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THE LASER AND ELECTRICAL KERR EFFECT IN PENTYLOXY - CYANOBIPHENYL

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ABSTRACT. The optical and dc pulsed field Kerr effects have been measured in 5 OCB in the isotropic phase and in dilute solution. The pretransitional behaviour has been examined in terms of the Landau-de Gennes model. The constants of this formalism have been given and a possible optical shutter has been suggested.

In continuation of our Kerr effect studies under both pulsed optical and d.c. electrical fields on liquid crystals we recently turned our attention to the stable and colourless cyano-biphenyls[1,2]. Such materials have phase transition temperatures that depend markedly on the nature (length or conformation) of the paraffinic tail. Whilst with the alkyl homologues the nematic-isotropic transition occurs in the range $\sim$30-40°C for the alkyloxy series this range is shifted to $\sim$70-80°C, and it is the purpose of this note to present preliminary results on one member of this family-pentyloxy cyanobiphenyl (5OCB) and to examine whether its pretransitional behaviour or electro-optical properties are significantly different from those recorded with 5CB (i.e. pentyl cyanobiphenyl). To our knowledge these are the first reported studies of this material by either the static or optical

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Kerr effects. In these measurements both the magnitudes and time dependence (relaxation) of the field induced birefringence are studied as a function of temperature. The applied fields used were either pulsed d.c. (0-10KV for durations up to 3μs with an electrode separation of 2mm) or pulsed optical (0-8MV.m^{-1} for 50ns single TEM_{00} unfocussed Nd^{3+}YAG laser pulses) and the birefringence was probed between a crossed polariser-analyser system using a He.Cd laser (λ_0 = 441.6nm) and a photomultiplier-oscilloscope recording system. The samples were used as supplied by Dr. B.Sturgeon of BDH Ltd (Poole, Dorset, U.K.) to whom we express our gratitude. Normal precautions were taken with respect to cleanliness of glassware etc. The thermostated cell has a 49 mm optical path length.

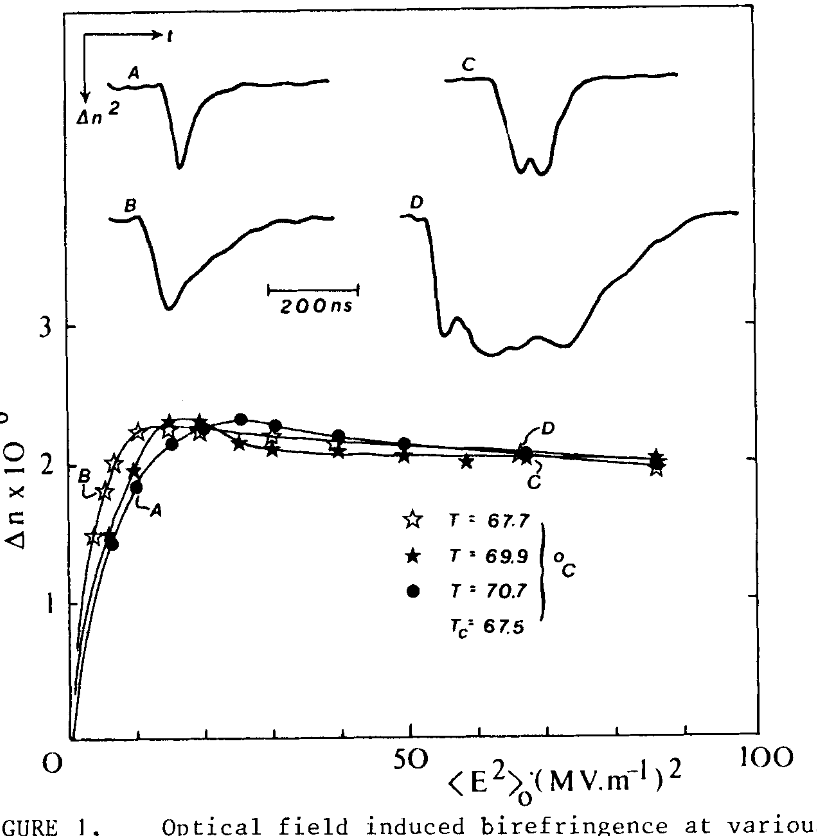

FIGURE 1, Optical field induced birefringence at various temperatures. The inset shows the recorded birefringent traces at high and low fields for T=67.7°C(B,D)and T=70.7°C(A,C

In figure I we have given the laser induced birefringence (Δn) as a function of optical field strength $\langle E^2 \rangle_0$. The birefringence appears to saturate and become essentially independent of field strength above $\langle E^2 \rangle_0 = 16$ $(\mathrm{MV.m^{-1}})^2$. This behaviour occurs for lower field strengths than that found for 5CB under equivalent temperature conditions and is therefore an indication of the increased optical anisotropy of 5 OCB. The optical Kerr effect depends, for a given temperature, only on the optical polarisability of the system being studied. This saturation should not be confused with a saturation of molecular orientation, and arises from the inhomogeneous field of the inducing laser beam. The field at the centre of such a gaussian (spatial) beam is greater than at the sides and, with the field strengths used herein, is sufficiently large to induce birefringences corresponding to phase changes larger than π . In birefringence measurements a phase change of $(2n+1)\pi$, where $n=1,2,3..$ corresponds to a maximum of transmitted intensity whereas a phase change of $2n\pi$ corresponds to zero intensity. Thus across the diameter of the probe laser beam we will have a distribution of intensities corresponding to the radial dependence of the induced birefringence. The recording photomultiplier sees only an average of this intensity distribution and from figure 1 it can be seen that above the critical field strength an approximately constant light level is recorded with increasing field strength. Further from the inset of figure 1, where we have traced the photographically recorded transients for low and high fields corresponding to two different temperatures, it can be seen that this effect is manifest in the time response to the applied laser pulse of 25ns half height width. Because at or near the centre of the laser beam the molecular system may have to relax back through several π changes the pulse appears to be prolonged with an almost constant light level. We have mentioned both the field and time dependences specifically as they may have applications in device physics for producing (a) a fast optically activated light switch (b) a constant light level device or (c) a method of producing prolonged optical pulses from a spiked input pulse. From the data we estimate the energy per 25nsec (half width) pulse required to induce a π phase change (or maximum transmitted light intensity) to be ~ 0.5mJ.

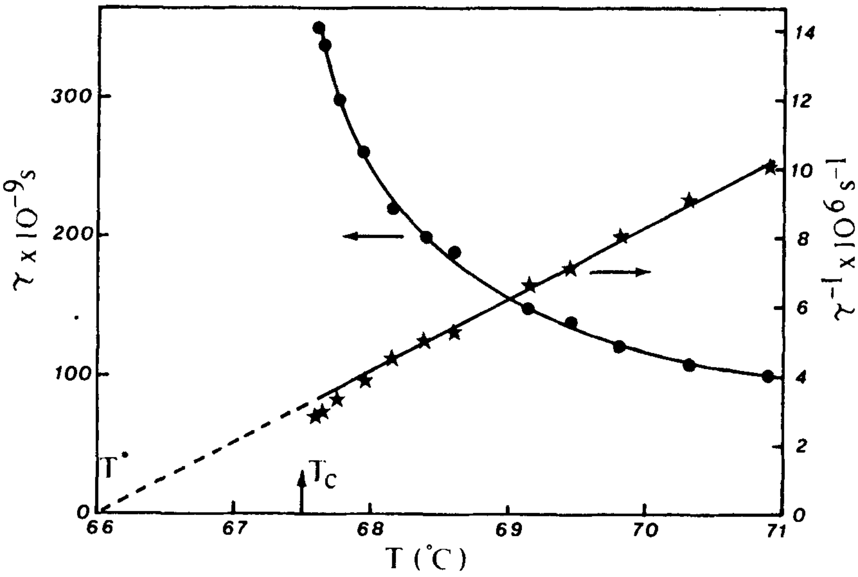

FIGURE 2. *Temperature dependence of τ and τ^{-1}*

From figure 2 it can be seen that the field free relaxation (τ) of the laser induced birefringence shows strong pretransitional behaviour with decreasing temperature. Such behaviour may be analysed[3] according to the phenomenological Landau-de Gennes model[4], and it can be shown that $\tau = \nu/a\ (T-T^*)^{-\gamma}$, where ν is a weakly temperature dependent viscosity ceofficient, T^* is the theoretical second order transition temperature and a is a constant of the free energy expansion of the model. The exponent $\gamma=1$ for a mean field theory. From figure 2 it can be seen that $\tau \alpha (T-T^*)^{-1}$ for 5 OCB and thus the Landau-de Gennes theory is upheld. For 5 OCB we find $T^*=66.0(\pm 0.1)$°C, $T_c-T^*=1.5$°C, where T_c is the nematic-isotropic transition temperature of 67.5°C and $\nu=0.48\times10^{-6}$, a $Jm^{-3}sec^{-1}$ (the units of a having already been included in the formula). This is identical to the value of ν determined for 5CB under applied laser fields.

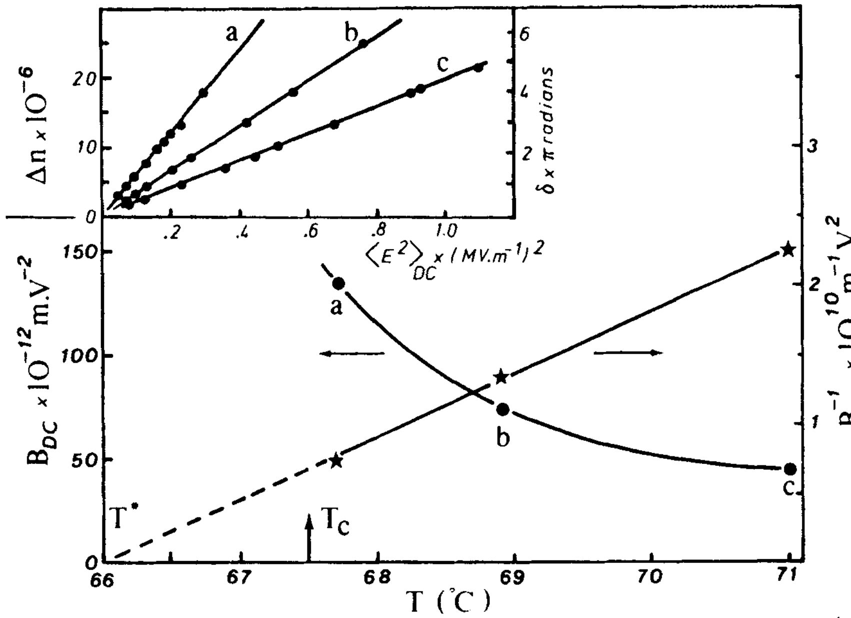

FIGURE 3, Temperature dependence of B_{DC} and B_{DC}^{-1}

We may further verify the applicability of the Landau-de Gennes model from the behaviour of the d.c. field Kerr constants. Following the laser results we have only analysed the behaviour of the d.c. field effect for a few temperatures, figure 3, although it should be remembered that each of these points is obtained from the slope of the Δn versus $\langle E^2 \rangle_{DC}$ plot (inset figure 3) which in turn has been found to be linear over a large range of Δn and $\langle E^2 \rangle_{DC}$. From the Landau-de Gennes theory it can be shown[5] that $B = \Delta n_o \, \Delta\varepsilon_o \, / \, 3a\lambda_o(T-T^*)$ and thus a graph of B^{-1} versus T should be linear. From our preliminary results of figure 3 it can be seen that this is the case and further $T^* = 66.0(\pm 0.1)$ °C in agreement with the value determined above. From the slope of the B^{-1} versus T graph we find $a = 3.41 \times 10^{15} \, \Delta n_o \Delta\varepsilon_o \, Jm^{-3}K^{-1}$ as compared with $3.37 \times 10^{15} \, \Delta n_o \Delta\varepsilon_o \, Jm^{-3}K^{-1}$ for 5CB. Whilst the publicity from BDH Ltd indicates a value of $\Delta\varepsilon_o = 12$ for 5 OCB we have no value of Δn_o to take this analysis further, although this is an optical constant of the molecular system.

From measurements of 5 OCB in CCl_4 solutions we find $B_{DC}^{SP} = 3.8 \times 10^{-12} m.V^{-2}$ and $B_{O}^{SP} = 3.9 \times 10^{-14} m.V^{-2}$ where these values have been extrapolated to zero concentration and the subscript o refers to optical pulsed fields. As shown previously (1) and using the constants for 5 OCB and CCl_4 listed below (7) we calculate the optical anisotropy factor $(g_1 - g_2)^\circ = 6.7 \times 10^{-2}$, the optical polarisability factor $\Delta\alpha^\circ = 36 \times 10^{-40}$ Fm^2, and a permanent dipole moment of $\mu = 16.7 \times 10^{-30} C.m$. These values compare with $(g_1 - g_2)^\circ = 6.0 \times 10^{-2}$, $\Delta\alpha^\circ = 30 \times 10^{-4\circ}$ $F.m^2$ and $\mu = 13.7 \times 10^{-30} C.m$. calculated for 5CB in CCl_4 solutions. The slight increase in these parameters for 5 OCB is presumably the result of the inclusion of the oxygen into the alkyl tail.

From the above results it would appear that the electro-optical properties of 5 OCB are similar to those of 5 CB, the phase transitions being merely transposed to a higher temperature range. As with 5 CB the Landau-de Gennes theory is seen to be obeyed over a temperature range of at least approximately 3°C, although within 0.5°C of the transition the experimental points fall consistently below the line given by τ^{-1} versus T, figure 2. As such behaviour can also be seen in other published data [6] on liquid crystal systems where the Landau-de Gennes theory holds it may be that this marks the lower bound of the applicability of the mean field approximation used in this formalism.

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7. Refractive index CCl_4 = 1.459 ; particle particle volume (5 OCB) = $0.048 \times 10^{-26} m^3$; particle semi-axes (5 OCB), 0.3,0.3,1.3nm ; local field factor f = 0.434 ; ε_{CCl_4}=2.238, ε_1(5 OCB)= 18 ; T = 298 K.