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Viscoelastic behaviour of a disk-like thermotropic nematic phase (N_D) versus temperature

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We have investigated 'hexa-*n*-alcanoyloxytruxene' HATXC_9H_{19} which exhibits a disk-like thermotropic nematic phase between 65 and 84°C. Using a light-beating technique we have measured the orientational diffusivities D_{twist} and D_{bend} for several temperatures, which correspond respectively to twist and bend deformations. D_{twist} increases monotonically as temperature increases, while D_{bend} remains constant. This result means that the curvature elastic constant K_{22} changes more rapidly than the viscosity η_{twist}, while K_{33} and η_{bend} change in the same ratio. This means also that in the discotic thermotropic nematic phase, when temperature increases the effective hydrodynamic object, in orientational fluctuation, changes shape to be disk-like rather than rod-like.

1. Introduction

In a nematic liquid crystal, the spontaneous alignment of molecular orientation is probably the most characteristic property of this phase. This orientational order undergoes thermal fluctuations about an equilibrium direction. Fluctuation amplitude is controlled by liquid crystal elasticity [1]. Therefore, information about elastic properties can be deduced from amplitude measurements, using light scattering to measure the intensity and spectrum of the light scattered by the angular fluctuations of the director **n** [2–9]. Consequently, one can, for instance, easily deduce orientational diffusivities D_{splay}, D_{twist} and D_{bend}, which are associated respectively with splay, twist and bend deformations. Then, an understanding of liquid crystal viscous and elastic properties can be reached.

It is well known that for the rod-like nematic phase (N_B), D_{splay} and D_{twist} are of the same order of magnitude, while D_{bend} is larger. This difference is generally attributed to backflow effects which reduce the bend viscosity relative to the twist viscosity.

Contrary to the nematic phase N_B, the disk-like nematic phase N_D is constituted by flat or nearly flat molecules [10, 11]. In this phase the director **n** lies along the molecular short axis. Based on the difference between geometrical shapes of the two kinds of molecules (rod and disk), one can expect an exchange between splay and bend distortions. The first check of these predictions was made on a disk-like nematic lyotropic phase [12], for which the authors measured D_{splay} and D_{twist} by the light-beating technique. They found a divergence between these two constants. For D_{bend}, they simply anticipated that the backflow effects must be very weak.

In previous work [8, 9], we used the light-beating technique to investigate the disk-like thermotropic nematic phase N_D. We measured D_{splay}, D_{twist} and D_{bend} at a fixed temperature. In spite of the difference between the geometrical shape of the two kinds of molecule the ratio $D_{\text{splay}}/D_{\text{twist}}$ and $D_{\text{bend}}/D_{\text{twist}}$ for the N_D phase exhibited the same behaviour as for the N_B phase. This result has been explained by the existence of a columnar order which can be manifest in the packing of a few (~ 25) molecules to form relatively short columns of the diameter of an individual disk. Each column would be equivalent to an individual rod in a conventional liquid crystal. The existence of columnar order in the N_D phase is probably due to a strong correlation between molecules, which is not the case for the discotic lyotropic nematic phase where disks seem to be less correlated. Based on these suppositions, one can expect for the disk-like thermotropic nematic phase a reduction of correlation effects if temperature increases. So the viscoelastic behaviour of the N_D phase is expected to be similar to that of a disk-like lyotropic phase and not as in the N_B phase.

In order to test these predictions, we have used quasi-elastic light scattering to investigate a disk-like thermotropic nematic phase for several temperatures, and to measure the damping times corresponding to each distortion mode.

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In this section we recall some theoretical predictions for a nematic liquid crystal used in the present study. In § 2, we describe experimental methods: materials, technique and scattering geometries. In § 3 we present measured data along with a discussion and a comparison with previous results.

First let us choose a coordinate system in which the mean direction $\mathbf{n}_0$ lies along the z-axis and the scattering wave vector $\mathbf{q} = \mathbf{k}_i - \mathbf{k}_s$ lies in the xz-plane (see figure 1). $\mathbf{k}_i$ and $\mathbf{k}_s$ are respectively the incident and scattered wave vectors. $\mathbf{e}_1$ and $\mathbf{e}_2$ denote the two unit vectors lying respectively along the x- and y-axis.

At a point $\mathbf{r}$, the local director $\mathbf{n}$ position is dependent in the sample and may be expressed as:

$$\mathbf{n}(r) = \mathbf{n}_0 + \delta n_1 \mathbf{e}_1 + \delta n_2 \mathbf{e}_2 \tag{1}$$

where the mode δn_1 is a combination of bend and splay deformations, and the mode δn_2 is a combination of bend and twist deformations.

At a fixed $\mathbf{q}$, the relaxation rate Γ_i corresponding to each mode is proportional to q^2 and can be given by the following expression:

$$\Gamma_i = (1/\eta_i)(K_{ii} q_\perp^2 + K_{33} q_{//}^2) \tag{2}$$

where i denotes the mode of fluctuation of δn parallel ($i = 1$) or normal ($i = 2$) to the $(\mathbf{q}, \mathbf{n}_0)$ plane. K_{11}, K_{22} and K_{33} are the Frank elastic constants associated with splay, twist and bend deformations, respectively; $\eta_1(\mathbf{q})$ and $\eta_2(\mathbf{q})$ are the viscosities attributed to modes 1 and 2; $q_\perp$ and $q_{//}$ are the perpendicular and parallel components of the wavevector $\mathbf{q}$ with respect to $\mathbf{n}_0$. Note that, according to equation (2) and from an appropriate choice of scattering geometries, one can deduce separately $D_{\text{splay}} = K_{11}/\eta_{\text{splay}}$, $D_{\text{twist}} = K_{22}/\eta_{\text{twist}}$ and $D_{\text{bend}} = K_{33}/\eta_{\text{bend}}$, which are respectively the splay, twist and bend orientational diffusivities.

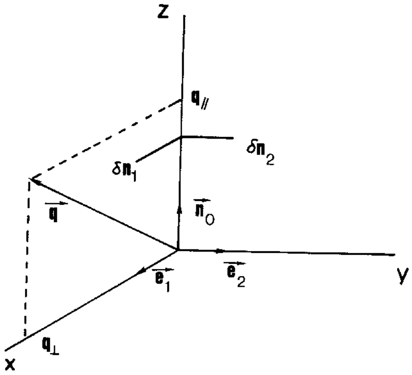


Figure 1. Fluctuation modes. The δn_1 mode which is in the $(\mathbf{q}, \mathbf{n}_0)$ plane is a combination of the bend and splay deformation. The δn_2 mode which is perpendicular to the $(\mathbf{q}, \mathbf{n}_0)$ plane is a combination of bend and twist deformation. $\mathbf{n}_0$ is the equilibrium direction.

2. Experimental method

The material used here is 'hexa-n-alcanoyloxytruxene' ($\text{HATXC}_9\text{H}_{19}$) which exhibits a disk-like thermotropic nematic phase (N_D) between 65°C and 84°C [11]. The thickness of the sample was adjusted with a mica spacer to 60 μm. To obtain a good homeotropic orientation ($\mathbf{n}_0$ aligned normal to the plates), we used the same orientation method as in [8].

The sample temperature was maintained at any desired value (to an accuracy of 0·1°C) in the nematic phase range by means of an electric oven. It was measured by means of a thermistor probe near the glass plates. The oven was then placed on a goniometer, allowing us to change the incidence air angle (angle between $\mathbf{n}_0$ and $\mathbf{k}_i$). To illuminate the sample, we used a 10 mW He–Ne laser whose polarization was selected as ordinary by means of a linear polarizer placed in front of the sample. The scattered light which was polarized extraordinary by an analyser, was detected along the direction $\mathbf{k}_s$ by a cooled S_{20} photomultiplier (PM). The PM was fixed on a rotatable arm which could be rotated around the vertical goniometer axis. After amplification, the photocurrent $i(t)$ was sent to a 64 channel digital correlator to be analysed. The experimental auto-correlation function $C_i(t)$ was sent to a computer to be adjusted against a theoretical model. Note that in the absence of multiple scattering $C_i(t)$ can be expressed as:

$$C_i(t) = (I_0 + I_s)^2 + I_s^2 \exp(-2t/\tau) + I_0 I_s \exp(-t/\tau) \tag{3}$$

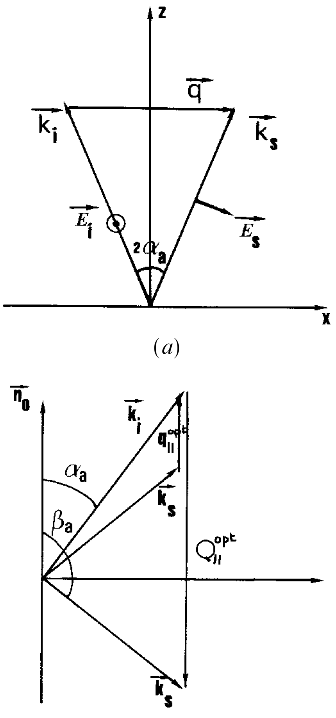
where I_0 is the intensity of the light scattered by a local oscillator in a heterodyne regime detection, and I_s is the intensity of light scattered by mode fluctuations. $\tau = 1/Dq^2$ is the damping time, where D is the orientational diffusivity.

To measure the damping time associated with pure twist deformations, we chose the scattering geometry in which the incident and scattering angles are equal in air and the wavevectors $\mathbf{k}_i$ and $\mathbf{k}_s$ are symmetric normal to the glass plates. The incident and scattered polarization are ordinary and extraordinary respectively (o, e) [see figure 2 (*a*)]. In this case, the wavevector $\mathbf{q}$ is closely perpendicular to $\mathbf{n}_0$.

For each temperature selected in the range 66–83°C in which we made measurements, we changed the air angle α_a between $\mathbf{k}_i$ and $\mathbf{n}_0$ from 0° to 20°. So the damping time corresponding to twist deformations is derived from a fitting of the experimental auto-correlation function with the following theoretical model:

$$C_{\text{th}}(t) = A \exp(-2t/\tau) + B \exp(-t/\tau) + C \tag{4}$$

where A, B and τ are the parameters to be adjusted and C is the baseline which is fixed to the measured value.



(*a*)

(*b*)

Figure 2. (*a*) Scattering geometry in air: $\mathbf{k}_i$ = incoming wave vector; $\mathbf{k}_s$ = scattering wave vector; $\mathbf{q} = \mathbf{k}_i - \mathbf{k}_s$. Depolarized scattering associated to twist deformations (mode 2). (*b*) Scattering geometry: $\mathbf{q}^{opt}$ and $\mathbf{Q}^{opt}$ correspond respectively to forward and backward scattering; $\mathbf{k}_i$ and $\mathbf{k}_s$ are the incoming and scattering wave vector, respectively; z is the optical axis

For pure bend deformations, we adopted the scattering geometry presented in figure 2 (*b*), in which the wavevector $\mathbf{q}$ is kept parallel to $\mathbf{n}_0$. So the light scattered when it exits must be centred outside the sample on the transmitted or reflected beam, because reflection and refraction across the plates containing the sample conserve the tangential components of light wavevectors along this interface [7]. Note that in our case and for each selected temperature, we have analysed the scattered light centred on the reflected beam. So for each incident angle α_a, we selected the scattering angle to be equal to $\beta_a = \pi - \alpha_a$ [see figure 2 (*b*)]. As in the case of twist deformation, the damping time associated with bend deformation modes is deduced from an adjustment of the experimental autocorrelation function $C_i(t)$ against the theoretical model formed by two exponential functions.

3. Results and discussion

We plot in figure 3, for each temperature selected in the range (66–83°C), the measured decay rate $\Gamma_2 = D_{\text{twist}} q_{\perp}^2$ versus $q_{\perp}^2$. Clearly, at a fixed $q_{\perp}$ (or fixed α_a), Γ_2 increases when the temperature increases from 66 to 83°C. For instance, at $\alpha_a = 7°$, Γ_2 increases from 1·52 to 5·10 s^{-1}, at $\alpha_a = 15°$, from 6·9 to 33·33 s^{-1}, at $\alpha_a = 19°$, from 12·40 to 46·00 s^{-1}. Figure 3 shows also that for each temperature experimental data are well fitted with a straight line. The corresponding slope gives the orientational diffusivity D_{twist}.

We plot in figure 4 D_{twist} versus temperature. D_{twist} increases monotonically with temperature, a behaviour which is habitually observed in rod-like nematic phases [13]. This result means that for the temperature range investigated the viscosity η_{twist} decreases more rapidly than the curvature elastic constant K_{22} as temperature increases. Note that in principle this result can be confirmed by direct measurement of the elastic constant versus temperature, for example by the Fréedericksz transition method, for planar orientation. In this way,

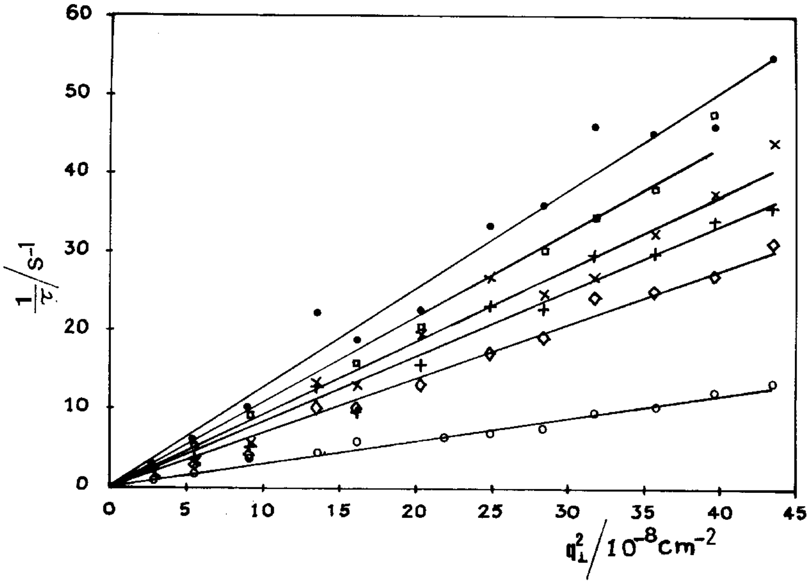


Figure 3. Decay rates $1/\tau$ versus $q_{\perp}^2$ corresponding to twist deformation: (○) $T = 66°C$; (◇) $T = 73°C$; (×) $T = 76·5°C$; (+) $T = 78·5°C$; (□) $T = 81°C$; (●) $T = 83°C$.

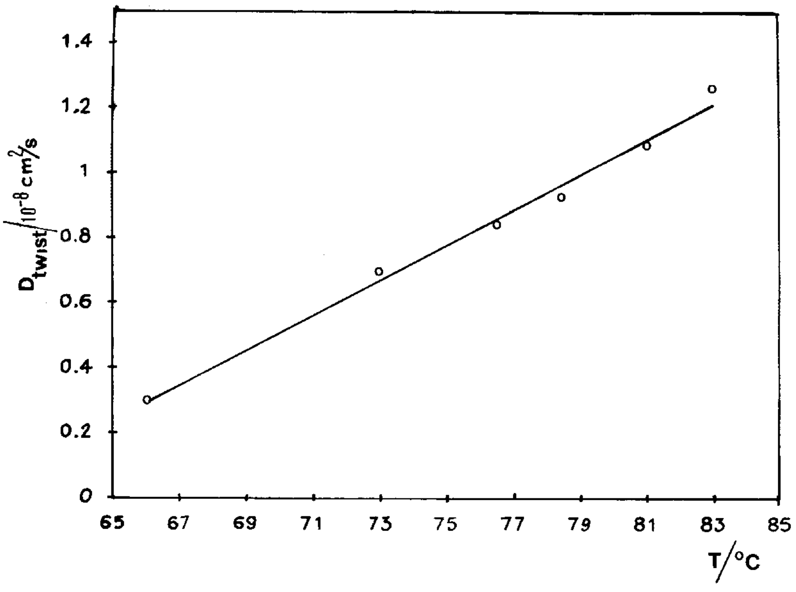


Figure 4. Orientational diffusivity D_{twist} versus temperature.

several attempts were made to orient our sample planarly, but we did not obtain satisfactory results. So our discussion concerning twist deformations is limited to the ratio $K_{22}/\eta_{\text{twist}}$.

Concerning bend deformations, we have analysed the scattered light centred on the reflected beam. The corresponding autocorrelation function is adjusted with a theoretical model with two exponential functions. The damping time deduced from this adjustment corresponds to bend deformation modes. In figure 5, for each temperature selected in the range (66–83°C) we plot the measured decay rates $\Gamma_2 = D_{\text{bend}} q^2_{//}$ versus $q^2_{//}$. Γ_2 increases monotonically with $q^2_{//}$ (or α_a). For each temperature, data are fitted with a straight line. The slope gives the bend orientational diffusivity D_{bend}. In figure 6 we plot D_{bend} versus temperature; in spite of experimental uncertainties, one can deduce that D_{bend} remains constant in the studied temperature range. So, following the bend orientational diffusivity expression, $D_{\text{bend}} = K_{33}/\eta_{\text{bend}}$, one can deduce that when the temperature changes, K_{33} and η_{bend} change in the same ratio. This result allows us to deduce that the ratio $D_{\text{bend}}/D_{\text{twist}}$ decreases when the temperature increases, a result found in the disk-like lyotropic nematic phase [12], where the effective hydrodynamic object is a disk and not a rod. This result can also be explained by a reduction of

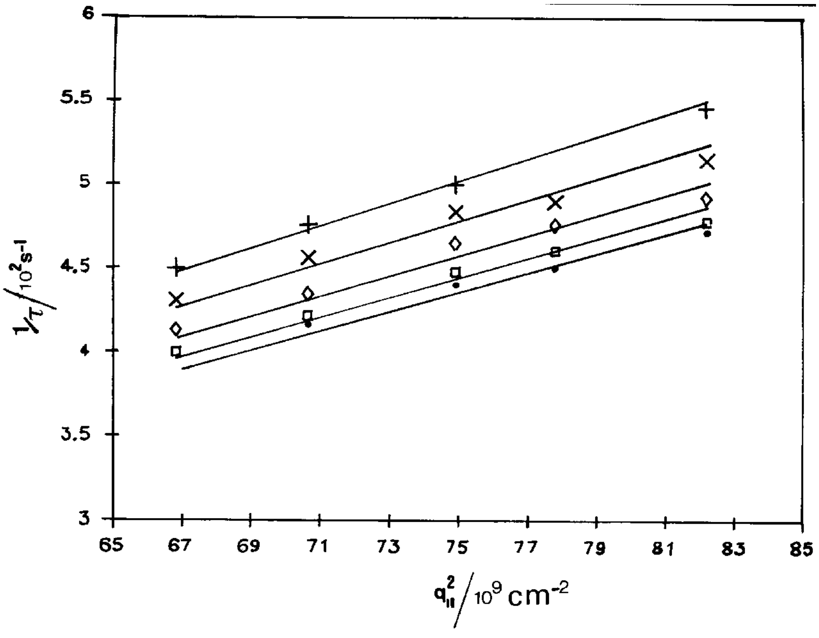


Figure 5. Decay rates $1/\tau$ versus $q^2_{//}$ corresponding to bend deformation: (●) $T = 68^\circ C$; (□) $T = 70{\cdot}4^\circ C$; (◇) $T = 75^\circ C$; (×) $T = 78^\circ C$; (+) $T = 83{\cdot}2^\circ C$.

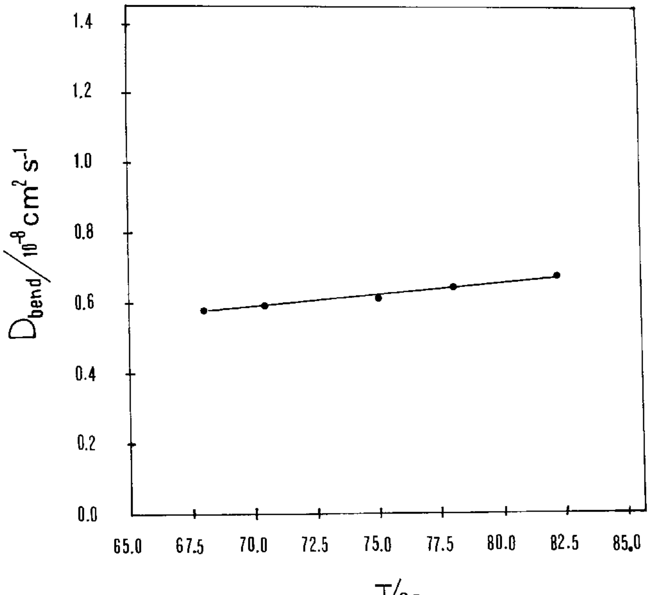


Figure 6. Orientational diffusivity D_{bend} versus temperature.

correlation between molecules. So in the thermotropic nematic phase N_D, the hydrodynamic object which was at first identified as an elongated rod formed by the packing of a few discotic molecules, becomes constituted as an individual disk.

4. Conclusion

We have here investigated the compound 'hexa-*n*-alcanoyloxtruxene' HATXC_9H_{19} which exhibits a disk-like thermotropic nematic phase between 65°C and 84°C. Using the light-beating technique, the behaviour of twist and bend deformations versus temperature has been examined. For appropriate scattering geometries, we have measured separately the decay rates corresponding to twist and bend deformations. D_{twist} increases monotonically as temperature increases, while D_{bend} remains constant. As a result, as temperature increases, the ratio $D_{\mathrm{bend}}/D_{\mathrm{twist}}$ decreases; consequently, there is reduction of divergence between D_{bend} and D_{twist}. Thus the disk-like thermotropic nematic phase exhibits the same viscoelastic behaviour as the disk-like lyotropic nematic phase. This result means also that as temperature increases the effective hydrodynamic object tends to be a disk and not a rod. Thus correlations between discotic molecules decrease as temperature increases. It would be of interest to test this result by X-ray diffraction or by independent measurements of curvature elastic constants and viscosity coefficients.

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