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Nematic–isotropic pretransitional behaviour in dimers with odd and even spacer lengths

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Magnetic field induced optical birefringence measurements in the isotropic phase are reported for two members of a series of phenyl benzoate dimers: one having an odd number of methylene units in the spacer and one having an even number. The discontinuity at the nematic–isotropic transition, as determined by the difference between the first order phase transition temperature T_{NI} and the supercooling limit of the isotropic phase T^*, is approximately 8 ± 3 times larger for the even species than for the odd. In addition, the product of the Cotton–Mouton coefficient $d\Delta n/dH^2$ and $T-T^*$ is the same for both materials. In terms of both steric and molecular field theories, the results indicate that the orientations of the terminal mesogenic groups are essentially uncorrelated in the isotropic phase.

Prior to recent experimental and theoretical work on oligomeric liquid crystals, it had been assumed that the flexible spacer groups of main chain polymeric liquid crystals in all cases act simply as inert solvents: they occupy volume but otherwise play little or no active role in the phase transitions of the material. Recent experimental results, however, have demonstrated the inadequacy of this picture, as NMR, magnetic susceptometry, and calorimetry measurements have shown that *certain* characteristics of the nematic–isotropic (NI) transition in polymers can be considerably different from those of the model monomer [1–11]. For example, it has been shown that the population of linear conformers increases at the expense of bent conformers in the nematic phase for a molecule with an even number of carbons in the spacer [2, 3, 12, 13]. This behaviour is reflected not only in the transition enthalpy [1], but in quantities such as $T_{NI}-T^*$ as well. Here T_{NI} is the first order NI transition temperature and T^* is the (extrapolated) supercooling limit of the isotropic phase. In one dimer, for

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example, T_{NI}–T^* was found to be 7 ± 2 times larger than in the model monomer [13], indicating a far larger entropy of transition ΔS for the dimer as compared with the monomer. Note that a small value of ΔS, which is associated with the monomer, is often a signature of a nearby biaxial nematic phase, which is likely to arise from a more strongly biaxial molecule.

Clearly, in some instances the spacer group can play a pivotal role in the phase diagram and behaviour of the phase transitions. Over the years countless observations of so-called odd–even effects have been made [14, 15], not only for the terminal alkyl chain(s) of monomers, but for oligomeric and polymeric liquid crystals as well [16–19]. For example, it is generally observed that the NI transition temperatures for dimers containing an even number N of methylene (or other linkage) groups is higher than for those containing $N-1$ or $N+1$ groups in the spacer. Physically, of course, the odd dimer is kinked (in the sense of being more biaxial), such that the mesogenic groups lie along different directions. Thus, the odd dimer tends to have a lower NI transition temperature than its even neighbours.

Only recently, however, have significant theoretical strides been made to understand odd–even effects as they relate to the pretransitional behaviour of oligomers. Building on a molecular field theory by Marcelja [20], Heaton and Luckhurst have developed a model which predicts both T_{NI} and T^* for flexible molecules [21]. For the case of the α,ω-bis(4,4′-cyanobiphenyloxy)alkane dimer, they predict that the supercooling temperature is relatively insensitive to the number of carbon atoms N in the spacer group, especially for $N>5$; on the other hand, they find that T_{NI} alternates significantly as a function of N. Using two members of this series, Dunmur and Wilson have recently performed light scattering measurements and have shown that T_{NI}–T^* for the ten carbon spacer is about three and a half times larger than that of the nine carbon spacer [22]. Thus, T^*/T_{NI} for the odd dimer (0·989) is larger and closer to one than for the even dimer (0·968), which is qualitatively consistent with the predictions of [21]. Nevertheless, the experimental values for T^*/T_{NI} are considerably larger than the theoretical values, which tend to lie closer to 0·9. These discrepancies are, of course, quite common for molecular field theories and reflect their omission of short range correlations, especially in the isotropic phase. The semi-quantitative success of the Heaton–Luckhurst model may nevertheless provide a springboard for future theoretical developments on the role of spacer length.

The purpose of this manuscript is to report on results from Cotton–Mouton measurements on two members of a series of nearly symmetric dimers formed from the 4,4′-dialkoxyphenylbenzoate monomer 5OO5

$$C_5H_{11}\text{–O–}\phi\text{–COO–}\phi\text{–O–}C_5H_{11},$$

where ϕ represents a benzene ring. The even dimer, which we refer to as 5–10–5, consists of a pair of monomers (minus two hydrogens) attached end-to-end; the spacer group contains ten methylene units. The odd dimer, referred to as 5–9–5, contains a nine methylene spacer. Analogous to the results from light scattering measurements on the cyanobiphenyl dimers [22], we found that T_{NI}–T^* for the odd dimer 5–9–5 is considerably smaller than for the even dimer. In addition, we found in the isotropic phase that the quantity Φ, which is defined as the Cotton–Mouton coefficient $d\Delta n/dH^2$ multiplied by $T-T^*$, is identical for both even and odd dimers to within experimental error. Here Δn is the optical birefringence and H the magnetic field. When analysed in terms of current models for nematic ordering of hard rods, the results indicate that for both species the spacers are completely flexible in the isotropic phase. (What is meant by *completely flexible* is a low degree of angular correlations between the terminal mesogenic groups.) Qualitatively similar results are obtained when the results are analysed in terms of a molecular field model. This represents the first odd–even comparison of spacer rigidity for main chain oligomers in the isotropic phase. In addition, comparison of our results for $T_{NI}-T^*$ with those of [22] indicates that physical dimerization may play an important role in the pretransitional behaviour of their material.

The molecules were synthesized according to procedures described elsewhere [17, 18, 23]. The samples were contained in a 1 cm pathlength cuvette housed in an oven temperature controlled to 25 mK. The oven was inserted into the bore of an 8·2 T superconducting magnet with transverse optical ports. Details of the oven and birefringence apparatus are described elsewhere [24]. The field was increased from zero to typically 2 or 3 T in approximately 5 min, and the field induced optical birefringence was computer recorded.

For both mesogens the birefringence was found to be linear in H^2 (see figure 1), and the temperature dependent Cotton–Mouton coefficient $C(T)$ $[\equiv d\Delta n/dH^2]$ was determined by a linear least squares fit of the data. Data were typically taken over a temperature range $T_{NI} \leq T \leq T_{NI}+5\,K$. C^{-1} was found to be linear in temperature (see figure 2), indicating mean field behaviour in the susceptibility. As a result the Cotton–Mouton coefficient can be shown to be [25]

$$C(T)=\frac{\Delta n_O \Delta \chi_O}{3a(T-T^*)} \equiv \frac{\Phi}{(T-T^*)}, \tag{1}$$

where Δn_O and $\Delta \chi_O$ are the birefringence and volume magnetic susceptibility anisotropy for fully saturated order, where it is assumed that the molecules can be treated as being in their all-*trans* conformations. The quantity a is the quadratic coefficient in the Landau free energy expansion

$$F=F_O+\tfrac{1}{2}a(T-T^*)\overline{P_2}^2-\tfrac{1}{3}b\overline{P_2}^3+\tfrac{1}{4}c\overline{P_2}^4-\tfrac{1}{3}\Delta\chi_O H^2\overline{P_2}, \tag{2}$$

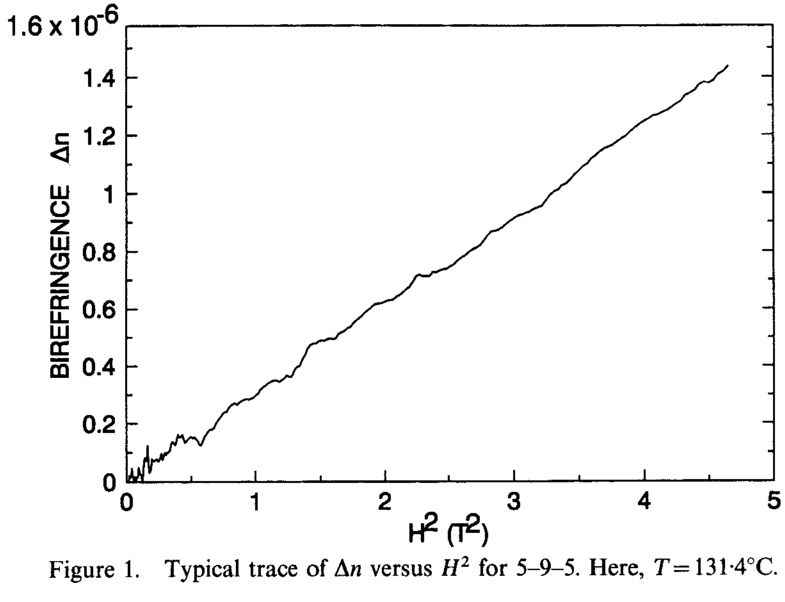

Figure 1. Typical trace of Δn versus H^2 for 5–9–5. Here, $T = 131{\cdot}4°C$.

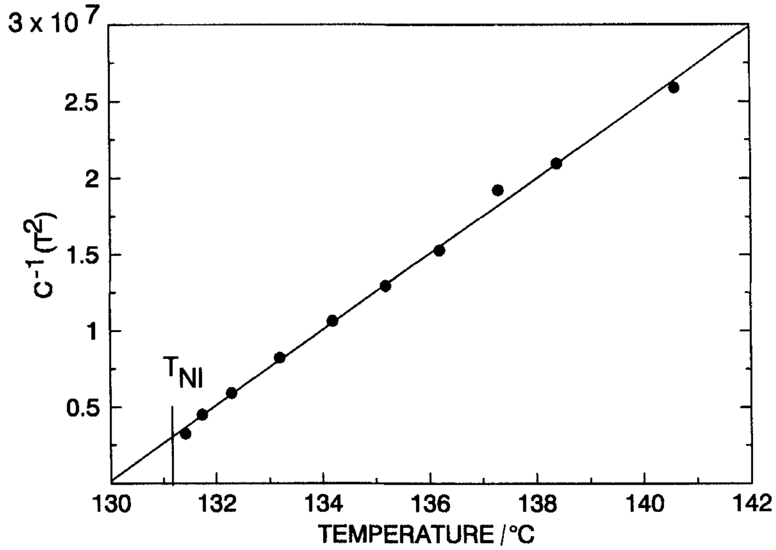

Figure 2. Cotton–Mouton coefficient $d\Delta n/dH^2$ versus temperature for odd dimer 5–9–5.

	Φ (K/T^2)	T_{NI}/°C	T^*	T_{NI}–T^*
5–9–5	$(4{\cdot}0\pm0{\cdot}5)\times10^{-7}$	$131{\cdot}1\pm0{\cdot}3$	$130{\cdot}0\pm0{\cdot}3$	$1{\cdot}1\pm0{\cdot}3$
5–10–5	$4{\cdot}1\times10^{-7}$	149·0	140·5	8·5

where $\overline{P_2}$ is the nematic order parameter and F_0 is the free energy of the isotropic phase. The Cotton–Mouton coefficient was measured as a function of temperature for each of the two species, and T^* and the quantity Φ were extracted by a linear least squares fit of C^{-1} versus T; the results are given in the table. Also given in the table are T_{NI}, the first order transition temperature, as well as T_{NI}–T^*, the difference between the first order phase transition temperature and the supercooling limit.

The first observation is that T_{NI}–T^* differs greatly between the two dimers, being about eight times larger for the even dimer than for the odd. Although qualitatively consistent with the predictions of [21], the ratio T^*/T_{NI} is still considerably closer to unity than predicted by theory. As already mentioned, this is likely the result of ignoring short range correlations in the molecular field theory. In addition, we note that the cubic coefficient b in equation (2) is proportional to $(T_{\mathrm{NI}}-T^*)^{1/2}$ [13], and thus is likely to be smaller for the odd dimer than for the even. The sign of coefficient b, of course, is related to whether the orientational distribution function in the nematic phase is prolate (+) or oblate (−): for the case at hand, involving elongated molecules, b is positive. However, if b were to change sign as a function of, for example, molecular length, the point $b=0$ on the molecular length–temperature phase diagram would correspond to a crossover from a uniaxial prolate to a uniaxial oblate nematic phase [26, 27]. It is important to note, however, that equation (2) disregards biaxiality and allows for only uniaxial phases. If instead we were to use an appropriate tensor order parameter and corresponding free energy, we would find that when the cubic coefficient is small, a biaxial phase might appear between the uniaxial prolate and oblate nematic phases. However, since the transition to the isotropic phase always occurs from a *uniaxial* nematic phase (except at an isolated Landau point [26, 27]), the uniaxial free energy equation (see equation (2)) is sufficient to describe our experimental results. Thus, given that T_{NI}–T^*, and therefore b, are found to be somewhat larger for 5–10–5 than for 5–9–5, we would expect 5–10–5 to exhibit more of a prolate character in the nematic phase than the corresponding odd dimer. This is consistent with the shape of the molecules in their fully extended conformations, the conformations which are favoured in the ordered nematic phase.

The second observation is that the quantity Φ is virtually the same for the two dimers, being $(4{\cdot}0\pm0{\cdot}5)\times10^{-7}\,\mathrm{K}/T^2$ for 5–9–5 and $(4{\cdot}1\pm0{\cdot}5)\times10^{-7}\,\mathrm{K}/T^2$ for 5–10–5. In fact, these values are not very much different from the 5OO5 monomer value of $(5{\cdot}1\pm0{\cdot}5)\times10^{-7}\,\mathrm{K}/T^2$ [13]. Lee [28] has used functional scaling to develop a spherocylindrical particle generalization of the Carnahan–Starling equation for the free energy of hard spheres [29]. His model, which reduces to the Onsager theory [30] in the low density, large aspect ratio limit, is in good agreement with Monte-Carlo simulations for short, high density rods at the NI transition [31–33]. Moreover, his results are in reasonable agreement with viscosity and elasticity data for tobacco mosaic virus in suspension [34–36]. After some calculation, the terms in Lee's free energy density relevant to our experiment can be shown to be [13]

$$F=F_0+\rho kT\overline{P_2}^2[5-0{\cdot}763\alpha\eta(4-3\eta)/(1-\eta)^2], \tag{3}$$

where ρ is the number density of rigid (persistence) lengths, k is Boltzmann's constant, α is an increasing function of the aspect ratio, and η is the packing fraction. In [13] it was argued that the quadratic coefficient a in the Landau expansion (see equation (2)) can be extracted from F, and is given by

$$a=2\rho k[5-0{\cdot}763\alpha\eta(4-3\eta)/(1-\eta)^2]. \tag{4}$$

Since the saturated birefringences, as well as the saturated magnetic susceptibility anisotropies, are nearly equal in both the fully extended 5OO5 monomer and 5–10–5 dimer, for these two species equation (1) reduces to $a\propto1/\Phi$. Flexibility in the dimer would be reflected in the quantity a through the parameters ρ and α. Since Φ (and thus a) differ little between the monomer and the even dimer, we concluded in [13] that, based upon a steric model for nematic order (such as that of Lee), the spacer in 5–10–5 is nearly completely flexible in the isotropic phase, such that the two mesogenic units which comprise the dimer are expected to behave as nearly free mesogens. Note that if, on the other hand, the fully extended conformation were to be heavily populated in the isotropic phase of 5–10–5 (i.e. a rigid spacer), then ρ would be decreased by a factor of 2 and α would be larger. The quantity Φ ($\propto 1/a$) would then have been expected to be about three to four times larger than for the monomer; this is clearly not the case experimentally.

Qualitatively, the odd dimer can be treated in a similar manner. First, we note that if the odd dimer were fully extended, both Δn_0 and $\Delta\chi_0$ would be smaller than the corresponding values for the even dimer; this, of course, is a result of the larger angle ($\sim25°$) between the mesogenic groups of the odd dimer as compared to the even dimer. More specifically, because most of the magnetic susceptibility resides in the aromatic groups, we would expect $\Delta\chi_0$ to be reduced by approximately $P_2(\cos 25°)$, or 0·73. The chromophore is not as well localized, however, and as a result the reduction factor for Δn_0 is likely to be a bit closer to unity. In addition, from equation (4) we would expect that a would be slightly larger for the fully extended 5–9–5 dimer because the parameter

α would be reduced. Thus, from equation (1), we would expect that Φ for a fully extended odd dimer is smaller than what would be expected for a fully extended even dimer. A quantitative estimate would be quite difficult, however, especially in light of the parameter α. We note that two limits can nevertheless be established: for an all-*trans* odd dimer, Φ should be somewhat less than the value expected for a *fully extended* even dimer, which is approximately three or four times the monomer value. On the other hand, an odd dimer in which the mesogens are uncorrelated should have a value of Φ comparable to the analogous even member of the series. The *measured* value of Φ for 5–9–5 is comparable to experimental results for both 5–10–5 and the monomer. Thus, since the odd and even dimers have virtually the same value of Φ, we conclude that the terminal mesogens are uncorrelated.

We now turn to the molecular field theory, developed by Heaton and Luckhurst [21], which allows for both the molecular flexibility and biaxiality. The flexibility is included via the Flory rotametric state theory [37], in which the conformational energy is determined by the number of gauche links in the chain and the energy difference E_{tg} between a *trans* and *gauche* bond. Within the theory [21] the angular correlations between two constituent groups are reflected by a J factor; thus for the two terminal mesogenic groups

$$J_{aa}=\sum_{ij}\overline{P_2(\cos\beta_{ij})}, \tag{5}$$

where β_{ij} is the angle between the assumed symmetry axes of the mesogenic groups i and j; the bar denotes a conformational average. When E_{tg} is large relative to $kT(E^*_{tg}\equiv E_{tg}/kT\sim 20)$ only the all-*trans* conformer is significantly populated, the mesogenic groups are totally correlated, and J_{aa} is determined simply by the molecular geometry. In contrast, when E^*_{tg} is about 1, as expected for the isotropic phases of mesogens, the angular correlations are found to be small. Indeed, J_{aa} for a dimer is predicted to be about 2 and, for spacers with more than six methylene groups, it is essentially independent of the spacer length. In the complete absence of correlations J_{aa} would be 2 because there are two self terms contributing to the sum in equation (5) [21]. The result is, of course, in accord with the conclusions drawn from our experimental findings on the basis of the steric model. The molecular field theory is, however, able to predict additionally the influence of the spacer length on both T_{NI} and T^* in reasonable agreement with experiment.

The theory can also be used to understand the behaviour of the Cotton–Mouton coefficient for the two dimers. The dominant contributions to the field induced birefringence comes from the two mesogenic groups. The field induced orientational order of such a group is given by a relatively complicated expression involving the molecular field interaction parameters and magnetic susceptibilities for the constituent groups within the molecule, as well as certain J factors [21]. However, in the limit that the magnetic susceptibility and molecular field interactions for the flexible spacer can be ignored, the field induced order parameter for a terminal mesogenic group takes the simple form

$$\overline{P^a_2}=\chi_a J_{aa}/5k(T-T^*), \tag{6}$$

where χ_a is the magnetic energy of such a group. Since J_{aa} is essentially independent of the length of the flexible spacer, the theory predicts that $\overline{P^a_2}(T-T^*)$, and hence $(d\Delta n/dH^2)(T-T^*)$ should be the same for both odd and even dimers, in good agreement with experiment.

Several points emerge from this work. First, $T_{NI}-T^*$ is much larger for dimers containing an even number of methylene units in the spacer group than for those containing an odd number; this is qualitatively as predicted by the model of Heaton and Luckhurst. For the extended conformations in the nematic phase, this result implies that the odd dimer might be more likely to exhibit a biaxial nematic phase. Although not a necessary condition, such a state is more likely if the molecule tends to be biaxial in character. In addition, $T_{NI}-T^*$ for the odd dimer (5–9–5) studied herein is yet a factor of approximately three *smaller* than that of the odd dimer studied in [22]. We speculate that this difference might be due to the nature of the two molecules. 5–9–5 is a relatively non-polar molecule, whereas that of [22] terminates in a cyano group at both ends. Given that the highly polar cyanobiphenyl monomers have a propensity to physically (as opposed to chemically) dimerize in the ordered states, such dimerization may tend to mitigate the effects of an otherwise bent molecular configuration. The result, of course, may be that the cyanobiphenyl dimers may aggregate to form a more prolate uniaxial particle. In addition, the magnetooptic response in the isotropic phase, as determined by the temperature dependent Cotton–Mouton coefficient, appears to be identical for both odd and even species studied herein, and similar to the response of the 5OO5 monomer. When analysed in terms of steric models of the nematic phase we conclude that the probability for the all-*trans* spacer conformation is low for both members of the series, and that the mesogens act nearly independently as contributors to the magnetooptic response. Similar behaviour might be inferred when the data is analysed in terms of a particular molecular field model. Overall, then, we present further evidence that the spacer group plays an important tole in *some* aspects of pretransitional behaviour (for example $T_{NI}-T^*$), but appears to play little or no role in other aspects, such as the susceptibility in the isotropic phase.

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