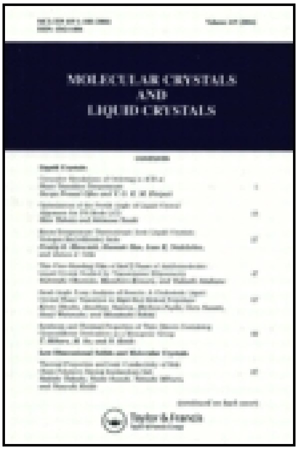

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Electro-Optical Effects of a Small-Pitch Blue-Phase System

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Electro-Optical Effects of a Small-Pitch Blue-Phase System

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A system which shows a relatively large blue-phase range is investigated. Owing to the small value of the cholesteric pitch the blue-phase shows no Bragg-reflections in visible light. Nevertheless, electric-field induced birefringence shows quite large values. The response times are a few tens of microseconds below 10°C. Crude estimates of the effects lead to values reasonably close to the experimental ones. Zero voltage birefringence effects are encountered, field induced and slowly decaying at higher temperatures and surface induced at lower temperatures where a uniaxial phase appears to be stable.

INTRODUCTION

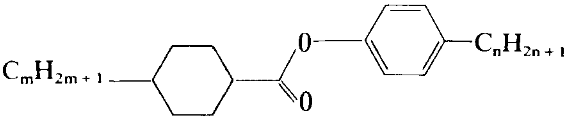
Recently blue-phases have attracted considerable attention principally for reasons of a fundamental understanding of their semimacroscopic structure.[1] Application of these interesting systems is hampered by the narrow temperature interval of about a degree in which they usually exist.[2] However, theoretical considerations[3–6] indicate that this may not be a fundamental limitation. In fact, blue-phase ranges proportional to P^{-2} are expected, where P is the pitch value entering the expression for the curvature elastic energy expression and thus determining the lattice constant of the blue-phase structures. Broad range blue-phases are expected to have lattice constants below the wavelength of visible light and thus to show no conspicuous optical properties at least in cubic structures. Nevertheless, one may expect high optical (and also other than optical) susceptibilities to applied fields.

Previously effects of electric fields on blue-phases have been reported.[7–9] These investigations concentrated on field induced structure and phase changes.

EXPERIMENTS

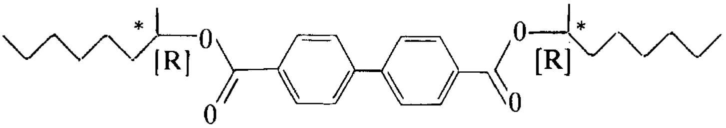
The present note reports on measurements of electro-optical effects of a system composed of several components which showed a fairly extended blue-phase range although some of it in coexistence with an isotropic phase.

The system under consideration was a nematic mixture composed of four homologues of the ester compounds[10]



(I)

namely 25% by weight of (m = 3, n = 2), (4,2), (5,1) and (4,6). As chiral additive we took the molecule[11]



(II)

which showed a helical twisting power

$$\frac{1}{cP} = 18.0 - 4.3 \cdot 10^{-2}\,(T\text{-}22°\text{C}) - 1.1 \cdot 10^{-3}\,(T\text{-}22°\text{C})^2 \quad (1)$$

where P is taken in μm and c in weight fraction of (II). These values were determined by pitch measurements of a 5.4 wt % mixture between 5 and 55°C.

The cholesteric helix is right-handed in this case. The comparatively high twisting power of compound II and its low melting point of 8°C make it suitable for producing low pitch mixtures at reasonable concentrations. However, with conventional positive dielectric nematic mixtures phase separation took place to such an amount that the mesophase part always showed cholesteric phases. For this reason we took the mixture of compounds I which, from the point of view of electro-optical effects, is less suited because of its low dielectric anisotropy of $\Delta\epsilon = \epsilon_{\parallel} - \epsilon_{\perp} = -.75$, as measured ten degrees below the clearing temperature.

Figure 1 shows a phase diagram as obtained by observation in a heating stage (Mettler FP 52, modified for convenient low-temperature observation). For concentrations up to about 20% observation

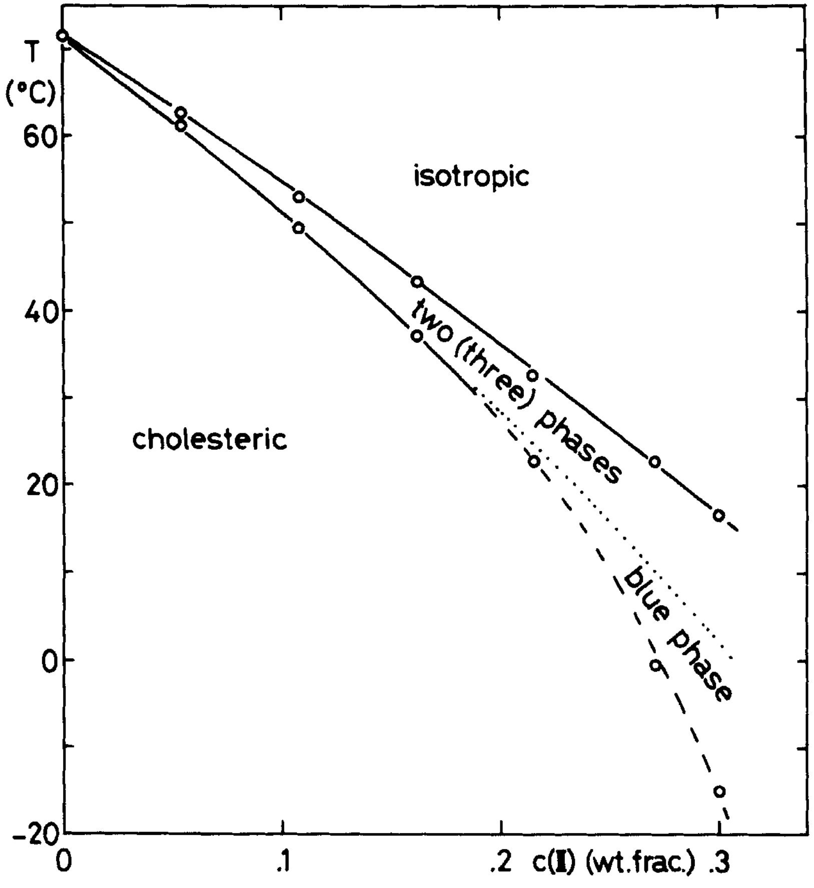


FIGURE 1 Phase diagram of mixtures of the nematic system (I) with the chiral molecule (II) for varying weight fraction of (II). The onset of mesophase ordering and the range of the two-phase region isotropic-cholesteric for concentrations below 0.2 could be determined quite accurately. However, the low-temperature end of the isotropic-blue phase two-phase region is subject to rather large uncertainties because of the extremely poor optical contrast. Similarly, the temperature of onset of cholesteric ordering is subject so substantial uncertanties owing to the extremely slow formation of cholesteric domains (at −20°C they grow on a time scale of several hours).

was straightforward since the occurring phases could be easily distinguished visually. For concentrations above 20% blue phases were hardly distinguishable from the isotropic one, which made the determination of the two phase region extremely difficult. In particular the temperature at which the isotropic phase disappears must be considered as a crude estimate. The onset of cholesteric ordering at still lower temperatures is again just an estimate owing to metastability of blue-phases and the extremely low speed of concentration changes at those low temperatures. Nevertheless the diagram illustrates that for concentrations above 20% a blue-phase can be observed over temperature ranges up to 30°C. This may give hope that in alternative systems large blue-phase ranges may also be obtained.

In the literature several types of blue phases have been reported. However, the poor visibility in our small pitch system did not allow to make such distinctions. Thus, in the following we use the term blue-phase without further specification.

To study electro-optical effects we took a 30% mixture and observed it in a conventional Kerr cell. The electrode spacing was 141 μm while the path of light was 1 mm long. The cell was placed under a polarizing microscope with the electric-field direction at 45° with respect to the polarizer. However, conventional Kerr measurements by compensating the optical path difference proved difficult for two reasons. Firstly, the blue-phase induced a rotation of the main polarisation axis by a few degrees and secondly, the sample had an inhomogeneous appearance owing to the presence of two phases and to possible domain structure in the blue-phase.

For this reason we preferred a more direct measurement. After the sample had reached equilibrium at a given temperature setting, the analyser was rotated to yield minimal transmission. The required deviation of the angle from the crossed position is shown in Figure 2. Then, a square wave voltage was applied to the sample and the corresponding change in transmission ΔI measured. This number was divided by the maximum transmission, $I_{\max}$, which occurred at nearly parallel setting of analyzer and polarizer. From these values a refractive index anisotropy δn was calculated with the expression

$$\frac{\Delta I}{I_{\max}} = \sin^2\left(\pi \frac{\ell}{\lambda} \delta n\right) \tag{2}$$

where ℓ is the light path and λ the wave length of light which was taken as 0.55 μm for white light. The corresponding values of δn are shown in Figure 2. The applied voltage has a value of 170 volts and

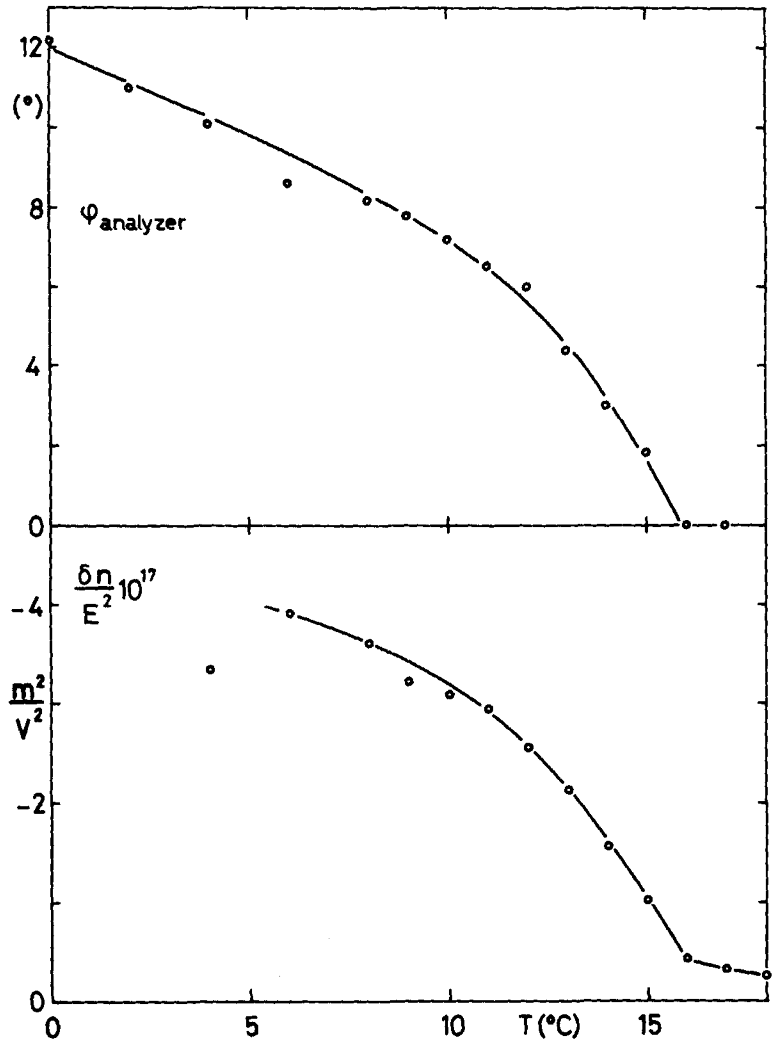


FIGURE 2 Fast response Kerr effect versus Temperature (bottom curve), as obtained from extrapolating the observed signal to time zero of applying the 170 V square wave signal of 50 Hz. Also shown is the angle of rotation of the analyser away from the crossed position which was needed to achieve minimal zero-voltage transmission(top). The polarization of light in the sample rotated according to a right handed screw in accordance with the cholesteric structure of low concentration mixtures.

the measurements were taken immediately after applying the voltage. The time of measurement was important because above 10°C the signal increased with the time the field was applied towards a stationary value of up to twice the initial value. A close examination utilizing an applied voltage of triangular form revealed that the signal changed from an initial V^4-dependence to a mixture of V^2- and V^4-dependence indicating that a zero field optical anisotropy was slowly developing. After removing the voltage, an increased transmission remained which slowly decreased towards the value which was found before applying the voltage. The characteristic times for these processes were on the scale of minutes. Below 10°C the applied voltage hardly influenced the zero field transmission. However, below 6°C a zero field anisotropy was found without an applied field. In fact, after rapidly cooling to temperatures between 0 and 4°C, a positive zero-field anisotropy was observable which in a few minutes changed sign without an applied field. In these cases the Kerr constant was evaluated by fitting an even fourth order polynomial to the transmission versus voltage characteristic. This procedure was subject to substantial uncertainties.

As an example of this effect we show in Figure 3 the time behaviour of $\delta n(V = 0)$ as obtained by fitting the transmission curves to a polynomial of the form

$$[\delta n(V)]^2 = [\delta n(V = 0) + \delta n_2 E^2]^2. \tag{3}$$

During these measurements no voltage was applied except for a few seconds for each measuring point. The zero field birefringence developed quite reproducibly from an initial value of about 5.10^{-5} to a final value of -3.10^{-5}.

Response times of the fast optical anisotropy occurring after a step function in the applied voltage were measured with a resolution time of the measuring equipment of 10 μs which proved to be sufficient for the low temperature range. Figure 4 shows the results of these measurements.

DISCUSSION

The presence of five components in our system with the corresponding possibility of coexistence of several phases complicates the discussion. The increase of the Kerr constant below 16°C is certainly mainly due to an increased content of blue-phase as compared to the isotropic

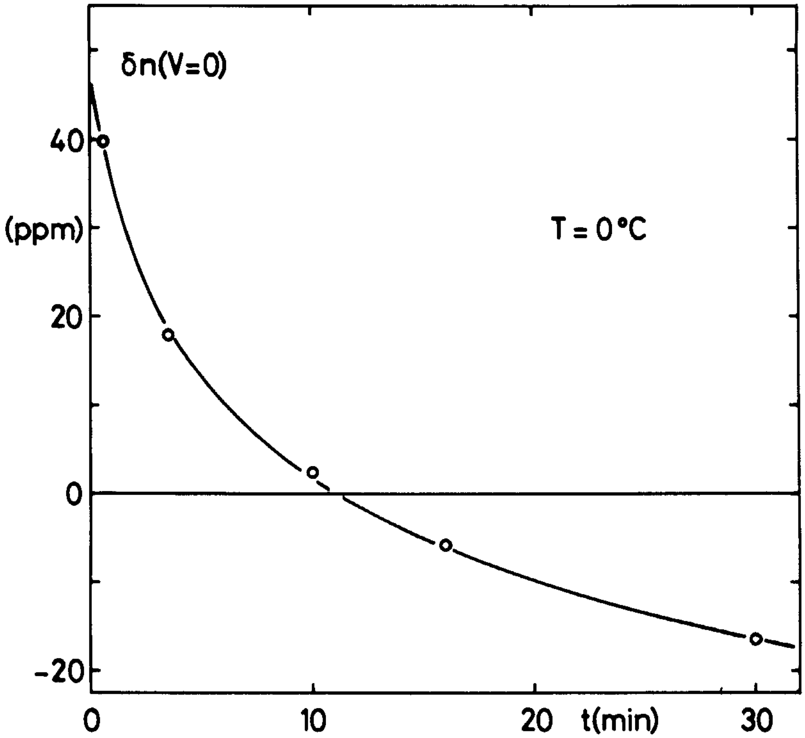


FIGURE 3 Development of the zero voltage birefringence with time at 0°C as obtained from a fit of the form (3) to signal versus voltage recordings. During the half hour shown on the plot the fast response Kerr signal decreased by about 25%. The sample developed in zero applied voltage.

phase content. Thus, we may estimate a value of 3 to $4.10^{-17}\ m^2\ V^{-2}$ for the blue-phase component alone, a value which certainly is also temperature dependent.

One expects from the model ideas proposed for the blue-phase[3-6] that elastic energies of deformations of wave numbers $q \approx 2\pi/P$ compete with electric reorientation energies. Neglecting all geometrical factors, this leads to an estimate for the Kerr constant

$$\frac{\delta n}{E^2} \approx \Delta n \cdot \Delta\epsilon \frac{\epsilon_0\, P^2}{k\,(2\pi)^2} \tag{4}$$

where Δn and $\Delta\epsilon$ are index of refraction—and dielectric anisotropies as observed on a scale small compared to P, where nematic order is present. In our system these quantities have estimated values of Δn

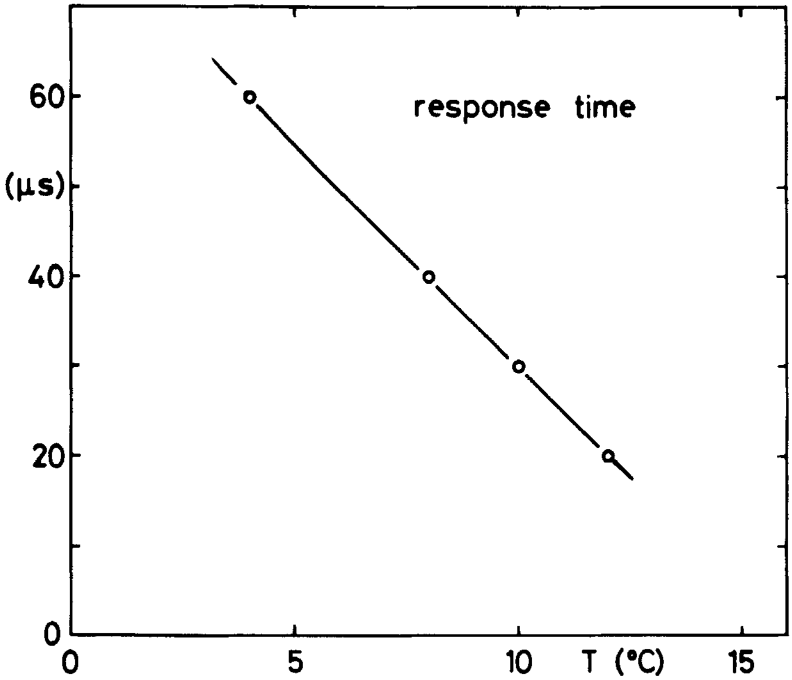


FIGURE 4 Exponential response of the fast Kerr signal versus temperature. Response time of the measuring equipment was 10 μs.

$\cong$ 0.07 and $\Delta\epsilon \cong -.7$ while for an elastic constant k—an estimate of 4.10^{-12} N—seems appropriate.[12] For the pitch P an extrapolated value of 0.2 μm was taken as obtained from (1) for a concentration of 0.3. These values lead to an estimated Kerr constant of

$$\frac{\delta n}{E^2} \cong 10^{-16}\, m^2\, V^{-2} \tag{5}$$

which gives the correct order of magnitude.

The response time τ may be estimated by comparing elastic and viscous torques leading to

$$\tau \cong \frac{\gamma_1 P^2}{k\,(2\pi)^2}, \tag{6}$$

where γ_1 is the rotational viscosity constant. At 10°C the mixture of components (I) showed a rotational viscosity of 2.74 Poise. This yields an estimate $\tau \cong 70\ \mu s$ at 10°C. This and the estimate (5) are somewhat high but sufficiently close to the measured values that uncertainties in k and P may account for the difference.

The zero field birefringence observed reproducibly below about 6°C must be induced by the orienting action of the electrodes, although it requires in addition the presence of axial symmetric structures. These may either stem from small domains of cholesteric structure[7] or alternatively from a non-cubic, axially symmetric blue-phase structure which may well occur since blue-phase often show a rich polymorphism. The generation of slowly decaying birefringence by the action of an electric field above 10°C indicates in addition that unaxial modification may exist which possibly become stable at low enough temperatures while at higher temperatures they are field induced. On the other hand cholesteric domains of observable size could only be observed at −10°C in the heating stage observations, where they stayed stationary in small size. Only at −20°C they grew very slowly.

The change in sign of the birefringence with time as displayed in Figure 3 may be attributed to either a slowly disappearing metastable modification or to some reorientational process.

It remains to be mentioned that similar effects are expected under the orienting action of a magnetic field, although they are expected to be of different sign in our system owing to the positive magnetic anisotropy $\Delta\chi$. On the other hand in alternative systems a considerable increase in the size of the effects may be expected since values for $\Delta\epsilon$ and Δn in nematics may be larger by factors 30 and 3 respectively for certain components. However, as mentioned, the chiral additive (II) could not easily be mixed with such components.

A second point to be made is that anisotropies of other quantities than the refractive index, such as the dielectric or magnetic susceptibilities are similarly induced by the orienting action of fields. An order of magnitude estimate of these effects is obtained from (4) by replacing Δn by the small scale anisotropy of the quantity of interest. Such measurements are valuable for a fundamental understanding of the blue phases structures and may eventually also become useful for the determination of material parameters such as curvature elasticity of rotational viscosity of these phases.

From a point of view of application the electro-optical effect may become of interest for relatively low voltage light modulators. However, the rotation of the plane of polarization, the inhomogeneity of the multidomain sample and the induced slowly decaying anisotropy may prove to be severe restrictions. The magnitude of the effect, if optimized, may be expected to surpass the pretransitionally enhanced Kerr effects as encountered just above the clearing temperatures of nematic phases.[13,14] In addition much larger temperature ranges may be envisaged.

Acknowledgments

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