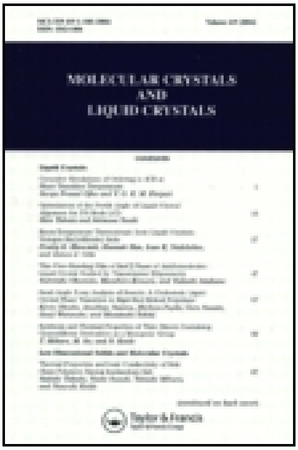

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Kerr Effect in the Isotropic Phase of Some Nematogenic Compounds

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Abstract—The exceptionally strong Kerr effect of some nematogenic compounds with strong electric dipole moments parallel to their long molecular axes was investigated. The Kerr constants just above the clearing point T_{cl} were about 100 times larger than with nitrobenzene. The temperature dependence of the Kerr effect obeyed $(T\text{–}T_{\text{cl}})^{-\gamma}$, with $0.5 < \gamma < 0.7$. The relaxation times were $4 \cdot 10^{-7}$ sec or less.

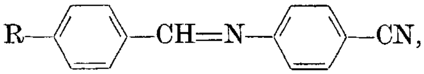
1. Introduction

Because of the weakness of the first-order phase transition nematic-isotropic only the long range ordering of the molecules is destroyed above the clearing temperature T_{cl}, whereas the short range order is largely preserved. The isotropic phase in the vicinity of the transition point may therefore be described as being composed of independently oriented " swarms " of more or less parallel molesules.(1) As the temperature is raised the swarms become smaller and finally vanish. The cooperative effect manifests itself in the huge birefringence in magnetic(2) and electric fields(3,4) or under shear flow.(2) It is also revealed by the high intensity and the spectrum of scattered laser light.(5)

In the following we wish to report on the electrically induced irefringence in the isotropic phase of nematic liquid crystals with strong positive dielectric anisotropy ($\epsilon_{\parallel} \gg \epsilon_{\perp}$). We took such materials to obtain a particularly large Kerr effect. The constituent molecules are characterized by a strong electric dipole moment terallel to their long axes. Also necessary, but not known, is a anonounced optical anisotropy of the molecules. We found Kerr constants which are indeed larger than all known values. The large effect facilitated a study of pretransitional phenomena, such as the temperature dependence of the dielectric birefringence and the relaxation time of the birefringence. The relaxation was observed by way of the frequency dependence of the Kerr effect, which is much simpler (though less instructive) than the determination through the study of laser light scattering by orientational fluctuations.(5)

2. Experimental

The substances studied in our experiments were the compounds



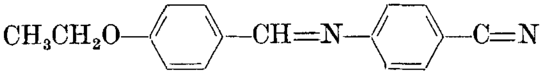
with

$$R_1 = n\text{—}C_7H_{15}\text{—COO—},\quad R_2 = n\text{—}C_6H_{13}\text{—O—}$$

and

$$R_3 = n\text{—}C_4H_9\text{—O—},$$

and a mixture in molar proportions of 1 : 1 : 1 of these components which is nematic between ca. 18 and 96.8 °C.(6) The compounds are nematic between 53.7–97.6 °C; 54.5–100.9 °C and 62.9–110.5 °C respectively. We also studied



(PEBAB)

with a nematic range from 105.5–128.9 °C. All substances were purified by standard chemical procedures,(7) the resulting conductivities being typically 10^{-9} ohm^{-1} cm^{-1}.

For measuring the electrical birefringence(8) (Kerr effect) we used a polarizing microscope with a built-in photomultiplier tube to detect small changes of light intensity. The electro-optical cell was made up of two parallel metal bars between glass plates. The bars served as spacers and electrodes and held the sample in place. Their height, i.e. the length of the light path, was 1 mm and their distance about 0.2 mm. Small differences $\Delta n = (n_e - n_0)$ between the two principal refractive indices were measured with an elliptical compensator ($\lambda/10$), for large Δn a Bereck compensator (4λ) was used. All measurements were performed in monochromatic green light ($\lambda = 546$ nm), i.e. far from any absorption bands of the practically colourless liquids. The cell was mounted in a Mettler heating stage permitting temperature stabilization within 0.02 °C. A sine wave generator and high voltage power amplifier were used to drive the cell. The generator frequency could be chosen such that it was high enough (~ 50 kHz) to prevent space charge formation and turbulence in the liquid which tended to reduce the accuracy of the measurements, but lower than the relaxation frequency of the swarms.

The relaxation time of the birefringence was measured via the frequency dependent modulation of the light transmitted by the Kerr cell which was driven by an alternating voltage. The light was detected by a photomultiplier tube and its intensity displayed on an oscilloscope. Unfortunately, the limited frequency range of our equipment permitted measurements only with the mixture and only in a very small temperature interval.

3. Results

Measurements of the electrical birefringence $\Delta n = (n_e - n_0)$ versus the electrical field F at different temperatures $T > T_{\mathrm{cl}}$ showed a strictly quadratic dependence. It may be written in the standard form

$$\Delta n = K\lambda F^2, \tag{1}$$

where K = Kerr constant, λ = wavelength of light. Δn was not influenced by the conductivity of the samples which is reasonable because any conduction-induced alignment effects⁽⁹⁾ should be negligible in comparison to the expectionally large Kerr effect.

In Fig. 1 we have plotted the time average of the electrical birefringence Δn versus temperature $(T - T_{\mathrm{cl}})$ for all five substances at fixed AC field. It is seen that Δn levels off near the transition temperature T_{cl} in a logarithmic plot and does not diverge as the earlier work of Tsvetkov and Ryumtsev seems to suggest.⁽²,³⁾ These authors investigated substances of weak dielectric anisotropy and did not come closer to the transition temperature than about 1 °C.

For temperatures $(T - T_{\mathrm{cl}}) \gtrsim 1$ °C the birefringence is proportional to $(T - T_{\mathrm{cl}})^{-\gamma}$, with $\gamma = 0.70 \pm 0.05$ for all substances except PEBAB where $\gamma = 0.51 \pm 0.05$ (see Fig. 1). (For reasons of sensitivity we could not go so high in temperature as to make the pretransitional

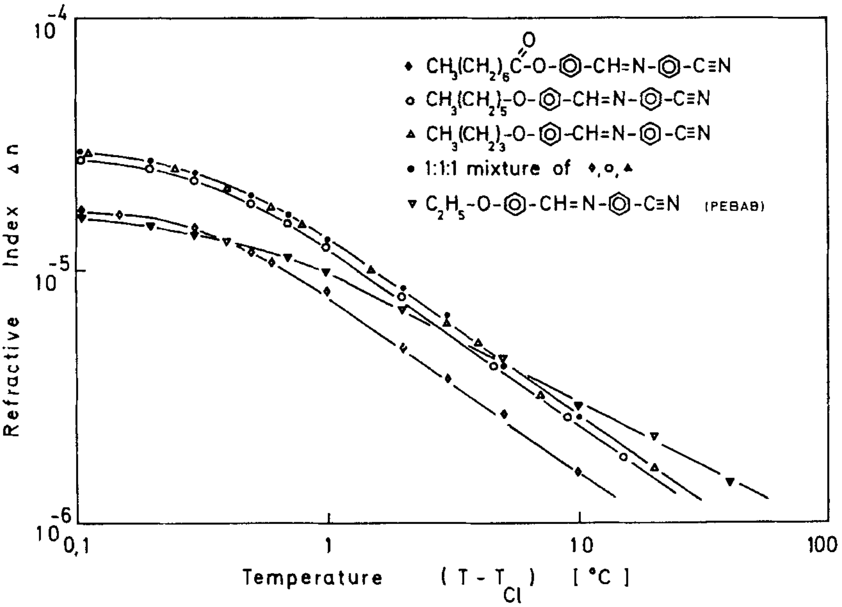


Figure 1. Electrical birefringence Δn versus temperature difference (T–T_{cl}), T_{cl} = clearing point, as measured for various nematogenic compounds. The alternating electric field $F_{\mathrm{RMS}} = 4$ kV cm^{-1} was held constant.

behaviour disappear). γ was found to be insensitive to impurities, even drastically impure samples with the clearing temperature reduced by several degrees centigrade gave the same results.

The standard form⁽¹⁰⁾ to express Δn versus T and F is

$$\Delta n \propto (T - T^*)^{-\gamma} F^2. \qquad (2)$$

The temperature $T^* < T_{\mathrm{cl}}$ may be obtained by extrapolating the linear part of $(\Delta n)^{-1/\gamma}$ versus T to the temperature axes. Apparently, the second-order phase transition at T^* suggested by Eq. (2) is cut off by a first-order transition at T_{cl}. Our measurements were not exact enough to determine $T_{\mathrm{cl}} - T^*$ which in all cases seems to be very small (< 0.2 °C).

The compound with $\mathrm{R_I}$ has the largest molecular volume and contains a COO group which may contribute to the permanent dipole moment a considerable component perpendicular to the long molecular axis. These differences may account for the comparatively weak dielectric birefringence, provided the optical properties of all molecules are similar. Again, PEBAB differs slightly from the other materials as its Kerr effect near T_{cl} is comparatively small despite a strong dipole moment almost parallel to the long molecular axis and a small molecular volume.

The relaxation time was obtained from the frequency dependence of the peak-to-peak amplitude of the light intensity transmitted by the Kerr cell. Theoretically, the AC birefringence as a function of time is

$$(\Delta n) = (\Delta n)_{\mathrm{DC}} \cdot \left(1 + \frac{\cos 2\omega t}{\sqrt{1+4\omega^2\tau^2}}\right)$$

Here $(\Delta n)_{\mathrm{DC}}$ is the DC birefringence, ω the frequency of the voltage applied to the Kerr cell, and τ the relaxation time. The light intensity I is proportional to $(\Delta n)^2$, which leads to

$$I = I_{\mathrm{DC}}\left(1 + \frac{2\cos 2\omega t}{\sqrt{1+4\omega^2\tau^2}} + \frac{\cos^2 2\omega t}{1+4\omega^2\tau^2}\right) \tag{3}$$

The peak-to-peak amplitude of this nonharmonic signal is easily seen to vary with frequency as $(1+4\omega^2\tau^2)^{-1/2}$. From the experimentally determined frequency ω_{c} where the peak-to-peak amplitude has fallen to $1/\sqrt{2}$ of its low frequency value we derive with $1+4\omega_c{}^2\tau^2 = 2$ a value of $\tau \approx 4 \cdot 10^{-7}$ sec for the relaxation time in the mixture at 0.1 °C above the clearing point. The measurements were not extended to higher temperatures and other materials for the reason mentioned earlier.

The Kerr constant at $\lambda = 540\,\mathrm{nm}$ derived from Fig. 1 and Eq. (1) for the mixture at $(T - T_{\mathrm{cl}}) = 0.1\,°\mathrm{C}$ is $K = (3.5 \pm 0.1) \cdot 10^{-10}\,\mathrm{mV}^{-2}$. It is by about a factor of 100 larger than that of nitrobenzene ($K = 2.9 \cdot 10^{-12}\,\mathrm{mV}^{-2}$), the substance most often used in actual applications.

4. Remarks

It is remarkable that our exponents γ are distinctly smaller than unity. A value $\gamma = 1$ is predicted by mean field theories of (nearly) second-order phase transitions and $(T - T^*)^{-1}$ is indeed obeyed by the magnetic birefringence of (p'-methoxybenzilidene)-p-n-butylaniline (MBBA)(11) and para-azoxyanisole (PAA).(12) It could be argued that the smaller exponents have a similar reason as does the change in sign of the Kerr effect of PAA. The reversal takes place at 5 °C above the clearing point and is attributed to the increase of orientational freedom which the individual molecule experiences with rising temperature.(3) However, our compounds have their electric dipoles almost parallel to their long molecular axes, while the dipole of PAA is at a large angle. It seems conceivable that critical exponents smaller than unity will also be observed in future studies of the magnetic birefringence of our materials. The compounds studied differ from most other nematogenic molecules by their very large dipole moments (5 debye) which perhaps influence the critical behaviour, rendering mean-field theory inapplicable.

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