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LASER AND ELECTRIC FIELD INDUCED BIREFRINGENCE STUDIES ON THE CYANOBIPHENYL HOMOLOGUES ★

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Abstract. The optical and d.c. pulsed field Kerr Effects have been used to study the pretransitional behaviour in the isotropic phase for the alkyl cyanobiphenyl homologues ($CN\phi.\phi C_nH_{2n+1}$) for n = 5-8. From the dynamic and static measurements both the relaxation time (τ) and the Kerr Constant B have been found to be proportional to $(T-T^*)^{-1}$. These results are interpreted in terms of the Landau - de Gennes model and the characteristic parameters of this formalism have been given. The results are discussed in terms of the changing chemical structure.

It has been demonstrated recently that both the optical (1) and electrical (2) Kerr effects may be used to study the pretransitional behaviour in the isotropic phase of liquid crystals. In the optical Kerr effect a pulsed laser is used to induce the birefringence whereas in the electrical Kerr effect a pulsed d.c. field is used, allowing us a method of examining the effects of ordering induced by the two different mechanisms (i.e. the interaction of the polarisability anisotropy or of the permanent dipole with the applied field). In the current work both methods have been used in the same experiment to determine the static properties and from the pulsed field free relaxation the dynamic properties of the cooperative behaviour. These results have been used to test the Landau - de Gennes model and the parameters of this formalism have been given for the mesophase-forming cyanobiphenyls (i.e. Pentyl to Octyl cyanobiphenyl). These parameters (see the table)

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+ Address for correspondence : CNRS, CRM, 6, rue Boussingault, 67083 Strasbourg-Cedex, France are important for characterising the properties of liquid crystals.

The cyanobiphenyl family of room temperature liquid crystals, which were recently synthesised by Gray and collaborators (3), are commercially of great interest because they are colourless and stable to moisture ; their use in electrooptic devices has been clearly demonstrated (4). It therefore seemed important to us to study the homologous series in order to ascertain whether changes in the alkyl tail length produced significant changes in the molecular properties as determined from the above electro-optic Kerr effects.

In the current work the Landau - de Gennes phenomenological model (5) of pretransitional behaviour is used to interpret the results. This model has recently been considered in greater detail elsewhere (6,7) and only the main definitions are listed below.

$$F - F_o = \frac{a}{2}(T-T^*)Q^2 - \frac{b}{3}Q^3 + \frac{c}{4}Q^4 - W + O(Q^5) \qquad 1$$

where F is the free energy, Q is the order parameter, T^* is the temperature of the theoretical second order phase transition, T is the absolute temperature, a,b,c are the phenomenological constants and $W = 1/3\ \Delta\varepsilon_o E^2 Q$. Then if Δn_o and $\Delta\varepsilon_o$ are the refractive index and dielectric anisotropies of the completely ordered liquid crystal molecule respectively, λ_o is the measuring vacuum wavelength and B is the Kerr constant it may be shown (6) that

$$B = \frac{\Delta n}{\lambda_o E^2} = \frac{\Delta n_o \Delta\varepsilon_o}{3a\lambda_o (T-T^*)^{\gamma}} \qquad 2$$

where Δn is the birefringence induced by an applied electric field E. Further, from the field free relaxation it has been shown for the Landau - de Gennes model (8) that

$$\tau = \frac{\nu}{a}(T-T^*)^{-\gamma} \qquad 3$$

where τ is the field free relaxation time and ν is a weakly temperature dependent viscosity coefficient. γ is an exponent that equals unity in any mean field theory.

In electric or laser field Kerr effect measurements for the isotropic phase the order parameter induced by the field is very small, and thus terms of $O(Q^3)$ and higher can be neglected. However if supplementary data, as from refractive index measurements, are available on the order parameter at temperatures below and near to the nematic isotropic clearing temperature T_c it is possible to determine the following relationships (6) between a, b and c :

$$Q_c = \frac{2b}{3c} = \frac{3a(T_c - T^*)}{b} \qquad 4$$

where Q_c is the order parameter at T_c, and thus the expansion of the free energy (1) may be determined up to $O(Q^5)$. From the original derivations (5) the latent heat L of the nematic-isotropic transition is given by

$$L = \frac{a}{2} \cdot T_c \cdot Q_c^2 \qquad 5$$

Both the d.c. and Optical Kerr effects were measured using a 10mW He-Cd laser as light source ($\lambda_o = 441.6$nm). The birefringence induced by the electrical (d.c. pulses of duration up to 25μs and between 0 and 10KV) and laser (Q-switched unfocussed TEM_{00} pulses of duration 50ns and of field strength 0 - 9MV.m^{-1} from an Nd^{3+}YAG laser) fields was measured between two glan-laser polariser prisms crossed with the azimuth at 45° to the applied field direction. The field direction for both the polarised optical and d.c. fields was horizontal. The beam passing through the analyser due to the field induced birefringence was detected by a fast blue sensitive photomultiplier (EMI type 9813QKB) amplified by a 100MHz preamplifier and displayed via a fast storage oscilloscope. The display could be photographed for later analysis. At the birefringence levels recorded in the current measurements (see Figure 1) the stray or strain birefringence in the cell was negligible ($\Delta n_{(stray)} \sim 10^{-9}$), and quadratic detection was used. The cell, which had an optical path length of 49mm and an electrode separation of 2mm, was thermostated to ±0.05°C, and normal precautions were taken with respect to cleanliness of glassware. The alkyl cyanobiphenyls were a gift from B.D.H. Ltd (Poole, Dorset, U.K.) which is gratefully acknowledged. These samples were used as supplied in their sealed containers, and the transition temperatures T_c were within 0.1°C of the accepted values (see the table). The notation n CB is used herein where n refers to the number of carbon atoms in the alkyl tail.

The Kerr constant B of a sample at a given temperature is obtained from the slope of the induced birefringence when plotted as a function of E^2. This has been illustrated for 5CB for d.c. fields in Figure 1, from which it can be seen that linearity is maintained up to field strengths of

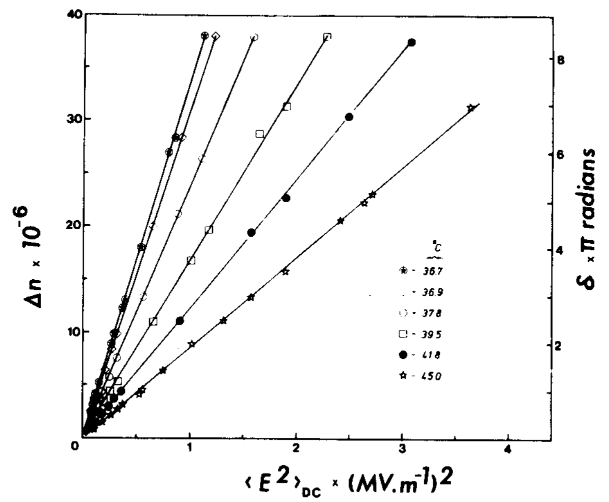

FIGURE 1. DC field induced birefringence for 5CB at various temperatures. The right hand ordinate gives the optical retardation where $\delta = \frac{2\pi\Delta n.l}{\lambda_o}$ and l is the cell path length.

2MV.m^{-1} depending on the temperature. For pulsed laser fields a departure from linearity was observed above a certain critical field strength for all of the nematogenic alkyl cyanobiphenyls, and this behaviour, because it has potential device applications, has been discussed elsewhere (9). The field free relaxation time τ shows strong pretransitional behaviour with decreasing temperature, and this has been shown for 6CB in Figure 2. In this case the relaxation which was monoexponential has been analysed from the laser induced birefringence. Because of the shorter pulse tail length i.e. $\sim$20ns the analysis is more accurate for laser fields than for d.c. fields where the pulse relaxation time, which is limited by cell impedance effects, is $\sim$120ns.

Following the Landau - de Gennes model, and from equations (2) and (3) both τ^{-1} and B^{-1} should be proportional to $(T-T^*)$ and this can be seen to be the case for 6CB from Figures 2 and 3. Knowing the constants Δn_o and $\Delta\varepsilon_o$ it is possible to determine the phenomenological constant a from the slope of Figure 3 and also ν from the slope of Figure 2.

Similar behaviour was determined for all the alkyl cyanobiphenyls from 5CB to 8CB and the constants determined for these systems have been given in the table. The critical

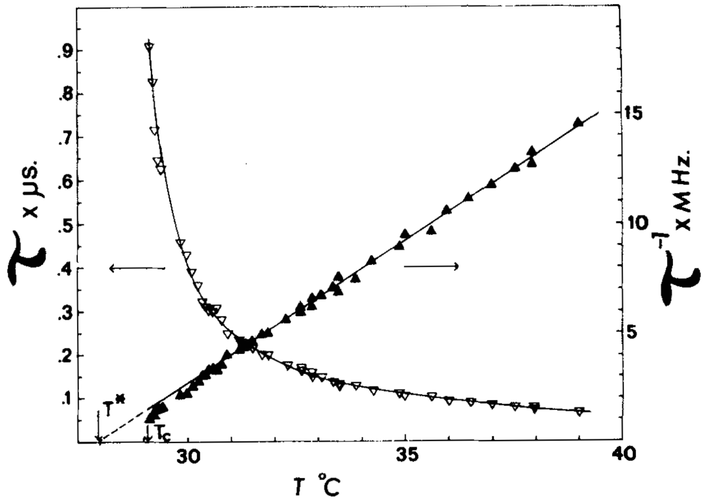

FIGURE 2. Temperature dependence of τ (relaxation time) and τ^{-1} from the pulsed laser measurements for 6CB.

exponent was always found to equal unity over the limited temperature range studied (i.e. within∿10°C of T_c). Then using the value of a and the other constants listed in the table the values of b,c and L were determined using relationships (4) and (5).

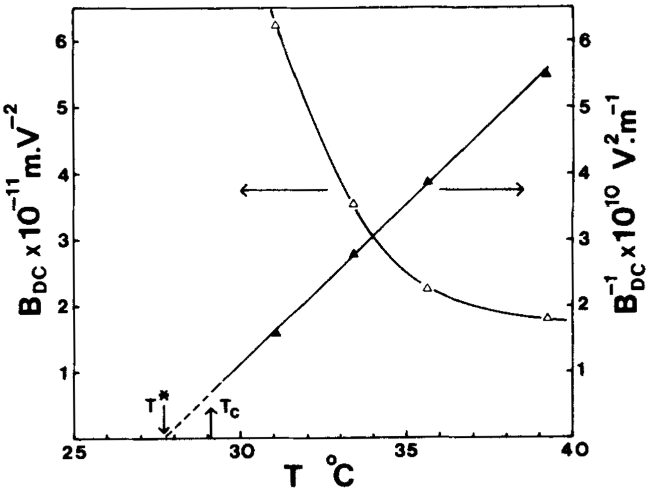

FIGURE 3. Temperature dependence of B_{DC} and B^{-1} for 6CB obtained from pulsed DC field measurements.

n CB	Units	5	6	7	8
$B_{DC}\Delta T$	$\times10^{-10}$ m.K.v^{-2}	2.24	2.10	1.37	1.25
$\tau\ \Delta T$	$\times10^{-6}$ s.K.($\pm$0.05)	0.48	0.76	0.29	0.46
T_c	°C ($\pm$0.1)	35.1	29.1	42.0	40.6
T^*	°C ($\pm$0.2)	34.0	27.8	40.6	39.3
a	$\times10^{6}$ J.m^{-3}K^{-1}($\pm$0.01)	0.13	0.15	0.21	0.18
b	J.m^{-3}K^{-1}($\pm$0.2)	1.6	2.3	3.3	2.3
c	J.m^{-3}($\pm$ 3)	3.9	6.2	8.1	5.2
ν°	$\times10^{-2}$ Kg m^{-1}s^{-1}($\pm$1.8)	7.3	11.5	6.1	8.3
Q_c^a	($\pm$0.01)	0.27	0.25	0.27	0.30
$\Delta n_o{}^b$	-	0.45	0.43	0.40	0.37
$\Delta\varepsilon_o^c$	-	9.9	9.8	9.7	8.5
L	$\times10^{3}$ J.Kg^{-1}($\pm$ 0.15)	1.47	1.41	2.41	2.54
L^d		1.41	1.05	2.10	2.48

a These values are extrapolated from the temperature dependence of Q established in reference (10) for the alkyl cyanobiphenyls.

b Using the data for n_e, n_o for λ_o = 546.1, 589.3 and 632.8nm & order parameters of reference (10) we have calculated the molecular $n_\parallel$ and $n_\perp$ and then used a Cauchy type dispersion (i.e. $\Delta n_\lambda = A + B/\lambda^2 + \ldots$) to determine Δn_o for λ_o = 441.6nm. Such a dispersion closely fitted the results.

c See reference (11)

d Values of L taken from reference (12)

The most striking feature of the current results is the agreement found experimentally between the dependence of both B^{-1} and τ^{-1} on temperature and the phenomenological Landau-de Gennes theory for all of the cyanobiphenyl homologues studied. Within the uncertainty quoted both sets of measurements gave identical values of T^*, and the values of L determined from the current measurements are in good agreement with those determined from differential scanning calorimetry (12). Given that the experimental values of L depend on an extrapolated value of Q_c, as well as a and T_c measured herein, it is difficult to envisage a different theory giving better agreement between a derived quantity and that measured independently. Thus the Landau - de Gennes model appears to be applicable to the cyanobiphenyl family of liquid crystals, and we use this as justification for calculating the other constants of the free energy expansion.

From the summary of the results given in the table several trends are obvious. Firstly the factor $B\Delta T$ decreases consistently with increasing tail length, and as the dipole moment factor (contained in $\Delta\varepsilon_0$) is approximately constant for the four homologues this suggests a continual decrease in the optical susceptibility anisotropy, a result reflected in the Δn_0 values determined independently (10). This would appear to be contrary to predictions for the optical polarisability for cyanobiphenyls (13) which might be expected to follow the oddeven effect and give an alternation in polarisability values. However as was recently pointed out (14) the molar volume effect which gives a lower molecular density with increasing n smoothes out the effective optical anisotropy and the alternations are not reflected directly in $B\Delta T$. Both $\tau\Delta T$ and the dependent constant ν do appear to exhibit an alternation effect that is in the opposite sense to that recorded for T_c and T^* although the effect is smaller for 7 and 8CB. This result is similar to that noted for the p-alkoxy-azoxybenzene homologues (14) and would appear to be typical alkyl chain behaviour, and is presumably linked to the increased flexibility or freedom of movement of the terminal links. The latent heat L follows the alternation in T_c and T^* for 5,6 and 7CB but the trend is not continued for 8CB whose value L is greater than that of 7CB. As 8CB is the first of the cyanobiphenyls to exhibit a smectic phase at lower temperatures it could be that this characteristic is influencing the pretransitional behaviour. Clearly much more energy is required to form the nematic phase in this case than for the purely nematic 5CB. The order parameter Q_c at the transition (T_c) is also alternating, being a maximum for 8CB. It will be interesting to examine this behaviour in the higher homologues. The phenomenological constants show an increase from 5 to 7CB and a decrease for 8CB but given the phenomenological nature of the model it is not clear that this trend is significant. It has been suggested (14) that as in the Maier and Saupe mean field theory (where $\gamma=1$) a should be constant, a departure from this condition implies the breakdown of the validity of the Landau expansion near to T_c. A breakdown of the mean field theory in the vicinity of T_c could explain the experimental points falling consistently below the straight line in Figure 3, a result also recently observed for pentyloxy cyanobiphenyl (9). However such a breakdown would be inconsistent with the work of reference (7), and given the experimental difficulties of measuring within $\sim 0.2°$ of the transition the problem probably cannot be resolved by optical methods alone. Further away from the transition (i.e. $T-T_c>0.2°C$) the model is valid.

Using transient optical and electrical Kerr effects the pretransitional behaviour of the cyanobiphenyl homologues has been studied. The Landau - de Gennes model has been found to be applicable and thus the phenomenological constants have been determined, and trends in these and other constants have been discussed in terms of the alkyl tail composition.

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