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Dynamics of the Frederiks transition in nematics consisting of disc-like molecules

Thermal dependence of a bend viscosity coefficient

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We report measurements of the dynamics of the magnetic Frederiks transition in nematics consisting of disc-like molecules. In this paper the results are presented for three 2, 3, 6, 7, 10, 11-hexakis(*p*-alkoxybenzoyloxy)triphenylenes, which exhibit a normal nematic phase, and for three 2, 3, 7, 8, 12, 13-hexa(alkanoyloxy)truxenes, which exhibit an inverted nematic phase. We find that the thermal dependence of a bend viscosity coefficient (γ_1^*) can be accurately described by the expression, $\gamma_1^* \sim S^2 \exp(E_a/kT)$. The absolute value of γ_1^* is found to be higher (by a factor of 10–100) than is commonly encountered in nematics consisting of rod-like molecules.

1. Introduction

Many of the interesting physical properties of nematic liquid crystals can be understood in terms of the continuum theory derived by Frank [1] on the basis of a phenomenological theory of Zocher [2] and Oseen [3]. From this continuum theory follows an expression for the free energy density (f_d) due to deformations of a uniaxially aligned nematic material (see, for example, [4]):

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

where $\mathbf{n}$ is the local axis of uniaxial symmetry, usually referred to as the director, and K_1, K_2 and K_3 are the curvature elastic constants associated with splay, twist and bend distortions, respectively. In a previous study the magnetic Frederiks transition technique was used to obtain information about these elastic constants for some liquid crystals consisting of disc-like molecules [5]. With this technique the measurements must be performed at or very close to the equilibrium state, so that the applied magnetic force is at all times exactly balanced by the restoring force against director deformations. As was reported in [5], due to the sluggish relaxation of the director distortion, it was found necessary to measure at different finite scanning speeds of the applied magnetic field and extrapolate to zero scanning speed in order to obtain the equilibrium value of the response to the applied magnetic field. In the present paper this relaxation of the director distortion is studied quantitatively.

The continuum theory proposed by Ericksen [6] and Leslie [7] gives a theoretical description of the relaxation behaviour in an (incompressible) nematic liquid. This hydrodynamical theory contains six viscosity coefficients, which are commonly

denoted by $\alpha_1, \ldots, \alpha_6$. The number of independent coefficients reduces to five due to an Onsager relation derived by Parodi [8]

$$\alpha_6 = \alpha_2 + \alpha_3 + \alpha_5.$$

Various methods can be used to measure viscosity coefficients in the nematic phase, for instance shear flow in a magnetic field, light scattering and ultrasonic shear waves [9–11].

Brochard *et al.* [12] and Pieranski *et al.* [13] have shown that information about the viscous behaviour of a nematic material can also be obtained by studying the response of the distortion of a well-oriented nematic liquid crystal film to a sudden change in the applied magnetic field, in the vicinity of the Frederiks transition. These authors derived the following relation between an effective viscosity constant γ_1^* and a relaxation time τ when deformations of a homeotropically aligned nematic material are studied (bend deformation):

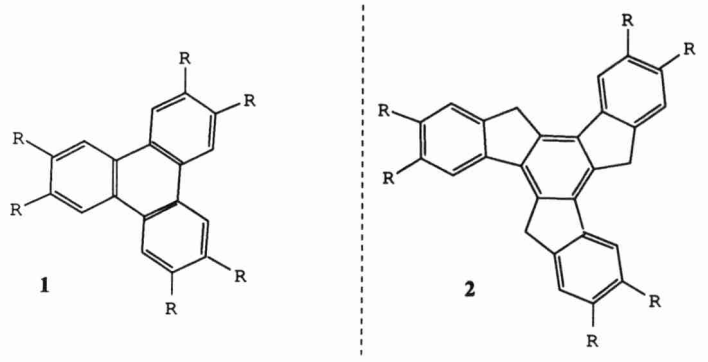
$$\gamma_1^* = 2\tau\Delta\chi B_c^2, \tag{2}$$

where τ is the measured relaxation time of the director distortion when a magnetic field (exceeding the Frederiks critical field value) is suddenly turned off, $\Delta\chi$ is the anisotropic part of the magnetic susceptibility and B_c is the Frederiks critical field value. The value of the bend viscosity γ_1^* is smaller than the kinematic value of the twist viscosity γ_1 due to backflow motion, which causes a decrease in the viscosity [13]. The effect of the backflow motion on the viscosity depends on the degree of distortion, decreasing when the distortions become smaller, but even in the limit of very small distortions γ_1^* remains smaller than γ_1;

$$\gamma_1^* = \gamma_1 - \alpha_2^2[3(\alpha_4 + \alpha_5 - \alpha_2)]^{-1}, \tag{3}$$

where $\gamma_1 = \alpha_3 - \alpha_2$ (see [13]). However, for small magnetic fields $B(B/B_c < 2{\cdot}5)$, the relative variation of γ_1^* with B is negligible and the dynamic behaviour should be rather similar to γ_1. For more detailed information about the relation between γ_1^* and γ_1 and the relation to the visocisty constants $\alpha_1, \ldots, \alpha_6$ we refer to [13] and [9].

The temperature dependence of γ_1 is described differently by different authors [14–20]. Imura and Okano [15] have given an extensive theoretical discussion of the temperature dependence of the viscosity coefficients leading to $\gamma_1 \sim \alpha S + \beta S^2$, where S is the nematic order parameter. Experimentally, the Arrhenius type of dependence (*vis.* $\gamma_1 \sim S\exp(E_A/kT)$) is well established for nematics consisting of rod-like molecules in the domain where S saturates [9, 16]. However, the temperature dependence of γ_1 for *o*-hydroxy-*p*-methoxybenzylidene-*p'*-butylaniline (OHMBBA) seems to be best described by $\gamma_1 \sim \exp(\alpha S/kT)$ [17], where α was found to be 0·22 eV. Molecular considerations have led Martins [18] to propose the form $\gamma_1 \sim S^2\exp(\xi S/kT)$, where ξ is given in terms of the Maier–Saupe molecular field theory [21]. In a more recent paper Diogo and Martins [19] modified their equation by a free volume term $\exp[AS^2/(T - T_0)]$. Summarizing these different equations for the thermal dependence of γ_1, it can be stated that an expression of the type $\gamma_1 = f(S)g(T)$ can be used, where $f(S)$ is a function of the degree of order of the type $f(S) = S$ or S^2 and $g(T)$ is mainly an exponential function of T with little, if any, dependence on S [20]. The temperature dependence of γ_1^* is expected to show a similar temperature dependence to γ_1 (see equation (3)), since in the limit of small deformations the ratio γ_1^*/γ_1 is not likely to differ much from unity [13].



(*a*) R = $OC(O)C_6H_4OC_6H_{13}$ (D $\overset{184°C}{\longleftarrow}$ N_D $\overset{274°C}{\longrightarrow}$ I)
(*b*) R = $OC(O)C_6H_4OC_7H_{15}$ (D $\overset{164°C}{\longleftarrow}$ N_D $\overset{255°C}{\longrightarrow}$ I)
(*c*) R = $OC(O)C_6H_4OC_{11}H_{23}$ (D $\overset{191°C}{\longleftarrow}$ N_D $\overset{199°C}{\longrightarrow}$ I)

(*a*) R = OC_9H_{19} (K $\overset{65°C}{\longleftarrow}$ N_D $\overset{84°C}{\longrightarrow}$ D′)
(*b*) R = $OC_{13}H_{27}$ (D $\overset{60°C}{\longleftarrow}$ N_D $\overset{84°C}{\longrightarrow}$ D′)
(*c*) R = $OC_{17}H_{35}$ (D $\overset{70°C}{\longleftarrow}$ N_D $\overset{82°C}{\longrightarrow}$ I)

Figure 1. Structure and nematic region of the triphenylene and the truxene derivatives studied in this paper. **1a**, 2,3,6,7,10,11-hexakis(*p*-hexyloxybenzoyloxy)triphenylene; **1b**, 2,3,6,7,10,11-hexakis(*p*-heptyloxybenzoyloxy)triphenylene; **1c**, 2,3,6,7,10,11-hexakis(*p*-undecyloxybenzoyloxy)triphenylene; **2a**, 2,3,7,8,12,13-hexa(decanoyloxy)-truxene; **2b**, 2,3,7,8,12,13-hexa(tetradecanoyloxy)truxene; and **2c**, 2,3,7,8,12,13-hexa(octadecanoyloxy)truxene. I indicates the isotropic liquid phase, N_D the nematic phase consisting of disc-like molecules and D and D′ indicate columnar phases.

2. Experimental

Information about the viscous behaviour of the nematic materials studied in this paper was obtained by studying the response to a sudden change in the applied magnetic field. We studied the relaxation of the director distortion when a magnetic field, which is stronger than the threshold field of the Frederiks transition, is suddenly turned off. The compounds studied in this paper are three triphenylene derivatives, which exhibit a normal phase sequence (*vis.* 2,3,6,7,10,11-hexakis(*p*-hexyloxybenzoyloxy)triphenylene (**1a**), 2,3,6,7,10,11-hexakis(*p*-heptyloxybenzoyloxy)triphenylene (**1b**) and 2,3,6,7,10,11-hexakis(*p*-undecyloxybenzoyloxy)triphenylene (**1c**)), and three truxene derivatives, which exhibit an inverted nematic phase (*viz.* 2,3,7,8,12,13-hexa(decanoyloxy)truxene (**2a**), 2,3,7,8,12,13-hexa(tetradecanoyloxy)truxene (**2b**) and 2,3,7,8,12,13-hexa(octadecanoyloxy)truxene (**2c**)) [22] (figure 1). Homeotropically aligned samples were prepared by placing the nematic material between two poly-imide coated (Dupont, P12566) [23] glass slides which were kept at a constant distance of some 50 μm by tungsten spacers [5]. The exact thickness of the sample cells was determined interferometrically. A single domain magnetic distortion of the initially homeotropic sample was prepared as described in [5].

The relaxation of the director distortion was followed optically. In the experiments the transmission of a polarized light beam through an analyser is monitored, where polarizer and analyser are mutually perpendicular and make an angle of $+45$ (-45) with the plane defined by the director and the direction of the magnetic field (see figure 2). The transmitted light intensity goes through a succession of minima and maxima as the field strength is varied, due to interference between the ordinary (perpendicular to the director) and the extraordinary ray (in the plane defined by the director and the direction of the magnetic field). A typical example of the transmitted light intensity as a function of time after the magnetic field has been removed is given in figure 3.

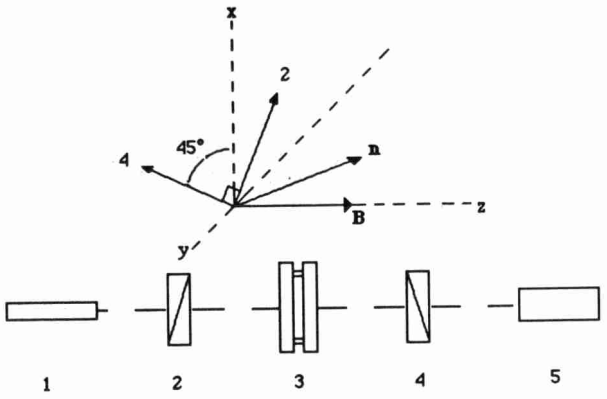


Figure 2. Experimental set-up to determine the relaxation of the director distortion in the homeotropic configuration. (1) He–Ne laser; (2) polarizer; (3) sample cell; (4) analyser; (5) photomultiplier tube. x, y and z indicate the axes of a right handed cartesian coordinate system, where the z axis is chosen parallel to the direction of the magnetic field.

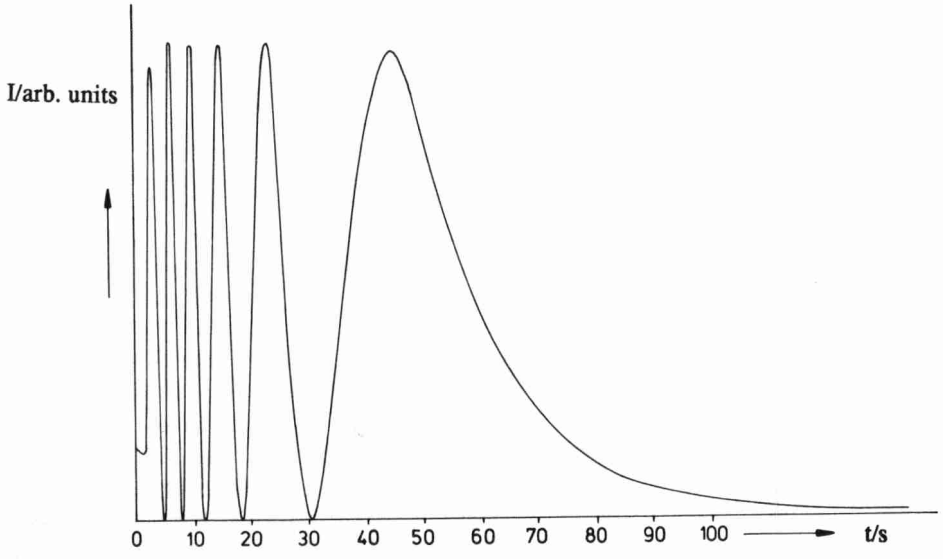


Figure 3. Typical example of the transmitted light intensity as a function of time after the magnetic field has been suddenly turned off. The curve shown was measured for compound **1b** at 198°C.

The transmitted light intensity (I) is related to the phase difference ($\Delta\phi$) between the ordinary and the extraordinary ray by the relation

$$I = I_{\max} \sin^2(\Delta\phi/2).$$

According to Pieranski *et al.* [13] this phase difference $\Delta\phi$ is proportional to the director distortion and should decrease exponentially with time (t). If we plot $\ln \Delta\phi$ against time a linear behaviour is indeed observed (except in the first part of the plot), and the relaxation time τ can be determined from the inverse of the slope. In figure 4 an example of such a plot is represented. The initial deviation from the straight

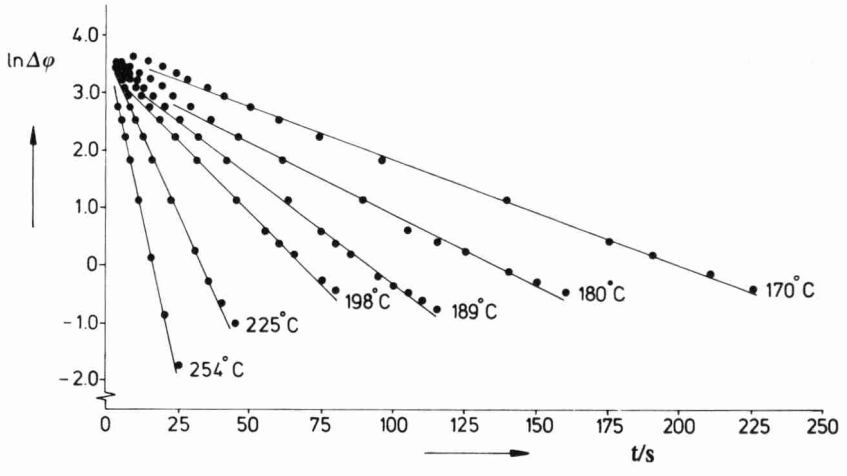


Figure 4. Typical example of $\ln \Delta\phi$ versus time curves at different temperatures. $\Delta\phi$ is the phase difference between the ordinary and the extraordinary ray. The data points shown were derived for compound **1b** from curves such as those presented in figure 3.

line can have several causes, such as backflow, non-equilibrium effects and the non-proportionality of Δn with the director distortion at larger deformations. However, we did not attempt to study these effects in more detail.

All measurements 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 were somewhat larger. The locations of all phase transitions were checked independently using a Mettler FP5 in combination with a Mettler FP52 hot stage. In order to prevent oxidation all measurements were carried out under a nitrogen atmosphere.

3. Results and discussion

From equation (2) and the value of the Frederiks critical field B_c ($\equiv \pi/d(K_3/\Delta\chi)^{-1/2}$) it follows that

$$\gamma_1^*/K_3 = \tau 2\pi^2/d^2 \tag{4}$$

Figures 5 and 6 show the results of this ratio γ_1^*/K_3 for the triphenylene derivatives **1a–c** (see figure 5) and the truxene derivatives **2a–c** (see figure 6) as a function of temperature. The temperature is expressed in reduced units T/T_{NI} or T/T_{ND}, where T_{NI} and T_{ND} are the transition temperatures from the nematic phase to the isotropic liquid and to the columnar phase, respectively. Using the values for $K_3/\Delta\chi$ from our previous experiments the ratio $\gamma_1^*/\Delta\chi$ can be calculated as a function of temperature [5, 24].

In order to check if the temperature dependence of γ_1^* for the investigated disc-like nematogens can be described by a similar functional dependence as found for γ_1, we plotted $\ln(\gamma_1^*/|\Delta\chi|)$ and $\ln[\gamma_1^*/(|\Delta\chi \cdot \Delta n|)]$ versus $1/T$. Assuming that the density ϱ is approximately constant, the replacement of S by $|\Delta\chi|$ should not change the relationship since $|\Delta\chi|$ is itself proportional to S. Instead of replacing S by $|\Delta\chi|$, S can be replaced by $|\Delta n|$ since the temperature dependence of both $|\Delta\chi|$ and $|\Delta n|$ is determined mainly by the temperature dependence of the nematic order parameter S [9]. Replacement of S by $|\Delta n|$ introduces a somewhat greater error, but due to the

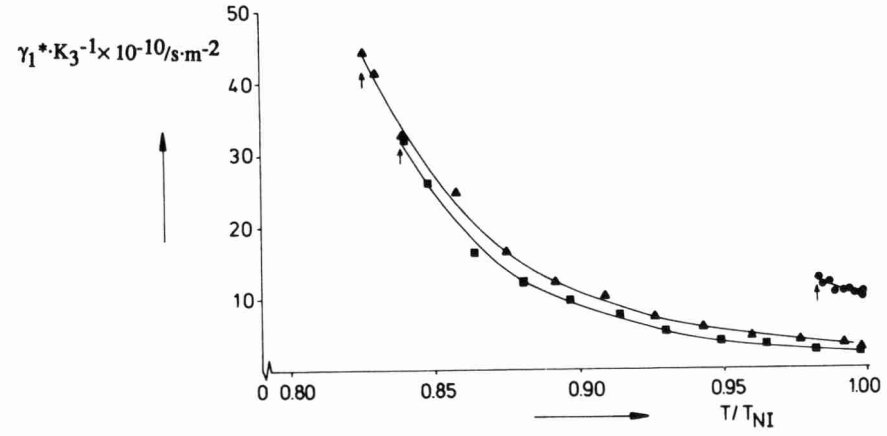


Figure 5. Temperature dependence of the ratio γ_1^*/K_3 in the nematic regime of the triphenylene derivatives **1a–c**. The temperature is expressed in reduced units T/T_{NI}, where T_{NI} is the transition temperature from the nematic to the isotropic phase. **1a**, T_{NI} = 545 K (squares); **1b**, T_{NI} = 528 K (triangles); **1c**, T_{NI} = 472 K (circles). The lower limit of the nematic regime is indicated by arrows.

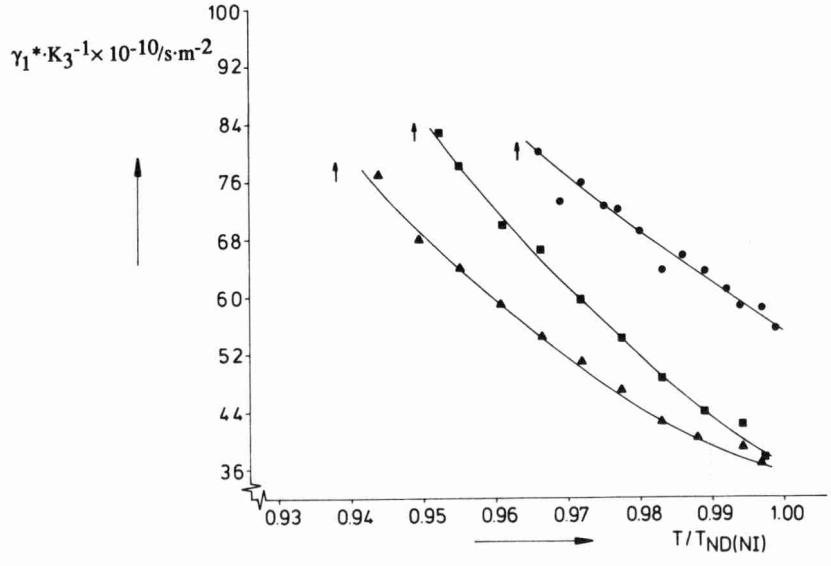


Figure 6. Temperature dependence of the ratio γ_1^*/K_3 in the nematic regime of the truxene derivatives **2a–c**. The temperature is expressed in reduced units T/T_{ND} for compounds **2a** and **2b** and T/T_{NI} for **2c**. T_{ND} indicates the transition temperature from nematic to columnar phase, whereas T_{NI} indicates the transition temperature from nematic to isotropic phase. **2a**, T_{ND} = 357 K (squares); **2b**, T_{ND} = 356 K (triangles), **2c**, T_{NI} = 355 K (circles). The lower limit of the nematic regime is indicated by arrows.

absence of $|\Delta\chi|$ measurements over the entire nematic range we had to use the anisotropy of the refractive index [5, 22] to estimate the temperature dependence of S. A more accurate estimate of S from refractive index measurements using the Vuk's equation [25] could not be used, because for the triphenylene derivatives we only know the value of $|\Delta n|$ [22]. Figures 7 and 8 represent plots of $\ln(\gamma_1^*/|\Delta\chi|)$ and

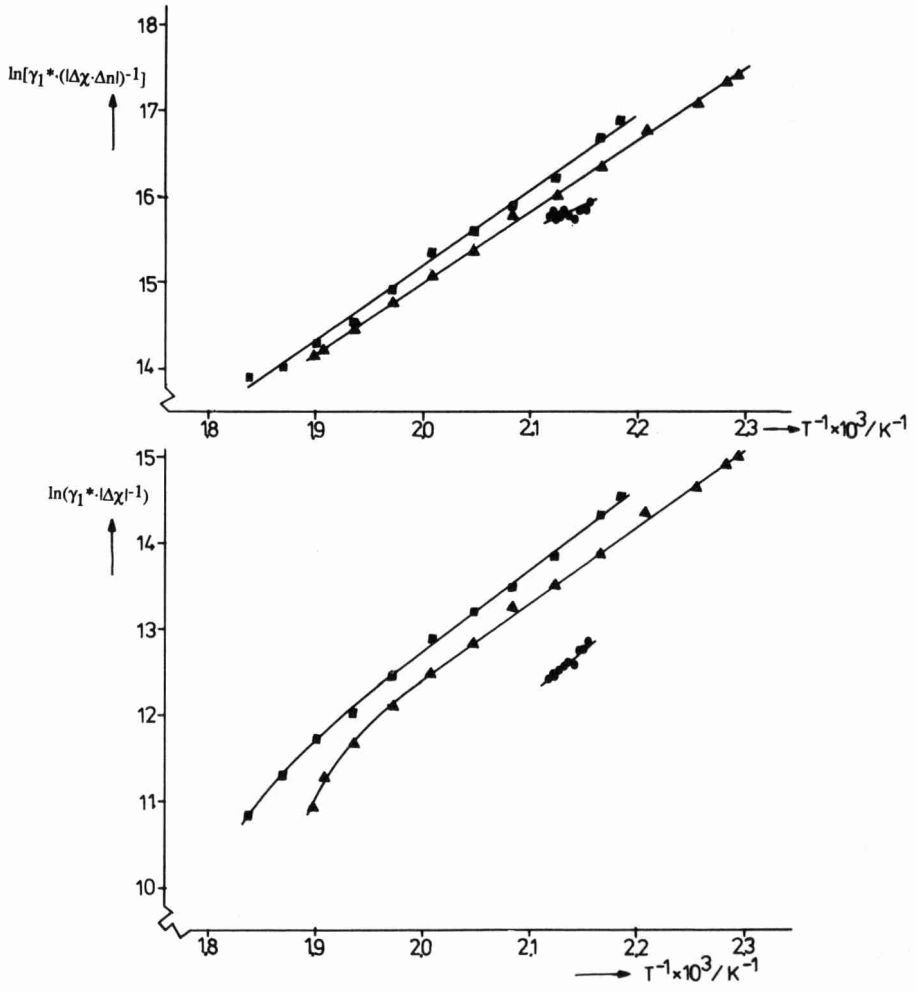


Figure 7. Temperature dependence of $\ln(\gamma_1^*/|\Delta\chi|)$ and $\ln[\gamma_1^*/(|\Delta\chi \cdot \Delta n|)]$ in the nematic regime of the triphenylene derivatives **1a–c**. **1a**, squares; **1b**, triangles; **1c**, circles.

$\ln(\gamma_1^*/|\Delta\chi \cdot \Delta n|)$ versus the inverse of the temperature for the triphenylene derivatives **1a–c** and the truxene derivatives **2a–c**, respectively. The corresponding data plotted in figures 5 to 8 have been collected in tables 1 to 6. These tables comprising seven pages have been deposited with the British Library Lending Division; copies of this Supplementary Publication may be obtained from the British Library by using the procedure described at the end of this issue and quoting the number SUP16507. The values of $K_3/|\Delta\chi|$ given in these tables are obtained from a quadratic fit to the data points presented in [5] and [24]. Figures 7 and 8 show a linear behaviour for all derivatives studied in this paper in the region where S saturates, but a departure from the linear behaviour is observed in the region close to the nematic-to-isotropic transition temperature for the triphenylene compounds **1a** and **1b** using the expression

$$\gamma_1^*/|\Delta\chi| \sim \exp(E_A/kT).$$

This is the region where S varies strongly and it seems likely that in this region the dependence of γ_1^* on S is more complicated. A good linear behaviour over the entire

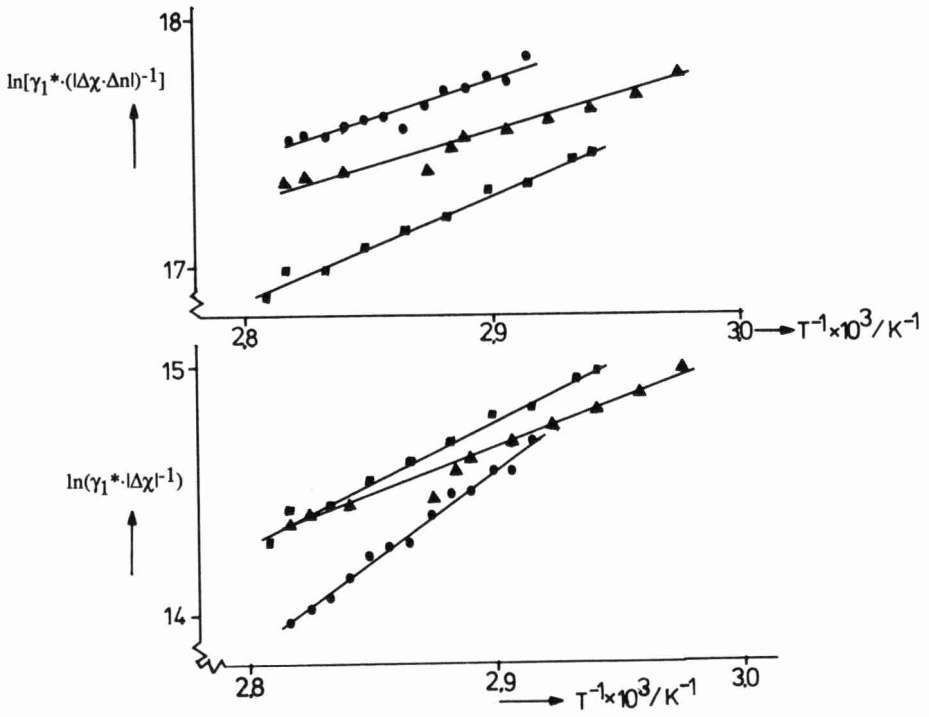


Figure 8. Temperature dependence of $\ln(\gamma_1^*/|\Delta\chi|)$ and $\ln[\gamma_1^*/(|\Delta\chi \cdot \Delta n|)]$ in the nematic regime of the truxene derivatives **2a–c**. **2a**, squares; **2b**, triangles; **2c**, circles.

nematic region is observed using the expression

$$\gamma_1^*/(|\Delta\chi \cdot \Delta n|) \sim \exp(E_A/kT),$$

showing that the temperature dependence of γ_1^* is accurately described by the relation

$$\gamma_1^* \sim S^2 \exp(E_A/kT).$$

Since deviations from the obtained linear behaviour are within experimental error we conclude that the exponential function $g(T)$ has little, if any, dependence on S. From the slope of the plot $\ln[\gamma_1^*/(|\Delta\chi \cdot \Delta n|)]$ versus $1/T$ an effective activation energy E_A can be determined; the results are presented in table 7.

The activation energies of these disc-like mesogens are comparable to values found for rod-like mesogens. For instance, for *N*-(4-methoxybenzylidene)-4′-butylaniline

Table 7. Activation energies of the disc-like mesogens studied in this paper. The estimated error in the activation energies is 10 per cent.

Compound	E_a/eV
1a	0·77
1b	0·71
1c	0·50
2a	0·36
2b	0·24
2c	0·28

(MBBA), E_a is 0·5 eV [9]. The active energies of the tripenylene derivatives are higher than those of the truxene derivatives. Although, at present, we can offer no explanation for this behaviour, we note that there appears to be no systematic dependence of the effective activation energy on the length of the alkyl chains within one group of compounds. Furthermore we note that the triphenylene derivatives exhibit a normal nematic phase, whereas the truxene derivatives exhibit an inverted nematic phase [22].

Using the values for $\chi_{\text{isotropic}} - \chi_\perp$ as reported by Levelut *et al*, [26] ($\Delta\chi = \chi_\parallel - \chi_\perp = 3(\chi_{\text{isotropic}} - \chi_\perp)$) an estimate of the absolute value of the bend viscosity constant γ_1* can be obtained. For compounds **1a** and **1c** a value of $\Delta\chi^m$ of $-0{\cdot}39 \times 10^{-7}$ and $-0{\cdot}21 \times 10^{-7}$ uem CGS g^{-1}, respectively, was reported close to T_{NI}. Assuming a value for $\varrho \approx 0{\cdot}8$ g/cm^3 and after converting the data to SI units, this leads to $\Delta\chi = -3{\cdot}9 \times 10^{-7}$ and $-2{\cdot}1 \times 10^{-7}$ for compounds **1a** and **1c**, respectively. The absolute value of γ_1* close to T_{NI} is then 0·02 kgm^{-1}s^{-1} for **1a** and 0·05 kgm^{-1}s^{-1} for **1c**. This value increases rapidly on cooling. For **1a** a value of $\gamma_1^* \approx 0{\cdot}1$ kgm^{-1}s^{-1} is reached at approximately 254°C (the lower limit of the $\Delta\chi$ measurements reported in [26]). From measurements of the electric Frederiks transition in the nematic phase of **1b** a value for $\gamma_1 \approx 3{\cdot}5$ P (= 0·35 kgm^{-1}s^{-1}) is reported at 230°C by Mourey *et al.* [27], which is somewhat higher than is found in the present experiments, but is of the same order of magnitude. However, we calculated a value for $\gamma_1 \approx 0{\cdot}11$ kgm^{-1}s^{-1} for **1b** at 230°C using the reported values of Mourey *et al.* for the relaxation time, thickness of the sample and the splay elastic constant K_1, which is in good agreement with the present experiments.

We cannot give the absolute values of γ_1* for the truxene derivatives as we do not know $\Delta\chi$. An estimate of $\Delta\chi$ can be obtained by assuming that the anisotropy in the magnetic susceptibility is due primarily to the aromatic rings [9]. This simple rule yields $\Delta\chi^a = -3{\cdot}0 \times 10^{-9}$ m^3/mol for a compound with an aromatic core consisting of four benzene rings (*vis.* the truxene core in figure 1), where $\Delta\chi^a$ is the molecular anisotropy of the magnetic susceptibility times N_A (the Avogadro constant). If, in addition, a value of 0·8 g/cm^3 is assumed for the density of the nematic material and a value of 0·7 for the nematic order parameter S, we arrive at the following order of magnitude estimate for $\Delta\chi$ of about -10^{-6}. The order of magnitude of γ_1* for the truxene derivatives is then approximately 2 kgm^{-1}s^{-1}. Comparing the values of γ_1* obtained for these nematic phases consisting of disc-like molecules with data of γ_1 obtained for nematics consisting of rod-like molecules (see, for example, [9]) we find that γ_1* of the disc-like molecules is significantly larger (by a factor 10–100) than γ_1 of rod-like mesogens. Only close to T_{NI} does the viscosity of the triphenylene compounds **1a** and **1b** ($T > 250$°C!) decrease to values comparable to their rod-like analogues.

4. Conclusions

Measurements of the dynamics of the magnetic Frederiks transition yields information about the bend viscosity coefficient γ_1*. The absolute value of this viscosity coefficient is significantly higher (by a factor 10–100) in the nematic phase consisting of the studied disc-like mesogens than is commonly encountered in nematics consisting of rod-like molecules. The temperature dependence of γ_1* is well fitted by the expression $\gamma_1^* \sim S^2 \exp(E_a/kT)$. The activation energies calculated for the disc-like mesogens have the same order of magnitude as found for rod-like mesogens.

References

[1] Frank, F. C., 1958, *Disc. Faraday Soc.*, **25**, 19.
[2] Zocher, H., 1933, *Trans. Faraday Soc.*, **29**, 945.
[3] Oseen, C. W., 1933, *Trans. Faraday Soc.*, **29**, 883.
[4] de Gennes, P. G., 1974, *The Physics of Liquid Crystals* (Clarendon Press).
[5] Warmerdam, T. W., Frenkel, D., and Zijlstra, R. J. J., 1987, *J. Phys., Paris*, **48**, 319.
[6] (*a*) Ericksen, J. L., 1960, *Arch. ration. Mech. Analysis*, **4**, 213; 1962, *Ibid.*, **9**, 371. (*b*) Ericksen, J. L., 1961, *Trans. Soc. Rheol.*, **5**, 23.
[7] Leslie, F. M., 1966, *Q. Jl mech. appl. Math.*, **19**, 357; 1968, *Ibid.*, **28**, 265.
[8] Parodi, O., 1970, *J. Phys., Paris*, **31**, 581.
[9] de Jeu, W. H., 1980, *Physical Properties of Liquid Crystalline Materials* (Gordon & Breach).
[10] O'Neill, G. J., 1986, *Liq. Crystals*, **1**, 271.
[11] Van der Meulen, J. P., and Zijlstra, R. J. J., 1984, *J. Phys., Paris*, **45**, 1347.
[12] Brochard, F., Pieranski, P., and Guyon, E., 1972, *Phys. Rev. Lett.*, **28**, 1681.
[13] Pieranski, P., Brochard, F., and Guyon, E., 1973, *J. Phys., Paris*, **34**, 35.
[14] Helfrich, W., 1972, *J. chem. Phys.*, **56**, 3187.
[15] Imura, H., and Okano, K., 1972, *Jap. J. appl. Phys.*, **11**, 1440.
[16] Prost, J., Sigaud, G., and Regaya, B., 1976, *J. Phys., Paris, Lett.*, **37**, 341.
[17] Van der Meulen, J. P., and Zijlstra, R. J. J., 1982, *J. Phys., Paris*, **43**, 411.
[18] Martins, A. F., 1974, *Port. Phys.*, **9**, 1.
[19] Diogo, A. C., and Martins, A. F., 1982, *J. Phys., Paris*, **43**, 779.
[20] Kneppe, H., Schneider, F., and Sharma, N. K., 1982, *J. chem. Phys.*, **77**, 3203.
[21] Maier, W., and Saupe, A., 1958, *Z. Naturf.* (*a*), **13**, 564; 1959, *Ibid.*, **14**, 882; 1960, *Ibid.*, **15**, 287.
[22] Destrade, C., Foucher, P., Gasparoux, H., Nguyen Huu Tinh, Levelut, A. M., and Malthete, J., 1984, *Molec. Crystals liq. Crystals*, **106**, 121.
[23] van Sprang, H. A., 1983, *J. Phys., Paris*, **44**, 421.
[24] Warmerdam, T. W., Frenkel, D., and Zijlstra, R. J. J., 1988, *Liq. Crystals*, **3**, 369.
[25] Vuks, M. F., 1966, *Opt. Spectrosc.*, **20**, 644.
[26] Levelut, A. M., Hardouin, F., Gasparoux, H., Destrade, C., and Nguyen Huu Tinh, 1981, *J. Phys., Paris*, **42**, 147.
[27] Mourey, B., Perbet, J. N., Hareng, M., and Le Berre, S., 1982, *Molec. Crystals liq. Crystals*, **42**, 193.