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Virtual isotropic-nematic transitions in alkyl cyanobiphenyls

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Pretransitional fluctuations in the isotropic phase of liquid crystalline and non-liquid crystalline alkyl cyanobiphenyls have been investigated using light scattering and magnetic birefringence measurements. We find evidence for a virtual isotropic-nematic phase transition in short-chain alkyl cyanobiphenyls with no observable nematic phase. The measured temperature dependence of fluctuations is well-described by mean-field theory. Virtual phase transition temperatures extrapolated from separate light scattering and magnetic birefringence experiments are in good agreement. Landau–de Gennes model parameters for the compounds investigated are calculated from the experimental results.

Keywords: virtual phase transition; liquid crystal phase transition; magnetic birefringence; light scattering

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1. Introduction

The boundary between those compounds that exhibit liquid crystalline phases and similar compounds that do not has been a subject of long-standing interest. It has long been recognised that some non-liquid crystalline materials behave analogously to liquid crystals and may exhibit a virtual isotropic-nematic phase transition, as revealed either by experiments on mixtures or by measurements of fluctuations in the isotropic phase. In mixture experiments, the non-liquid crystal is mixed with a liquid crystal to make a mixture that exhibits an actual isotropic-nematic phase transition; extrapolation of the concentration-dependence of transition temperature T_{ni} to pure non-liquid crystal can be used to estimate the virtual transition temperature of the non-liquid crystalline material (*1*). In fluctuation experiments, the temperature dependence of nematic fluctuations within the isotropic phase is measured using such methods as light scattering or magnetic or electric field-induced birefringence (*2–4*). Mean-field theory predicts a divergence like $(T-T^*)^{-1}$ of scattered light and field-induced birefringence at a temperature T^* which can be measured from the experimental data.

Despite their intrinsic interest, systematic investigations of virtual phase transitions are rare. In this paper, we report an investigation of virtual phase transitions in some non-liquid crystalline alkyl cyanobiphenyls using two experimental techniques, light scattering and magnetic birefringence. We find both experiments well-described by mean-field theory. Further, we find the extrapolated temperatures T^* (theoretical minimum super-cooling temperature of the isotropic phase) in excellent agreement for both experiments, confirming that the mean-field theory of liquid crystals gives a consistent description of the virtual phase transition in non-liquid crystalline materials. We investigated the following compounds: 5CB (4′-*n*-pentyl-4-cyanobiphenyl, a liquid crystal), 3CB (4′-*n*-propyl-4-cyanobiphenyl, a monotropic liquid crystal which can be super-cooled to a metastable nematic phase), and 2CB (4′-*n*-ethyl-cyanobiphenyl), 0CB (4-phenylbenzonitrile) and biphenyl (non-liquid crystals). In the case of 0CB, the virtual isotropic-nematic transition is very far below (163°C below) the observed isotropic-crystal transition temperature. Previous experiments have been limited to identifying virtual phase transitions much closer to the crystallisation temperature (allowing for a stronger temperature dependence of fluctuations) or were beset by uncertainties in making a large extrapolation of a weakly temperature-dependent signal. In our experiment, the excellent consistency between different experimental techniques and the agreement of both with mean-field theory provides compelling confirmation of the virtual phase transition and accurate identification of T^*.

The value of the transition temperature provides an indication of a material's affinity for nematic ordering. Hence, by measuring the virtual transition temperatures in a homologous series, one can obtain more information about the influence of molecular parameters on liquid crystallinity. Measurement of pretransitional fluctuations also allows for the calculation of the model parameters describing the isotropic-nematic transition; we provide estimates for the Landau–de Gennes (LdG) free energy parameters for the materials investigated.

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2. Theory

Following the LdG model (*5, 6*), the free energy density Φ in the isotropic phase may be approximated as a truncated power series in terms of the tensor order parameter $Q_{\alpha\beta}$ as

$$\Phi = \Phi_o + \frac{1}{2} A Q_{\alpha\beta} Q_{\beta\alpha} - \frac{1}{3} B Q_{\alpha\beta} Q_{\beta\gamma} Q_{\gamma\alpha} + \frac{1}{4} C \left(Q_{\alpha\beta} Q_{\beta\alpha} \right)^2 - \frac{1}{2\mu_o} \chi_{\alpha\beta} B_\alpha B_\beta. \qquad (1)$$

The last term in equation (1) represents the free energy contribution due to interaction with the magnetic field, B_α. In the LdG model, which applies in the isotropic phase for temperatures in the vicinity of the isotropic-nematic transition, A has temperature dependence given by $A = a(T - T^*)$ and the parameters a, B, C and T^* are temperature-independent material parameters. The anisotropy of the diamagnetic susceptibility tensor $\chi_{\alpha\beta}$ is related to the nematic order parameter $Q_{\alpha\beta}$ by

$$\chi_{\alpha\beta} = \bar{\chi} \delta_{\alpha\beta} + \frac{2}{3} \Delta\chi_m Q_{\alpha\beta}, \qquad (2)$$

where $\bar{\chi}$ is the magnetic susceptibility per unit volume when $Q_{\alpha\beta} = 0$ and $\Delta\chi_m$ is the maximum anisotropy of magnetic susceptibility per unit volume in a perfectly aligned nematic. For uniaxial liquid crystals, $Q_{\alpha\beta}$ is related to the scalar order parameter S and the molecular axis direction u_α by (*6*)

$$Q_{\alpha\beta} = \frac{1}{2} S \left(3 u_\alpha u_\beta - \delta_{\alpha\beta} \right). \qquad (3)$$

Using Equations (2) and (3), Equation (1) can be written in the simpler form (*6*)

$$\Phi = \Phi_o + \frac{3}{4} a (T - T^*) S^2 - \frac{1}{3\mu_o} \Delta\chi_m S B^2, \qquad (4)$$

where higher order terms in the series are neglected. Upon minimising the free energy density in Equation (4) with respect to variations in S, one can show that the birefringence Δn induced in the isotropic phase by a magnetic field is given by

$$\Delta n = \frac{\Delta\varepsilon_m \Delta\chi_m B^2}{9 \bar{n} a (T - T*)}, \qquad (5)$$

where $\Delta\varepsilon_m$ is the maximum optical dielectric anisotropy of the perfectly aligned nematic and $\bar{n} = \sqrt{\bar{\varepsilon}}$.

We now consider the light scattering experiment. As shown in detail elsewhere, the depolarised light intensity I_{sc} scattered at 90° is given by

$$I_{sc} = \frac{\gamma T}{a(T - T^*)}, \qquad (6)$$

where the constant of proportionality γ depends on the sample geometry, optical wavelength and detector parameters (*6*). We will use Equation (5) to analyse the results of the magnetic birefringence experiments and Equation (6) for the light scattering experiments.

3. Experimental

Samples of the liquid crystal 5CB, the monotropic liquid crystal 3CB and the non-liquid crystals 2CB, 0CB and biphenyl were obtained from EM Industries (5CB, 3CB, 2CB) or Aldrich (0CB, biphenyl) and used without further purification.

The apparatus for the magnetic birefringence measurements has been described in detail elsewhere (*7*). Briefly, light from a helium-neon laser was directed through a polariser, the sample cell and a crossed analyser, then focused by a lens on to a silicon photodiode detector. Polariser and analyser axes were oriented at ±45° with respect to the magnetic field. In this geometry, the transmitted light intensity I_t is given by

$$I_t = I_o \sin^2 \left(\frac{\pi d \Delta n}{\lambda} \right), \qquad (7)$$

where I_o is the incident light intensity, d is the length of the sample, $\lambda = 632.8$ nm is the laser wavelength, and Δn is the magnetically induced birefringence in the sample. Equation (7) was used in measuring the birefringence at different temperatures. The dependence of birefringence on magnetic field predicted in Equation (5) was also confirmed. The isotropic-nematic phase transition was easily recognisable by the sudden large increase in light scattered by the sample when cooling from the isotropic phase. The sample cell was made from an aluminium tube (3.3 cm long) with optical glass windows epoxied on the ends; liquid crystal was introduced through a transverse port drilled in the tube wall and subsequently sealed. The sample tube was housed in a copper block with Teflon cladding for thermal isolation, resistively heated by a commercial temperature controller with ±0.03°C stability.

The apparatus for the light scattering experiments has been described previously (*8*). Briefly, a vertically polarised helium-neon laser was weakly focused on the sample cell, a square optical cuvette residing in a thermally controlled copper chamber. Light scattered from the sample at a 90° angle was collected by a lens and focused through a laser-line bandpass filter on to

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a photomultiplier tube detector. Care was taken to shield the detector from sources of stray light. The predicted 4:3 ratio of vertically to horizontally polarised scattered light intensity was confirmed (*6*). Having a long thermal time constant, the sample was allowed to cool from its initial high temperature while the sample temperature was monitored by thermistor. The cuvette was thoroughly rinsed in acetone and cleaned using chromic acid between samples.

4. Results and discussion

Experimental results for the magnetic birefringence measurements are shown in Figure 1, and results for the light scattering measurements are given in Figure 2. In the experiments on 5CB, 3CB, 2CB and 0CB the $(T-T^{*})^{-1}$ dependence of experimental signal (birefringence or scattered intensity, respectively) *vs.* temperature predicted in Equations 5 and 6 was confirmed, within experimental uncertainty, over a wide temperature range (>15°C) approaching the transition from the isotropic to the nematic (5CB), metastable nematic (3CB) or crystalline phase (2CB, 0CB). A small deviation of the data from the predicted temperature dependence within about 1°C of the phase transition, noted by others, was visible in 5CB and 3CB, indicating the inadequacy of mean-field theory in the close vicinity of the phase transition (*9, 10*). Extrapolation of the data line yielded values for T^{*}, the minimum super-cooling temperature of the isotropic phase, for each sample; in all cases, the T^{*} values determined from both magnetic birefringence and light scattering experiments were in close agreement. We note that in Figures 1 and 2 the temperatures are given relative to T_c, the transition temperature between isotropic and nematic, metastable nematic or crystalline phases, observed as the samples were cooled from the isotropic phase. Experimental results are summarised in Table 1. The sample of biphenyl showed no measurable temperature dependence in its magnetic birefringence or scattered light intensity; within our experimental resolution, we conclude that biphenyl has no measurable fluctuations indicative of a virtual nematic phase.

Using the LdG theory outlined above, it is possible to estimate values for the LdG parameters *a, B* and *C* for the materials investigated. First, we rewrite Equation (4) in the conventional form

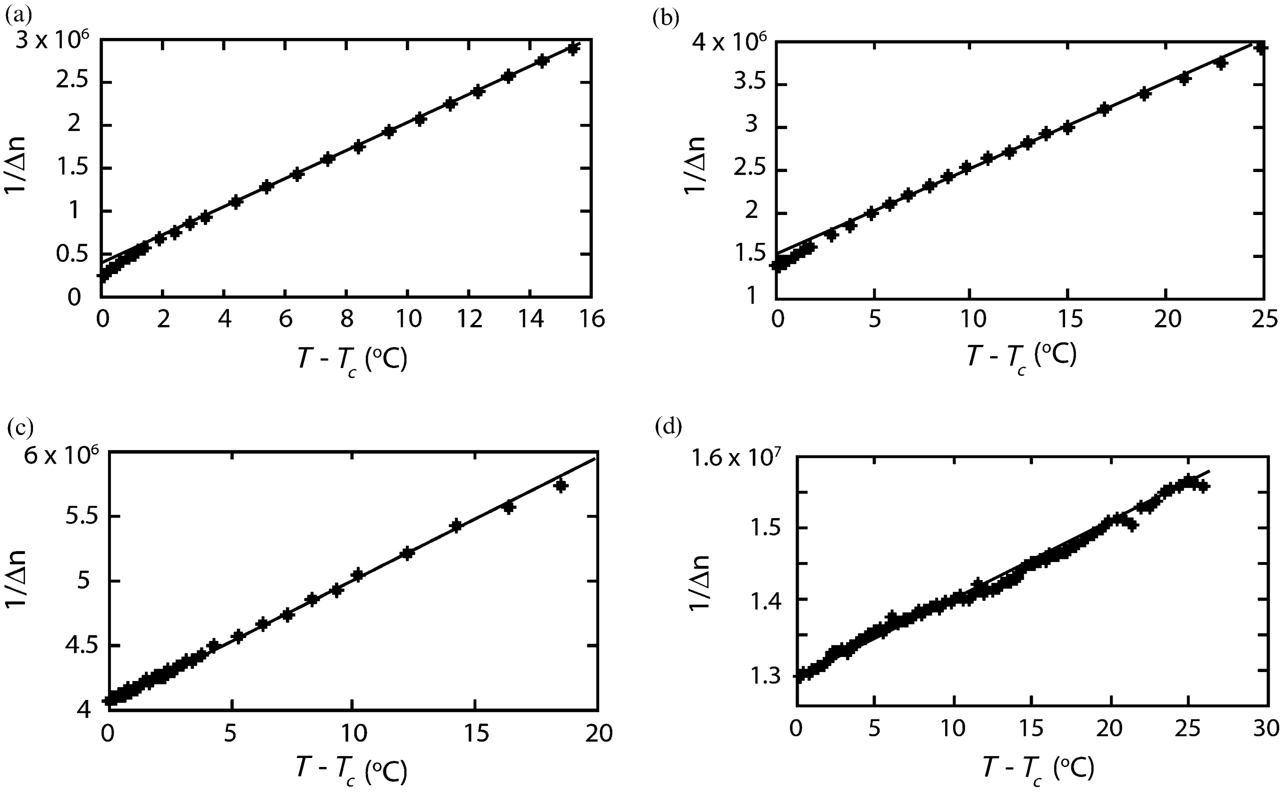

Figure 1. Inverse of magnetic field-induced birefringence *vs.* temperature for (a) 5CB, (b) 3CB, (c) 2CB and (d) 0CB. The magnetic field was $B=2.00\,T$. The solid lines are fits to Equation (5).

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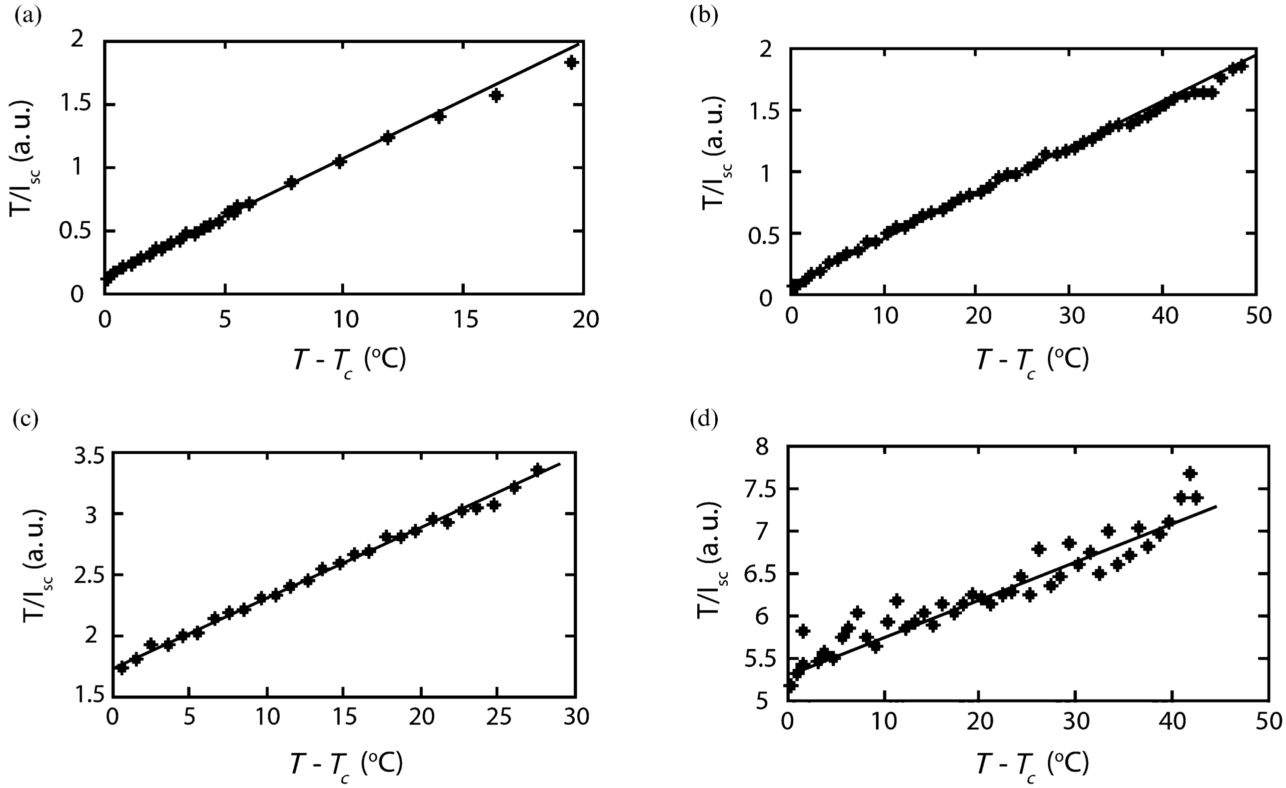

Figure 2. Temperature (K)/scattered light intensity (arb. units) *vs.* temperature for (a) 5CB, (b) 3CB, (c) 2CB and (d) 0CB. The solid lines are fits to Equation (6).

$$\Phi = \Phi_o + \frac{1}{2}a'(T - T^*)S^2 - \frac{1}{3}B'S^3 + \frac{1}{4}C'S^4 - \frac{1}{3\mu_o}\Delta\chi_m S B^2, \tag{8}$$

where the coefficients a', B' and C' are related to a, B and C by $a' = \frac{3}{2}a$, $B' = \frac{3}{4}B$ and $C' = \frac{9}{4}C$. We use equation (5) to find a', using literature values for $\Delta\chi_m$ (*11, 12*), $\Delta\varepsilon_m$ (*13*) and $\bar{n}$ (*13*). Minimising Φ with respect to variations in S leads to the result (*6*)

$$S_c = \frac{2B'}{3C'} = \frac{3a'(T_c - T^*)}{B'}, \tag{9}$$

which may used to estimate the parameters B' and C'. However, since T_c (the isotropic-nematic transition temperature of the virtual transition) is not measurable, only order-of-magnitude estimates for B' and C' can be made, using $S_c \approx 0.35$ and $T_c - T^* \sim 1.5$°C as is typical for the cyanobiphenyls (*13, 14*). A further complication is that data for *n*CB for $n<5$ is not available, but the necessary values can be estimated with reasonable confidence from known results for the homologous series 5–9CB. The procedure used to find a' is outlined below. To estimate $\Delta\chi_m$, the value of maximum molar magnetic susceptibility anisotropy density, observed to be quite constant (0.1% variation) for 5CB–9CB (*11*), was

Table 1. Molecular parameters and LdG theory parameters for *n*CB.

	*n*CB			
Parameter	0	2	3	5
T^{*1} K	203.5	286.7	299.7	306.5
T^{*2} K	195.5	290.5	301.8	307.6
a' $\times 10^5\,\mathrm{J\,K^{-1}\,m^{-3}}$	1.25	0.895	0.917	1.19
$\Delta\chi_m$ $\times 10^{-6}$	3.43	2.89	2.68	2.33
$\Delta\varepsilon_m$	1.074	1.028	1.005	0.926
$\bar{n}$	1.624	1.609	1.601	1.586

Note: T^{*1} is the minimum super-cooling temperature of the virtual isotropic-nematic transition determined from the magnetic birefringence measurements; T^{*2} is determined from the light scattering measurements.

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scaled by the molecular weight and mass density (*15*), to calculate $\Delta\chi_m$ values for 3CB, 2CB and 0CB. Values for $\bar{n}$ were estimated by linear extrapolation of the fairly linear plot of $\bar{n}$ *vs.* N (hydrocarbon chain length) for $N=5$–8, taken from the data of Karat and Madhusudana (*13*). The value of $\Delta\varepsilon_m$, the maximum optical dielectric anisotropy, for 5CB was found using the relation $\Delta\varepsilon(T_c)/\Delta\varepsilon_m=S_c$, with $\Delta\varepsilon(T_c)$ taken from Karat* (*13*) and S_c from Sherrell and Crellin (*11*). The $\Delta\varepsilon_m$ values for 3CB, 2CB and 0CB were estimated by linear extrapolation from a linear plot of $\Delta\varepsilon_m$ vs. N for $N=5$–8. Values of LdG parameters a' and T^*, as well as the material parameters $\Delta\chi_m$, $\Delta\varepsilon_m$ and $\bar{n}$, are given in Table 1. We note that the LdG parameters we found for 5CB are in close agreement with those found earlier by Coles (*14*) and Coles and Strazielle (*10*). Also, we observe that the a' values obtained for 3CB, 2CB and 0CB are quite comparable to those found in the *n*CBs having a thermodynamically stable nematic phase, so there appears to be nothing extraordinary about the isotropic-nematic phase transition of 3CB, 2CB and 0CB, except that in the case of 2CB and 0CB, it is pre-empted by the onset of crystallinity.

5. Conclusion

Our experiments support the existence of a virtual isotropic-nematic transition in the cyanobiphenyls down to 0CB. Orientational fluctuations in the isotropic phase, sensed by separate light scattering and magnetic birefringence measurements, exhibited a temperature dependence in good agreement with the mean-field LdG theory. The virtual isotropic-nematic transition can be identified with confidence since fluctuations sensed by independent experiments extrapolate to the same T^* value (minimum supercooling temperature of the isotropic phase). It is interesting that the polar molecule 0CB, wholly lacking a hydrocarbon chain, exhibits a measurable liquid crystalline character in its isotropic-phase orientational fluctuations, whereas the non-polar molecule biphenyl did not. This result suggests that the existence of molecular polarity in combination with phenyl rings can generate measurable anisotropic molecular interactions even when a liquid crystalline phase is absent, and that a wide class of compounds having these characteristics but lacking liquid crystal phases may nonetheless exhibit *virtual* nematic phases.

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