Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713926090

Study of the nematic electroclinic effect in mixtures

J. Zubia[a]; J. Etxebarria[b]; M. Perez Jubindo[c]
[a] Departamento de Automática, Electrónica y Telecomunicaciones, E.T.S.I.I.T., Alameda de Urquijo s/n, Universidad del Pais Vasco, Bilbao, Spain [b] Departamento de Física de la Materia Condensada, Facultad de Ciencias, Universidad del País Vasco, Bilbao, Spain [c] Departamento de Física Aplicada II, Facultad de Ciencias, Universidad del Pais Vasco, Bilbao, Spain

To cite this Article Zubia, J. , Etxebarria, J. and Jubindo, M. Perez(1994) 'Study of the nematic electroclinic effect in mixtures', Liquid Crystals, 16: 6, 941 — 954

To link to this Article: DOI: 10.1080/02678299408027865

URL: http://dx.doi.org/10.1080/02678299408027865

LIQUID CRYSTALS, 1994, VOL. 16, NO. 6, 941–954

Study of the nematic electroclinic effect in mixtures

by J. ZUBIA†, J. ETXEBARRIA*‡ and M. A. PEREZ JUBINDO§

† Departamento de Automática, Electrónica y Telecomunicaciones, E.T.S.I.I.T.,
Alameda de Urquijo s/n, Universidad del País Vasco, 48013, Bilbao, Spain

‡ Departamento de Física de la Materia Condensada, Facultad de Ciencias,
Universidad del País Vasco, Apartado 644, 48080 Bilbao, Spain

§ Departamento de Física Aplicada II, Facultad de Ciencias,
Universidad del País Vasco, Apartado 644, 48080 Bilbao, Spain

(Received 26 April 1993; accepted 23 September 1993)

The temperature dependence of the nematic electroclinic effect has been studied in binary mixtures prepared from two chiral compounds with nematic–smectic A–smectic C and nematic–smectic C phase sequences. The data obtained show a substantial difference in the magnitude of the effect, not only with the type of phase sequence, but also with the temperature range of the subsequent smectic A phase. These results suggest that short-range smectic fluctuations can play an important role in the nematic electroclinic effect at least when a smectic C phase is close to the nematic. In addition, the dynamic behaviour of the electroclinic effect has been investigated in the compound with the nematic–smectic A transition. As in previous work, an anomaly in the electroclinic response time has been found around the nematic–smectic A transition. This fact is analysed qualitatively assuming two different mechanisms contributing to the electroclinic effect.

1. Introduction

The electroclinic effect (EE) was first described by Garoff and Meyer [1] two years after the discovery of ferroelectricity in liquid crystals. The effect can be predicted by means of a symmetry argument similar to that allowing the existence of ferroelectricity in a chiral smectic C (S_C). It can be shown that when an orthogonal smectic mesophase composed of chiral molecules is subjected to an electric field parallel to the layers, an inclination of the molecules is induced in a plane normal to the field. If the applied field E is not too high, the magnitude of the induced tilt θ is linear in the field, i.e. $\theta \propto E$.

Since the discovery of the EE, a lot of effort has been devoted to the study of this phenomenon due to its considerable interest, not only from a fundamental, but also from a practical point of view [2–9]. Most of this work has been centred on smectic A (S_A) materials although the effect has also been observed in other smectic orthogonal phases such as smectic B and smectic E [10]. However, recently, it has been demonstrated that the presence of smectic layers is not essential for the appearance of an optical tilt proportional to the applied field [11, 12]. In the chiral nematic (N) phase of a material with a long pitch, a tilt of the optical tensor can be induced by an electric field if the cholesteric helix is unwound by means of surface stabilization. This is the so-called nematic electroclinic effect (NEE).

---

* Author for correspondence.

0267–8292/94 $10·00 © 1994 Taylor & Francis Ltd.

From the theoretical point of view, the NEE is far from being well understood. Even its origin is a matter of discussion. In principle, the nature of the effect is different from that of the conventional EE in smectics, because in the N phase two configurations which differ in a rotation of the nematic director are equienergetic. One possible mechanism which can give rise to the effect is the biasing of the rotation of the molecules around their long axes as a consequence of the electric field [12, 13]. If the optical dielectric tensor of a molecule is not codiagonal with its inertial tensor, the molecular rotational hindrance causes appearance of an optical tilt that, in a first approximation, is proportional to the applied field [13, 14]. An alternative to this explanation can be given by considering the NEE as originated by the biasing of the optically biaxial S_C fluctuations due to the electric field [15]. On the other hand it is known that electroclinic phenomena can be induced by an interface [16–18] and, in this context, the NEE can also be attributed to a flexoelectric surface mechanism [19]. There is little reason to consider one particular model preferable to the others since, up to now, very few studies have been published on this subject. It is therefore interesting to provide more experimental information in order to test the above models with the new data.

The purpose of this paper is to give some new insight into the origin of the NEE. In this sense, we have studied the temperature dependence of the induced tilt in two chiral compounds with N–S_A and N–S_C phase sequences, respectively, and in their mixtures. The magnitude of the induced tilt and its temperature behaviour have been found to present a clear dependence not only upon the phase sequence, but also upon the S_A range of existence. In addition, we have studied the dynamic response of the NEE in the compound with the N–S_A transition. As in previous work [20, 21], it has been found that the NEE is very fast and its response time shows an anomalous behaviour in the proximity of the N–S_A transition. In view of the results obtained some hypotheses about the origin of the NEE are suggested.

2. Experimental

The materials studied, SCE9 and SCE10, were purchased from Merck Ltd., U.K., and used without further purification. These compounds are multicomponent mixtures with a large cholesteric pitch over a temperature range several degrees above the nematic to smectic phase transition. The transition temperatures as determined by polarizing microscopy are as follows:

$$S_C\ 56{\cdot}2°C\ S_A\ 87{\cdot}3°C\ N\ 115°C\ \text{Isotropic}. \qquad \text{(SCE9)}$$

$$S_C\ 70°C\ N\ 110°C\ \text{Isotropic}. \qquad \text{(SCE10)}$$

Both materials have a negative value of the dielectric anisotropy which make them suitable for studying the electroclinic response in the N phase. For our measurements, we employed glass cells coated with indium tin oxide (ITO), having an area of 4 × 4 mm^2 and a nominal thickness of 4 μm. The plates were treated with nylon 6/6 and rubbed undirectionally in order to achieve the desired bookshelf geometry. Compounds SCE9 and SCE10 and the binary mixtures made from them were introduced into the cells by capillary action in the isotropic phase. Previously to the experiments, all samples were rigorously examined to check the alignment quality and to verify that in all cases the helix remained unwound at least 10°C above the N–S_A and N–S_C phase transitions. Electro-optical investigations were carried out by means of the typical arrangement for measuring the EE [3]. The sample, housed in a hot stage, was situated between crossed polarizers with the nematic director making an angle of 22·5 degrees with respect to the first polarizer. The sample was subjected to a sine-wave voltage which produced a modulation of the intensity of a He–Ne laser beam passing through the set polarizer–sample–analyser. The modulated light intensity δI was detected with a photodiode and a lock-in amplifier. Simultaneously the transmitted DC intensity I_0 was determined with a digital voltmeter. Under these conditions the induced tilt angle is simply given by

$$\theta = \delta I / 4I_0. \tag{1}$$

For measurements of the NEE as a function of temperature, the driving frequency was kept fixed at a value of 1 kHz. This frequency is high enough to prevent the appearance of electrohydrodynamical instabilities which were observed below 100 Hz. The measurements were performed dynamically at a constant rate of 0·1°C min^{-1} both on heating and cooling. Data were stored in a microcomputer every 10 s.

The study of the relaxational dynamics of the NEE was based on the assumption that its time dependence is well described by a Debye-type equation, i.e.

$$\Gamma d\theta/dt + A\theta = cE, \tag{2}$$

where Γ is a viscosity, c is the coupling constant between θ and E in the Landau free-energy expansion and $A = \alpha\,(T - T_{AC})$. Here α is a constant, T is the temperature and T_{AC} the S_A–S_C transition temperature. If a sinusoidal electric field $E = E_0 \exp(i\omega t)$ of angular frequency ω is applied to the sample, the induced tilt angle is given by the expression

$$\theta = (cE/A)/(1 + \omega^2\tau^2) \tag{3}$$

and the phase delay δ of the tilt relative to the applied field is given by

$$\delta = \tan^{-1}(\omega\Gamma/A) = -\tan^{-1}(\omega\tau), \tag{4}$$

where $\tau = \Gamma/A$ is the relaxation time.

Thus, by measuring the slope of a plot of $\tan\delta$ versus ω the relaxation time can be determined. For these measurements, the voltage across the sample was fixed at 2·5 V, well inside the region of linear response, while the frequency of the electric field was varied from 3 kHz to 100 kHz, which was the upper limiting frequency of our lock-in amplifier. The drift of the phase with frequency (arising from the electronic circuitry and, in particular, from the lock-in) was corrected using a sinusoidal voltage of 1 mV for calibration purposes. There was no necessity of introducing new corrections due to the non-null response time of the photodiode since, in all cases, this time was found to be several orders of magnitude smaller than the relaxation time of the material.

3. Results

In this section we will describe the main features of the temperature dependence of the EE in the N and S_A phases of SEC9, SCE10 and the binary mixtures formed with these materials. We will also present the results of the relaxational behaviour of the NEE in the compound SCE9.

Figure 1 shows the temperature dependence of the induced tilt angle for SCE9. Data were taken over a temperature range from 56°C (slightly below the S_A–S_C phase transition) up to 90°C (above the N–S_A transition). Both transition temperatures T_{NA} and T_{AC} were found to be somewhat different from those published recently by us for the same compound [14]. The reason for this discrepancy may be related to the period of time that elapsed between these two sets of measurements, during which some degradation of the material could have occurred.

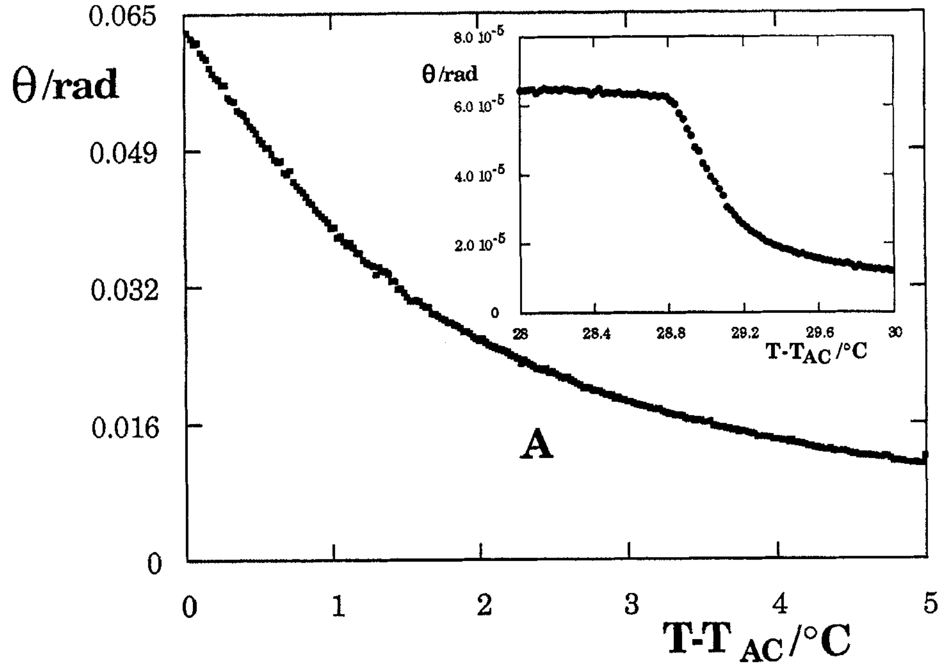


Figure 1. Temperature dependence of the tilt angle induced by a sinewave voltage of 2·5 V and 1 kHz around the S_A–S_C and N–S_A (inset) phase transitions of compound SCE9.

Within the S_A phase and near the S_A–S_C phase transition temperature, the usual pretransitional divergence of the EE is observed. In this region, data were successfully fitted to a function of the type $\theta \propto (T-T_{AC})^{-\gamma}$. The stability of the fit was good and no appreciable dependence of the exponent γ on the number of points taken to fit the results could be noted. The best fit corresponds to a transition temperature $T_{AC} = 56{\cdot}23°C$ and a susceptibility critical exponent $\gamma = 1{\cdot}04 \pm 0{\cdot}05$ which, according to the expectations, is in good agreement with the predictions of a mean-field model.

Approximately at 87°C, the tilt angle drops suddenly down to a small fraction of the value taken just below the transition. Finally, well inside the N phase, θ is extremely low, showing a monotonous decreasing tendency with increasing temperature. As found in previous work, the pretransitional behaviour of the NEE is so strong that no reliable fit of the results could be performed in the framework of the available theories [12, 13]. Details of the fitting attempts can be found in [14]. Here we will briefly review the main aspects of the analysis carried out with the data. According to the model proposed in [13], the induced tilt in the N phase should be proportional (except for an additive constant) to the square of the smectic order parameter $|\psi|^2$. Therefore θ must have a temperature dependence given by the renormalization-group expression

$$\theta = \theta_0 + A|t|^{1-\alpha} + B|t| \tag{5}$$

where α is the critical exponent for the specific heat, A and B are constants, $t = (T - T_{NA})/T_{NA}$ is the reduced temperature and θ_0 the tilt at T_{NA}. In performing the fits, only α, A and B were allowed to vary. The transition temperature was taken, as the formula above suggests, at the point at which the slope of the curve $\theta(T)$ is a maximum and θ_0 was held fixed at its experimental value at T_{NA}. The resulting fits were not bad, presenting χ^2 values close to unity. However, no convergence for the parameters could be achieved as stability of the fits was tested by range shrinking. Furthermore, the range in which the resulting critical exponent α varied was completely unrealistic. We will point out some reasons for this anomalous behaviour in the next section.

An analogous study to that described above was repeated for SCE10. In figure 2 we have plotted the temperature dependence of the induced tilt angle. As can be seen, θ changes very little over a broad range in the N phase and then grows suddenly in the proximity of the N–S_C transition temperature, T_{NC}. This temperature was difficult to locate accurately since there is not a precise point where the growing tendency of θ stops as the temperature is lowered. By analogy to the preceding case, T_{NC} was situated at the temperature at which $d\theta/dT$ is a maximum, although it could be placed at a slightly lower value. Anyway, it can be seen that the induced tilt angle in the N phase of this compound is much higher than that of SCE9, with a N–S_A phase transition. This is in qualitative agreement with the behaviour of the NEE estimated from dielectric measurements in a short-pitch cholesteric material [15], although the numerical values reported in that work are much larger than those found here and in other studies using optical techniques [11–14]. In any case, an increase of the NEE near a N–S_C transition is what can be expected from the diverging coherence length of the S_C fluctuations at T_{NC}. No attempt was made to fit the pretransitional behaviour of the NEE in this material. As indicated in [12], equation (5) is not expected to be valid when the N phase is followed by a tilted smectic phase.

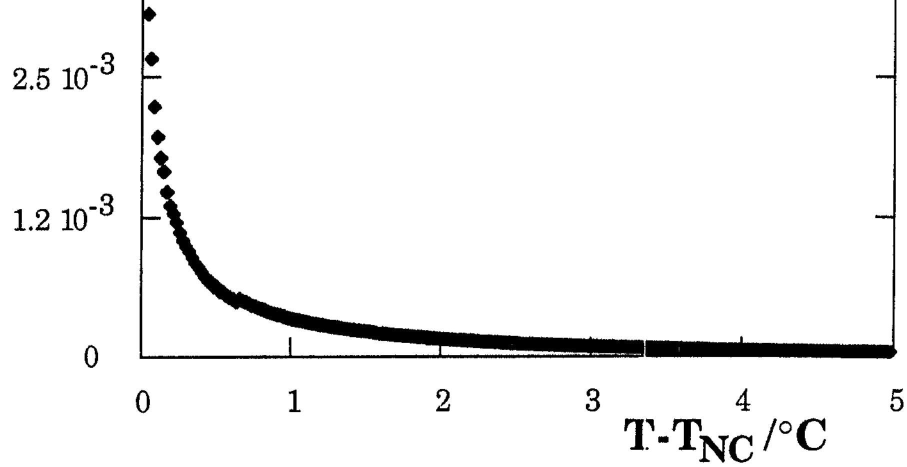


Figure 2. Nematic electroclinic effect of SCE10 near the N–S_C phase transition.

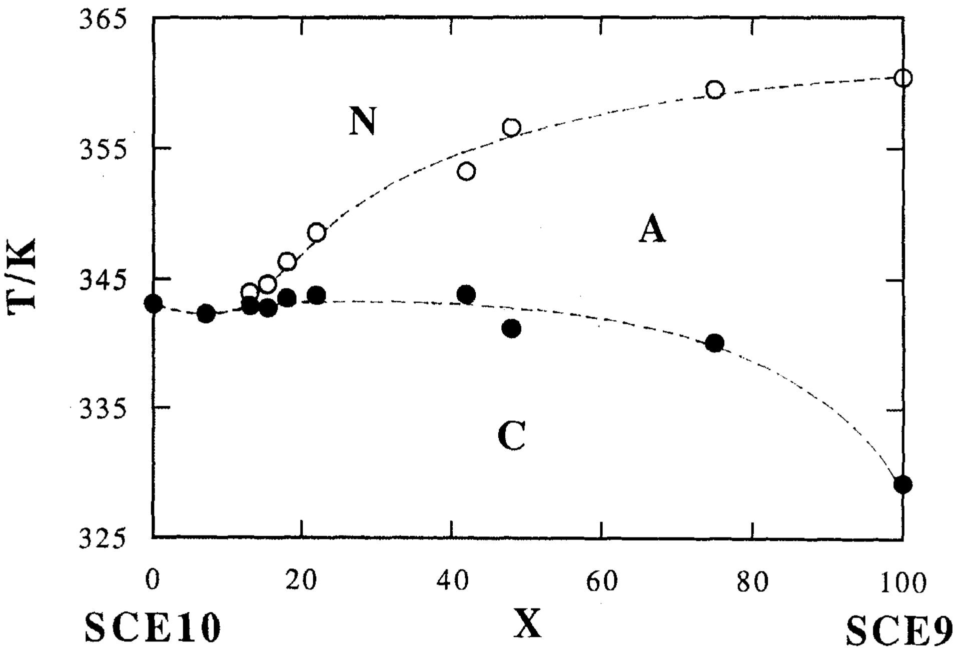


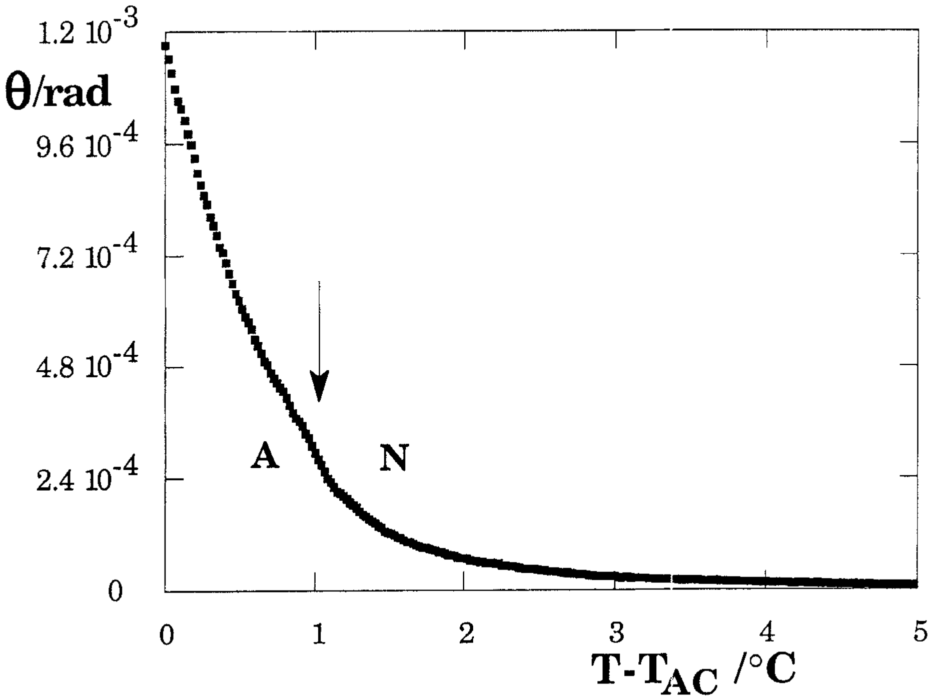
Figure 3. Phase diagram of the binary system SCE9 + SCE10. X represents the wt percentage of SCE9 in each mixture.

In order to get a better understanding about the effect of the phase sequence on the magnitude and evolution of the NEE, we measured the induced tilt angle in N phases of the mixtures made from SCE9 and SCE10. As will be shown below, these results have also allowed us to analyse the role of the S_A range on the magnitude of the NEE.

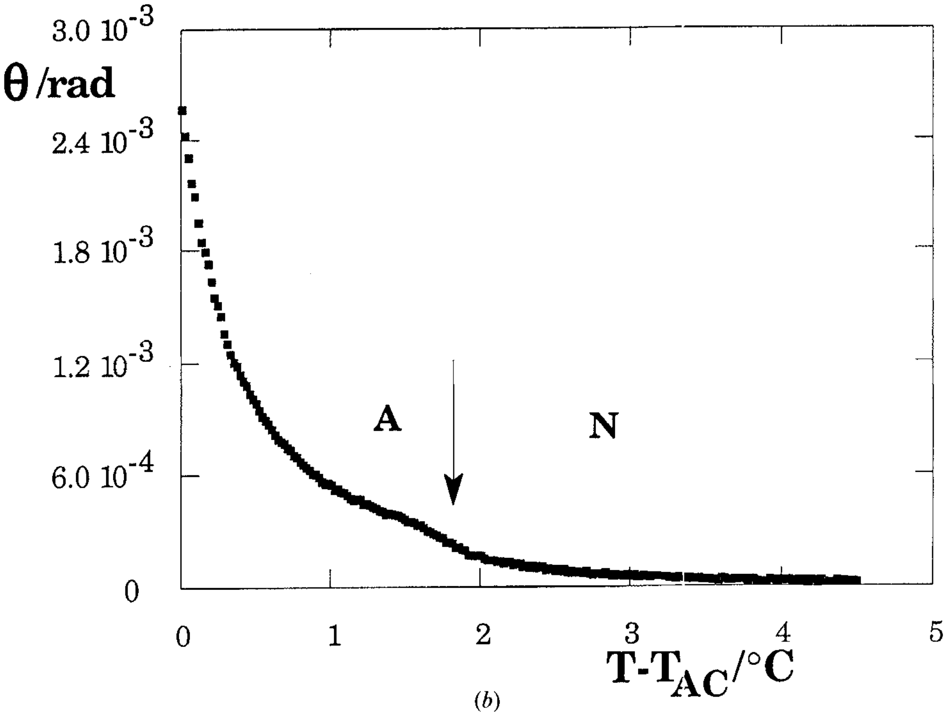
The phase diagram of the binary system is shown in figure 3. The transition temperatures were obtained from measurements of the EE and DSC data. The error of this procedure was estimated to be about 0·1°C. These temperatures are compatible with those obtained by direct microscopic observation. As can be seen, the first-order N–S_C line splits into two S_A–S_C and N–S_A lines at the N–S_A–S_C multicritical point. The concentration of the compound SCE9 at this point is $X = 12 \pm 1$ (wt%). All the S_A–S_C phase transitions are continuous and show a mean-field to tricritical cross over behaviour as the S_A phase range decreases [22]. The N–S_A transitions are always second-order.

Figure 4 shows the temperature dependence of the NEE for several mixtures. The plots are arranged as a function of the concentration X. It can be seen that, as a general trend, when the range of the S_A phase is reduced or, what is the same thing, when the temperature interval from the N phase to the ferroelectric phase is lowered, the magnitude of the NEE increases. In contrast, the opposite evolution is displayed by the induced tilt close to T_{AC}.

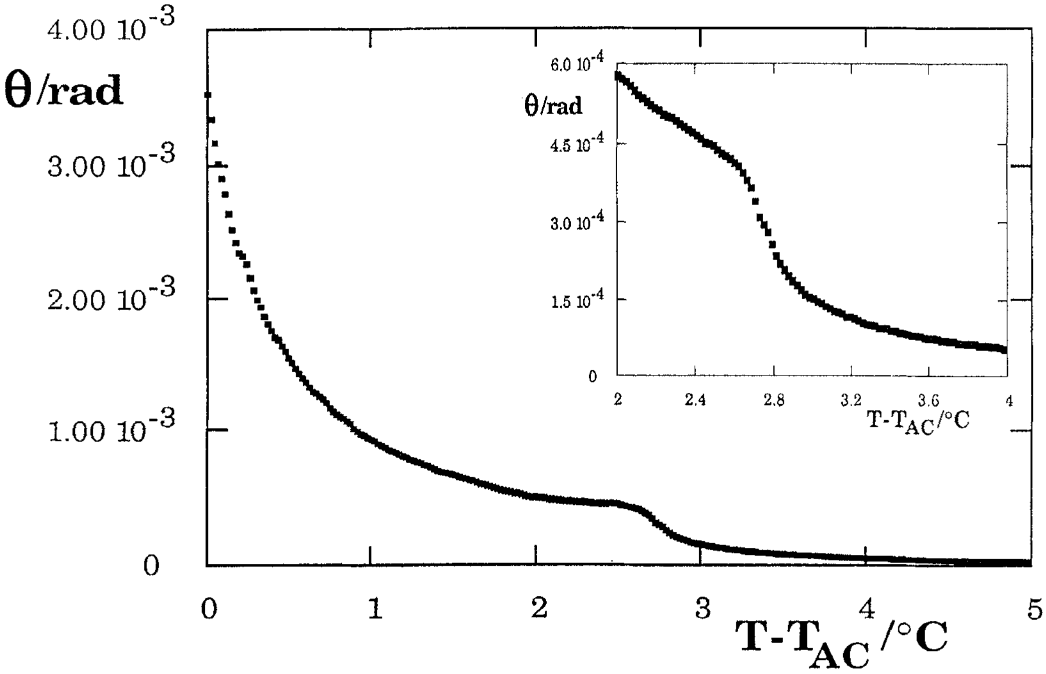
One way to characterize the behaviour and size of the NEE for the different mixtures is by means of the value and the slope of θ at T_{NA}. The table shows these quantities for all mixtures. For the mixtures close to the N–S_A–S_C point, both the NEE and its derivative are much greater than those obtained for 100 per cent SCE9 or for mixture 5 ($X = 75$) that also possesses a broad S_A range. In fact, for mixture 1 ($X = 13$), with only one degree of S_A phase, the N–S_A transition temperature does not appear


θ/rad
1.2 10^{-3}
9.6 10^{-4}
7.2 10^{-4}
4.8 10^{-4}
2.4 10^{-4}
0
A
N
0
1
2
3
4
5
T-T$_{AC}$ /°C

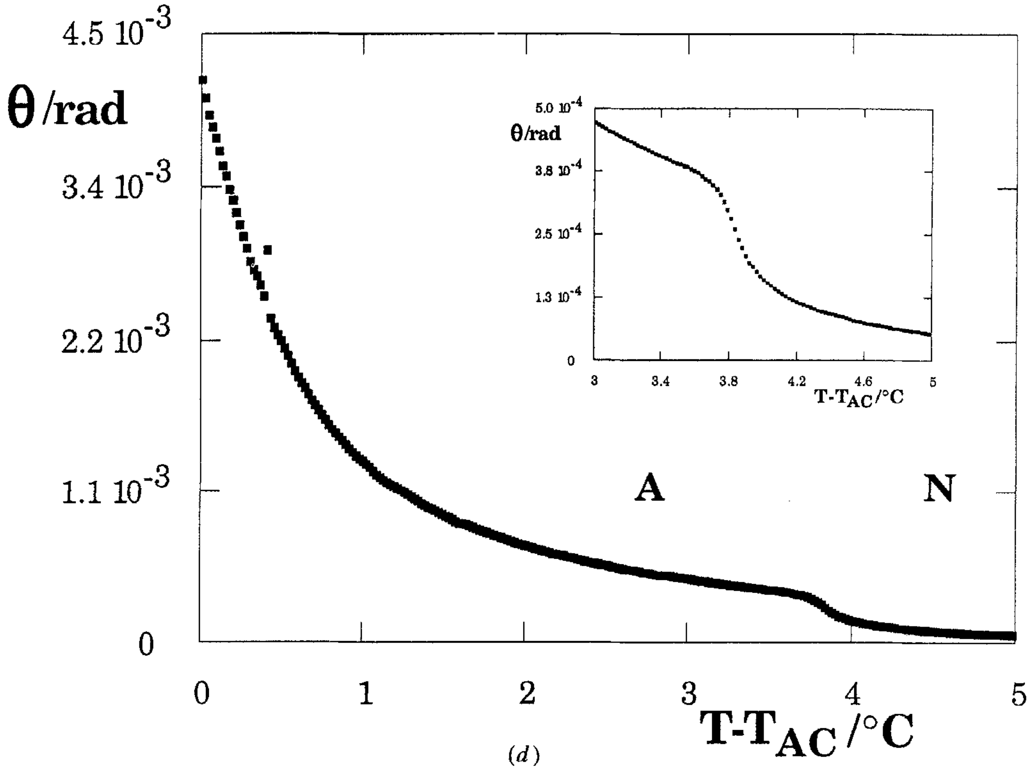
(*a*)


θ /rad
3.0 10^{-3}
2.4 10^{-3}
1.8 10^{-3}
1.2 10^{-3}
6.0 10^{-4}
0
A
N
0
1
2
3
4
5
T-T$_{AC}$/°C

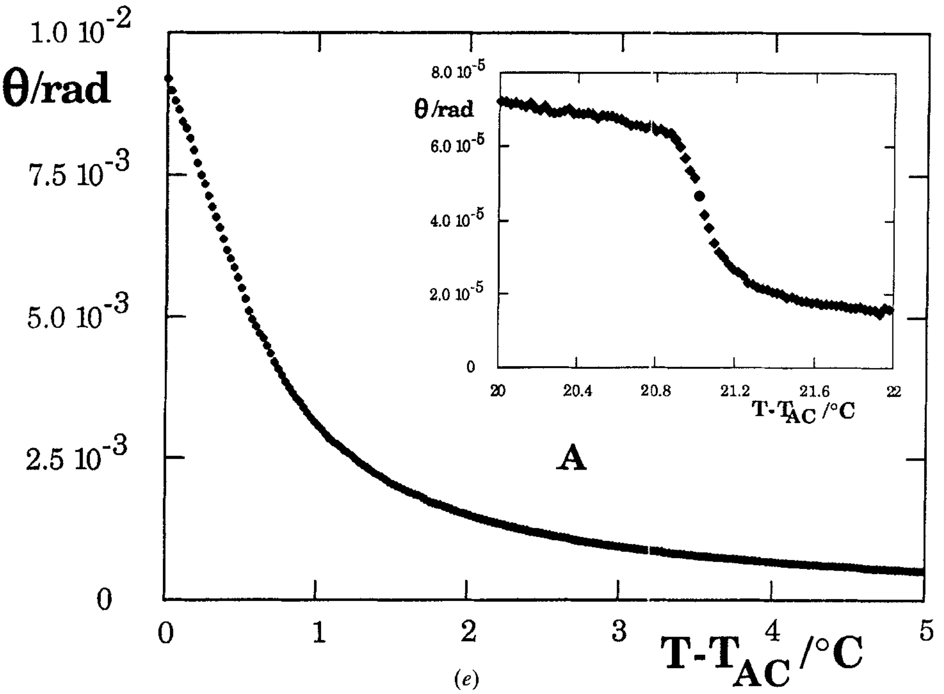
(*b*)


θ/rad
4.00 10^{-3}
3.00 10^{-3}
2.00 10^{-3}
1.00 10^{-3}
0
0
1
2
3
4
5
T-T$_{AC}$ /°C
6.0 10^{-4}
θ/rad
4.5 10^{-4}
3.0 10^{-4}
1.5 10^{-4}
0
2
2.4
2.8
3.2
3.6
4
T-T$_{AC}$/°C

(*c*)


θ/rad
4.5 10^{-3}
3.4 10^{-3}
2.2 10^{-3}
1.1 10^{-3}
0
0
1
2
3
4
5
T-T$_{AC}$ /°C
A
N
5.0 10^{-4}
θ/rad
3.8 10^{-4}
2.5 10^{-4}
1.3 10^{-4}
0
3
3.4
3.8
4.2
4.6
5
T-T$_{AC}$/°C

(*d*)



(*e*)

Figure 4. Temperature dependence of the induced tilt angle for several SCE9+SCE10 mixtures around the N–S_A phase transition. The weight percentage of SCE9 and the temperature range of the S_A phase are the following: (*a*) $X=13$; $T_{NA}-T_{AC}=1{\cdot}0$°C, (*b*) $X=15{\cdot}4$; $T_{NA}-T_{AC}=1{\cdot}9$°C, (*c*) $X=18$; $T_{NA}-T_{AC}=2{\cdot}8$°C, (*d*) $X=22$; $T_{NA}-T_{AC}=3{\cdot}8$°C, (*e*) $X=75$; $T_{NA}-T_{AC}=21$°C.

Magnitude and slope of the induced tilt θ at the N–S_A transition temperature T_{NA} as a function of the S_A range. X represents wt percentage of SCE9 in each SCE9+SCE10 mixture. For pure SCE10 we have written the values of θ and its derivative at the N–S_C transition temperature. In all cases the applied field amplitude was 2·5 V/4 μm.

X/per cent	S_A range/°C	$\theta(T_{NA})$/rad	$(d\theta/dT)(T_{NA})$/rad °C^{-1}
0	0	$4{\cdot}01\times10^{-3}$	$2{\cdot}10\times10^{-2}$
13	1·0	$2{\cdot}53\times10^{-4}$	$7{\cdot}10\times10^{-4}$
15·4	1·9	$2{\cdot}99\times10^{-4}$	$6{\cdot}11\times10^{-4}$
18	2·8	$2{\cdot}81\times10^{-4}$	$5{\cdot}00\times10^{-4}$
22	3·8	$2{\cdot}69\times10^{-4}$	$3{\cdot}47\times10^{-4}$
75	21	$4{\cdot}16\times10^{-5}$	$1{\cdot}71\times10^{-4}$
100	29	$3{\cdot}05\times10^{-5}$	$1{\cdot}60\times10^{-4}$

sharply defined, the only noticeable effect of the transition being a slight modification of the shape of the curve around this position. In these cases, and at a first glance, the EE behaves as if it was due to a unique continuous process, identical in both the N and S_A phases and only smoothly altered by the N–S_A phase transition.

In parallel to the study carried out on the compound SCE9, we tried to fit the curves $\theta(T)$ in the N phase to equation (5). The validity of these fits was checked by range shrinking using three different temperature ranges and, as before, we failed to fit data to that expression.

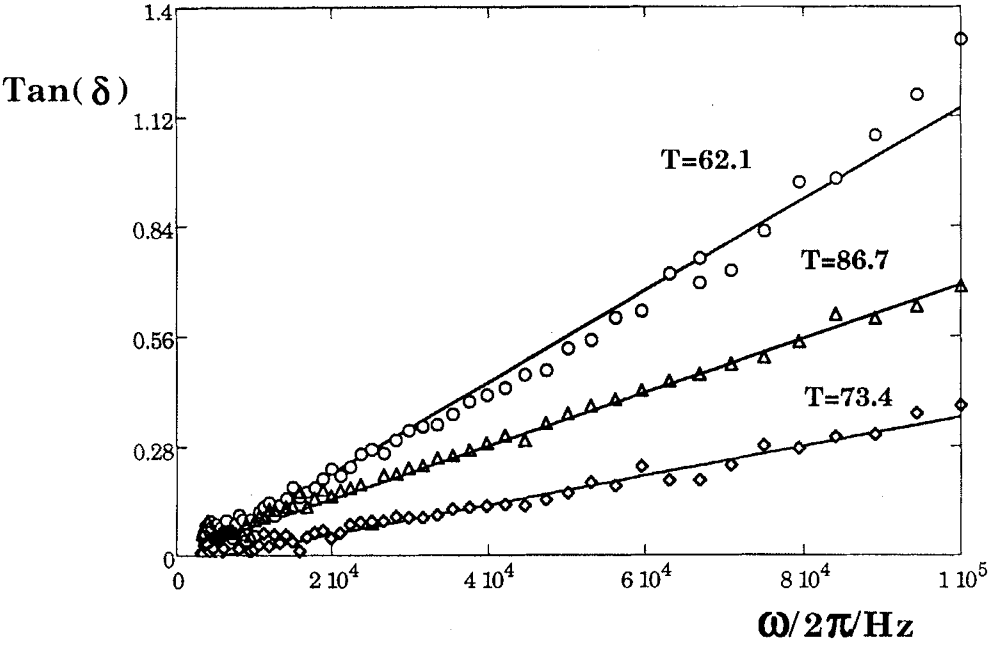


Figure 5. Tangent of the phase angle δ between the induced tilt angle and the applied electric field as a function of frequency at several temperatures in the S_A phase of compound SCE9.

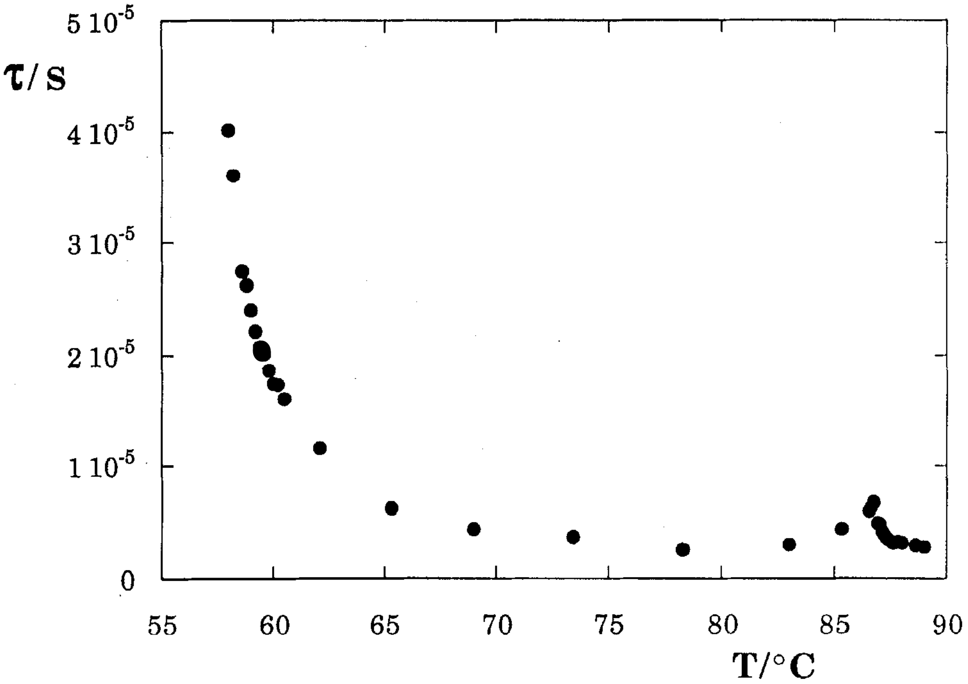


Figure 6. Response time τ of the electroclinic effect versus temperature for compound SCE9.

We now turn to describe the dynamics of the EE in the N and S_A phases of SCE9. Figure 5 represents the tangent of the phase δ versus frequency for three chosen temperatures in the S_A phase. The relaxation time is directly inferred from the slope of these plots. As can be seen, the expected linear relationship between $\tan\delta$ and ω (equation (4)) is reasonably well followed, although some small deviations from this behaviour appear at low temperatures. In any case, the variations of the slope are small enough to assume that, at least, in the frequency range 10^3–10^5 Hz, only one important mechanism is involved. The relaxation times obtained from the linear fits are shown in figure 6. At low temperatures in the S_A phase, τ presents the usual diverging behaviour which corresponds to the soft-mode evolution. However, on approaching the N–S_A transition from below, an unexpected increase of the relaxation time is observed, very similar to that reported by Li *et al.* [20, 21]. We will discuss this point in the next section. Finally, above the N–S_A transition, the relaxation time is a monotonically decreasing function of temperature with a sharp slope near T_{NA}. A few degrees within the N phase τ values are very small.

4. Discussion

As has been pointed out in the Introduction, when dealing with the EE we must distinguish between the effect in orthogonal smectic mesophases and the effect in chiral phases without layers, such as the nematic or even isotropic [23]. In smectic phases, the layer normal provides a reference direction that permits one to distinguish energetically between untilted and tilted configurations. This allows the molecules to tilt physically when an electric field is applied. As a consequence of this mechanism, the smectic layers are forced to lower their thickness and, in order to avoid this contraction (quite unfavourable from the energetic point of view), the planes should deform. The actual existence of this physical tilt in the conventional EE has been indirectly observed by some authors, who have proposed an undulation of the planes [24, 25] or the bending or tilting of the layer structure [26] when an electric field is applied.

In contrast, in the case of N phases, this mechanism is, in principle, not allowed if the NEE is assumed to be a bulk effect. Without considering for the moment surface processes, the only possibility to impose locally a preferred axis in a nematic is to include the presence of smectic cybotactic groups. Since, on average, the molecular director in these groups is parallel to the director in the N phase, the process responsible for the EE in smectics could also operate for the NEE.

On the other hand, it is clear that the NEE can also appear as an inclination of the optical indicatrix without any tilt of the (usual) nematic director. Although this process does not produce a net restoring torque linear in the electric field, there is no reason that prevents this contribution from working also in smectic phases. However, presumably, this mechanism is much less efficient than the former and, given the small value of the NEE, it is expected to be negligible in phases with translational order.

Having stated these ideas, we begin comparing the results obtained for the compounds SCE9 and SCE10. Although the chemical structure of these materials is unknown to us, it seems reasonable to assign similar values to the molecular transverse dipole moment, since the spontaneous polarization in the corresponding S_C phases is quite the same in both cases (about 25 nC cm^{-2} at room temperature). Therefore, the strong difference exhibited by the observed NEE can only be related with the kind of phase sequence. Since the effect is two orders of magnitude higher in SCE10, with a S_C phase below the N phase, it seems likely that the S_C fluctuations play an important role in the explanation of the phenomenon [15]. This idea is supported by the behaviour displayed by the SCE9 + SCE10 mixtures, which show an increasing magnitude of the tilt and its derivative as the S_A range is reduced and the tilted smectic fluctuations become more important.

It can be argued that this increasing effect is reasonable because the induced tilt in the S_A phase must also grow, due to its proximity to a S_C phase, where θ diverges. In addition, as has been pointed out above, the hypothesis of proportionality between θ and $|\psi|^2$ may fail if the N–S_A transition is close to a S_A–S_C transition. Nevertheless, we can also notice that for mixtures close to the N–S_A–S_C multicritical point, the EE appears as if it were driven by a single process both in the N and S_A phases. Thus, this seems to suggest a unique main mechanism for the induced tilt in both phases. Furthermore, if the contribution of the smectic cybotactic domains is relevant in the explanation of the NEE, it is not clear that the induced tilt should be well approximated simply by a term proportional to $|\psi|^2$. In this approach, the problem becomes more complicated. Only one part of the induced tilt would behave like $|\psi|^2$. It is therefore not surprising that equation (5) cannot account properly for the results obtained. An expression for the other contributions would involve material quantities such as the correlation lengths of the smectic domains and the elastic constants of the nematic, that present abrupt changes at nematic to smectic transitions. In principle we consider that this could give rise to the observed anomalous behaviour of the NEE.

Another possible explanation of the NEE was suggested in [19]. In this hypothesis the NEE is considered as a surface flexoelectric effect of a chiral nature rather than an actual bulk EE effect. In the presence of an electric field, the surface molecules would tilt with respect to the rubbing axis and the rotation of the alignment at the surface would be transmitted to the whole sample thickness via the twist elastic constant K_2. Nevertheless, there exists a serious drawback in considering the NEE as a surface effect. The problem is the order of magnitude of the response time predicted by the model, which is not consistent with that experimentally observed. If the NEE were driven by an interfacial mechanism, the response time τ would be expected to be of the order of $\tau = \eta d^2/\pi^2 K_2$ [27]. Taking a typical viscosity $\eta = 0{\cdot}1$ P and $K_2 = 10^{-11}$ N, τ results to be in the range 10^{-2}–10^{-3} s for our $d = 4\,\mu$m sample. As has been shown before (see figure 6), this is 3 or 4 orders of magnitude greater than the measured times. It is worth pointing out however, that recently a surface-mediated NEE has been in fact observed in homeotropic cells [28], so this new phenomenon actually does exist as expected from the above argument. The effect presents relaxation times as high as 10^{-2} s and its size is much larger than that which we have observed. However, given the frequency range used in our measurements and the size of the induced tilt we have observed, the contribution from this interfacial process to our signal is expected to be negligible.

At this point it is interesting to discuss the temperature dependence of τ both in the S_A and N phases. Near T_{AC}, τ increases abruptly as we approach the S_C phase. This behaviour is classical and corresponds to the critical slowing down of the mode whose softening gives rise to the S_C phase. Similar behaviour is seen in the dielectric response [29]. However, at the S_A side, near the N–S_A transition, τ increases again with increasing temperature. As has been pointed out before, the temperature dependence is similar to that found by Li *et al.* [20, 21], and differs considerably from the behaviour predicted by the available theoretical models. Above the N–S_A transition, τ decreases again, and at temperatures well inside the N phase, the effect is so small and fast that reliable measurements become problematic. In the case of the material with the N–S_C transition, preliminary results indicate a similar tendency for the temperature dependence of the response time of the NEE.

It is difficult to explain the results obtained around the N–S_A point, especially those at the S_A side. Given our current understanding of the EE and since apparently there is only one relaxation mechanism, τ should be proportional to the induced tilt angle both in the S_A and N phases. In [20], the cusp-like anomalous slowing down of τ in the S_A phase has been explained in terms of two relaxation mechanisms whose contributions to the tilt susceptibility subtract, thus giving an effective time larger than either of the two individual processes. In the referred work, these two relaxations are associated with the 'in-phase' and 'out-of-phase' amplitude fluctuations in the tilt and polarization as described in [30]. However, several difficulties arise when comparing the experimental data and the predictions of this model. First, unless the two relaxation frequencies have quite similar values, the deviation of the effective τ from the relaxation time of the slower process is negligible. Furthermore, if the temperature dependence of the characteristic times of the two modes follow the classical predictions [30], it is difficult to reproduce the sharp experimental behaviour near T_{NA}. Finally, the fact that a similar anomaly has been found at least in two compounds near a N phase suggests that the existence of the N–S_A transition must presumably be involved in the effect.

Here we propose another scheme for the EE which, at least, is able to connect the anomaly of τ with the presence of the N–S_A transition. In the line of the above reasoning and using two different processes for the EE, one could think of the biasing of the rotation of the molecules around their long axes as one fast mechanism competing simultaneously with the physical tilt of the molecules (tilt of the nematic director) in the S_A phase. The last contribution would be driven by the usual process which softens at the S_A–S_C transition. On the other hand, the fast process would be associated with the rotational hindrance aroung the molecular long axes. Well inside the N phase, only this fast process would operate. However, in order to explain the shape of the observed τ curve it is necessary that the contributions to the tilt susceptibility of both mechanisms are of similar size or their characteristic frequencies become of the same order of magnitude in this region. Neither of these two possibilities seems to be very likely, but in order to elucidate the question it would be worth examining the relaxational behaviour of this material in a broader frequency range. Presently we intend to carry out this study using high-frequency dielectric measurements. If this model is correct, the anomaly of τ at the N–S_A transition could have a different shape in other materials. This would occur if the contributions of both processes to the tilt susceptibility add instead of subtract.

In conclusion, we have analysed the origin of the NEE for several compounds. Results of the induced tilt magnitude as a function of the temperature range of the subsequent S_A phase suggest that short range smectic fluctuations can play an important role in the NEE at least when a S_C phase is close to the nematic. On the other hand, from the dynamical behaviour of the NEE we have deduced that the effect is mainly driven by bulk processes. Although the biasing of the molecular rotation by the field seems to be the principal cause of the NEE, the anomaly of τ around the N–S_A transition indicates the existence of, at least, another competing mechanism. In order to achieve a definitive conclusion about the origin of the NEE a systematic study of the phenomenon in other materials is necessary. In this sense, complementary measurements such as X-ray and high-frequency dielectric spectroscopy can be particularly helpful.

One of us (JZ) wishes to thank Dr L. Komitov for fruitful discussions. This work is supported by the Comisión Interministerial de Ciencia y Tecnología (CICYT) of Spain under project No. MAT91-0962-C02-02.

References

[1] Garoff, S., and Meyer, R. B., 1977, *Phys. Rev. Lett.*, **38,** 848.

[2] Andersson, G., Dahl, I., Keller, P., Kuczynski, W., Lagerwall, S. T., Skarp, K., and Stebler, B., 1987, *Appl. Phys. Lett.*, **51,** 640.

[3] Bahr, Ch., and Heppke, G., 1987, *Liq. Crystals*, **2,** 825.

[4] Nishiyama, S., Ouchi, Y., Takezoe, H., and Fukuda, A., 1987, *Jap. J. appl. Phys.*, **26,** L1787.

[5] Qiu, R., Ho, J. T., and Hark, S. K., 1988, *Phys. Rev.* A, **38,** 1653.

[6] Li, Z., and Rosenblatt, C., 1989, *Phys. Rev.* A, **39,** 1594.

[7] Etxebarria, J., Remón, A., Tello, M. J., and Serrano, J. L., 1989, *Liq. Crystals*, **4,** 543.

[8] van Haaren, J. A. M. M., and Rikken, G. L. J. A., 1989, *Phys. Rev.* A, **40,** 5476.

[9] Andersson, G., Dahl, I., Komitov, L., Lagerwall, S. T., Skarp, K., and Stebler, B., 1989, *J. appl. Phys.*, **66,** 4983.

[10] Bahr, Ch., and Heppke, G., 1988, *Phys. Rev.* A, **37,** 3179.

[11] Komitov, L., Lagerwall, S. T., Stebler, B., Andersson, G., and Flatishler, K., 1991, *Ferroelectrics*, **114,** 169.

[12] Li, Z., Petschek, R. G., and Rosenblatt, C., 1989, *Phys. Rev. Lett.*, **62,** 769; 1989, *Ibid.*, **62,** 1577(E).

[13] Li, Z., Lisi, A. D., Petschek, R. G., and Rosenblatt, 1990, *Phys. Rev.* A, **41,** 1997.

[14] Etxebarria, J., and Zubia, J., 1991, *Phys. Rev.* A, **44,** 6626.

[15] Legrand, C., Isaert, N., Hmine, J., Buisine, J. M., Parneix, J. P., Nguyen, H. T., and Destrade, C., 1992, *J. Phys. II, France*, **2,** 1545.

[16] Xue, J., and Clark, N. A., 1990, *Phys. Rev. Lett.*, **64,** 307.

[17] Patel, J. S., Lee, S. D., and Goodby, J. W., 1991, *Phys. Rev. Lett.*, **66,** 1890.

[18] Chen, W., Ouchi, Y., Moses, T., Shen, Y. R., and Yang, K. H., 1992, *Phys. Rev. Lett.*, **68,** 1547.

[19] Dahl, I., 1990, Ph.D. Thesis, Göteborg.

[20] Li, Z., Atkins, R. B., Dilisi, G. A., Rosenblatt, C., and Petschek, R. G., 1991, *Phys. Rev.* A, **43,** 852.

[21] Li, Z., Ambigapathi, R., Petschek, R. G., and Rosenblatt, C., 1991, *Phys. Rev.* A, **43,** 7109.

[22] Zubia, J., Castro, M., Puértolas, J. A., Etxebarria, J., Pérez, Jubindo, M. A., and de la Fuente, M. R., 1993, *Phys. Rev.* E, **48,** 1970.

[23] Lee, S. D., and Patel, J. S., 1991, *Phys. Rev.* A, **44,** 2749.

[24] Pavel, J., and Glogarova, G., 1991, *Ferroelectrics*, **114,** 131.

[25] Pavel, J., and Glogarova, G., 1991, *Liq. Crystals*, **9,** 87.

[26] Johno, M., Chandani, D. L., Takanishi, Y., Ouchi, Y., Takezoe, H., and Fukuda, A., 1991, *Ferroelectrics*, **114,** 123.

[27] de Gennes, P. G., 1974, *The Physics of Liquid Crystals* (Clarendon Press), pp. 178–180.

[28] Crandall, K. A., Tripathi, S., and Rosenblatt, C., 1992, *Phys. Rev.* A, **46,** R715.

[29] Zubia, J. (unpublished results).

[30] Blinc, R., and Zeks, B., 1978, *Phys. Rev.* A, **18,** 740.