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Measurements of the ratio of the Frank constants for splay and bend in nematics of disc-like molecules

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Résumé. — Nous présentons une étude de la transition magnétique de Frederiks dans des nématiques formés de molécules discotiques (2, 3, 7, 8, 12, 13-hexa(alkanoyloxy)truxènes). Nous trouvons que, dans toute la plage nématique de ces matériaux, la constante élastique K_1 pour les déformations en éventail est plus grande que la constante de flexion K_3 . Ce comportement est à l'opposé de ce qu'on observe couramment dans les nématiques calamitiques ; il est en accord avec les prédictions de la théorie de champ moyen [1]. A la transition entre la phase nématique et la phase haute température en colonnes le rapport K_1/K_3 s'approche de l'unité. Nous n'observons pas d'accroissement prétransitionnel du rapport K_1/K_3 lié aux fluctuations du paramètre d'ordre des colonnes [2].

Abstract. — We report measurements of the magnetic Frederiks transition in nematics consisting of disc-like molecules (2, 3, 7, 8, 12, 13-hexa(alkanoyloxy)truxenes). We find that in these materials the splay elastic constant K_1 is larger than the bend elastic constant K_3 throughout the nematic regime, in contrast to what is commonly observed in fluids of rodlike mesogens. This behaviour is in agreement with the behaviour predicted by mean-field theory [1]. At the transition from the nematic to the high-temperature columnar phase the ratio K_1/K_3 appears to approach unity. We find no evidence for the predicted pretransitional enhancement of the ratio K_1/K_3 due to columnar order parameter fluctuations [2].

1. Introduction.

The spontaneous alignment of molecular orientations is probably the most characteristic property of nematic liquid crystals. Distortion of the uniform orientational alignment in a nematic increases its free energy. The lowest order expression for this distortion contribution to the free energy in terms of gradients of the nematic director $\mathbf{n}(r)$ (the local axis of uniaxial symmetry) is the following [3]:

$$f_d = \frac{1}{2} [K_1 (\nabla \cdot \mathbf{n})^2 + K_2 (\mathbf{n} \cdot \nabla \times \mathbf{n})^2 + K_3 (\mathbf{n} \times \nabla \times \mathbf{n})^2], \quad (1)$$

where f_d is the distortion free energy per unit volume, and K_1 , K_2 and K_3 are the elastic constants, usually referred to as Frank constants, associated with « splay », « twist » and « bend » distortions, respectively. The absolute values and the ratios of the Frank constants are very sensitive to the non-spherical part of the intermolecular interactions. Unfortunately, although theoretical expressions for the Frank constants

exist (see e.g. [4, 5]), explicit answers can only be obtained for a limited number of simple model systems [6, 7]. In particular, calculation of the elastic constants of hard spherocylinders seem to indicate that for such rodlike particles the bend elastic constant K_3 is in general larger than the splay constant K_1 . In fact such behaviour is indeed observed both in thermotropic [8, 9] and lyotropic [10-12] liquid crystals consisting of « rodlike » particles. Much less is known about the elastic constants of liquid crystals consisting of disc-like molecules [13]. A simple mean-field theory due to Sokalski and Ruijgrok [1] predicts that for disc-like molecules K_1 would be larger than K_3 . Thus far, direct experimental tests of this prediction were lacking.

In this paper we present the results of measurements of the ratio K_1/K_3 for two nematic liquid crystals consisting of disc-like molecules, viz. 2, 3, 7, 8, 12, 13-hexa(decanyloxy)truxene and 2, 3, 7, 8, 12, 13-hexa(tetradecanyloxy)truxene (1. and 2. respectively in Fig. 1). Both materials, which had been first synthesized by Destrade *et al.* [14], have a nematic phase

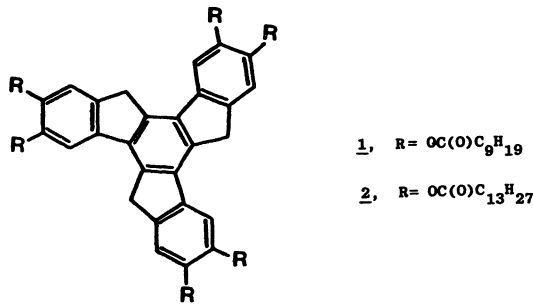


Fig. 1. — Structure of the truxene derivatives studied in this paper. 1: 2,3,7,8,12,13-hexa(decanoxy)truxene and 2: 2,3,7,8,12,13-hexa(tetradecanoxy)truxene.

around 350 K. On heating, the nematic phase goes over into a columnar phase. At lower temperatures, the nematic either freezes or transforms into a reentrant columnar phase [15]:

$$1 \text{ K} \xrightarrow{\frac{68}{\text{K}}} \text{N}_D \xrightarrow{\frac{85}{\text{K}}} \text{D}_{rd} \xrightarrow{\frac{138}{\text{K}}} \text{D}_{ho} \xrightarrow{\frac{280}{\text{K}}} \text{I}$$

$$2 \text{ K} \xrightarrow{\frac{61}{\text{K}}} \text{N}_D \xrightarrow{\frac{84}{\text{K}}} \text{D}_{rd} \xrightarrow{\frac{112}{\text{K}}} \text{D}_{hd} \xrightarrow{\frac{241}{\text{K}}} \text{I}$$

↓⁵⁶
D_{hd}

In order to obtain information about the Frank constants of these compounds, we employed the magnetic Frederiks-transition technique (see e.g. Ref. [16]). In the presence of a magnetic field \mathbf{B} the expression for the free energy density of a nematic material becomes:

$$F_{\text{total}} = f_d - 1/2 \mu_0^{-1} \Delta\chi (\mathbf{B} \cdot \mathbf{n})^2, \quad (2)$$

where f_d is the distortion free energy density (Eq. (1)). For certain experimental geometries the magnetic field counteracts the restoring force against director deformations described by f_d . Above a well defined threshold field the original director pattern becomes unstable and starts to deform. The amplitude of this deformation can be determined optically. For the geometry used in the experiments described below, the measurement of the field-induced director distortion yields information about $K_3/\Delta\chi$ and K_1/K_3 .

2. Experimental.

The synthesis of the truxene compounds used in the present experiments was carried out using a modification of the approach described by Destrade and Gasparoux [14]; details of our synthesis will be described elsewhere [17]. The transition temperatures, as observed by a polarizing microscope agree to within 1 K with the values reported by Destrade *et al.*

The nematic material was placed between two flat, parallel glass plates which were kept at a constant distance of some 30 μm by tungsten spacers. The exact

thickness of the sample cells was determined interferometrically. In order to insure uniform alignment of the nematic liquid crystals, the glass surfaces were coated with a thin poly-imide film (Dupont, PI2566) [18]. In this way we could make samples in which the director was everywhere perpendicular to the glass surface (« homeotropic » alignment). As the director in discotic materials is normal to the molecular plane, this implies that the plane of the molecules was, on average, parallel to the walls. Other coating materials which induce alignment have been reported in the literature [19]. We tried to use coatings of mellitic acid and 2,3,6,7,10,11-hexahydroxytriphenylene to induce homeotropic alignment. But we found that the resulting samples were of insufficient quality to perform Frederiks transition measurements. The same was true for the samples with homogeneous alignment, induced by glass plates coated with silicon oxides deposited at oblique incidence. Hence all measurements reported below were carried out on homeotropic samples. Measurements on homeotropic samples can only yield information about the Frank constants for splay and bend (K_1 and K_3). Actually, the information that is derived directly from the Frederiks transition data is: 1) the ratio K_1/K_3 and 2) the ratio $K_3/\Delta\chi$, where $\Delta\chi$ is the anisotropic part of the magnetic susceptibility of the nematic material. If $\Delta\chi$ were known, the absolute values of K_1 and K_3 could have been determined. However, we did not attempt to measure $\Delta\chi$.

Essential for the analysis of the Frederiks-transition data is the knowledge of the ordinary and extraordinary refractive indices of the materials studied. These measurements were carried out over the entire nematic range with a temperature controlled Abbe refractometer. The results have been collected in table I.

Studying the magnetic Frederiks transition in disc-like nematics requires special care for two reasons. In most rodlike nematics $\Delta\chi$ is positive and, as a consequence, the director tends to align parallel to an applied magnetic field. In contrast, for disc-like materials such as the ones studied in the present experiments, $\Delta\chi$ is negative and hence we would expect that all configurations with the director in a plane perpendicular to the magnetic field are equally favoured. The problem is that if we switch on a magnetic field parallel to the director, we cannot tell in advance in which direction the director will distort once the Frederiks transition is reached. To circumvent this problem we used the following approach. Initially, the normal to the plane of the sample was rotated to an angle of 45° with the axis of the electromagnet. Then the magnetic field was increased gradually to a strength well above the threshold value for the Frederiks transition. This caused the director to rotate, but in a well defined plane, namely the one defined by the magnetic field axis and the sample normal. Next, with the field still on, the sample was slowly rotated back to the position where sample normal and magnetic field

Table I. — Temperature dependence of the ordinary (n_o) and extraordinary (n_e) refractive index, the ratio of the splay and bend Frank constants K_1 and K_3 , and the ratio $K_3/\Delta\chi$ for hexa(decanyloxy)truxene (columns 1 through 5) and for hexa(tetradecanyloxy)truxene (columns 6 through 10). The reduced temperature is defined as T/T_{ND} , where T_{ND} is the transition temperature from the nematic phase to the (high temperature) columnar phase. The estimated error in the K_1/K_3 ratios is 10 % and 5 % for $K_3/\Delta\chi$.

hexa(decanyloxy) truxene					hexa(tetradecanyloxy) truxene				
T/T_{ND}	n_o	n_e	K_1/K_3	$K_3/\Delta\chi \times 10^6$ [N]	T/T_{ND}	n_o	n_e	K_1/K_3	$K_3/\Delta\chi \times 10^6$ [N]
0.999	1.531	1.454	1.01	4.43	0.999	1.511	1.459	0.89	4.81
0.997	1.531	1.454	0.96	4.60	0.996	1.512	1.459	1.05	4.67
0.996	1.532	1.454	1.05	4.42	0.990	1.513	1.459	1.25	4.41
0.993	1.532	1.454	1.15	4.23	0.990	1.513	1.459	1.35	4.20
0.989	1.533	1.454	1.14	3.88	0.987	1.513	1.459	1.28	4.28
0.982	1.535	1.454	1.38	4.23	0.984	1.514	1.459	1.00	4.71
0.982	1.535	1.454	1.23	4.01	0.984	1.514	1.459	1.08	4.88
0.976	1.536	1.454	1.49	3.86	0.982	1.515	1.459	1.38	4.44
0.975	1.536	1.455	1.36	3.64	0.979	1.515	1.459	0.90	5.04
0.970	1.537	1.455	1.48	3.98	0.973	1.516	1.459	1.15	4.63
0.967	1.538	1.455	1.48	4.42	0.970	1.517	1.459	1.26	4.53
0.967	1.538	1.455	1.22	4.06	0.965	1.518	1.459	1.52	4.27
0.962	1.539	1.455	1.29	4.07	0.962	1.518	1.459	1.57	4.38
0.960	1.539	1.455	1.67	3.55	0.956	1.520	1.460	1.62	4.07
0.953	1.541	1.456	1.76	4.11	0.951	1.521	1.460	1.54	4.11
0.953	1.541	1.456	1.55	3.96	0.945	1.522	1.461	1.45	4.46
0.950	1.542	1.456	1.61	3.72	0.939	1.523	1.461	1.78	3.99
0.948	1.542	1.456	2.01	3.85	0.934	1.524	1.462	1.83	3.97

were parallel. This procedure allowed us to prepare the magnetic distortion of the sample in a reproducible way (see Fig. 2). This is important because in the experiments one monitors the transmission of a polarized light beam through an analyser, where polarizer and analyser are mutually perpendicular and make an angle of $+45^\circ$ (-45°) with the plane defined by the director and the magnetic field axis. In the actual measurements, the magnetic field is decreased gradually (a typical field sweep takes about one hour). As the field strength is varied, the intensity of the transmitted light goes through a succession of maxima and minima. Below a critical field strength B_c , the homeotropic alignment is restored and the transmitted intensity drops to zero. From the positions of the maxima and minima, the ratios K_1/K_3 and $K_3/\Delta\chi$ can be determined using a non-linear least squares fit. However, for the present experiments it was found that, due to the high viscosities of the truxene derivatives [16], the relaxation of the director distortion was extremely sluggish. Consequently, the positions of the minima and maxima in transmitted intensity were measured as a function of scanning speed. In all cases studied, we found that positions of the minima and maxima depended linearly on the scanning speed. A typical example is shown in figure 3. Estimates for the positions of the extrema at zero scanning speed were obtained

from the intercepts of the straight lines that were fitted to the data points such as shown in figure 3. These extrapolated values of the magnetic field strength were then used to determine the ratio K_1/K_3 and $K_3/\Delta\chi$ by non-linear least squares fitting. In the experiments reported here we found no evidence for a break-up or rotation of the aligned domain after it had been prepared. All measurements of the Frederiks transitions were carried out using a temperature controlled cell. In this cell the temperature could be held constant to better than 0.1 K, although the estimated error in the absolute temperature readings was somewhat larger. The locations of all phase transitions were checked independently using a Mettler FP5 hot stage.

3. Results and discussion.

Figures 4 and 5 show the results for the ratios K_1/K_3 of the decanyloxy and tetradecanyloxy derivatives of truxene, as a function of temperature. The corresponding numbers have been collected in table I. We have expressed the temperature in reduced units T/T_{ND} , where T_{ND} is the transition temperature from the nematic phase to the high-temperature columnar phase: $T_{ND} = 354.5$ K for the decanyloxy derivative and $T_{ND} = 353.5$ K for the tetradecanyloxy derivative. The values of T_{ND} given here were measured after

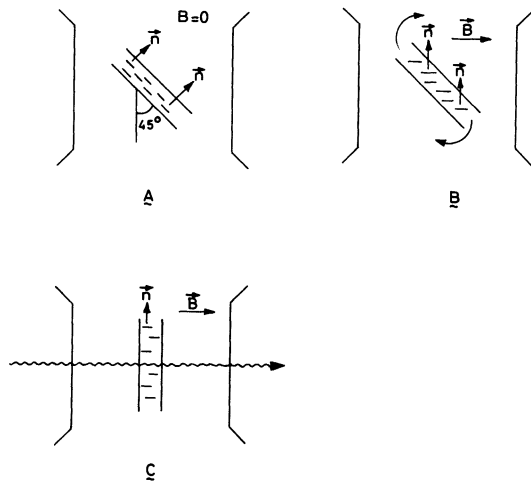


Fig. 2. — Schematic drawing of the preparation of a single-domain magnetic distortion in an initially homeotropic sample. A : With the magnetic field off, the homeotropic sample is rotated such that the director makes a 45° angle with the axis of the electromagnet. B : Next the magnetic field is switched on. The director in the bulk of the sample rotates in the plane spanned by the sample normal and the magnetic field. At sufficiently high field strengths the director makes an angle of almost 90° with the field axis. With the field on, the sample is now slowly rotated back such that the sample normal is parallel to the magnetic field. During this rotation the director remains perpendicular to both the rotation axis and the magnetic field. C : Once the sample normal is parallel to the magnetic field, the sample is illuminated by a laser beam directed along the sample normal. The polarization of the laser light makes a 45° angle with the plane spanned by the magnetic field and the nematic director. In this configuration the Frederiks transition is measured.

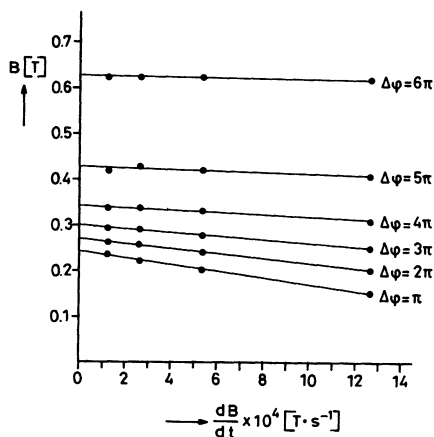


Fig. 3. — Typical example of the dependence on scanning speed of the magnetic field strengths corresponding to the minima and maxima of the optical interference pattern. The data shown were measured for hexa(decanyloxy)truxene at $T/T_{ND} = 0.999$. Note that over the range of scanning speeds which we employed the relation between the positions of the extrema and the rate of change of the field strength is linear. Estimates of the positions at zero scanning speed were obtained by linear extrapolation.

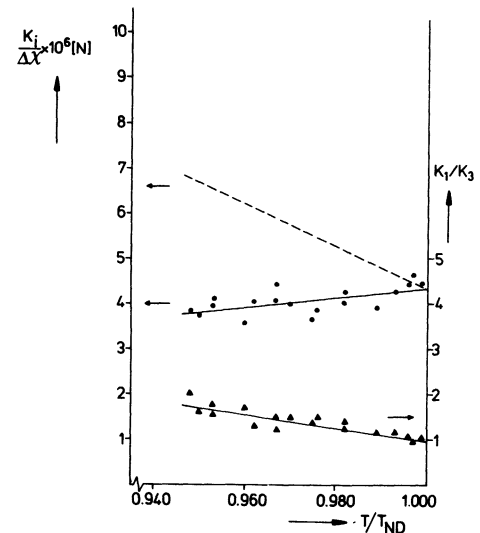


Fig. 4. — Temperature dependence of the ratio $K_3/\Delta\chi$ (closed circles) and K_1/K_3 (closed triangles) in the nematic regime of hexa(decanyloxy)truxene. The temperature is referred to the high-temperature nematic-to-columnar transition temperature, $T_{ND} = 353.5$ K. The drawn lines are linear least-squares fits to the experimental data. Using these fits, the temperature dependence of $K_1/\Delta\chi$ could be estimated (dashed line).

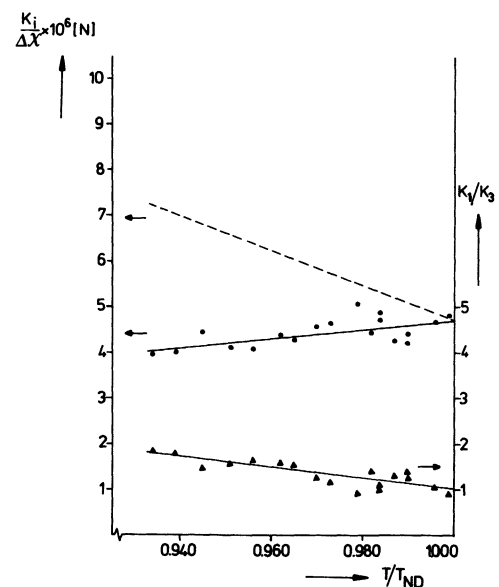


Fig. 5. — Temperature dependence of the ratio $K_3/\Delta\chi$ (closed circles) and K_1/K_3 (closed triangles) in the nematic regime of hexa(tetradecanyloxy)truxene. The temperature is referred to the high-temperature nematic-to-columnar transition temperature, $T_{ND} = 354.5$ K. The drawn lines are linear least-squares fits to the experimental data. Using these fits, the temperature dependence of $K_1/\Delta\chi$ could be estimated (dashed line).

preparing the samples for the Frederiks transition measurements. Note that these transition temperatures are slightly lower than those observed directly after the compounds were synthesised. During the course of an experiment, which typically took about 2 weeks, T_{ND} tended to decrease further by 1 to 2 degrees. This suggests that even at these rather low temperatures some chemical decomposition of the truxenes took place, even though the samples were sealed. The lower limit of the temperature range is determined by the point where the compounds either freeze or form a reentrant columnar phase. We found no dependence on time of the temperature of the lower phase transition. From figures 4 and 5 it is clear that for both compounds K_1 is larger than K_3 by up to a factor of 2. This ratio is seen to approach 1 as the transition to the high temperature columnar phase is approached. The mean-field theory of Sokalski and Ruijgrok [1] does predict that K_1 would be larger than K_3 for disc-like nematics. But the observation that both Frank constants become equal at the transition to the high-temperature columnar phase is not explained by this theory. As we do not know $\Delta\chi$ we cannot give the values for K_1 and K_3 . However, we can estimate $\Delta\chi$ assuming that the anisotropy in the magnetic susceptibility is primarily due to the aromatic rings [16]. This simple rule yields $\Delta\chi = 3.0 \times 10^{-9} \text{ m}^3/\text{mole}$. If, in addition, we assume a value of 0.7 for the nematic order parameter S and a value of 0.8 g/cm^3 for the density, we arrive at the following order-of-magnitude estimates for K_1 and K_3 : $K \approx 5 \times 10^{-12} \text{ Newton}$. This value is comparable to what is commonly found in rodlike nematics. We note that measurements of the electric Frederiks transition in the nematic phase of another disc-like molecule, viz. 2, 3, 6, 7, 10, 11-hexa(4-heptyloxybenzoyloxy)triphenylene [20], yields a comparable value for K_1 ($K_1 = 3.5 \times 10^{-12} \text{ N}$). If both $K_1/\Delta\chi$ and $K_3/\Delta\chi$ are plotted individually (see Figs. 2 and 3), we see that the former quantity decreases with increasing

temperature while the behaviour of the latter is opposite. It is reasonable to assume that the variation with temperature of $K_3/\Delta\chi$ is primarily due to the temperature dependence of $\Delta\chi$, because the relative increase in $K_3/\Delta\chi$ is almost equal to the relative decrease in the anisotropy of the refractive index (see Table I). It should be recalled that the variation with temperature of both $\Delta\chi$ and Δn is dominated by the same effect, viz. the temperature dependence of the nematic order parameter. The different temperature dependence of K_1 and K_3 is not predicted by the mean-field theory of reference [1]. We should add however that this theory does not consider the possibility of a transition to a columnar phase. A Landau theory which does take pretransitional effects due to fluctuations of a columnar order parameter into account has been proposed by Swift and Andereck [2]. This theory predicts that K_1 would be enhanced due to fluctuations, while K_3 would not exhibit pretransitional effects. If the transition nematic-to-columnar is an (almost) second order phase transformation, the theory of reference [2] predicts that the ratio K_1/K_3 would in fact diverge at the transition. We find no evidence for such behaviour, neither in the absolute values of the Frank constants nor in their ratio. In fact, the trend which we observe seems to be opposite to these predictions. To our knowledge a theoretical explanation for this behaviour is, as yet, lacking.

Acknowledgments.

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