both electric and magnetic birefringence over a temperature range $(T^* + 15 > T > T^* + 2)$K. Close to the transition temperature $T_{NI} \sim (T^* + 1)$, deviations from the predictions with $\gamma = 1$ have been noted by some authors[12,13] but not others.[14,15]

The purpose of the work described in this paper was to investigate the applicability of the Landau-de Gennes theory to the description of the electric field-induced birefringence in 4-*n*-pentyl-4′-cyanobiphenyl. This material has been studied by other workers,[14,15] and no deviation from the theory with $\gamma = 1$ was observed. We have performed experiments at much lower field strengths, and at temperatures closer to T_{NI}, and we have observed a deviation from the $\gamma = 1$ prediction. In an attempt to explain this deviation, we have extended the Landau-de Gennes theory to include a field-dependent T^*, and have also included higher terms in the Landau free energy expansion. Inclusion of a field-dependent T^* can lead to differences in results obtained at high and low field strengths. However it does not explain the divergence from the $\gamma = 1$ prediction noted at temperatures close to the transition.

THEORY

Following Landau and de Gennes, the free energy density of a fluid in the presence of an electric field may be written as:[16]

$$g = g_0 + \tfrac{1}{2}aQ^2 - \tfrac{1}{3}bQ^3 + \tfrac{1}{4}cQ^4 - \tfrac{1}{8}\epsilon_0(2\Delta\epsilon^{(0)}Q + 3\bar{\epsilon} - 3)E^2 + 0(Q^5) \quad (1)$$

$Q = \Delta\epsilon/\Delta\epsilon^{(0)}$ is the macroscopic order parameter, $\Delta\epsilon = (\epsilon_{\parallel} - \epsilon_{\perp})$ is the dielectric anisotropy of the fluid (assumed to be unaxial) and $\Delta\epsilon^{(0)}$ is the dielectric anisotropy of the perfectly ordered fluid with $Q = 1$; $\bar{\epsilon}$ is the mean permittivity. The parameters a, b and c are characteristic of the fluid, and in general are functions of temperature and pressure. However in this theory the temperature dependence of b and c is neglected, and a is assumed to vary according to the mean field result $a = a_0(T - T^*)$. For an isotropic fluid in the absence of an electric field the average of Q is zero, but $\overline{Q^2}$ is non-zero and diverges as the critical temperature T^* is approached. T^* is the temperature of the second order phase transition predicted by Eq. (1) when $b = 0$. For $b \neq 0$, the order/disorder transition is first order, and T^* is a temperature below the transition temperature at which the turning point in $(g - g_0)$ at $Q = 0$ changes from being a maximum to a minimum i.e. T^* is the lowest temperature at which the disordered phase can be metastable.

In the presence of an electric field, $\bar{Q}$ is no longer zero, and its value can be determined by the minimization of Eq. (1). A further effect of the electric field is to shift the first order transition temperature, and also change the value of T^* below which the disordered phase is absolutely unstable. Since it is $(T - T^*)^{\gamma}$ which determines the divergence of the electric birefringence, a field-dependent T^* can influence the interpretation of experimental results.

To find the turning points in $(g - g_0)$ the following equation is solved:

$$\frac{d(g - g_0)}{dQ} = aQ - bQ^2 + cQ^3 + z = 0 \qquad (2)$$

where $z = -\epsilon_0 \Delta\epsilon^{(0)} E^2/3$. The region of thermodynamic phase space where two states of different Q correspond to minima in $(g - g_0)$ is determined by the range of values of a, b, c and z for which Eq. (2) has three real roots. Assuming that b and c are independent of temperature, the limits of this region for a given value of z are fixed by the values of a for which Eq. (2) has two equal real roots. This is illustrated schematically in Figure 1 for the field-free situation: only for values of $a_2 < a < a_1$ does the free energy as a function of Q have two minima corresponding to the possible stability of two phases of different Q.

The limiting values of a_1 and a_2 may be found for various values of the field (i.e. z) by solving:

$$4a^3c - a^2b^2 - 4b^3z + 18abcz + 27c^2z^2 = 0 \qquad (3)$$

which states the condition that Eq. (2) has three real roots of which two are equal. In fact Eq. (3) gives three roots for a, but the two significant roots can be selected on physical grounds. The roots of Eq. (3) can now be used to determine the field dependence of T^*. For $z = 0$,

$$a_2(0) = a_0\,(T - T^*(0)) = 0$$

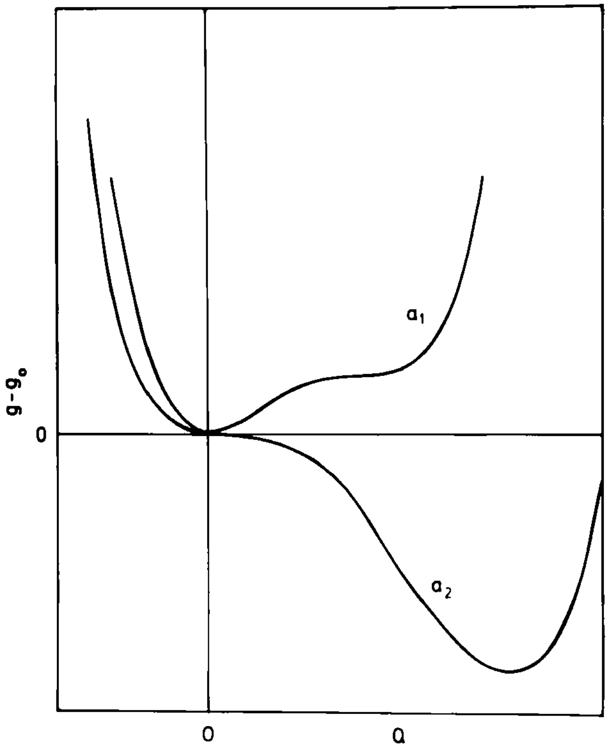

FIGURE 1 Free energy as a function of order parameter.

and in the presence of an electric field whose strength corresponds to z:

$$a_2(z) = a_0\,(T^*(z) - T^*(0)) \tag{4}$$

$T^*(z)$ is the temperature which determines the lower limit of the two phase region in the presence of a field, and since the field stabilizes the ordered phase $a_2\,(z) > 0$. The upper limit of the two phase region is determined by the root a_1.

Above the transition temperature T_{NI}, the stable state is one of zero Q. In the presence of an electric field the stable state becomes one having a small but non-zero Q. For a particular value of z the corresponding $T^*\,(z)$ can be obtained from Eq. (4), and using $a = a_0(T - T^*\,(z))$ in Eq. (3), the field-induced order may be found to be:

$$Q = \frac{-z}{a} + \frac{bz^2}{a^3} - \frac{2b^2z^3}{a^5} + 0(z^4) \tag{5}$$

In practice, for accessible field strengths $|z| < 10^2\ \mathrm{Jm}^{-3}$, only the first term of Eq. (5) is significant.

CALCULATIONS

To examine the effect of including a field-dependent T^* on the calculation of Q, we have solved Eqs. (3) and (5) for different values of the field strength. Approximate values of the parameters a_0, b, c, and $\Delta\epsilon^{(0)}$ have been obtained from previous experimental work on the nematogen 4-*n*-pentyl-4′-cyanobiphenyl.

In Figure 2 are plotted the solutions to Eq. (3) for various values of the field strength up to 10^7 V/m. The roots a_1 and a_2 define the limits of the region of possible co-existence of an ordered and disordered phase, but the physical significance of the third root is not clear to us. Using values of $T^*(z)$ obtained from $a_2(z)$ we have calculated the field-induced order from Eq. (5), and our results (full lines) are presented in Figure 3 as a function of electric field strength for different values of $(T - T^*)$. Also plotted (broken lines) are the values for Q obtained by neglecting the field dependence of a. The results show that the inclusion of a field dependent T^* is only significant at high field strengths, and at temperatures close to T^*. Unfortunately measurements of Q are restricted to temperatures such that $(T - T^*) > 1\text{K}$ because of the existence of the isotropic to nematic transition at about $T = T^* + 1\text{K}$.

COMPARISON WITH EXPERIMENT

The order induced in a fluid by an electric field results in a corresponding birefringence (the Kerr effect), and by measuring this birefringence in the pre-

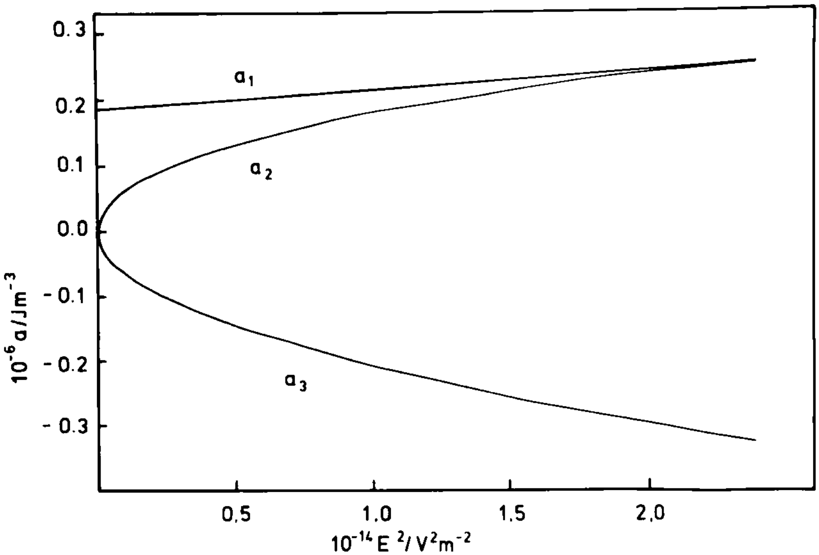

FIGURE 2 Solutions to Eq. (3): $a_0 = 0.2 \times 10^6\ \text{J m}^{-3}\text{K}^{-1}$, $b = 1.5 \times 10^6\ \text{J m}^{-3}$, $c = 3 \times 10^6\ \text{J m}^{-3}$, $\Delta\epsilon^{(0)} = 21.3$.

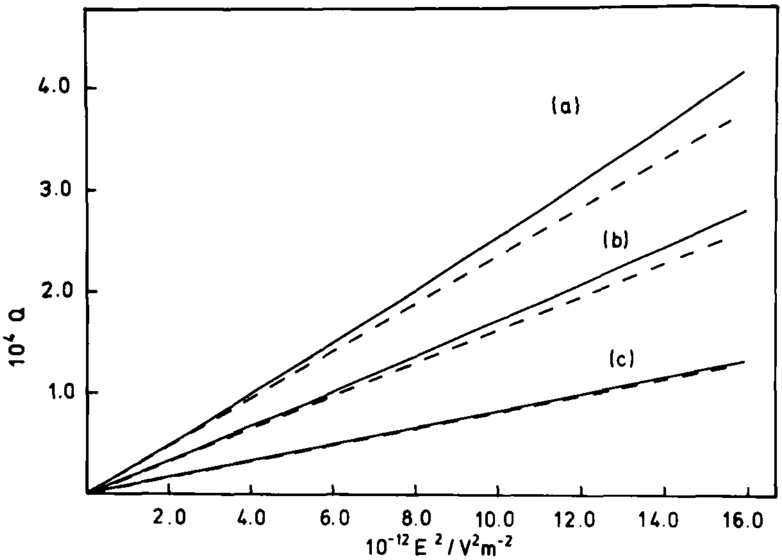

FIGURE 3 Q as a function of E^2. $(T - T^*) = 1.3$ (a), 1.9 (b), 3.9 (c).

transitional region of an isotropic nematogen it is possible to test the validity of the theory outlined above.

The Kerr constant is defined as $B = \Delta n/\lambda E^2$, and is related to the order parameter by:[17]

$$B = \frac{\Delta n^{(0)} Q}{\lambda E^2} \tag{6}$$

where $\Delta n^{(0)}$ is the birefringence of the perfectly aligned liquid crystal. Our experimental method for measuring the electro-optic Kerr effect in liquid crystals is based on a sensitive null technique that we have previously used[18] to study the Kerr effect in gases. The birefringence induced by a low frequency electric field is balanced by an equal birefringence induced in a calibrated standard Kerr cell. A phase-sensitive detection system enables us to measure birefringences down to 10^{-13}, and so we are able to study pretransitional effects in liquid crystals at very low field strengths ($\sim 10^4$ Vm^{-1}). Accurate control of temperature is essential, and our sample cell is contained in a thermostatted enclosure, whose temperature is maintained constant to ±0.005 K by a proportional controller. The temperature was measured by a platinum resistance probe immersed in the sample cell.

In Table I and Figure 4 we give our results for the Kerr constant of 4-*n*-pentyl-4'-cyanobiphenyl measured at $\lambda = 633$ nm. Also presented in Figure 4 are results taken from Ref. 15 corrected by us to the same wavelength. The results

TABLE I

Kerr constants of 4-*n*-pentyl-4′-cyanobiphenyl for $\lambda = 633$ nm

Temperature ($T - T_{NI}$)	$10^{11}B/C^2$ mJ^{-2}	Temperature ($T - T_{NI}$)	$10^{11}B/C^2$ mJ^{-2}
0.13	14.86	0.47	9.43
0.13	13.47	0.48	8.68
0.14	13.36	0.62	7.77
0.17	12.41	0.74	7.50
0.20	11.79	0.79	7.33
0.23	12.00	0.87	6.86
0.29	11.15	1.02	6.45
0.35	9.85	1.10	6.23
0.36	9.71	1.65	5.00
0.43	9.17	2.06	4.40
		2.50	3.86

($T_{NI} = 35.2$°C)

are in reasonable agreement at temperatures greater $T_{NI} + 0.5$ K, but close to the transition temperature our results are significantly different.

At the field strengths used in our experiment the corrections to Q which result from a field dependent T^* or from terms other than the first in Eq. (5) are negligible, and so the Landau-de Gennes theory with $\lambda = 1$ predicts that B^{-1} is

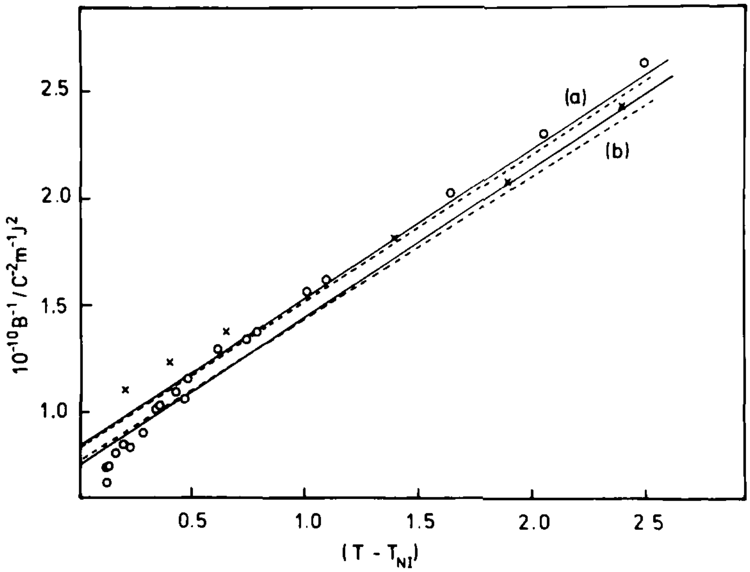

FIGURE 4 Kerr constant of 4-*n*-pentyl-4′-cyanobiphenyl at $\lambda = 633$ nm. Experimental results: O = this work, X = Ref. 15. Calculations: broken line = constant Q, full line = constant E; (a) = this work, (b) = Ref. 15.

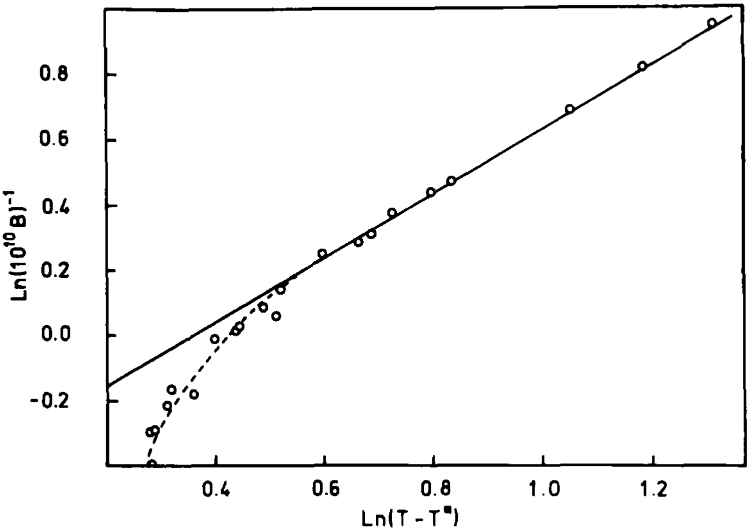

FIGURE 5 Ln B^{-1} as a function of Ln($T - T^*$).

directly proportional to T. This prediction is confirmed by our measurements for $T > T_{NI} + 0.5$ K, but at temperatures close to the transition there is a departure from the theory. Extrapolation of the linear portion of the graph in Figure 4 gives a value for T^* at effectively zero field strength. Using this value we have plotted $\ln B^{-1}$ against $\ln(T - T^*)$ in Figure 5, and we find that for $T > (T^* + 1.7)$K the slope is -1. Close to the transition, our experimental measurements indicate that either the mean field exponent $\gamma = 1$ is incorrect, or that the real T^* differs from that predicted by the mean field theory.

As well as making predictions about the variation with temperature of B, the Landau-de Gennes theory also allows the calculation of the slope of the graph of B^{-1} against T. a_0 and hence a can be obtained from latent heat measurements,[19] since $\Delta H_{NI} = \frac{1}{2} a_0 T_{NI} Q_{NI}^2$ according to the Landau-de Gennes theory. A value for $Q_{NI} = 0.3$ has been assumed. This value has also been used to obtain estimates of $\Delta n^{(0)}$ and $\Delta\epsilon^{(0)}$ from the relation: $\Delta n_{NI}/\Delta n^{(0)} = \Delta\epsilon_{NI}/\Delta\epsilon^{(0)} = Q_{NI}$. The coefficients b and c have been obtained from Q_{NI} and $(T_{NI} - T^*)$.[17] The small corrections to the electric field-induced birefringence calculated from Eqs. (5) and (6) lead to a non-linear dependence of Δn on E^2. In fact this is so small that it is not experimentally detectable within the limits of the range of field strengths and precision of the measurements. Therefore to compare the calculations with experiment we have calculated the apparent Kerr constant as defined by Eq. (6) for two experimentally realizable situations, (i) constant electric field strength, and (ii) constant induced birefringence. In the former situation the precision of the measurement decreases as Δn decreases, while the latter corresponds to an approximately constant precision since Δn is always the same.

In Figure 4 calculated values for B^{-1} are plotted against temperature for (i) and (ii) for constant E^2 and Δn that correspond approximately to our experiments and those performed at higher field strengths.[15] Agreement with both sets of experimental results is good, apart from the divergence close to T_{NI} already noted.

DISCUSSION AND CONCLUSIONS

In this paper we have presented some new measurements of the Kerr constant of 4-*n*-pentyl-4′-cyanobiphenyl in the pretransitional isotropic phase. These measurements have been performed at lower field strengths than other workers, and we have observed a previously undetected deviation from the Landau-de Gennes theory for this material at temperatures close to T_{NI}. Such a deviation has been observed in magnetic birefringence,[20] light scattering intensity[21] and in the electric birefringence of a related nematogen.[13]

Extension of the Landau-de Gennes theory to include a field dependent critical temperature has predicted that measurements made at high field strengths may differ slightly from those made at low electric field strengths, and these predictions are confirmed by the experimental results. We have shown that calculations are in agreement with experiment for temperatures greater than $T_{NI} + 0.5$ K if we assume values for $\Delta n^{(0)}$ and $\Delta\epsilon^{(0)}$ of 0.30 and 21.3 respectively. Accurate values for the birefringence and dielectric anisotropy of the hypothetical fully aligned nematic phase are extremely useful in assessing molecular statistical theories of nematic alignment.[16]

Close to the transition temperature the experimental measurements of the Kerr constant are not in accord with the mean field predictions. By going beyond the mean field approximation, Lin Lei has shown[22] that for a particular lattice model the deviation of the inverse magnetic birefringence from a linear dependence on temperature may be explained. This explanation may also hold for the deviation of electric birefringence from the mean field theory, but further experimental tests of Lei's model are necessary before it can be firmly accepted.

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