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Structural and dynamic properties of a new type of discotic nematic compounds†

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Thermodynamic, structural and dynamical properties of a new type of discotic compounds, a hydrocarbon without any heteroatoms, displaying a nematic discotic phase have been investigated by means of X-ray diffraction, electro-optical relaxation, and calorimetric studies. Of particular interest are the strength of the first order nematic–isotropic phase transition and the nature of the orientational fluctuations in the isotropic phase. The short range positional order was found to be biaxial in both the isotropic and the nematic phase. The isotropic phase displays strong pretransitional effects originating from orientational fluctuations in the neighbourhood of the transition to the nematic phase. The character of these pretransitional effects differs from that found for calamitic systems in that the number of correlated molecules g_2 is extremely large, of the order of 600 at the clearing temperature and the electro-optical relaxation time is very large, caused by the large value of g_2.

1. Introduction

This paper is concerned with the characterization of the nematic–isotropic phase transition, including its strength as a first order transition, and with the pretransitional effects in a new type of discotic compound which is a hydrocarbon without any heteroatoms [1, 2]. The majority of studies concerned, so far, with this topic were performed on calamitic compounds and only a few on discotic systems.

It is a characteristic feature of the nematic–isotropic transition that it is only weakly first order: a second order nematic–isotropic transition is located just below the first order phase transition [3–7]. According to a phenomenological Landau type theory due to de Gennes [3] the characteristic features of the transition are represented as follows. The free energy density $F(T, S)$ in the vicinity of this transition is expressed as a function of the nematic order parameter, S, as

$$F(T, S) = F_0(T) + (a(T)/2)S^2 - (b(T)/3)S^3 + (c(T)/4)S^4 + \dots.$$

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† Part 45 on liquid-crystalline compounds; part 44: A. Eckert, B. Kohne, K. Praefcke, *Z. Naturf.* **43b** (1988), 878.

The coefficient of the quadratic term $a(T)$ is given by

$$a(T) = a_0(T - T^*)^\mu;$$

with $\mu = 1$ in the mean field approximation where T^* is a hypothetical second order phase transition temperature. The assumption is that this second order phase transition is located in the neighbourhood but below the first order phase transition which occurs at a temperature T_{NI}. The expansion coefficients a, b, c are available from macroscopic, predominantly thermodynamic, properties such as the heat of transition ΔH, the temperature difference ΔT between T_{NI} and T^* and the nematic order parameter at the phase transition S_{NI}. The coefficient a_0 is given, for instance, by

$$a_0 = 2\Delta H/T_{NI}S_{NI}^2$$

and is thus strongly related to the heat of transition. The relative magnitudes of the expansion coefficients can be used as a measure of the strength of the nematic-isotropic phase transition.

It is a second characteristic feature of the nematic–isotropic transition that strong pretransitions occur within the isotropic phase which originate from fluctuations of the nematic order parameter S about its mean value of zero. These fluctuations can be characterized, for instance, by depolarized light scattering, by magneto-optic or by electro-optic relaxation studies [3–7]. The experimental finding is that the mean square value of the order parameter fluctuations and the corresponding correlation time diverge with decreasing temperature as the temperature T^* is approached. Parameters characteristic of the static and dynamic properties of the orientational fluctuations such as their correlation length and their relaxation time may again be used as a measure of the strength of the phase transition. They are related to the thermodynamic parameters, characteristic of the transition, as we shall see.

Thus by studying both the thermodynamic properties together with the static and dynamic aspects of the pretransitional effects we are able to gain an insight into the interrelations between the thermodynamics of the nematic–isotropic phase transition, into structure formation processes as well as into the dynamics of reorientational motions. This aspect has been considered predominantly for low molar mass and polymeric calamitic liquid crystals formed by rigid rod-like particles [6–12]; only a few such studies were concerned with discotic systems formed by disc-like mesogenic units [13, 14]. We would like to know whether the change from a calamitic to a discotic system gives rise to strong variations of the strength of the transition, and the nature of the pretransitions as well as whether the modifications of the intermolecular interactions has an impact on the nature of the nematic–isotropic transition. The paper considers, in addition, the positional order in the isotropic and nematic discotic phase and compares it with that characteristic of calamitic systems. Additional studies were performed on a compound which differed from the pure hydrocarbon by replacement of the alkyl groups by alkoxy groups of approximately the same length.

2. Experimental considerations on pretransitional effects

The orientational fluctuations are known to couple to the electro-optic properties, i.e. they may be characterized experimentally by Kerr relaxation studies [6–14]. The Kerr relaxation experiment consists of applying an electric field to the macroscopically isotropic liquid and the determination of the optical birefringence resulting from the induced reorientational motions of the molecules. The Kerr law states that the induced birefringence increases linearly with the square of the applied field E [15, 16]

$$\Delta n = \lambda B E^2,$$

where B is the Kerr constant and λ the wavelength of the light. The dynamic aspect of the Kerr relaxation is investigated by determining the time evolution of the birefringence after switching the field on or off. Both the Kerr constant and the Kerr relaxation time are usually rather weak functions of the temperature as far as normal fluids are concerned [15, 16]. This is, however, not the case for liquid crystals in the isotropic liquid in the neighbourhood of the nematic phase [6–14].

The theoretical treatment of the static and dynamic electro-optical properties of the isotropic phase in the neighbourhood of the nematic phase is based on the simple phenomenological Landau theory of phase transitions, as proposed by de Gennes [3]. The phenomenological theory may also be used to express the temperature dependence of the Kerr constant B as

$$B(T) = (\Delta n^0 \Delta \varepsilon^0 \varepsilon_0)/3a_0(T - T^*),$$

where Δn^0 and $\Delta \varepsilon^0$ are the anisotropy of the refractive index and of the dielectric constant for the completely ordered system. The phenomenological approach can also be taken to derive an expression for the relaxation time characteristic of the electro-optic response. The prediction of its temperature dependence is

$$\tau = 3\eta(T)/2a_0(T - T^*),$$

where η is the viscosity which controls the time scale of the reorientational motion.

The prediction is therefore that the Kerr relaxation is characterized by the occurrence of pretransitional effects leading to a divergence both of the Kerr constant B and of the Kerr relaxation time at the temperature T^*. The divergence of the Kerr constant B and of the relaxation time are caused by the divergence of the correlation length for reorientational motions. Using a molecular statistical approach we may express this divergence via a correlation parameter g_2 which is directly related to the orientational pair correlation function and which is defined as:

$$g_2 = 1 + \sum_{i \neq j} (1/2)\langle 3 \cos^2 \theta_{ij} - 1 \rangle,$$

where θ_{ij} is the angle between the long or symmetry axes of molecules i and j. g_2 represents, to a first approximation, the number of mesogenic units which reorient in a correlated fashion and it can be calculated from

$$g_2 = (45NkT)/((\bar{n} + 2)^2 a_0(T - T^*)),$$

where N is the number of units per unit volume. The important parameters which can be derived from the Kerr relaxation studies are the correlation parameter g_2 which represents structural features, the Kerr relaxation time and the Kerr viscosity, representing the dynamic properties, all of which are evidently connected to the phenomenological coefficient a_0.

3. Experimental

The chemical structure of the discotic compounds studied are shown in figure 1 (1, 2). The preparation of mesogen **2** is described here and that of mesogen **1** has been reported previously [1]. The calorimetric investigations were performed with

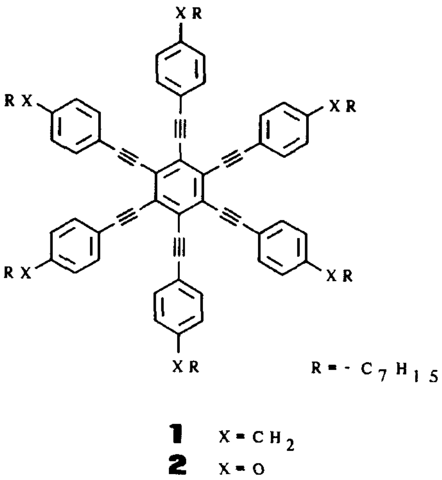

Figure 1. Chemical structure of the discotic mesogens.

a DSC 4 (Perkin Elmer) calorimeter. The X-ray data were taken with a flat camera, for samples which were oriented in a magnetic field, and with a wide angle X-ray diffractometer (Siemens D500) for isotropic samples. Both set-ups were equipped with a heating cell. The small angle X-ray studies were performed with a Kratky compact small angle X-ray camera which was also equipped with a thermostatted cell. The distances corresponding to the observed reflections were calculated from the Bragg equation

$$d = \lambda/2 \sin\theta.$$

The Kerr relaxation studies were made with an experimental set-up, constructed by us; details of this have been published previously [9, 10]. In each of the experiments described we checked whether the induced birefringence depended linearly on the square of the electric field as required by the Kerr law.

4. Synthesis of mesogen *hexakis(4-heptyloxyphenylethinyl)benzene* [2]

A stirred mixture of 1·10 g (2 mmol) hexabromobenzene, 3·24 g (15 mmol) 4-heptyloxyphenylacetylene [17], 100 mg cuprous iodide, 200 mg triphenylphosphine, 100 mg bis(triphenylphosphine)palladium-(II)-chloride and 20 ml dried triethylamine was refluxed under argon for 20 hours [18]. After cooling to room temperature and addition of 300 ml diethylether the dark brown reaction mixture was poured into water. The organic layer was washed two times with water, two times with 0·1 N hydrochloric acid and three times with a saturated aqueous solution of sodium chloride, dried over magnesium sulphate, filtered and evaporated to dryness. The crude product (3·68 g dark brownish solid) was purified by filtration through a column of silica ($\approx$ 100 g, 70–230 mesh, $\phi \approx 2$ cm) in petroleum ether (30–70°C)/ethyl acetate 20 : 1, boiling over charcoal in ethylacetate and successive recrystallisations (3 ×) from methylacetate yielding 1·21 g (44 per cent) of bright yellow crystals, m.p. ($K \rightarrow N_D$) 108·8°C, cl.p. ($N_D \rightarrow I$) 192·5°C (D.S.C. data, Mettler TA 3000/DSC-30 with silver oven); in reality **2** exhibits a rather complex polymorphism which will be discussed in more detail elsewhere.—IR (Beckman IR 9, $CHCl_3$): $\nu_{C\equiv C}$ = 2205 cm^{-1}.—UV (Cary 118, C = 2·96 × 10^{-6} mol/l in CH_2Cl_2): λ_{max} (log ε) = 268·0

(4·77), 366·5 (5·22), 389·0 (sh, 5·04).—^{1}H-NMR (Bruker WM400, $CDCl_3$): δ = 7·55, 6·87 (2 d, $J \approx$ 8·5 Hz; 2 × 12 H, AA′BB′), 3·99 (t, $J \approx$ 7 Hz; 12 H, OCH_2), 1·81 (tt, $J \approx$ 7 and 7 Hz; 12 H, OCH_2CH_2), 1·53 – 1·29 (m; 96 H, CH_2), 0·93 (t, $J \approx$ 7 Hz; 18 H, CH_3).—^{13}C-N.M.R. (Bruker AM 270, off-resonance, $CDCl_3$ as solvent and internal standard with δ = 77 ppm): δ = 159·62 (s; 6 C, aromatic C–O), 133·28 (*d*; 12 C, aromat. C–H), 126·90 (s; 6 C, central ring), 115·35 (*s*; 6 C, aromat. C–C≡C), 114·62 (*d*; 12 C, aromat. C–H), 99·07, 86·61 (2 *s*; 2 × 6 C, C≡C), 68·12 (*t*; 6 C, CH_2O), 31·78, 29·22, 29·06, 25·99, 22.60 (5 *t*; 6 × 6 C, CH_2), 14·08 (*q*; 6 C, CH_3). —MS (Varian MAT 711, 440°C): *m*/*z* (per cent) = M^+ < 0·001 per cent, 282 (10), 207 (100), 206 (33), 133 (12), 120 (12), 192 (37), 108 (31), 94 (31), 91 (12).—$C_{96}H_{114}O_6$ (1364·0) Calc.: C 84·54 H 8·42 Found: C 84·47 H 8·22 (Perkin-Elmer 240 C Elemental Analyser).—

5. Results and discussions

(*a*) Calorimetric results

Compound 1

Figure 2 shows D.S.C. traces of discotic compound **1** obtained for a heating rate of 20 K/min. It is obvious that **1** displays two major transitions, one at a temperature of 71·5°C and one at 96·5°C, as far as the onset temperatures are concerned. The peak maxima are located at 85·8°C and 97·1°C respectively. The corresponding transition enthalpies are displayed in table 1. The X-ray studies to be discussed here and a photograph of the mesophase texture of compound **1** shown in figure 5 reveal that the transition at 71·5°C is connected with the destruction of the crystalline state and the formation of an anisotropic fluid state whereas the high temperature transition corresponds to the destruction of the anisotropic fluid and the formation of an isotropic liquid. An additional weak transition which is observed at lower temperatures

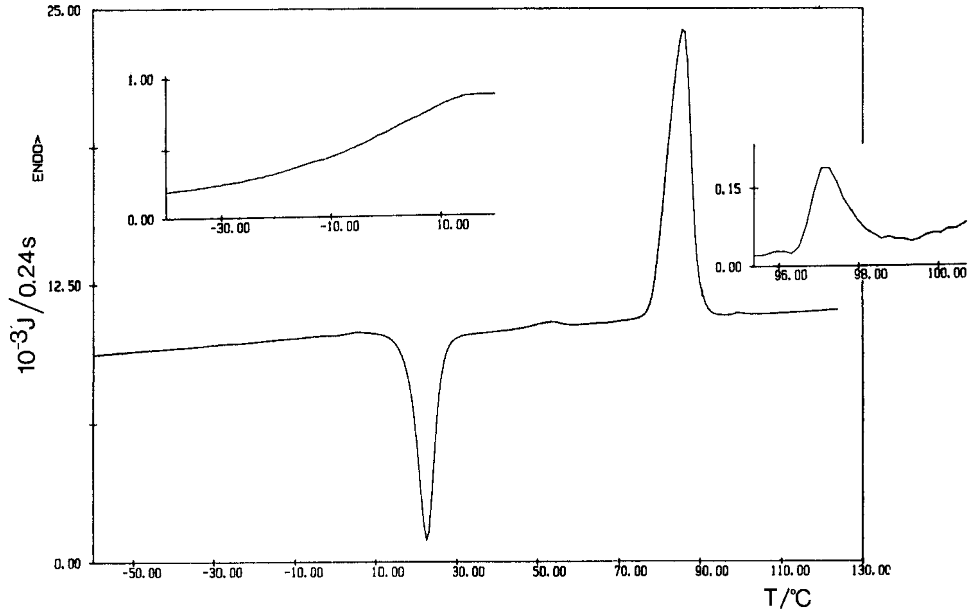

Figure 2. D.S.C. trace for compound **1**.

Table 1. Transition temperatures and the corresponding enthalpies for compounds **1** and **2**.

	Compound **1**	Compound **2**
T_g/°C	−5·4	−7·8
T_{m1}†/°C	41·7	
ΔH_{m1}/J g^{-1}	1·42	
T_{m2}†/°C	71·5	107·1
ΔH_{m2}/J g^{-1}	59·5	48·1
T_{NI}/°C	96·5†; 96·1‡	190·6†
ΔH_{NI}/J g^{-1}	0·119	0·279

† Onset temperature of the transition. ‡ Calculated from Kerr-relaxation studies.

(around 42°C) results, apparently, from structural variations taking place within the crystalline state (1). In addition, it is, apparent from the D.S.C. trace of the sample which was quenched rapidly down to low temperatures that compound **1** exhibits a glass transition temperature at −5·4°C. However recrystallization sets in on heating once the temperature becomes sufficiently high, i.e. above 0°C.

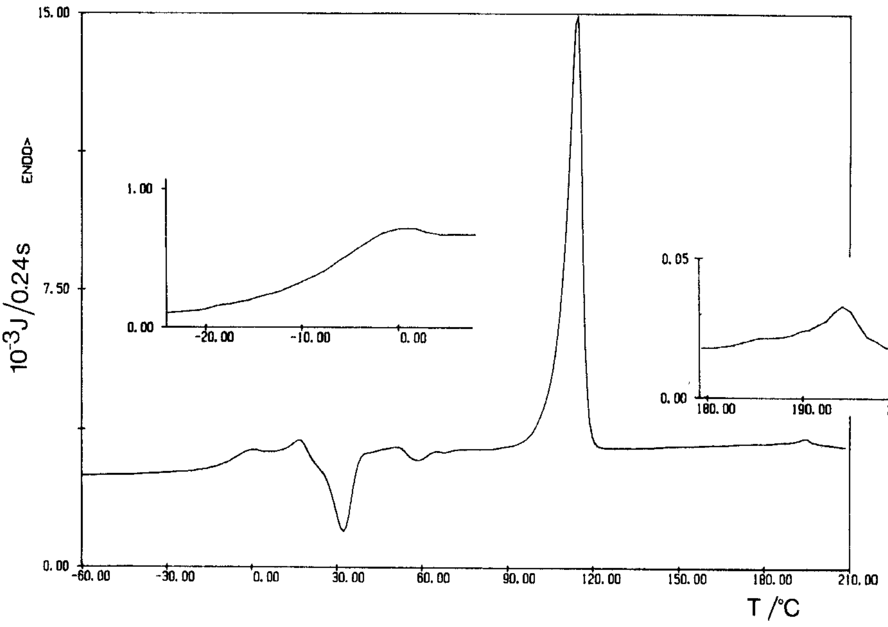

Figure 3. D.S.C. trace for compound **2**.

Compound 2

Compound **2** shows qualitatively similar transitional properties as compound **1**, as is apparent from figure 3. The glass transition temperature is located at −7·8°C, the melting process occurs at 107·1°C and the transition from the anisotropic to the isotropic fluid state takes place at 190·6°C (peak positions: 114·4°C and 193·8°C respectively). The absolute values of the clearing temperature and of the corresponding enthalpy of transition are increased quite strongly by the structural modification: the replacement of the alkyl group in **1** by the alkoxy group of approximately the same length in **2** results in a shift of the nematic discotic to isotropic transition temperature by as much as 100 K.

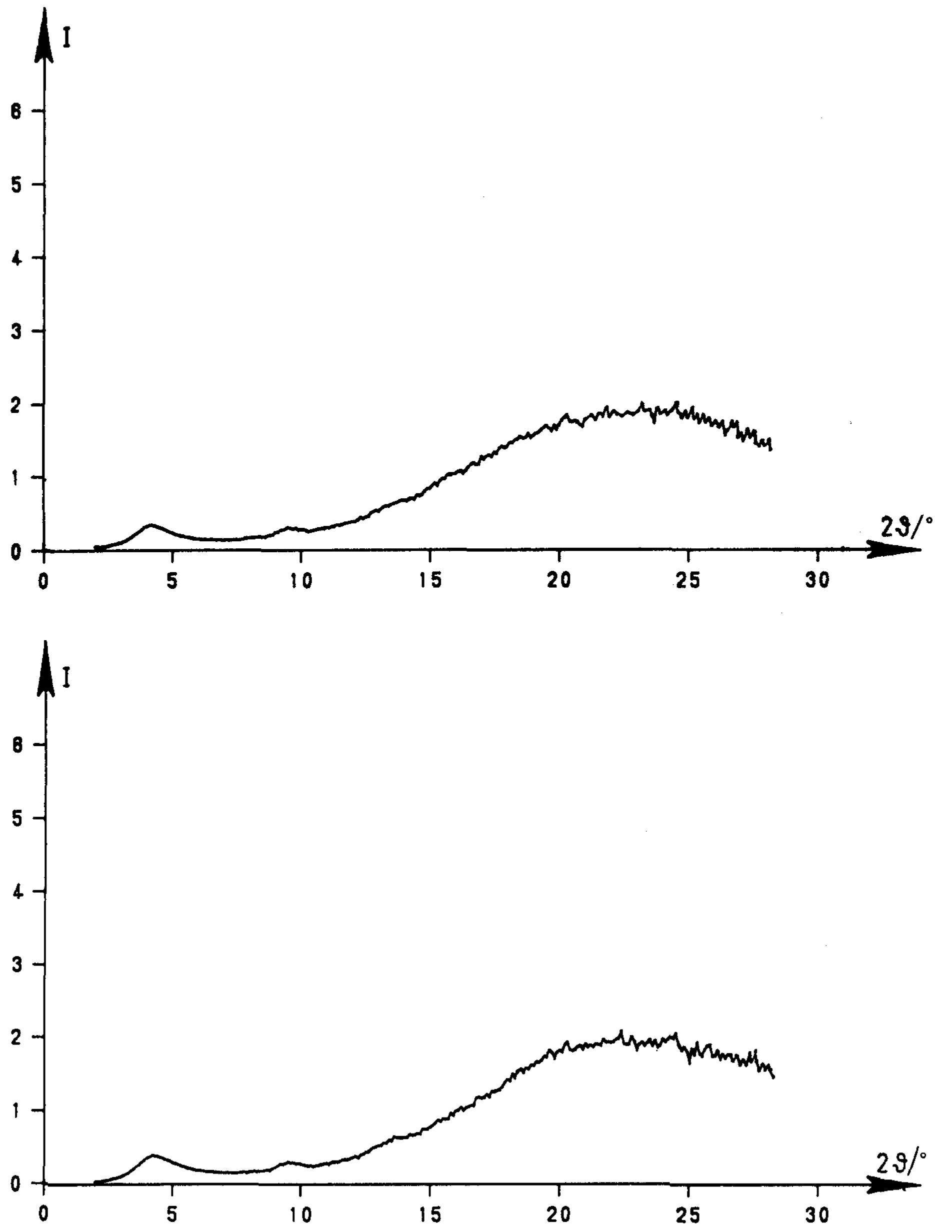

Figure 4. Wide angle X-ray diffraction diagram of compound **1**. (*a*) isotropic phase; (*b*) discotic nematic phase.

(*b*) *X-ray scattering results*

Compound 1

The X-ray studies performed on mesogen **1** revealed the occurrence of several amorphous halos, at least two halos occur in the small angle X-ray range and one in the wide angle range (see figure 4). These diagrams were obtained in the isotropic phase well above the clearing temperature and in the anisotropic phase about 6 K below the nematic-isotropic transition temperature. So we conclude, that no long

Figure 5. Schlieren texture of compound **1** at 95·2°C.

range positional order is present in the anisotropic state in agreement with the polarizing microscopical observation of a Schlieren texture which is shown in figure 5.

The distances derived from the location of the first small and the wide angle halos are about 22·2 Å and 4·6 Å, respectively. It thus seems that these dimensions correspond roughly to the thickness and the diameter of the discotic units and that a biaxial short range order rather than a uniaxial one exists, in agreement with similar data on other discotic systems [19, 20]. This biaxial order is, however, not a peculiar feature of the anisotropic state but apparently of the condensed state in general, since it is also observed in the isotropic phase (see figure 4(*a*)). The small angle X-ray results obtained by a Kratky small angle camera which are displayed in figure 6(*a*) clearly indicate that the transition from the nematic to the isotropic transition does not change the biaxial short range order to an appreciable extent. The second small angle halo with a distance of 9·4 Å which is apparent in both X-ray diagrams shown in figure 4 cannot be a higher order reflection of the first broad small angle halo. It is apparently a reflection arising from the interior structure of the molecule, as in the case of the meridional reflections observed for rigid chain random copolyesters [21, 22]. Finally figure 7 shows the X-ray diagram obtained for room temperature. It is evident that the room temperature state crystalline.

Compound 2

Compound **2** is characterized by a scattering behaviour in the nematic phase which is very similar to that reported for mesogen **1**. Figure 6(*b*) shows the Kratky small angle X-ray diagram as obtained for compound **2** in the nematic state. The location of the halo is shifted to larger scattering angles i.e. the corresponding distance of 20·5 Å is decreased relative to that found for component **1** with 22·2 Å and the halo

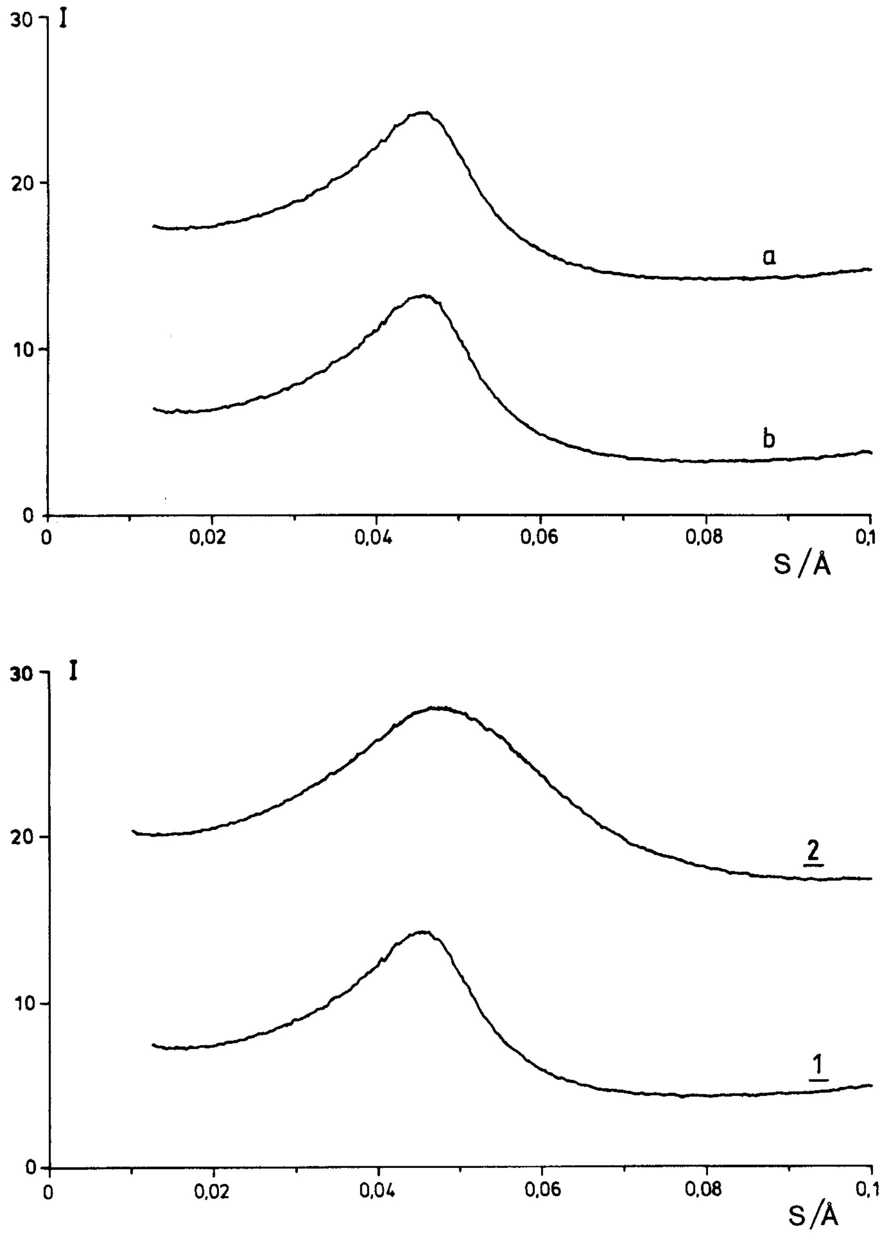

Figure 6. (*a*) Small angle X-ray diffraction diagrams of compound **1** (upper curve *a*: isotropic phase; lower curve *b*; discotic nematic phase). (*b*) Small angle X-ray diffraction diagrams for the discotic nematic phase of compound **2** (upper curve) and compound **1** (lower curve).

is broader. It has, however, to be pointed out that the diagram was taken at a temperature which was significantly higher than in the case of compound **1**.

So we find that these compounds display a short range order which is biaxial and which does not change at the transition into the isotropic liquid. Similar results have been reported for other discotic nematic systems [19, 20]. One important difference

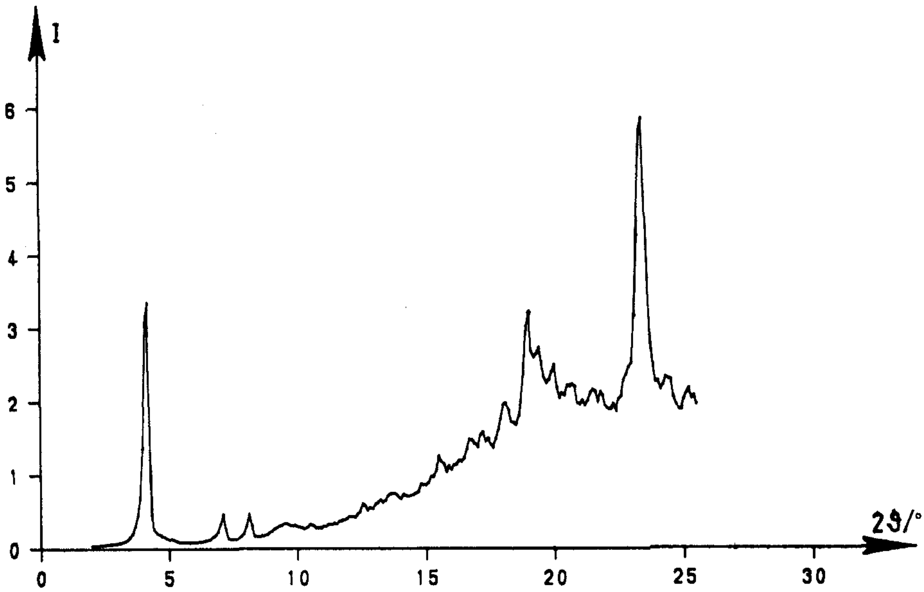

Figure 7. Wide angle X-ray diffraction diagram for the crystalline phase of compound **1**.

between the isotropic and the anisotropic phases is apparent however if the influence of a magnetic field on the scattering behaviour is studied. The finding, which is based on the analysis of flat camera diagrams, is that the samples remain unoriented in the isotropic state, as expected, and that they become highly oriented in the anisotropic fluid state (magnetic field 0·1 T). This allows the determination of the singlet orientational distribution function and so of the order parameter S from the azimuthal intensity distribution $I(\theta)$ of the X-ray reflections displayed in figure 8 for compound **1**:

$$S = \langle (3\cos^2\theta - 1)/2 \rangle$$

$$\langle \cos^2\theta \rangle = \int I(\theta) \cos^2\theta \sin\theta \, d\theta,$$

where $I(\theta)$ is already normalized. The value obtained for S is 0·42 + 5 per cent and was obtained for a reduced temperature T/T_{NI} of 0·96. This value will be used later in the analysis of the Kerr relaxation data.

The general conclusions which can be drawn are that the structural properties of compound **1** and of the slightly modified compound **2** agree qualitatively with those found for other discotic systems. The short range order is locally biaxial, in contrast to the case of calamitic systems, magnetic fields give rise to macroscopic orientations and the nematic order parameter just below T_{NI} is approximately 0·4.

(*c*) *Electro-optic* (*Kerr*) *relaxation studies*

These studies were only performed on compound **1** because of the limited thermal stability of compound **2** at elevated temperatures. The application of an electric field to the discotic substance within the isotropic melt gives rise to an equilibrium induced birefringence which increase linearly with the square of the electric field E_0, as expected from the Kerr law (see figure 9). The slopes of the lines are directly

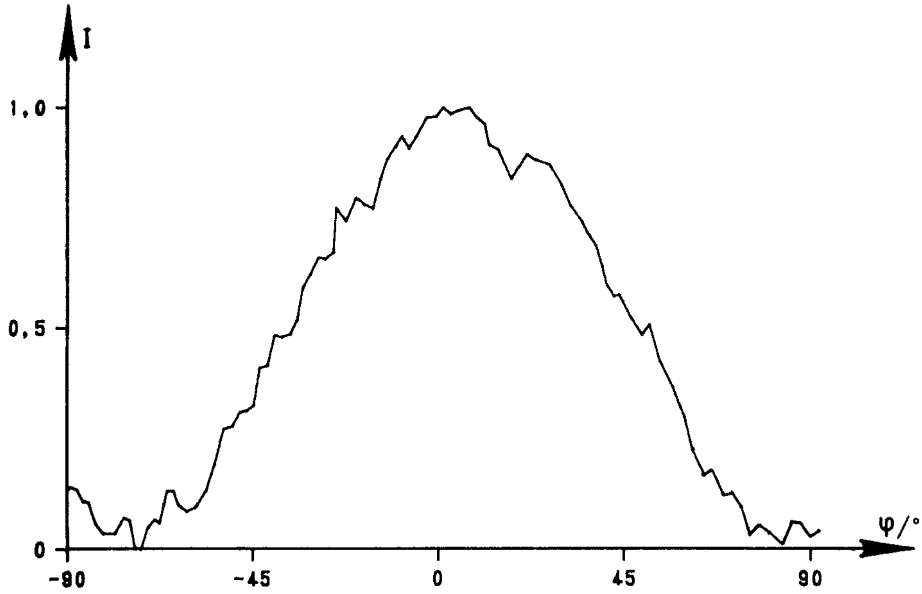

Figure 8. Azimuthal intensity distribution of the small angle reflection for 22·2 Å of compound **1** in the discotic nematic phase, oriented by a magnetic field of 1 T.

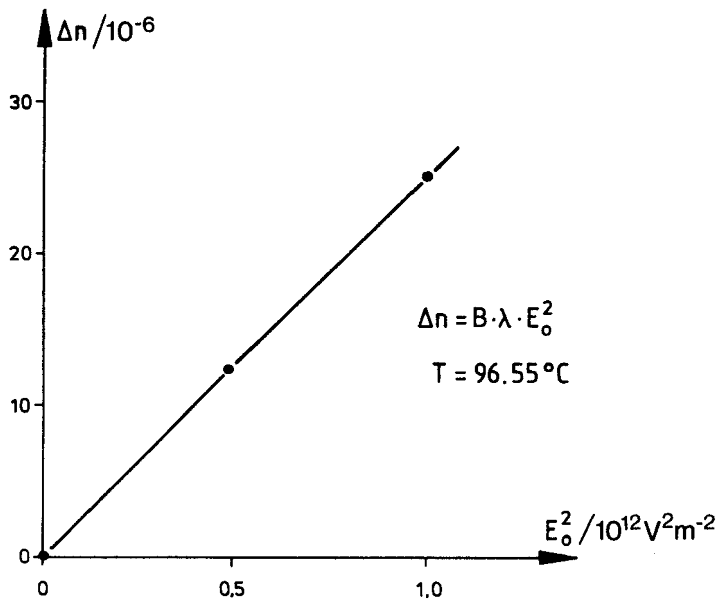

Figure 9. Dependence of the induced birefringence on the electric field for compound **1** at $T = 96{\cdot}55°C$.

correlated with the absolute value of the Kerr constant *B* and its sign which is positive at all temperatures.

The Kerr constant is found to depend strongly on temperature and diverges with decreasing temperature. A plot of the inverse of the Kerr constant versus temperature, which is shown in figure 10 reveals that the Kerr constant behaves as expected on

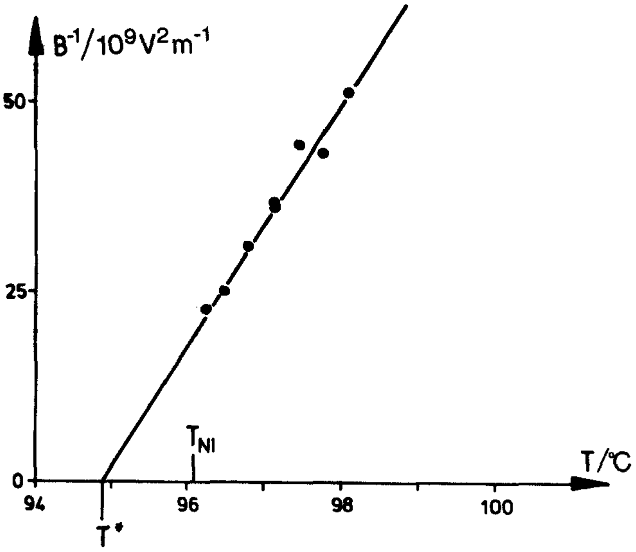

Figure 10. Variation of the inverse of the Kerr constant B with temperature for compound **1**.

the basis of the phenomenological theory

$$B \propto (T - T^*)^{-\gamma}$$

and that the critical exponent γ is approximately 1. The characteristic temperature is found to be 94·9°C which is about 1·2 K below the first order phase transition temperature T_{NI}. The latter temperature is available from calorimetric experiments but is also evident from the Kerr relaxation studies (see table 1). The samples turn turbid below this temperature so that no Kerr relaxation data can be obtained below this temperature.

The discussion has been limited so far to the equilibrium values of the induced birefringence. In the following we consider the dependence of the induced birefringence on the time after switching the field on and off. The observation is that the magnitude of the relaxation time is identical for both rise and decay. This is in agreement with the fluctuation model devised by de Gennes [3]. These Kerr relaxation times depend only on the temperature but not on the magnitude of the electric field (as found for optical switching). The relaxation time is found to increase strongly with decreasing temperature and to diverge at T^*, as expected from the theoretical treatment. The temperature dependence of the inverse relaxation time is linear as for the static constant B as expected from theory. This is shown in figure 11.

We now analyse the data within the framework of the phenomenological theory previously introduced. Using the values of the transition temperatures, the heat of transition, the temperature difference $\Delta T = (T_{NI} - T^*)$ and the jump in the order parameter S_{NI} at the transition we are able to calculate the important coefficient a_0

$$a_0 = 2\Delta H/T_{NI}S_{NI}^2$$

as well as b and c. The results are given in table 2 and they are compared to those which are typical for calamitic nematic compounds. These results will be discussed later.

The Kerr relaxation data allow us to calculate the correlation parameter g_2 based on a knowledge of a_0 and on the mean value of the refractive index n. The latter value is 1·68. The absolute value of the correlation parameter g_2 and its dependence on the

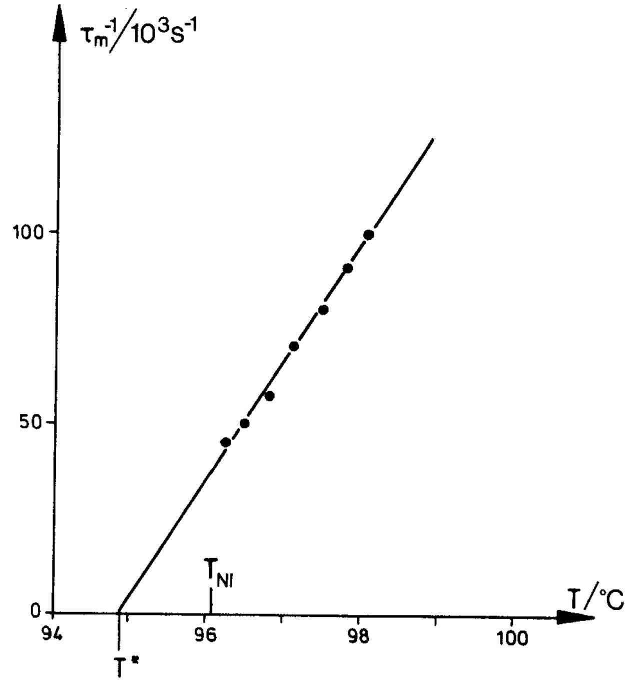

Figure 11. Variation of the inverse of the Kerr relaxation time (decay) with temperature for compound **1**.

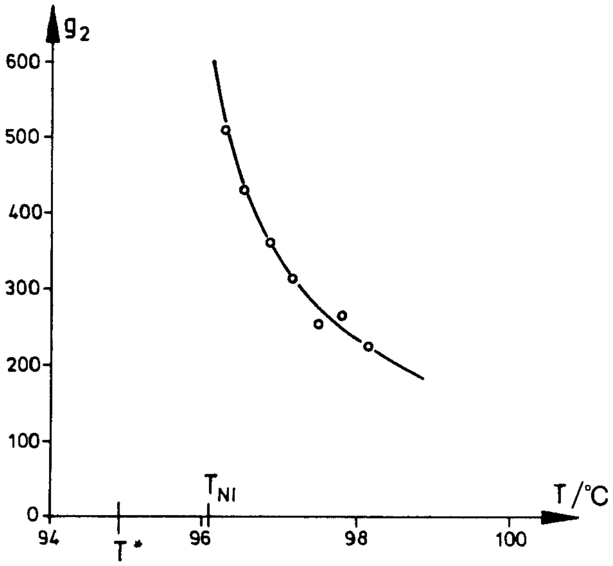

Figure 12. Variation of the correlation parameter g_2 with temperature for compound **1**.

temperature are shown in figure 12. It is apparent that g_2 diverges as T^* is approached and that g_2 is of the order of 600 at the first order phase transition T_{NI}.

Next we analyse the Kerr relaxation times in order to obtain the basic dynamic viscosity which controls the reorientational motions. Using the experimentally

Table 2. Analysis of the properties of compound **1** on the basis of the Landau–de Gennes approach (comparison with *n*CB series, $n = 4$–8 [8])

Discotic nematic Compound **1**	Calamitic nematic typical values [8]
$a_0 = 6{\cdot}1 \times 10^3\,\mathrm{J/Km^3}$	$a_0 = 95 \times 10^3\,\mathrm{J/Km^3}$
$b = 67{\cdot}7 \times 10^3\,\mathrm{J/m^3}$	$b = 850 \times 10^3\,\mathrm{J/m^3}$
$c = 139{\cdot}0 \times 10^3\,\mathrm{J/m^3}$	$c = 1700 \times 10^3\,\mathrm{J/m^3}$
$\Delta T = (T_{\mathrm{NI}} - T^*) = 1{\cdot}2\,\mathrm{K}$	$\Delta T = 1\,\mathrm{K}$
$g_2(\Delta T = 1\,\mathrm{K}) = 720$	$g_2 = 250$
$\Delta S_{\mathrm{NI}} = 0{\cdot}33$	$\Delta S_{\mathrm{NI}} = 0{\cdot}45$
$\bar{n} = 1{\cdot}68$	$\bar{n} = 1{\cdot}57$

Table 3. Results of the dynamic studies, analysed in terms of the Landau–de Gennes approach (comparison with *n*CB series, $n = 4$–8 [8]).

Discotic system Compound **1**	Calamitic system typical values [8]
$\tau_{\mathrm{Kerr}} = 31{\cdot}7\,\mu\mathrm{s}\ (\Delta T = T - T^* = 1\,\mathrm{K})$	$\tau_{\mathrm{Kerr}} = 0{\cdot}2 - 0{\cdot}5\,\mu\mathrm{s}\ (\Delta T = 1\,\mathrm{K})$
$\eta_{\mathrm{Kerr}} = 129\,\mathrm{mPa\,s}$	$\eta_{\mathrm{Kerr}} = 10$–$29\,\mathrm{mPa\,s}$

obtained values for the Kerr relaxation time and for a_0 we are able to calculate the viscosity η. The values are given in table 3 and compared again with those of a typical calamitic nematic system.

(*d*) *Conclusions*

Table 2 lists the results obtained for the Landau–de Gennes expansion coefficients for the free energy in the neighbourhood of the discotic nematic–isotropic transition from mesogen **1**. They are compared to characteristic values found for low molar mass systems displaying calamitic nematic phases. It is evident that the values obtained for a_0, b, c are definitely smaller than those usually found for the nematic isotropic transition of calamitic systems, due to the very small enthalpy of transition observed for the discotic system **1**. It is in particular the smallness of a_0 which causes the strong pretransitional effects. The Kerr constant B is relatively large and the correlation parameter g_2 approaches values which are much larger than usually encountered at similar temperature distance ΔT from T^* (see table 2). These results show that the correlation is much stronger than normally experienced for the isotropic phase of calamitic systems, the correlation length is of the order of 120 Å at 1 K above T^*. We thus conclude that the transition strength is small, i.e. it is only very weakly first order.

According to these results the relaxation times are relatively large although the viscosities are not much larger than usually encountered for low molar mass systems calamitic systems. Again this has to be taken as an indication for the weakness of the phase transition. The Kerr relaxation times of calamitic systems and that studied here differ by a factor of more than 100 whereas the ratios of the corresponding viscosities amount to about 4. The reason, quite obviously, is that the thermodynamic driving force, which controls the relaxation time:

$$\tau \propto \eta/a_0 \propto \eta/(d^2G/dS^2)_{S=0}$$

is much smaller for the compounds considered here in comparison to calamitic systems.

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