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Flow-alignment and the sign of κ_2 in nematic liquid crystals

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Résumé. — On présente des résultats pour θ_0, l'angle d'alignement des nématiques par l'écoulement. Des mesures sur deux composés qui ne diffèrent que dans la présence d'un groupe de cyano terminal fortement polaire, n'indiquent aucune influence de ce groupe sur θ_0. Des résultats pour une série homologue montrent que θ_0 décroît avec la longueur des chaînes d'alkyl, jusqu'à perdre l'alignement en raison d'un changement du signe de κ_2. Ces effets sont attribués à l'ordre smectique prétransitionnel.

Abstract. — Results are presented for the flow-alignment angle θ_0 of various nematics. Measurements for two compounds that differ mainly in the presence of a strongly polar terminal cyano-group indicate that this has no influence on θ_0. Results for a homologous series give a decrease of θ_0 with increasing alkyl chain lengths, until finally no flow-alignment exists due to a change in sign of κ_2. This is attributed to pre-transitional smectic order.

The hydrodynamic properties of nematic liquid crystals [1] are complicated in the first place because the flow depends on the angles between the preferred orientation of the long molecular axis (director **n**) and the flow direction **v** and the velocity gradient ∇**v**. Secondly, translational motions are coupled to inner, orientational motions of the molecules and the flow will cause **n** to rotate. In the absence of external constraints this leads to flow-alignment, which means that **n** orientates in the shear-plane at an angle θ_0 with respect to **v**. The flow-alignment angle θ_0 is given by [2]

$$\tan^2 \theta_0 = -\kappa_2/\kappa_1 \tag{1}$$

where κ_1 (or α_2) and κ_2 (or $-\alpha_3$) are the shear-torque coefficients that determine the torques on **n** when it is parallel to ∇**v** and **v**, respectively. These shear-torque coefficients are of special interest because they have no isotropic counterpart. For some nematogenic compounds κ_2 has been found to change sign as a function of temperature [3]. In that case there is no real solution to equation 1 anymore. It is the purpose of this letter to report on the physical origin of this effect. In particular it will be shown that it is not related to association between strongly polar molecules as has been suggested [3*a*, 4]. It is due to the influence of smectic short-range order on κ_2 [5], for which flow-alignment turns out to be an extremely sensitive probe.

The set-up used to determine θ_0 is essentially as described in reference 6. The optical detection system has been improved along similar lines as used by Lim *et al.* [7] to determine the birefringence of liquid crystals. Referring to figure 1 we note that the light emerging from the sample is elliptically polarized, with a phase shift δ between the components parallel and perpendicular

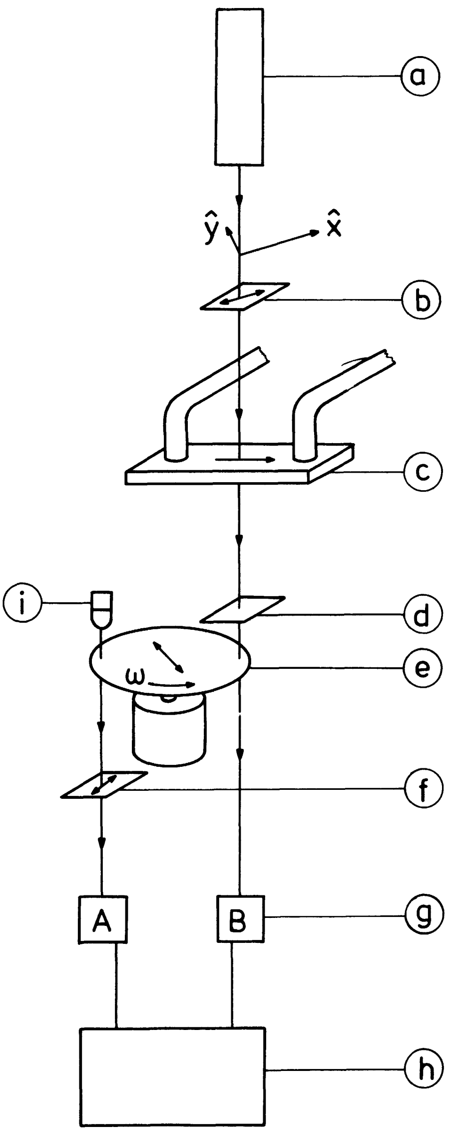


Fig. 1. — The optical part of the set-up used to determine θ_0. a — He-Ne laser, b — polarizer, c — flow-cell, d — λ/4-plate, e — rotating polaroid, f — analyser, g — photodiodes, h — phase meter, i — LED.

to **n**, respectively. The intensities of the reference beam (I_A) and of the light beam from the sample (I_B) are given by

$$\begin{aligned} I_A &= I_1[1 + \cos(2\,\omega t)] \\ I_B &= I_2[1 + \cos(2\,\omega t + \delta)]\,, \end{aligned} \tag{2}$$

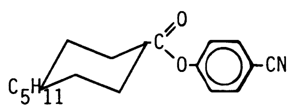
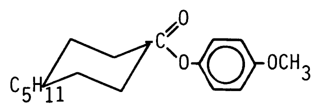
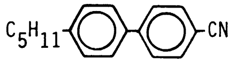
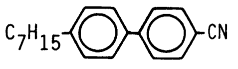
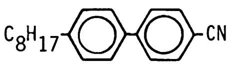
where ω is the frequency of the rotating polaroid. This allows us to measure the change $\Delta\delta$ in the phase shift δ comparing the situations $\mathbf{n} /\!/ \mathbf{v}$ (using an external magnetic field) and **n** at θ_0 with **v** (field switched off). Now, $\Delta\delta$ is given for a parabolic velocity distribution by [3*a*, 6]

$$\Delta\delta = -\frac{\pi}{\lambda} n_e\, d[(n_e/n_o)^2 - 1]\sin^2\theta_0\,. \tag{3}$$

Here n_o and n_e are the ordinary and extraordinary refractive index, respectively, at a wavelength λ, while d is the thickness of the flow cell. In the derivation of equation 3 the optical effect of the boundary layers and of the transition layer in the middle of the cell has been neglected. Furthermore it has been assumed that $\sin^2\theta_0 \ll 1$. Thus, θ_0 can be determined from $\Delta\delta$ by means of equation 3.

The compounds investigated are given in table I, together with their transition temperatures. The first two differ in the presence or absence of a strongly polar CN-group; otherwise they are as similar as possible. This should allow the observation of any effect of molecular association on the flow-alignment, as this association is directly connected with the presence of a strongly polar end group [4]. The other compounds serve to investigate any effect of increasing smectic order in a homologous series, which is expected with increasing alkyl chain length.

Table I. — *Compounds studied.*

1.		K 47.6 N 79.5 I
2.		K 40 N 71,8 I
3.		K 24 N 34.7 I
4.		K 30 N 42,7 I
5.		K 21 S_A 32,6 N 40,5 I

The results for θ_0 of the two esters are given in figure 2. Within the experimental error they have the same values, excluding any important effect of anti-parallel molecular association on the flow-alignment. The results of the *n*CB-series are given in figure 3. Here we note a trend of decreasing θ_0 with increasing chain length, until finally for 8CB the flow-alignment disappears (κ_2 changes sign) about 1^0 below the nematic-isotropic transition. There has been some disagreement about the (non)-existence of flow-alignment in 7CB [3*f*, 8]. Our measurements do not give any evidence for a change of sign of κ_2 in that case. The trend of decreasing θ_0 with increasing alkyl chain length was also found for the series of p, p'-dialkylazoxybenzenes. This will be reported elsewhere in combination with results of a homologous series without smectic phases.

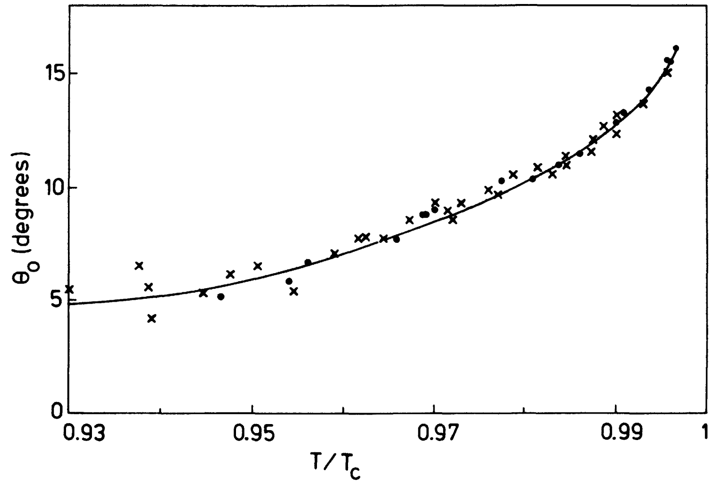


Fig. 2. — Flow-alignment angle of compound 1 (●) and 2 (×).

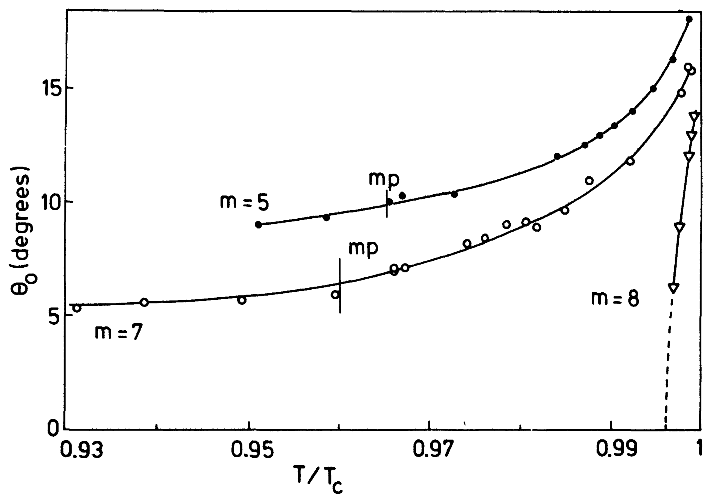


Fig. 3. — Flow-alignment angle of 5CB (●), 7CB (○) and 8CB (▽).

From time-dependent Landau theory a renormalization of κ_2 due to pre-transitional short-range smectic order is predicted [5], finally leading to κ_2 diverging in the smectic phase. On the other hand, κ_1 is not sensitive to this effect. The divergence is well-known from measurements of $\gamma_1 = \kappa_1 + \kappa_2$ [9]. However, for rod-like nematogenic molecules κ_1 is necessarily positive [10], and usually one or two orders of magnitude larger than $| \kappa_2 |$. Hence γ_1 is rather insensitive to changes in κ_2, in contrast to the flow-alignment angle θ_0. This latter quantity provides an extremely sensitive and useful probe for smectic short-range order, which might even be found without a smectic phase actually having been observed.

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