Eur. Phys. J. B **1**, 179-187 (1998)

THE EUROPEAN
PHYSICAL JOURNAL B

Effect of a strong electric field on a nematogen: evidence for polar short range order

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Received: 15 July 1997 / Received in final form: 24 September 1997 / Accepted: 29 October 1997

Abstract. We present experimental studies on the effect of strong electric fields on the nematogen p-cyanophenyl p-n-heptyl benzoate which has the strongly polar cyano end group and a large positive dielectric anisotropy. We use a local temperature measurement to take into account heating effects and an electrical impedance analysis to determine both the dielectric constant ($\epsilon_{\|}$) and the resistance *(R)* of the sample. We also measure the higher harmonic responses of the medium. The new results obtained in this study are: (i) a detailed temperature dependence of the terms which describe (a) the quenching of macroscopic thermal fluctuations of the nematic director and (b) the enhancement of the orientational order parameter due to Kerr effect, (ii) clear evidence for the critical divergence of susceptibility as reflected in the third harmonic signal, (iii) an unusual enhancement of the conductivity which shows a large peak just below the critical point T_c, (iv) a significant peak in the second harmonic signal at T_c and (v) evidence for a field induced nematic-nematic transition well inside the nematic range. We argue that the results (iii)-(v) indicate the presence of *polar* short range order in the medium and hence support a molecular model in which such an order has been proposed.

PACS. 61.30.Gd Orientational order of liquid crystals; electric and magnetic field effects on order – 64.70.Md Transitions in liquid crystals

1 Introduction

Liquid crystals made of compounds with the highly polar cyano or nitro end groups show several unusual features [1]. The dipolar interaction energy usually favours an antiparallel association between neighbouring molecules [2]. As the aromatic cores have the strongest attractive interaction, such *pairs* will have a length l_d $(= a + 2c)$ which is incommensurate with the molecular length l_m $(= a + c)$ where a is the length of the aromatic core and c the chain length [3]. Many such compounds exhibit reentrant nematic and smectic phases, as well as smectic A polymorphism [1]. More recently, the possibility of a nematic-nematic transition has also been discussed [4,5]. These phenomena have been successfully explained on the basis of a Landau theory [4,6] with two coupled smectic order parameters whose layer spacings correspond to l_d and l_m mentioned earlier. The origin of l_d is clear, as described above. In all compounds with aromatic cores l_d is found to be the layer spacing of either short or long range layer ordering in higher temperature ranges of liquid crystals. On the other hand the spacing shifts towards l_m as the temperature is lowered in such compounds. For example the smectic A phase with the partial bilayer structure occurs at higher temperatures while the reentrant smectic A phase which occurs at lower temperatures has a monolayer spacing [7]. Thus, the origin of l_m is *not* due to the break up of the antiparallel pairs which can only occur at very high temperatures. In a model proposed earlier [8,9] it was pointed out that the dipole induced in the highly polarizable aromatic core by the permanent dipole of a neighbouring molecule can effectively reduce the net dipole moment if the molecules have a *parallel* configuration. Further, in this configuration, the chains of neighbouring molecules have an attractive interaction. Both these interactions are $\propto 1/r^6$ where r is the intermolecular separation. The dipole-dipole interaction which favours antiparallel configuration is $\propto 1/r^3$. Hence a *parallel* configuration with a spacing $\sim l_m$ is favoured at higher densities or *lower* temperatures. This mechanism provides the molecular justification for the two order parameter model of Prost and coworkers [4,6].

The highly polar compounds also have a large positive dielectric anisotropy $\Delta\epsilon = \epsilon_{\|} - \epsilon_{\perp}$, the subscripts referring to orientation with respect to the director $\mathbf{n}$, which is the unit vector along the average orientation direction of the long axes of the molecules. The liquid crystal couples to an external electric field through this anisotropy and the square of the field is conjugate to the orientational order of the medium. The nematic-isotropic transition is weakly first order in nature. The transition temperature is shifted to higher values under the action of the field which

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induces a weak orientational order in the higher temperature *paranematic* phase (Kerr effect). At a critical field, the nematic to field induced paranematic transition vanishes so that at higher fields, there is a continuous evolution between the two phases in analogy with the liquid-gas transition [10–12]. A quantitative experimental study of this critical field was made by Durand and coworkers only recently [13,14]. The main problem in applying strong electric fields to liquid crystals is the heating of the medium due to ionic conductivity. This problem was overcome by Durand *et al* by using short electric pulses separated by long equilibration times. We have recently designed an alternative experimental technique in which we monitor the *local* temperature of the sample using an evaporated thin film of nickel as a thermometer to study the electric field phase diagrams of liquid crystals [15,16]. Using this setup we have studied the effect of a strong electric field on the nematic-isotropic, nematic-smectic A_d and smectic A_d-reentrant nematic transitions in a few different compounds.

In the present paper we report extensive investigations on the effect of strong electric fields on a highly polar compound which exhibits a wide nematic range (~ 30 °C). We also measure the second and third harmonic components of the electrical output of the cell. We report the following results: (a) an analysis of the electric field enhancement of the order parameter, (b) the divergence of susceptibility near the critical temperature as measured by the 3rd harmonic signal, (c) a small but unusual *2nd harmonic* signal which again diverges near the critical point T_c, (d) a significant peak in the electrical conductivity close to T_c and (e) evidence for a field-induced phase transition at a low temperature which we identify tentatively as a nematic-nematic transition, brought about by a discontinuous change in the short range order.

2 Experimental

The experimental technique has been described in our earlier papers [15,16]. The *local* temperature of the sample subjected to a strong electric field is measured using a thin film nickel thermometer etched from a nickel coated glass plate. This is covered with an insulating silicon monoxide layer on which an aluminium electrode is vacuum evaporated. The top plate of the cell has a circular ITO electrode. The electrode configuration also has a guard ring to minimize temperature gradients near the edge of the measuring area [16]. Both the electrodes are treated with octadecyloxy silane (ODSE) to obtain a homeotropic alignment of the sample. The sample thickness is measured using an interferometric technique. A Trek (model 601B) amplifier is used to generate the high voltages needed. The sinusoidal input at 4111 Hz to this amplifier is derived from an SRS 830 lock-in-amplifier which is used to analyse the electrical impedance of the cell [16]. The latter allows us to measure higher harmonic signals as well. The light scattered by twist fluctuations of the nematic director is monitored in the reflection mode.

The sample used in the present experiment is p-cyanophenyl p-n-heptyl benzoate (CP7B) obtained from Merck which has the following sequence of phase transitions: crystal $\xrightarrow{43.5\ ^{\circ}\mathrm{C}}$ nematic $\xrightarrow{56.0\ ^{\circ}\mathrm{C}}$ isotropic. The nematic phase readily supercools so that the experiments can be conducted down to ambient temperature. This compound was chosen as the dielectric anisotropy ($\Delta\epsilon = 20$ at 35°C) is considerably larger than that of other compounds like cyanobiphenyls used in earlier experiments [13–16]. The homeotropic alignment of the sample is stabilized by the large electric field applied as the dielectric anisotropy is large and is positive. Thus, all the results reported in the next section correspond to monodomain samples, with the director oriented along the field direction.

3 Results and discussion

3.1 Low field dielectric measurements

The temperature dependence of the magnetic susceptibility of CP7B has been measured in our laboratory [17] and agrees to within ~ 8% with the values reported earlier by Buka and de Jeu [18]. Using the Haller extrapolation procedure [19], we have calculated the absolute order parameter from this data as a function of temperature (Fig. 1). Using the impedance analysis of the cell filled with CP7B we have measured $\epsilon_{\|}$. The sample thickness is $\simeq 16\ \mu$m and the applied voltage is 10 V (~ 20 esu) which is sufficiently low so that the $\epsilon_{\|}$ data can be considered as *zero field* values. Our dielectric measurement of $\epsilon_{\|}$ agrees to within 2% with the values reported earlier by Titov *et al.* [20]. We can write [21]

$$\epsilon_{\|} \simeq \bar{\epsilon} + \left\{ \frac{2}{3} A \left(\Delta\alpha + \frac{F\mu^2}{k_B T} \right) \right\} S \tag{1}$$

where $\bar{\epsilon}$ is the average dielectric constant, A and F are correction factors for local field effects, $\Delta\alpha$ the anisotropy of polarizability and μ the dipole moment assumed to be parallel to the long axis and k_B the Boltzman constant.

The main contribution to the dielectric constant comes from the orientation polarization arising from the *effective* dipole moment μ of the molecule. Hence one would expect from equation (1) that $(\epsilon_{\|} - \bar{\epsilon})$ is a measure of S/T. Normalizing the order parameter near T_{NI} with respect to the magnetic susceptibility data, and correcting for the above temperature dependence, we have calculated the "order parameter" S_e from the dielectric data as a function of temperature (Fig. 1). It is clear that S_e increases substantially at lower temperatures compared to the true order parameter S, indicating that the effective μ is also increasing at lower temperatures. This is possible if the short range order changes with temperature. Indeed in the molecular theory of such highly polar compounds referred to in the introduction [8,9], the relative concentration of *parallel* configuration which has a higher effective dipole moment increases at lower temperatures. It is clear that in CP7B, this mechanism appears to lead

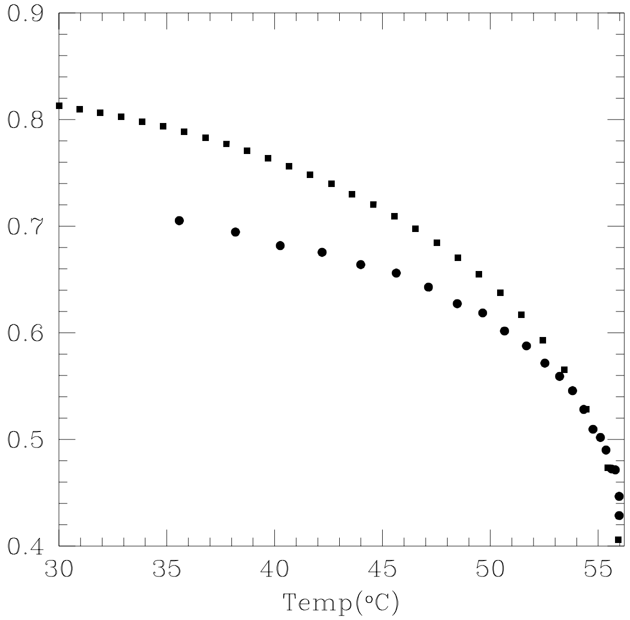

Fig. 1. Comparison between the orientational order parameter measured from magnetic susceptibility (filled circles) and the effective order parameter S_e calculated from the dielectric constant $\epsilon_{\|}$ (filled squares) in the compound CP7B. The dielectric data has been normalized at $T - T_{NI} = 2$ °C with respect to the magnetic data, and the higher effective values of S_e compared to the true values S indicate a change in the short range order of the medium at lower temperatures.

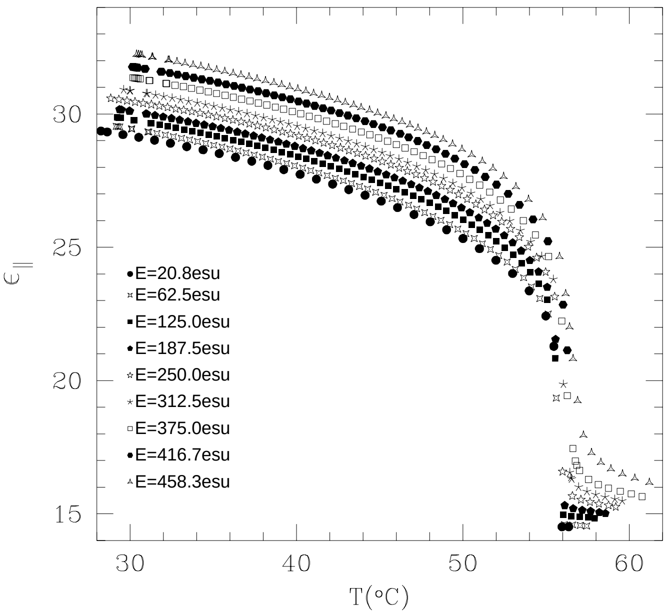

Fig. 2. Temperature variations of the dielectric constant $\epsilon_{\|}$ of CP7B at different values of the applied electric field. Note that the curves remain almost parallel even at the lowest temperatures. $d = 16$ μm.

to the strong variation in $\epsilon_{\|}$ in the temperature range of interest. On the other hand, in compounds like 5CB, 7CB *etc.*, the order parameter calculated from the dielectric measurement is proportional to that of the magnetic susceptibility measurement to a good approximation [22]. (It is likely that the concentration of parallel configuration increases noticeably only at temperatures far below the observed nematic range in these cases).

3.2 Field induced enhancement of the order parameter

The electrical measurements were carried out as the sample was cooled under different sinusoidal AC electric fields across the paranematic-nematic (PN-N) transition. The variations of $\epsilon_{\|}$ as a function of temperature at different fields are shown in Figure 2. As expected, $\epsilon_{\|}$ in general increases with field. The PN-N transition temperature shifts to higher values. It is interesting to note that the experimental curves remain roughly parallel to one another even when the temperature is ~ 25° below the transition point. One would have expected that as the order parameter susceptibility decreases rapidly at lower temperatures, the different curves would have crowded together. The latter trend is in fact seen in some other systems that we have studied.

As we discussed in the previous section, in CP7B $\epsilon_{\|}$ varies more rapidly than implied by the order parameter as the temperature is lowered. By identifying the $\epsilon_{\|}$ measured at low fields with the order parameter at the same temperature got by magnetic data, we have calculated the "order parameter" as a function of temperature at different fields (Fig. 3). It is obvious that even the order parameter curves at different fields do not crowd together at lower temperatures. The increase in the order parameter with field $\delta S(E) = S(E) - S(0)$, arises due to two physical mechanisms. As pointed out by de Gennes [1] the macroscopic thermal fluctuations of the director are suppressed by the external field which couples to the order parameter through the dielectric anisotropy. In a simple one constant approximation this effect is given by:

$$\delta S_{\mathrm{l}} = \frac{k_{\mathrm{B}} T (\Delta\epsilon)^{1/2}}{4(\pi K)^{3/2}} |E| \tag{2}$$

where K is an average curvature elastic constant. Note that δS_{l} depends *linearly* on the *magnitude* of the applied field. The other mechanism is the Kerr effect which is microscopic in origin. The dielectric anisotropy and hence the order parameter tend to have a higher value under the field to lower the electric energy density of the medium. The corresponding increase in order parameter is given by:

$$\delta S_{\mathrm{qk}} = \frac{\chi_{\mathrm{k}} \Delta\epsilon}{12\pi} E^2 \tag{3}$$

where χ_{k} is an appropriate susceptibility. This effect is *quadratic* in E. To take account of both the effects, we write [13]

$$\delta S(E) = c_{\mathrm{l}} |E| + c_{\mathrm{q}} |E|^2. \tag{4}$$

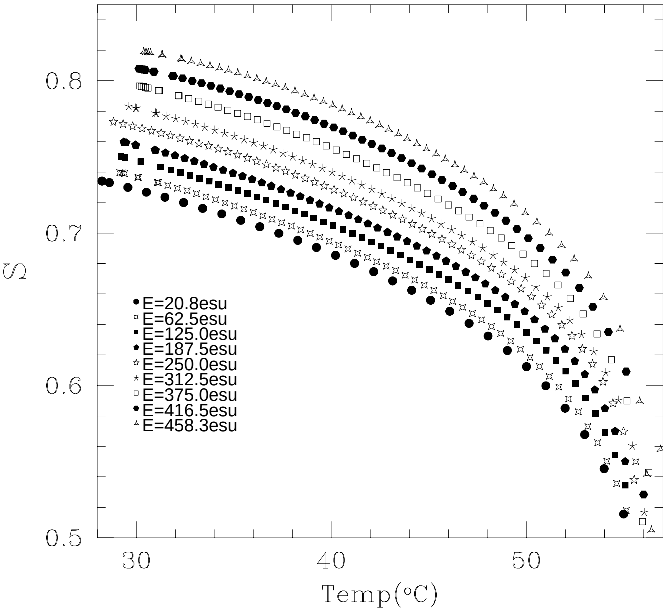

Fig. 3. Temperature variations of the "order parameter" at different fields calculated from the data shown in Figure 2.The values have been calculated by identifying $\epsilon_{\|}$ (at low fields) with the orientational order (from magnetic susceptibility data) at the corresponding temperature.

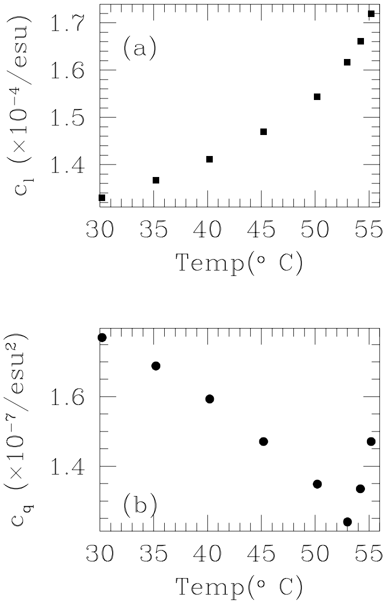

Fig. 4. Temperature variations of (a) c_l and (b) c_q as defined in equation (4).

The temperature variations of c_l and c_q are shown in Figure 4. c_l decreases as the temperature is lowered, a trend which can be expected from equation (2). c_q initially shows a decrease with decrease in temperature and below ~ 53 °C it *increases*. Roughly, one expects that $\Delta\epsilon \propto S$ and $K \propto S^2$ and as such $c_l \propto S^{-5/2}$. However, the actual variation of c_l with S is much less rapid. Though $\Delta\epsilon$ varies more rapidly than S as described in the previous section, it cannot account for the relatively weak dependence of c_l on S. Indeed, Malraison *et al.* [23] measured the magnetic quenching of thermal fluctuations in 7CB and used their own measured values of the susceptibility anisotropy $\Delta\chi$, and the elastic constants K_{ii}, and found that the theoretical variation was considerably steeper than the experimental one near $T_{\rm NI}$. As such the mean field theoretical calculations on the quenching of fluctuations appear to be inadequate. If we assume that $c_l \propto S_o^x$, in CP7B we find that $x \simeq -0.94$ rather than -2.5. Further, as pointed out by Lelidis *et al.* [13], c_l depends on S, which itself changes with field. Thus the quenching of thermal fluctuations itself gives rise to a change in order parameter which contributes to the quadratic component c_q. Using a Taylor expansion we can write

$$\delta S = \left(\frac{\partial S}{\partial E}\right) E + \frac{1}{2}\left(\frac{\partial^2 S}{\partial E^2}\right) E^2. \tag{5}$$

The total quadratic effect is then $c_q = c_{qk} + c_{ql}$. Using the empirical value of $c_l = \partial S/\partial E = \lambda S_o^{-0.94}$, we obtain $c_{ql} = \frac{1}{2}\partial^2 S/\partial E^2 = -0.47\lambda^2 S_o^{-2.88}$ which produces a saturation, as it has a negative sign. Though $|c_{ql}|$ decreases with decrease of temperature, it is too small to account for the increase of c_q at lower temperatures. By taking out this contribution due to c_{ql} we can calculate the variation of the susceptibility χ_k with temperature (Fig. 5) using equation (3) and the known $\Delta\epsilon$ values [20]. As the temperature is lowered from $T_{\rm NI}$, χ_k decreases at first rapidly and at lower temperatures rather slowly. $\Delta\epsilon$ increases by a factor ~ 4 as the temperature is lowered from $T_{\rm NI}$ to ~ 30 °C, and the large increase in $\Delta\epsilon$ accounts for the unusual temperature dependence of c_{qk}. Our calculations on χ_k do not extend upto the critical temperature T_c. The main reason is that due to additional heating effects to be described in the next section, at temperatures below T_c the data points become sparce as the field is increased.

3.3 Electrical conductivity

The electrical resistance of the sample was also measured by using the impedance analysis of the current passing through the sample [15,16]. The field and temperature dependences of the resistance are shown in Figure 6, from which we note the following features.

(i) At low applied fields upto 187.5 esu the resistance decreases with increase of temperature in the nematic range, and has a positive jump of ~ 25 − 30% across the nematic-paranematic transition temperature, and decreases again at higher temperatures. (ii) In the lower temperature range (around 30 °C), the resistance *increases* with field upto ~ 416.7 esu and then starts to decrease. (iii) The last observation is also related with an actual *increase* of resistance with temperature at higher fields in the lower temperature range. (iv) Beyond ~ 312.5 esu the resistance drops substantially as the nematic-paranematic transition temperature is approached. As the applied fields

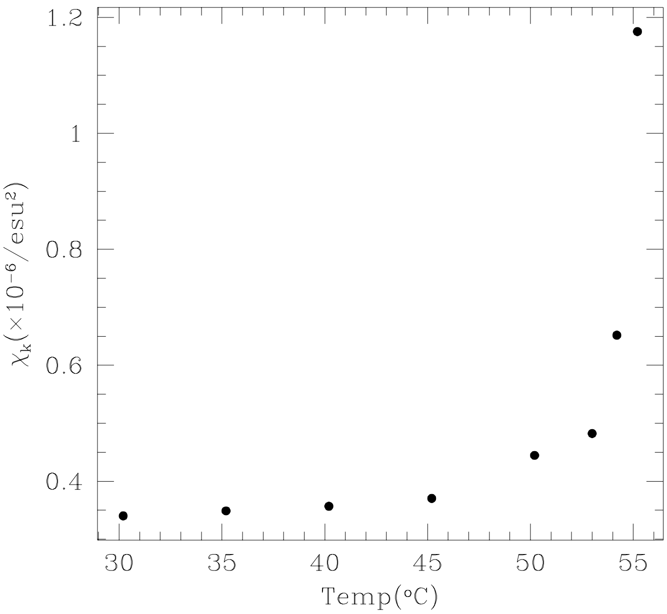

Fig. 5. Temperature variation of the susceptibility for Kerr effect.

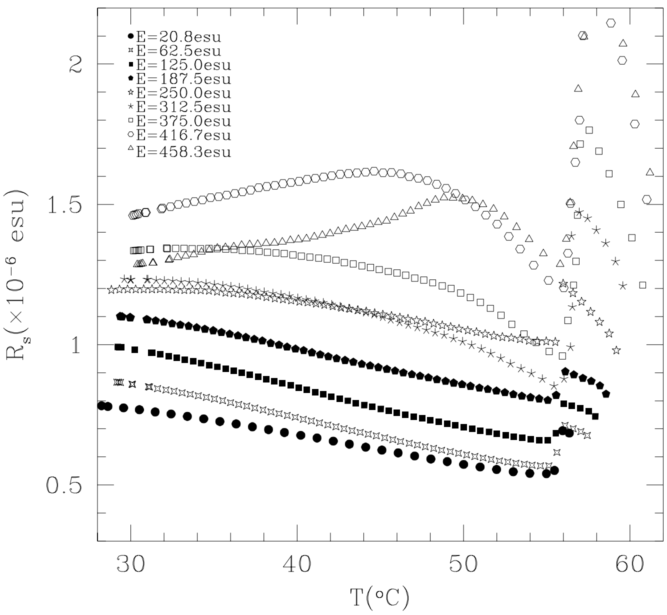

Fig. 6. Temperature variations of the resistance of a 16 μm thick sample of CP7B at different values of the applied electric field.

are now close to the critical value, this clearly indicates a critical enhancement of the electrical conductivity of the sample. (v) The last two effects which have opposite trends with temperature result in a broad peak in the resistance of the sample as a function of temperature at higher fields (Fig. 6). The peak shifts to higher temperatures at higher fields. (vi) Beyond the transition temperature, there is a very large increase in resistance in a narrow temperature range. The resistance shows a relatively sharp maximum and decreases at higher temperatures.

The anisotropic electrical conductivity in the nematic phase of the highly polar compound used in our experiment has two contributions: (i) The medium has unknown species of ionic impurities which contribute to the DC as well as AC conductivity of the sample. (ii) The dielectric constant $\epsilon_\parallel$ relaxes at relatively low frequencies ($\omega_\mathrm{r} \sim$ MHz) in the nematic phase because of the nematic potential which generates an additional barrier for reorientation of the dipoles about the short axes of the molecules. As discussed by Schadt [24], the relaxation process increases the effective conductivity $\sigma_\parallel$ of the medium. The excess conductivity increases as ω_r is approached. The strong heating effect due to this excess conductivity near ω_r has been experimentally studied by Schadt [25]. However, this contribution normally *decreases* at higher temperatures as the order parameter, and hence the nematic potential as well as the friction coefficient for rotational motion decrease with increase of temperature, resulting in an increase in ω_r.

The ionic contribution to the conductivity is anisotropic as the mobility of the charges is higher along the director compared to its value in an orthogonal direction. The nematic is a weak electrolyte because of the impurity ions. Thus, electrolytic processes become relevant in the conduction mechanism [26]. In our experiment, the minimum field applied to the sample is 20.8 esu and if the dissociation constant producing ions in the medium is sufficiently small, we can expect that the bulk of the ions flow towards the electrodes under the action of the field to give rise to an initial surge after the field is reversed. It also leads to a depletion of charges in the bulk and hence to a reduced conductivity. In turn, there is a saturation of current at higher fields [27]. As the field is increased the effective average resistance of the sample *increases* as is indeed seen at low temperatures between 20.8 to 416.7 esu.

Another concurrent effect of the field is the increase in the orientational order parameter, which in the compound used is quite considerable even at low temperatures, as discussed in Section 3.2. An increased order parameter would imply an increased conductivity both due to the greater mobility of ionic impurities along **n**, the director, and due to a lowering of the dielectric relaxation frequency. This effect due to the field is opposite to the charge depletion effect discussed above. Apparently at ∼ 30 °C beyond 416.7 esu the former effect overtakes the latter and at higher fields the resistance *decreases* with field (Fig. 6). Further, at low fields the temperature coefficient of resistance is negative, as the mobility of ions increases with temperature. As the field is increased to ∼ 250 esu, the resistance of the cell is practically independent of temperature at ∼ 30 °C due to the compensation of the pure temperature effect by that due to the decrease in orientational order at higher temperatures. Indeed above 375 esu the temperature coefficient of resistance has a *positive* sign at 30 °C.

The most important effect on conductivity arises close to the nematic-paranematic transition point when

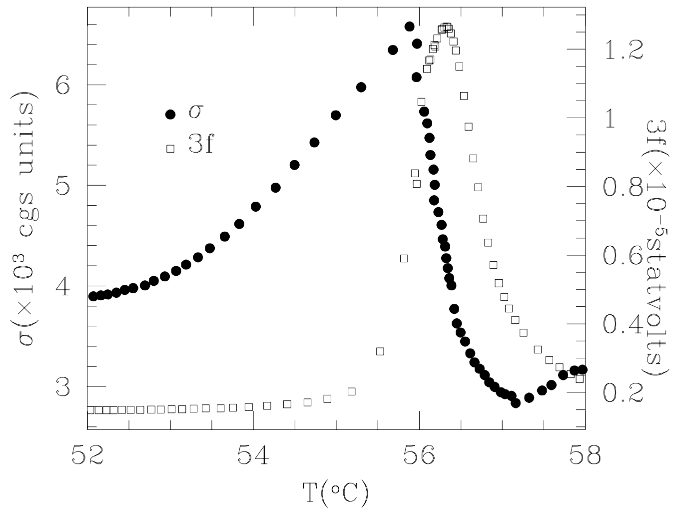

Fig. 7. Temperature variations of the electrical conductivity and third harmonic signal of CP7B of a 12 μm thick sample under an applied field of 472 esu.

the applied field is above 312.5 esu. We clearly see a sharp dip in R as this transition point is approached and a subsequent rise in R which is even sharper. As usual, the resistance starts decreasing with temperature after attaining a maximum. The first dip in resistance is obviously connected with the field-induced critical point in the sample. We have made detailed measurements on the resistance of a 12 μm thick sample close to the critical point at 170 V ($E = 472$ esu) which corresponds to a field close to the critical value. The conductivity of the sample is shown in Figure 7 on an enlarged temperature scale. We have also shown in the figure the temperature variation of the third harmonic signal which was also simultaneously measured. As will be discussed in the next section, the third harmonic signal is a direct measure of the susceptibility of the system and exhibits an enhancement by an order of magnitude as the temperature approaches the critical point. The third harmonic signal shows a nearly symmetric and narrow peak. The conductivity shows a peak at a temperature which is ~ 0.4 °C *below* that corresponding to the third harmonic signal. Moreover, the conductivity shows a broader maximum, with a characteristic asymmetry with temperature.

Electrical resistance has been measured in other liquids exhibiting critical phenomena. Both in a binary mixture of two metals *viz.*, bismuth and gallium as well as in an aqueous solution of isobutyric acid, the resistance has been shown to dip by a small fraction as the liquid-liquid critical temperature is approached from above [28, 29]. In these cases, $\mathrm{d}R/\mathrm{d}T$ exhibits a critical divergence as T_c is approached. In our system, the enhancement in conductivity is indeed much larger, and as mentioned earlier, occurs at a temperature below T_c. We believe that the enhancement is *not* connected with ionic conductivity. It is probably caused by the critical slowing down of fluctuations as T_c is approached. As we have discussed earlier, the compound used in this experiment *viz.* CP7B appears to have a fraction of the molecules in the *parallel* configuration. We can expect that unlike molecules with antiparallel configuration which form *pairs* due to a frustration effect, the parallel molecules will form relatively larger *polarized* domains [9,16]. The orientation polarization of such domains begins to have a collective response as T_c is approached. The critical slowing down will in turn enhance the effective conductivity due to the dielectric relaxation which occurs at lower and lower frequencies. The Landau-Khalatnikov model predicts that [28]

$$\frac{1}{\tau} \propto \left(\frac{T_\mathrm{c} - T}{T_\mathrm{c}}\right) \tag{6}$$

where τ is the relaxation time for the collective behaviour. The dielectric relaxation will give rise to an effective conductivity [24]

$$\sigma_\parallel(\omega) = \frac{\epsilon_\mathrm{o}(\delta\epsilon_\parallel)}{1 + \omega^2\tau^2}\tau\omega^2 \tag{7}$$

where ϵ_o is the vacuum dielectric constant and $\delta\epsilon_\parallel$ is the difference between the low frequency and high frequency dielectric constants. As the peak in conductivity occurs at $\omega\tau = 1$, and we have used $\nu = \omega/2\pi$ of 4111 Hz in our experiments, we can calculate the proportionality constant in relation (6) from the experimental data. Using relations (6, 7) we can then calculate $\sigma_\parallel$ as a function of temperature at the measuring frequency. We compare this with the measured excess conductivity due to the critical slowing down, which is obtained by subtracting a linearly interpolated *background* value from the measured value of $\sigma_\parallel$. The calculated value agrees with the measured excess at the peak position if we assume $\delta\epsilon_\parallel \simeq 3$. This is much smaller than $\epsilon_\parallel - n^2 \simeq 20$ (where n is the refractive index) which would be the value if the entire medium contributed to the relaxation mechanism. The small value of $\delta\epsilon_\parallel$ indicates that only a relatively small fraction of the molecules form the polarized domains which exhibit this collective response. Indeed with this assumption, the temperature variation of the excess conductivity is reasonably well reproduced (Fig. 8). We may also note that according to the molecular model mentioned earlier [9,16] the antiparallel configuration can be expected to have a much larger concentration at higher temperatures compared to the parallel configuration.

As a result of this excess conductivity the sample heats up around this temperature much more than at temperatures far away from that corresponding to the peak in $\sigma_\parallel$. Consequently there is a scarcity of data points around this temperature. It is interesting to note that in other compounds like octyloxycyanobiphenyl, the conductivity shows a smaller enhancement as T_c is approached. Indeed in this case, the parallel configuration appears to be practically absent near T_c. The above interpretation is supported by the fact that we have seen a small but clear peak in the *second harmonic* signal near T_c of CP7B (Fig. 9). The peak shows up better if we apply a larger field than for the other studies. Such a signal implies that the medium

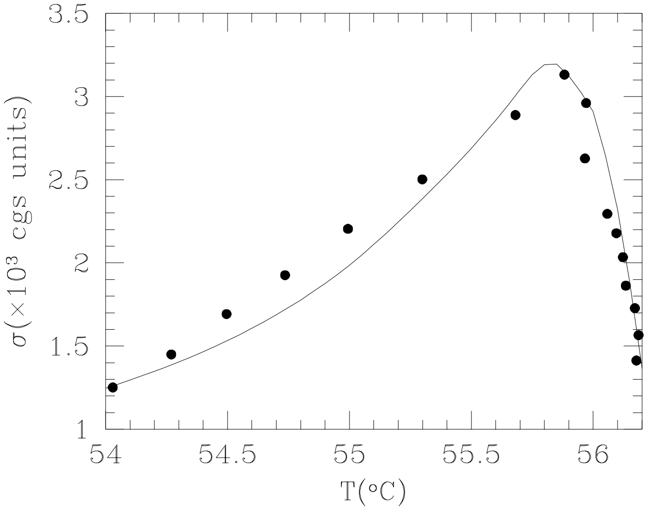

Fig. 8. The fluctuation dependent part of the conductivity compared with the theoretical variation assuming a Landau-Khalatnikov slowing down of polarized domains.

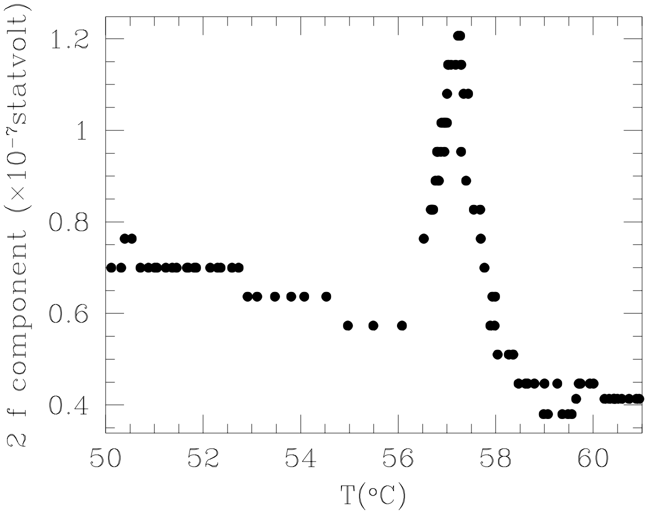

Fig. 9. Divergence of the second harmonic signal in a 10 μm thick sample of CP7B under a field of 600 esu.

has polarized domains which are unable to reorient at the frequency of the applied field. Interestingly, we could not detect a second harmonic peak in other compounds like, for example, pentyl cyanobiphenyl.

3.4 Third harmonic signal

Assuming that the nonlinear response of the system is entirely capacitive, the current though the sample is given by

$$I = \frac{\mathrm{d}}{\mathrm{d}t}(CV) \qquad (8)$$

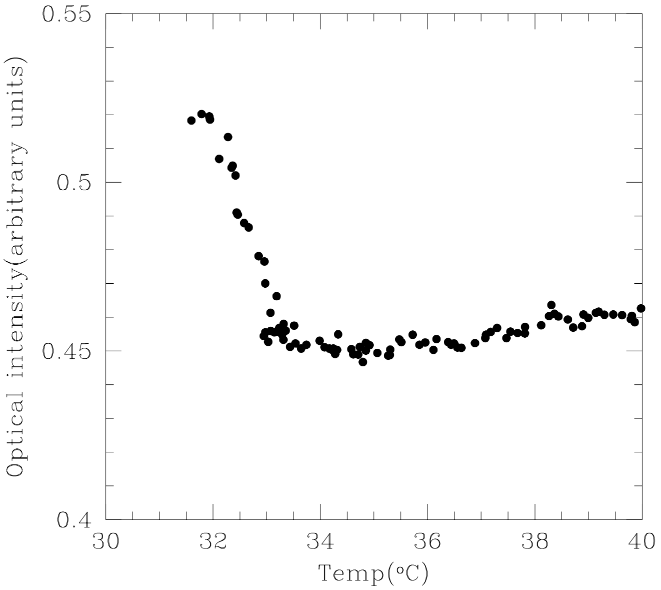

Fig. 10. Temperature variation of the light scattered from twist fluctuations in a 10μm thick sample of CP7B subjected to a field of 600 esu. Note the large enhancement as the temperature is lowered below 33 °C.

where $C = C_{\mathrm{o}}\epsilon_{\|}$, C_{o} being the capacitance of the empty cell and $V = V_{\mathrm{o}} \sin \omega t$ the applied voltage. In a simple approximation, $\epsilon_{\|} = \bar{\epsilon} + \frac{2}{3}\Delta\epsilon_{\mathrm{o}} S$ and $S = S(0) + \chi_E E^2$, $S(0)$ being the order parameter in the absence of E, and χ_E is an effective susceptibility. Using these equations we get

$$I = V_{\mathrm{o}}\omega[(C_{\mathrm{a}} + \frac{3}{4}V_{\mathrm{o}}^2 C_2)\cos\omega t - \frac{3}{4}V_{\mathrm{o}}^2 C_2 \cos 3\omega t] \qquad (9)$$

where $C_{\mathrm{a}} = C_{\mathrm{o}}(\bar{\epsilon} + \frac{2}{3}\Delta\epsilon S_{\mathrm{o}})$ and $C_2 = 2C_{\mathrm{o}}\Delta\epsilon_{\mathrm{o}}\chi_E/3d^2$, where d is the thickness of the cell.

Equation (9) shows that the third harmonic signal is proportional to the susceptibility χ_E. The third harmonic signal has already been shown in Figure 7. The critical divergence of χ_E near T_{c} is evident from the figure. The extraction of a critical index from this data is somewhat delicate. As the conductivity is also quite nonlinear around the critical point, the contribution from $\sigma_{\|}$ to the above response has to be accounted for, which we do not take up in this paper. Further from the above derivation it is clear that to get a second harmonic signal, it is necessary for a part of the capacitance to vary *linearly* with E. This is possible only if there are polarized domains which do *not reorient* with the field, as we discussed in the previous section.

3.5 Field induced nematic-nematic critical point?

In two independent experiments we noticed that the intensity of light scattered by twist fluctuations in the medium showed a sharp increase at ~ 33 °C when the sample was cooled under a field of ~ 600 esu (Fig. 10). This clearly indicates that a phase transition occurs under these conditions. We did not notice this enhancement when the field was significantly smaller than the value given above. Also, the slope of the temperature dependence of $\epsilon_{\|}$ increases by a small amount around this temperature and the resistance shows a small jump. Conoscopic observations on thick enough samples under a similar field indicated that the medium continues to be uniaxial below this temperature. We subjected a *homogeneously* aligned sample to a transverse field of a similar magnitude in a gap etched in an ITO coated plate, and did not find any evidence for a transition to the smectic A phase by direct texture observations. As we discussed in Section 3.1. the molecular theory in which the polar molecules can have antiparallel and parallel mutual configurations, predicts that the concentration of the latter increases as the temperature is lowered. In CP7B this leads to an excess $\epsilon_{\|}$ at lower temperatures. Further the possibility of a jump in the concentration of parallel configuration and hence a nematic-nematic transition, such that the long range order has the same nature in the two phases has also been predicted [5, 16]. This transition is rather weak and hence hard to detect and can exhibit a critical point under the action of the field. Indeed we think that the large increase in the scattered intensity implies that we may be close to a field-induced critical point in the present case. If this is true it once again confirms that the compound used in the present experiments has a fraction of the molecules in the parallel configuration, the remaining ones having the antiparallel short range order. Indeed using specific heat measurements a nematic-nematic transition has been reported in a binary mixture of strongly polar compounds [30]. This transition line occurs as a continuation of a smectic $\mathrm{A_1}$-$\mathrm{A_d}$ transition. In CP7B that we have studied, there is no smectic phase. Further studies on this transition will be reported elsewhere.

4 Conclusions

We have presented detailed measurements on the effect of strong electric fields on various properties of the nematogen p-cyanophenyl p-n-heptyl benzoate. The low field dielectric measurement shows that $\epsilon_{\|}$ increases more rapidly as the temperature is lowered than warranted by the enhancement of the order parameter. The order parameter itself is significantly enhanced by the applied field, and unusually the relevant susceptibility does not decrease rapidly at lower temperatures. The third harmonic signal which is a measure of the susceptibility of the medium exhibits a characteristic divergence as T_{c} is approached. The conductivity measurement shows the usual effects of a weak electrolyte, *viz.*, a reduction in the conductivity at higher fields deep in the nematic phase due to the sweeping of the ions by the field. As the field is increased to large values, the conductivity again increases due to an increase in the order parameter. Close to the critical point T_{c}, the conductivity shows an unusually large increase exhibiting a peak at a temperature slightly lower than T_{c}.

These results are consistent with the trends expected on the basis of a molecular model in which the highly polar compounds prefer to have antiparallel pairs at higher temperatures and parallel configurations at lower temperatures. We may mention here that from dielectric measurements on dilute solutions of a lower homologue of CP7B, *viz.*, CP4B, Dunmur [31] found evidence for parallel correlations between the polar molecules when the concentration was *quite low*. As the concentration was increased the antiparallel correlation was favoured. On the other hand our results on the pure compound show that parallel correlations are favoured especially at lower temperatures, or higher densities, as predicted by our molecular model. We interpret the conductivity peak near T_{c} as arising from a critical slowing down of macroscopic polarized domains of molecules which have the parallel orientation. Indeed the detection of a significant second harmonic peak at T_{c} which implies the presence of polarized domains that do not reorient with the field, appears to support this idea.

Finally, we have found evidence for a field induced transition deep inside the nematic range. As the lower temperature phase is neither biaxial in nature nor exhibits the textures of smectic A, we interpret this to be a nematic-nematic phase transition in which the fraction of molecules with the antiparallel orientation increase as the temperature is raised across the transition. We may also note that there is a considerable body of theoretical work on the possibility of a *polar* nematic phase when the molecules carry a large dipole moment (see for example [32]). To our knowledge such a phase has not yet been discovered. Our observation of a strong *polar short range order* may indicate one possible route to the realisation of a polar nematic liquid crystal.

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