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On the observation of flow-induced order in the isotropic phase of a nematic discogen

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The phenomenon of flow-induced order observed in the isotropic phase of nematic discotic materials is studied and the orientation of the induced director explained by the existence of the molecules in short columns. The occurrence of this order in both the isotropic and nematic phases explains the low transition enthalpy, agreeing with the inferences made in the literature.

1. Introduction

Previous work on the triphenylene hexa-alkoxybenzoate nematic discogens [1] has shown a variety of interesting effects which have been attributed to the large amount of short-range columnar order in these materials. In particular, the materials exhibit very small transition enthalpies [2], around 100–200 J mol^{-1}, a large drop in the mean permittivity as the material is cooled into the nematic phase [2], and some unusual elastic constant effects [2], as well as a very large degree of anti-parallel dipole correlation [2,3]. Recently, some new materials have been made with two methyl groups on the substituent benzene rings [4], and these have been studied by their inclusion in a number of binary mixtures. A new and interesting effect, namely that of a large degree of flow-induced order in the isotropic phase (easily visible with the naked eye), has been observed. The effect is discussed in this paper.

2. Experimental

2.1. *Materials*

The mixture detailed in this paper [5] consists of a methylated triphenylene hexa-alkoxybenzoate, DB126 [1], together with a doubly-methylated compound, PH8 [4]. The structures of the materials are shown in figure 1. The doubly-methylated compounds, where the groups both point in towards the core, are found to have much lower transition temperatures than the singly methylated ones [4], while retaining the nematic character of the previous materials. The two compounds were mixed, with the resultant phase diagram shown in figure 2. There is some depression of transition temperatures, but the best mixture is still inferior to a previous mixture **T1a** [6], having a similar clearing point of ~90°C, but now a rather higher melting point at ~80°C (cf. 66°C for **T1a**). The nematic discotic phase is continuous across

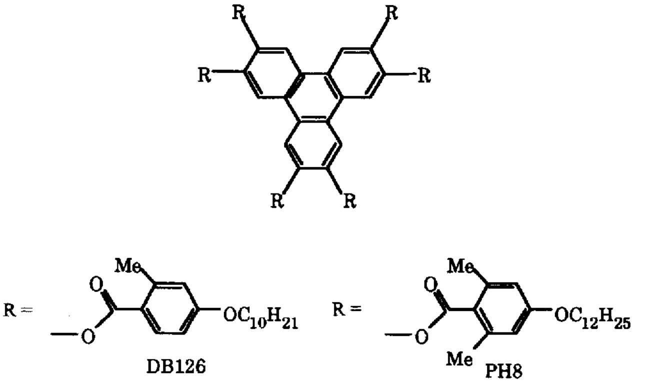

Figure 1. Mixture components.

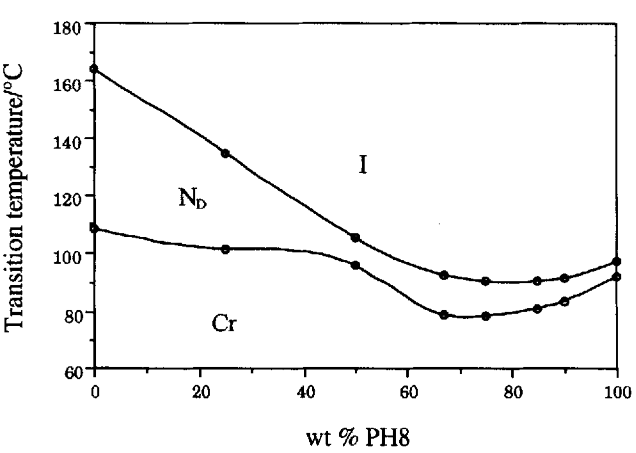

Figure 2. Phase diagram for mixtures of DB126 and PH8.

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the phase diagram, and the clearing line is strongly curved.

2.2. *Flow-induced order*

The mixtures on the right-hand side of the phase diagram (for example the 75% mixture) shown an unusual phenomenon. When the sample is heated into its isotropic phase by a few degrees, between two glass slides, and then sheared, a brief flash of light is seen when the sample is viewed between crossed polarizers. This is visible up to 10°C above the transition, though the size of the effect decreases as the distance from the transition increases. The effect is superficially similar to that seen when homeotropically aligned sample of a nematic material, in the nematic phase, is sheared. In that case, the sample, which initially appears black because it is viewed along its optic axis, has its director tilted over due to the flow in the cell (figure 3). This tilt decays after the flow stops, and the sample returns to homeotropic alignment. The process appears as a brief flash of light when viewed with a polarizing microscope.

The effect in the discotic is significantly different, as can be seen with transient conoscopy (see figure 4, which is only a schematic because of the difficulty of photographing the short-lived resultant). The initial (unsheared) conoscopic figure shows that the material is truly isotropic, rather than homeotropic uniaxial (which would give a dark cross on a light background [7]). When sheared, the figure is that for a tilted uniaxial sample. This suggests that the shear is inducing order, as well as tilting over the director that it creates. This is shown schematically in figure 5, where the amount of order, as well as the orientation of the director created, is shown using the vector $\mathbf{n} = S\hat{\mathbf{n}}$.

Flow induced birefringence is known to occur in calamitic materials, but the effect is extremely small ($\Delta n_{\mathrm{flow}} \sim 10^{-5}$) and needs careful experimentation to detect it [8]. In contrast, the effect in these materials is easily seen with the naked eye, and the induced birefringences are of the order of that in the nematic phase, i.e. $\sim 0{\cdot}1$ [6]. There is clearly an important distinction here between the behaviour of discotics and calamitics near the isotropic–nematic transition. This effect has not been noted in previously studied materials.

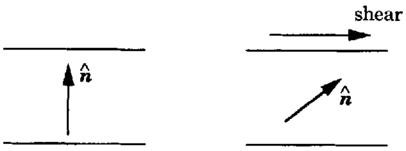
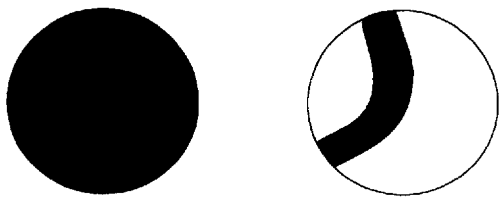


Figure 3. Shearing a homeotropically aligned nematic.



unsheared sheared (example)

Figure 4. Schematic representation of the results from transient conoscopy.

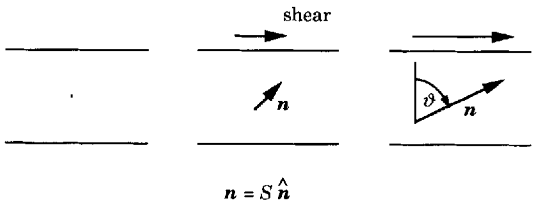


Figure 5. Shearing an isotropic phase to induce order. An attempt is made to show the amount of order by the magnitude of the vector **n**.

3. Discussion

3.1. *Direction of shear*

An interesting part of this phenomenon is that the director formed by the shear has a component in the direction of the shear—this is confirmed by noting the directions of the fast and slow axes as the sample is sheared. As the director in the homeotropic calamitic nematic case is tilted parallel to the direction of shear, it might be expected, due to the reverse aspect ratio of the discotic, that the created director would tend to be perpendicular to the shear direction. This expectation is confirmed by the work of Carlsson [9,10], who discussed the case of a discotic nematic in terms of the Leslie viscosity coefficients [11]. The viscous torque exerted on the director in the steady state, Γ^h_y, is given by

$$\Gamma^h_y = (\alpha_3 \sin^2 \vartheta - \alpha_2 \cos^2 \vartheta) u', \qquad (1)$$

where u' is the local shear rate, and ϑ is the angle between the director and the normal to the plates (figure 5). Flow alignment is then possible when Γ^h_y is zero, giving a solution for the flow alignment angle

$$\tan \vartheta = \pm (\alpha_2/\alpha_3)^{1/2}. \qquad (2)$$

Carlsson suggested the discotic nematic as an example of a system where the coefficients α_2 and α_3 were both positive, rather than both negative as is the case with most calamitics (the others have α_3 positive and α_2 negative—they do not flow align). An inevitable consequence of this, within the framework of the Leslie theory, is that the flow alignment angle will be negative. In fact, a further restriction on the angle comes from the inequality [11]

$$\alpha_3 - \alpha_2 \geqslant 0, \qquad (3)$$

which restricts stable solutions for ϑ to the range $-45° \leqslant \vartheta \leqslant 0°$.

Now the parameter λ, given by

$$\lambda = \frac{\alpha_2 + \alpha_3}{\alpha_2 - \alpha_3}, \tag{4}$$

so that

$$\frac{\alpha_2}{\alpha_3} = \frac{\lambda + 1}{\lambda - 1}, \tag{5}$$

is predicted by Volovic [12] to be equal to -1 for infinitely thin discs; he predicted small deviations from this result for discs of finite thickness. Carlsson assumes $\lambda \lessgtr -1$, so $\alpha_2/\alpha_3 \rightarrow 0^+$, in agreement with Helfrich [13,14], as long as the axes in his prolate calculation can be interchanged without over changes (Helfrich finds for the prolate case that $\alpha_2/\alpha_3 = a^2/b^2$, where $2a$ and $2b$ are the long and short axes, respectively). This then implies that ϑ is very small and negative, in other words that the discs lie roughly parallel to the flow, and the director roughly normal to it. This is in direct conflict with the experimental observation presented above.

The disagreement discussed above is found to arise for flow alignment in the nematic phase of these discotics, where the director lies roughly in the shear direction, as well as in the case of the flow-induced order presented here.

3.2 *Implications of short-range columnar order*

The observation of this flow-induced order agrees with other observations and inferences made previously [5]. The materials discussed in this paper are found to have an extremely small enthalpy of transition at $T_{\rm NI}$ ($\sim 20 \pm 10\,\mathrm{J\,mol^{-1}}$), suggesting a very small change in order at this transition. This value is even smaller than the enthalpy changes seen with DB126 [2] or **T1a**, for example, and in those cases the effect was attributed to a large degree of short-range order that persists into the isotropic phase [5]. This comparison also suggests that the disagreement with the continuum theory described above is also due to the fact that the molecules in these systems are associated into short columns. In this case, the aggregate may have an aspect ratio approaching unity, while still being slightly oblate or possibly becoming slightly prolate. In the oblate case, the most extreme case is when the aspect ratio approaches unity, so that $\lambda \rightarrow -\infty$, in which case the alignment angle approaches $-\pi/4$. This is certainly a possibility as seen from the transient conoscopy, where the dark ring is the 'equator' of the nematic conoscopic figure [7]. There remains the possibility that the cybotactic columns are sufficiently long to have a prolate aspect ratio, and as such comprise a nematic columnar, or $\mathrm{N_c}$, phase. Such a phase has been noted [15,16], with columns consisting of about 20–30 discs. It is the elastic constant data for similar materials [2] that suggest this is not the case here. Firstly, the ratio k_{11}/k_{33} was found to be that for an oblate aspect ratio, and secondly the values for the elastic constants were approximately similar to those for calamitic examples. The $\mathrm{N_c}$ phase is found to have very large elastic constants [17].

4. Conclusions

The observed phenomenon of flow-induced order in the isotropic phase of some nematic discotic materials has been studied. It is suggested that the orientation of the induced director is only explainable if the molecules are assumed to exist as very short columns. In addition, the very small enthalpy of transition is believed to be due to the fact that most of this order occurs in both the isotropic and nematic phases. This conclusion is in correspondence with all inferences presented in previous papers.

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