Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713926090

On the influence of short range order upon the physical properties of triphenylene nematic discogens

T. J. Phillips[a]; J. C. Jones[a]; D. G. McDonnell[a]
[a] Defence Research Agency, Worcestershire, WR, England

To cite this Article Phillips, T. J. , Jones, J. C. and McDonnell, D. G.(1993) 'On the influence of short range order upon the physical properties of triphenylene nematic discogens', Liquid Crystals, 15: 2, 203 — 215
To link to this Article: DOI: 10.1080/02678299308031951
URL: http://dx.doi.org/10.1080/02678299308031951

LIQUID CRYSTALS, 1993, VOL. 15, NO. 2, 203–215

On the influence of short range order upon the physical properties of triphenylene nematic discogens

by T. J. PHILLIPS*, J. C. JONES and D. G. McDONNELL
Defence Research Agency, St. Andrews Road,
Malvern, Worcestershire WR14 3PS, England

(*Received 14 December 1992; accepted 10 March 1993*)

The dielectric and elastic properties of two novel triphenylene nematic discogens are measured and compared with those of calamitic nematics and the known material H7OBT. The new compounds have nematic phases at much lower temperatures than H7OBT. All three compounds have a small positive permittivity anisotropy, indicating the presence of a permanent dipole contribution parallel to the director. Measurement of the molecular moment dipole provides a value consistent with nearly-free rotation of the substituent groups. The temperature dependence of $\bar{\varepsilon}$ and the concentration dependence of the dipolar strength Δ show evidence of antiparallel dipole correlations in the N_D phase. The strong temperature dependence of $|k_{33}/\Delta\chi|$, the large value of k_{11}/k_{33} and the rise in k_{11}/k_{33} as the temperature approaches the clearing point are believed to be due to short range columnar order. Theoretical study suggests that dipole correlations favour local columnar order, and we predict that antiparallel dipole correlations require that the molecules be tilted within the columns.

1. Introduction

Since the discovery of discotic phases [1], and especially the nematic discotic N_D phase [2], several studies have been made of electro-optic effects that occur in these materials. Heppke *et al.* [3], have measured the dielectric and elastic properties of the hexakis((4-alkylphenyl)ethynyl)benzene nematic discotic compounds, which have no permanent dipole moment. Warmardam *et al.* [4], and Raghunathan *et al.* [5], have studied truxene esters, which have incommensurate nematic discotic phases, and Mourey *et al.* [6], and Dubois *et al.* [7], have made measurements on the original nematic triphenylene hexa(alkoxybenzoate) materials. Meanwhile, many new discotic compounds have been synthesized, the various discotic phases classified and possible non-display applications of the materials examined.

Recently, some new triphenylene materials have been synthesized with N_D phases at considerably lower temperatures [8]. This is achieved by the addition of a methyl group onto each of the substituent benzene rings, which tends to favour a nematic phase by disrupting long range columnar order. The advent of these new materials suggested the following work, which consists of a study of their phase characteristics, dielectric behaviour and elastic properties. Three comparisons are made: two novel materials, one *ortho*- and one *meta*-substituted, are compared with a literature nematic discotic, with calamitic nematics, and with each other. Particular reference is made to the influence of short range columnar order on the measured properties.

* Author for correspondence.

2. Experimental

2.1. *Phase behaviour and microscopy*

The materials studied are shown in figure 1; the first, triphenylene hexa(heptoxybenzoate) H7OBT is a literature material [2]; the second and third are new materials [8]. The phase behaviour of the materials was studied by polarizing optical microscopy and differential scanning calorimetry (Du Pont DSC 2910) and is shown in the table. The transition temperatures and enthalpies were obtained by taking measurements at 4, 7, 10 and 20°C min^{-1} and extrapolating any significant variation to zero heating rate. The enthalpies of transition ΔH_{NI} for the materials are rather small (cf. 4-*n*-octyloxyphenyl-2-fluoro-4′-*n*-pentyl biphenyl-4-carboxylate (MB8O5F) [9]: $\Delta H_{\mathrm{NI}} = 1{\cdot}6\,\mathrm{kJ\,mol^{-1}}$); the transitions are effectively second order. DB119 behaved rather differently from the other two materials: instead of a first order transition to a crystal phase, this material underwent a series of weakly first order transitions down to room temperature and below. All the mesophases in this material had the optical appearance of a nematic phase; the viscosity of these phases increased markedly at temperatures similar to the DSC transitions.

The nematic discotic phase of all three materials could be aligned successfully using a thin layer of polyimide (PI) or poly-vinyl alcohol (PVA). Conoscopic observation confirmed that the samples were homeotropically aligned (i.e. the director perpendicular to the plane of the cell) and that the phase is uniaxial and has negative

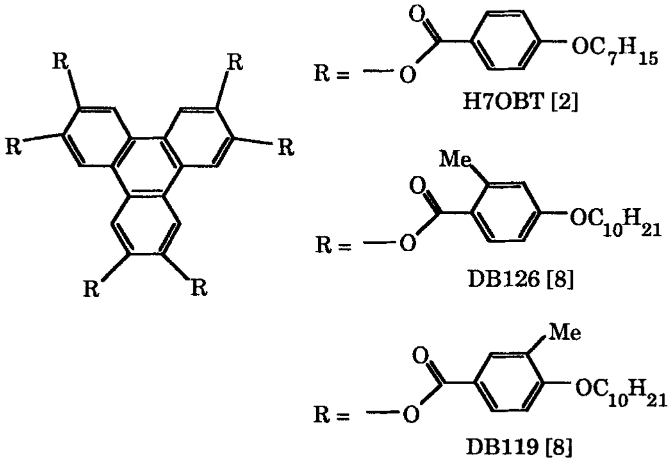

Figure 1. Material structures.

Phase transitions. Positive values of ΔH indicate exotherms on heating. Unidentified phases with nematic-like textures are represented by '?'. Square brackets indicate temperatures obtained on cooling.

H7OBT/°C	C_1	132	C_2	142[129]	N_D	248	I			
$\Delta H/\mathrm{kJ\,mol^{-1}}$		−0·5		−7·1		−0·3				
DB126/°C	C_1	23	C_2	67	C_3	109[75]	N_D	164	I	
$\Delta H/\mathrm{kJ\,mol^{-1}}$		1		28		−33		−0·06		
DB119/°C	?	2·9	?	84[68]	?	129	N_D	170	I	(±2)
$\Delta H/\mathrm{kJ\,mol^{-1}}$		−0·5		−1·4		−0·3		−0·6		(±5 per cent)

birefringence. An approximate value of the birefringence of H7OBT was measured microscopically and found to be $\approx -0{\cdot}12$ at 150°C. Microscopic investigation of electro-optic effects demonstrated that the material has a positive permittivity anisotropy.

2.2. *Permittivity and elastic constant measurements*

A computer controlled Hewlett–Packard HP4192A impedance analyser was used to make permittivity measurements. The response of each empty cell was measured as a function of temperature and frequency in order to determine the empty cell capacitance C_0, the lead resistance and the lead inductance [10]. Temperature control was provided by a Mettler FP 80 hot-stage controller and FP 82 hot-stage, controlled by an RS 232 interface with the computer, to provide temperatures up to 180°C. The cells used were of thickness 10, 25 or 50 μm and had $5\,\Omega\,\mathrm{sq}^{-1}$ ITO conductors of area 1 cm^2 with polymer aligning layers.

The data are plotted in terms of the complex relative permittivity tensor

$$\varepsilon_{ij}^* = \begin{pmatrix} \varepsilon_\perp^* & 0 & 0 \\ 0 & \varepsilon_\perp^* & 0 \\ 0 & 0 & \varepsilon_\parallel^* \end{pmatrix} \text{(for the uniaxial } \mathrm{N_D} \text{ phase)}, \qquad (1)$$

where

$$\varepsilon_\gamma^* = \varepsilon_\gamma' - i\varepsilon_\gamma'', \quad \gamma = \perp, \parallel, \qquad (2)$$

versus frequency and temperature, where

$$\varepsilon_\gamma'(\omega, T) = \frac{C_\gamma(\omega, T)}{C_0(\omega, T)}, \qquad (3)$$

and

$$\varepsilon_\gamma''(\omega, T) = \frac{G_\gamma(\omega, T)}{\omega C_0(\omega, T)}. \qquad (4)$$

C_γ and G_γ are the capacitance and conductivity, respectively, of a cell with the relevant alignment geometry; ω is the measuring frequency.

The measurement of the permittivity parallel to the director, $\varepsilon_\parallel^*$, used the homeotropic alignment conferred by the polymer layer and gave an absolute tolerance of 1 per cent. A magnetic field parallel to the cell normal was used to distort the director and $\varepsilon_\perp^*$ measured by extrapolating $1/\varepsilon_{\mathrm{meas}}^*$ versus $1/B$ to infinite field [11], giving a tolerance of ~ 3 per cent. This technique relied on $\Delta\chi$ for these materials being negative. The field was varied at $\approx 0{\cdot}2\,\mathrm{T\,h^{-1}}$ and the results were taken from the average of the permittivity measured while increasing and then decreasing the field; this eliminated the slight effects of experimental hysteresis. An attempt was made, following Warmadam *et al.* [4], to solve the problem of degeneracy of distorted director orientation by rotating the sample in the field prior to inducing the Fréedericksz transition. This was found to make little difference to either the absolute values of the permittivity or the value of the threshold field, and the technique was not used subsequently.

Plots of measured permittivity versus magnetic field at various temperatures allow $k_{33}/\Delta\chi$ to be determined, to within 6 per cent, from the threshold field B_c [12]

$$\left|\frac{k_{33}}{\Delta\chi}\right| = \frac{1}{\mu_0}\left(\frac{B_c d}{\pi}\right)^2, \tag{5}$$

where d is the cell thickness, and k_{11}/k_{33}, to within ~8 per cent, from the initial slope, m, of the $\varepsilon'_{\text{meas}}$ versus B curve above the threshold [13]

$$\frac{k_{11}}{k_{33}} = -\frac{2\Delta\varepsilon}{B_c m}. \tag{6}$$

2.3. *Dipole moment measurement*

The dipole moment of the DB126 molecule was measured using several isotropic solutions in the non-polar compound PCH32 according to the method of Raynes [14], giving a tolerance of 5 per cent. The refractive index and permittivity of solutions of various (low) concentrations were measured and the quantity $\Delta/(x/V)$ plotted against (x/V), where

$$\Delta = \frac{(\varepsilon - n^2)}{(\varepsilon+2)(n^2+2)} - \frac{(\varepsilon_1 - n_1^2)}{(\varepsilon_1+2)(n_1^2+2)}, \tag{7}$$

is the dipolar strength, (ε, n), (ε_1, n_1) are the permittivities and refractive indices of the solution and solvent respectively, x is the mol fraction of the solute and V the mean molar volume of the solution. Debye's equation

$$\frac{\Delta}{(x/V)} = \frac{N_A}{27\varepsilon_0 k_B T}\,\mu^2_{\text{solution}} \quad \text{(SI units)}, \tag{8}$$

implies that the plot will be a horizontal line if there is no dipole correlation. However, if the effective dipole moment of the solution varies as

$$\mu^2_{\text{solution}} = \mu^2_{\text{molecule}} + (g-1)\kappa^2_{\text{corr}}\left(\frac{x}{V}\right) + o\left(\left(\frac{x}{V}\right)^2\right), \tag{9}$$

(as implicitly assumed by Raynes [14]), where g is the relevant Kirkwood factor, defined by [15]

$$\mu^2_{\text{solute}} = g\mu^2_{\text{molecule}}, \tag{10}$$

and κ^2_{corr} is a constant to correct the units, the graph plotted will be a straight line at low concentrations. This extrapolates to μ^2_{molecule} at infinite dilution and has a gradient related to the type and degree of correlation.

3. Results

3.1. *Permittivity measurements*

The two measured permittivities and $\bar{\varepsilon}' = \frac{1}{3}(\varepsilon'_{\parallel} + 2\varepsilon'_{\perp})$ for H7OBT are shown in figure 2. The graph shows that $\Delta\varepsilon$ for this material is ~ +1, in agreement with the results of Mourey *et al.* [6]. The alignment deteriorates when the sample is cooled into the C phase (crystal) and the measured permittivity approximates to $\bar{\varepsilon}'$. Figures 3 and 4 show equivalent results for DB126 and DB119. The fact that $\Delta\varepsilon'$ is positive and $\Delta\alpha$ negative for these materials implies there must be a significant contribution from the

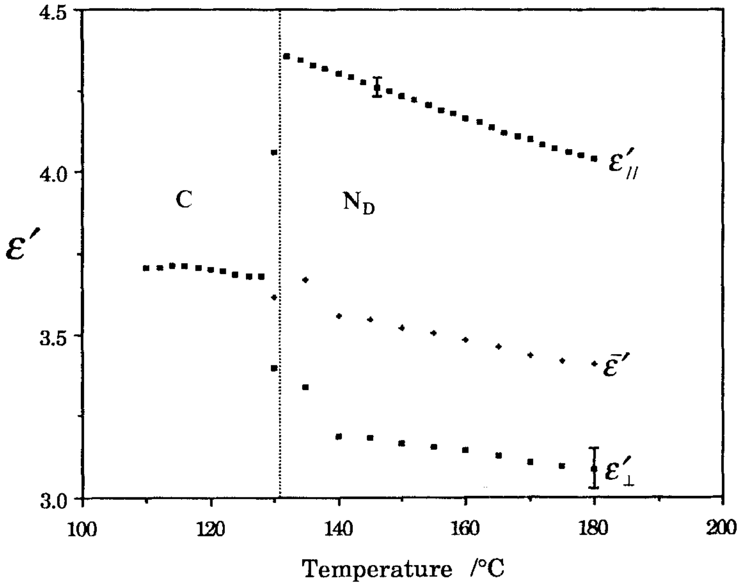

Figure 2. Permittivity versus temperature for H7OBT (100 kHz, 50 μm PVA cell).

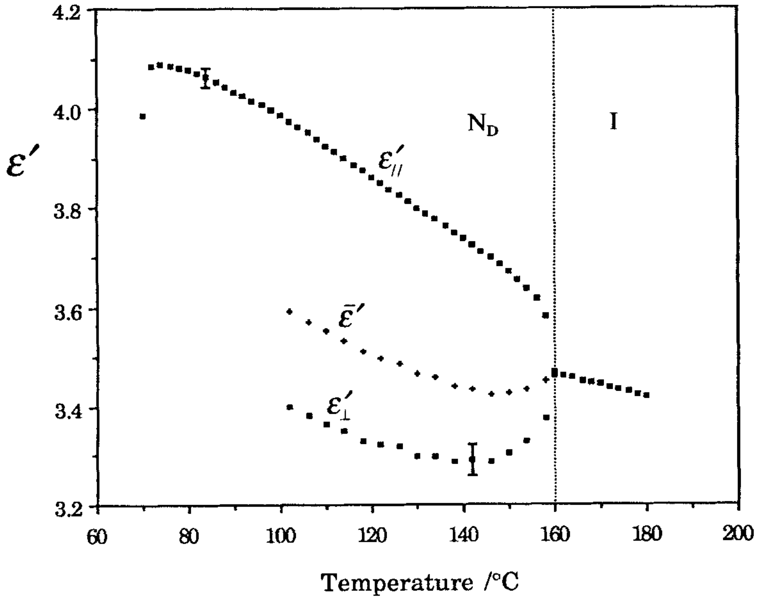

Figure 3. Permittivity versus temperature for DB126 (100 kHz, 10 μm PI cell).

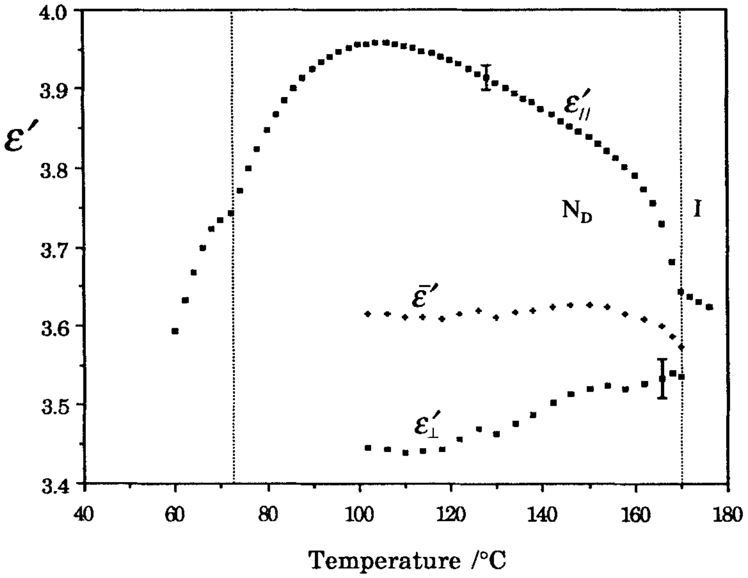

Figure 4. Permittivity versus temperature for DB119 (100 kHz, 10 and 25 μm PI cells).

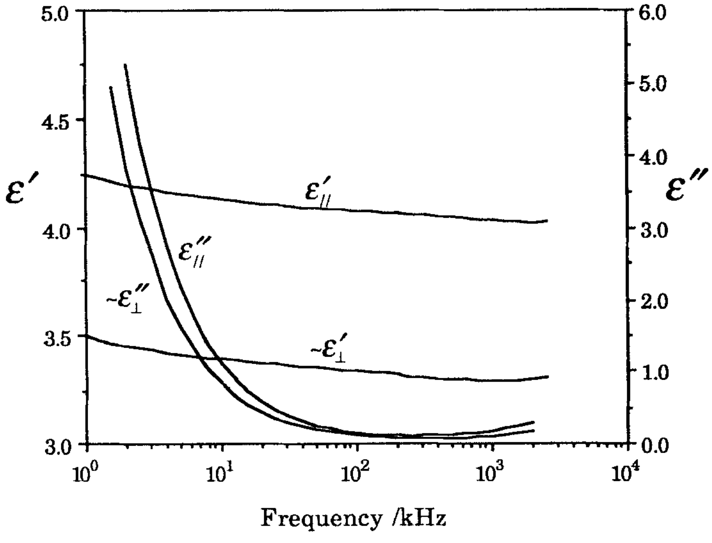

Figure 5. Plot of ε^*_{ij} versus frequency for H7OBT (150°C, 50 μm PVA cell).

reorientation polarizability, i.e., a permanent dipole moment along the molecular short axis, μ_s, which is greater than that transverse to the short axis μ_t.

ε_{ij}^* is plotted against frequency for H7OBT in figure 5 (the other materials behaved similarly), where "$\sim\varepsilon'_\perp$" and "$\sim\varepsilon''_\perp$" are the values measured at the maximum field available (1·2 T). These were only about 2 per cent higher than the extrapolated values. No evidence is seen for a relaxation in ε' below the ~2 MHz high frequency limit of the experiment, which suggests that the reorientation effect is not of the molecule as a whole; such an effect is likely to have a relaxation frequency well into the measurable range. The reorientation effect must arise from rotation of the ester linkages in response to the external field, with a correspondingly high relaxation frequency, probably ~1 GHz [16]. From the symmetry of the molecule, one would expect μ_t to be very small; the only dipolar contributions to $\varepsilon'_\perp$ coming from the orientational fluctuations of the molecule as a whole.

The two novel compounds have lower permittivity anisotropies, possibly because the ester linkages are more constrained to lie in the plane of the molecule than before due to the steric effect of the methyl substituents.

3.2. *Dipole moment measurement*

The results for DB126 (figure 6) show a negative gradient, which suggests $g < 1$ (i.e. antiparallel dipole correlation) from equation (9). The extrapolated value of $\Delta/(x/V)$ gave the result $\mu_{\text{molecule}} = 25{\cdot}1 \pm 1{\cdot}3 \times 10^{-30}$ Cm for temperatures of 50 and 80°C. A literature value [17] for the dipole moment of the phenyl benzoate molecule is $6{\cdot}5 \times 10^{-30}$ Cm, which is taken to be oriented at 55° to the molecular long axis [18]. In addition we take the components of the dipole due to the alkoxy chains [17], as shown in figure 7. If we assume that these two dipoles can rotate freely with respect to each

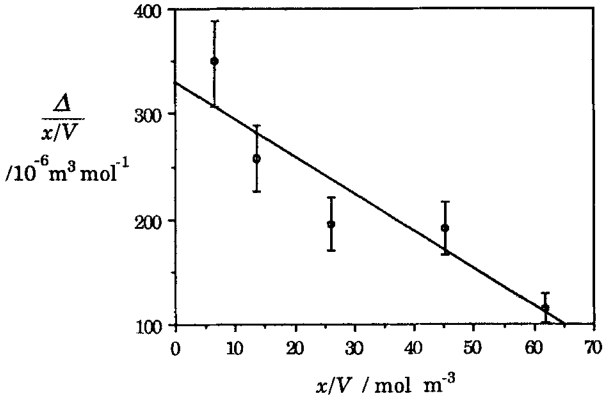

Figure 6. Dipole moment measurement: $\Delta/(x/V)$ versus x/V for DB126.

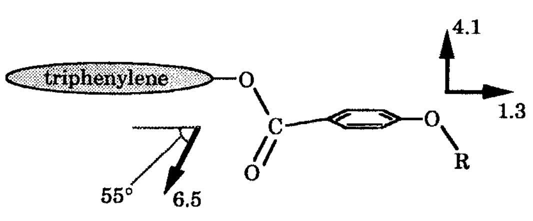

Figure 7. Calculation of dipole moments in DB126.

other, then the resultant dipole of one of the six substituent groups, parallel to the molecular short axis, is obtained by adding the two components in quadrature [17]: we obtain $\sqrt{[(6\cdot5 \sin 55^\circ)^2 + (4\cdot1)^2]} = 6\cdot7 \times 10^{-30}$ C m. Taking the parallel dipole moment of DB 126 as comprising six of these, the resultant short axis moment, μ_s, of the whole molecule may be calculated by assuming two possible configurations: if the component dipoles are parallel and all directed along the molecular short axis, the resultant is $6 \times 6\cdot7 = 40\cdot2 \times 10^{-30}$ C m, whereas if the dipoles have free rotation about a molecular long axis the resultant is $\sqrt{6} \times 6\cdot7 = 16\cdot4 \times 10^{-30}$ C m. As the experimental value is between these two, but nearer the free rotation value, nearly-free rotation of the dipoles is implied, with the dipoles favouring orientation along the molecular short axis. The transverse dipole moment, μ_t, is assumed to be very small because of the symmetry of the molecule.

3.3. *Elastic constant measurements*

At 150°C ($T/T_{NI} = 0\cdot81$), H7OBT has a value of $k_{33}/\Delta\chi = -5\cdot5 \pm 0\cdot3 \times 10^{-6}$ N. The slope above the transition gives $k_{11}/k_{33} = 4\cdot3 \pm 0\cdot3$. This result is distinct from most calamitic nematics in that k_{11}/k_{33} is greater than unity (cf. the calamitic nematic E7, which has $k_{11}/k_{33} = 0\cdot7$ at the same reduced temperature [19]). Assuming the Tsvetkov expression for the nematic order parameter [20]

$$\Delta\chi = \chi_{\parallel} - \chi_{\perp} = S(\chi_l - \chi_t) = S\rho(\chi_l^m - \chi_t^m) \tag{11}$$

and taking $\chi_l^m - \chi_t^m = -1\cdot4 \times 10^{-9}\,\mathrm{m^3\,kg^{-1}}$ [15], $S = 0\cdot7$ and the density $\rho = 900\,\mathrm{kg\,m^{-3}}$, we estimate $\Delta\chi = 8\cdot8 \times 10^{-7}$ SI units. The values $k_{11} \sim 20 \times 10^{-12}$ N and $k_{33} \sim 5 \times 10^{-12}$ N are then obtained for the elastic constants. These are comparable with those of other nematics, both calamitic and discotic [19].

Figure 8 shows $|k_{33}/\Delta\chi|$ versus reduced temperature for the methylated compounds. The results lie between 2 and 6×10^{-6} N, implying values for k_{33} between 1·4

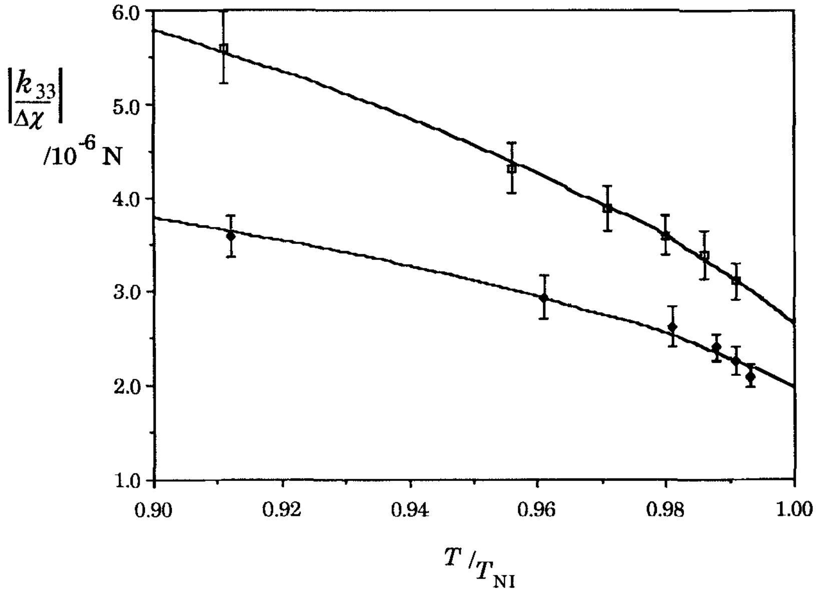

Figure 8. $|k_{33}/\Delta\chi|$ versus reduced temperature for DB126 (◆) and DB119 (□) (100 kHz, 10 and 25 μm PI cells).

and 4×10^{-12} N, assuming the same values as above for $\chi_l^m - \chi_t^m$ and ρ, but taking into account variation in order parameter, S, according to [15]

$$S = (1 - 0{\cdot}98T/T_{NI})^{0{\cdot}22}. \tag{12}$$

The values of $|k_{33}/\Delta\chi|$ for the two materials, if extrapolated to lower temperatures, are found to lie either side of the value of $5{\cdot}5 \times 10^{-6}$ N for H7OBT. Mean field theories of long range order only imply that $|k_{33}/\Delta\chi|$ should vary roughly as S, since $k_{ii} \sim S^2$ [21, 22] and $\Delta\chi \sim S$ [20]. The solid lines on the graph are fits of the experimental data to

$$\left|\frac{k_{33}}{\Delta\chi}\right| = cS^n, \tag{13}$$

where $n = 1{\cdot}67$ and $2{\cdot}01$ for DB126 and DB119 respectively, implying that a theory of this type is inapplicable to these N_D phases due to the existence of short range order.

Figure 9 shows k_{11}/k_{33} versus reduced temperature for both novel materials. The ratio appears to stay roughly constant at ~3–4 (similar to that of H7OBT) until values of $T/T_{NI} > 0{\cdot}98$, where the value increases markedly.

4. Discussion

Figures 3 and 4 show a noticeable drop in $\bar{\varepsilon}'$ as the materials are cooled into the N_D phase. Similar effects in calamitic mesogens are due to the presence of antiparallel dipole correlations [15] in the form of short range smectic ordering. By analogy this suggests that antiparallel dipole correlation is present in the discotic nematic phase of these materials. The dipole moment measuring technique confirms that antiparallel dipole correlations exist in DB126 and, as we have seen, an attempt to understand the molecular dipole as resulting from nearly-free rotation of the substituent polar groups is successful within the tolerance of the experiment.

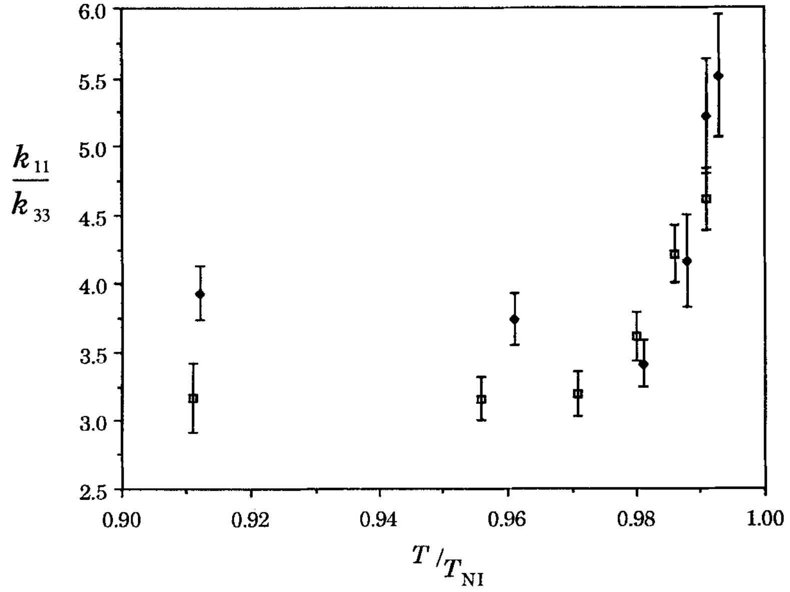

Figure 9. Elastic constant ratio k_{11}/k_{33} versus reduced temperature for DB126 (◆) and DB119 (□) (100 kHz, 10 and 25 μm PI cells).

X-ray measurements [23] show that short range columnar order exists in these systems and we suggest that this affects the elastic behaviour of these compounds. For example, the variation of $|k_{33}/\Delta\chi|$ with temperature is rather stronger than expected from mean field theories of long range order only. This is analogous to calamitic materials where the variation of elastic constants with S^2 is dependent on the degree of short range smectic order [19]. The elastic constant ratio, k_{11}/k_{33}, is found to have a rather high value (much larger than unity) and an unusual variation with temperature; previous results are few. Heppke *et al.* [3], find k_{11}/k_{33} slightly greater than unity and decreasing slightly with temperature for a non-polar discotic compound with a $N_D \rightarrow I$ transition. Ragunathan *et al.* [5], find $k_{11}/k_{33} < 1$ for a polar incommensurate N_D, and Warmardam *et al.* [4], report k_{11}/k_{33} just greater than unity and decreasing slowly with temperature for a polar incommensurate nematic. As far as theoretical results are concerned, Sokalski and Ruijgrok [24] predict $k_{11}/k_{33} > 1$ for a nematic discotic with long range order only (largely confirmed), and Swift and Andereck [25] predict an increase in k_{11}/k_{33} as a nearly second order $N_D \rightarrow D$ transition is approached, due to fluctuations in a local columnar order parameter. Consideration of the symmetry and the requirement of conservation of columns lead to the conclusion that divergence of the director is not allowed within a columnar phase, implying that a large increase in k_{11} would occur as a columnar phase is approached (see Appendix).

Hence, there is little experimental or theoretical precedent for the measured k_{11}/k_{33} magnitude and temperature dependence, as most results are for incommensurate nematics, which are expected to have different behaviour. The only results for a $N_D \rightarrow I$ compound are obtained for a non-polar mesogen, where short range order is not expected. Columnar order is believed to increase k_{11}, as discussed in the Appendix, and here short range order of this type is the probable cause of the unexpectedly large value of k_{11}/k_{33}. The reason for the enhancement in k_{11}/k_{33} as the clearing point is approached remains unclear: there appears to be an increase in k_{11} near the almost second order $N_D \rightarrow I$ transition. This may arise from the fluctuations of a local columnar order parameter (e.g. $\langle P_2(\cos\theta_{0j})\rangle$ in the work of Madhusudana and Chandrasekhar [26]).

We now attempt a theoretical investigation of dipole correlations in discotic systems and its relationship with columnar order. Adapting the argument given by de Jeu [15], for molecules with one dipole, μ_s, in the centre of the molecular spheroid, by making the spheroid oblate (short axis $2a$, long axes $2b$) and using nematic-like order ($S \approx 0{\cdot}5$), we obtain for the Kirkwood correlation factor parallel to the director in a nematic phase

$$g_{\|,\text{nematic}} = 1 + \frac{2N\mu_s}{3k_BT}\int_V dVE_\mu. \tag{14}$$

In this equation, E_μ is the field due to a central dipole, $N = 3/(4\pi ab^2)$ is the dipole density, and V is the volume of a sphere of radius b outside the molecular spheroid. The integral is given by

$$\int_V dVE_\mu = +\frac{\Omega_s\mu_s}{\varepsilon_0}, \tag{15}$$

where $\Omega_s \approx 0{\cdot}04$ for $b = 6a$ [15]. Note that the integral gives a positive result, in contrast to the calamitic case. Then

$$g_{\|,\text{nematic}} \approx 1 + \left(\frac{2\mu_s^2}{3k_BT}\right)\left(\frac{3\times 0{\cdot}04}{4\pi\varepsilon_0 ab^2}\right). \tag{16}$$

For a columnar phase, we assume, in addition to $S \approx 0{\cdot}5$, that the centres of mass of molecules in a column are arranged in a straight line. The integration over the volume V reduces to that over a line l of length $2b$

$$g_{\|,\text{columnar}} = 1 + \frac{2N''\mu_s}{3k_BT} \int_l dl\, E_\mu, \tag{17}$$

where $N'' = 1/2a$ is the line dipole density. Along the line,

$$\int_l dl\, E_\mu = \frac{\mu_s}{2\pi\varepsilon_0} (1/a^2 - 1/b^2), \tag{18}$$

and using $b \gg a$, we find

$$g_{\|,\text{columnar}} \approx 1 + \left(\frac{2\mu_s^2}{3k_BT}\right)\left(\frac{1}{4\pi\varepsilon_0 a^3}\right). \tag{19}$$

Hence the theory predicts a *parallel* dipole correlation in both nematic and columnar phases. This is found to be a consequence of the assumption that the dipole is buried in the centre of the molecule. Figure 10 (*a*) demonstrates the physical argument. Molecule **1** can interact with other molecules in two basic ways, illustrated by molecules **2** and **3**. The position of **2** is more energetically favourable, because the dipoles are closer due to the molecular aspect ratio, and gives parallel correlation. However, a more realistic schematic of the triphenylene benzoate esters is shown in figure 10 (*b*); the molecules have peripherally arranged dipoles. With molecules of this type, antiparallel dipole correlation may be possible in the manner shown. The intermolecular one-to-one correlation is parallel (the molecules cannot pack closely enough to allow the overlap necessary for antiparallel correlation), but over a column the correlation is antiparallel. The requirement that the dipoles are parallel leads to prediction of a tilt of the molecules within the columns. The magnitude of this tilt is predicted to be about 35° due to the angle the dipolar groups make with the molecules; this is supported by the X-ray results [23], which gave the tilt to be approximately 50°.

The experimental results showing antiparallel correlation allow an *ad hoc* reversal of sign in equations (16) and (19). Comparing the magnitudes, we find that the correction to μ_s in the columnar phase is a factor of $10b^2/a^2 \approx 360$ larger than for the nematic phase (the correlation calculated will be too large due to the assumption of

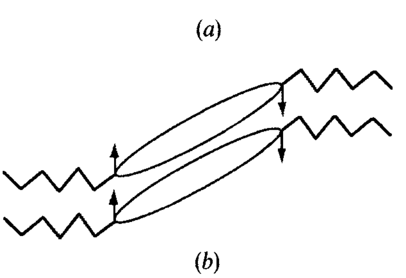

Figure 10. Physical model of dipole correlation in discotic phases.

perfect order). In conclusion we find that any short range columnar order would be expected to enhance antiparallel dipole correlations, as suggested by the experimental results.

The above analysis also suggests the interesting possibilities that a molecule with a dipole buried in the core may exhibit parallel dipole correlations, and also that a molecule with dipoles nearer to the extremities of the disc may allow lamellar ordering by antiparallel dipolar interaction. Further work is needed to investigate the relationship between the position of dipole moments and phase behaviour.

5. Conclusions

The methylation of the benzoate groups in these materials reduces the phase transition temperatures to more accessible levels, with the position of methylation affecting the phase behaviour markedly. Many physical aspects of these compounds are similar to those of calamitic nematics, but often an inversion occurs: the polarizability anisotropy, $\Delta\alpha$, and hence the birefringence, Δn, become negative, as does the magnetic susceptibility anisotropy $\Delta\chi$. However, in these materials, the permittivity anisotropy $\Delta\varepsilon'$ is positive because of a permanent dipole moment parallel to the director; other workers have found that non-polar materials have a negative $\Delta\varepsilon'$. The elastic constants are found to have similar magnitudes to calamitics, but the ratio k_{11}/k_{33} is greater than unity, in contrast with most calamitics.

Evidence is found for antiparallel dipole correlations and short range columnar order in the nematic phase of these materials. This combination of effects has an interesting and important effect on the relevant physical properties. We suggest that dipole correlations favour local columnar order, and predict that antiparallel dipole correlations require that the molecules be tilted within the columns.

The authors thank the University of Hull for the synthesis of the materials described in this paper, R. Bannister and the clean-room staff for provision of the test cells, and M. J. Towler and I. C. Sage for valuable discussions

Appendix

Effect of long range columnar order on elastic constants

Consider a small, cubical box, of total area S, volume V, within the columnar phase: for conservation of columns, the number of columns entering the box is equal to the number of columns leaving, or

$$\int_{S} \mathbf{n}\cdot d\mathbf{S}=0. \tag{A 1}$$

Hence, from the divergence theorem,

$$\int_{V} \nabla\cdot\mathbf{n}\, dV=\int_{S} \mathbf{n}\cdot d\mathbf{S}=0, \tag{A 2}$$

i.e. $\nabla\cdot\mathbf{n}=0$ in a columnar phase.

Since the elastic free energy density of the nematic phase, f, is given by

$$f=\tfrac{1}{2}k_{11}(\nabla\cdot\mathbf{n})^2+\tfrac{1}{2}k_{22}(\mathbf{n}\cdot\nabla\times\mathbf{n})^2+\tfrac{1}{2}k_{33}(\mathbf{n}\times\nabla\times\mathbf{n})^2, \tag{A 3}$$

it follows that splay distortions become disallowed as a columnar phase is approached, and k_{11} becomes infinite. The other two distortions, twist and bend, become more difficult as they involve the distortion of columns, but they are still allowed. This is in contrast with the case of a smectic A phase, where both k_{22} and k_{33} become infinite, but k_{11} remains finite.

References

[1] Chandrasekhar, S., Sadashiva, B. K., and Suresh, K. A., 1977, *Pramana*, **9,** 471.

[2] Nguyen Huu Tinh, Destrade, C., and Gasparoux, H., 1979, *Physics Lett.* A, **72,** 251.

[3] Heppke, G., Kitzerow, H., Oestreicher, F., Quentel, S., and Ranft, A., 1988, *Molec. Crystals liq. Crystals Lett.*, **6,** 71. Heppke, G., Ranft, A., and Sabaschus, B., 1991, *Molec. Crystals liq. Crystals Lett.*, **8,** 71.

[4] Warmerdam, T., Frenkel, D., and Zijlstra, R. J. J., 1987, *J. Phys., Paris*, **48,** 319.

[5] Raghunathan, V. A., Madhusundana, N. V., and Chandrasekhar, S., 1987, *Molec. Crystals liq. Crystals*, **148,** 77.

[6] Mourey, B., Perbet, J. N., Hareng, M., and Le Berre, S., 1982, *Molec. Crystals liq. Crystals*, **84,** 193.

[7] Dubois, J. C., Hareng, M., Le Berre, S., and Perbet, J. N., 1981, *Appl. Phys. Lett.*, **38,** 11.

[8] Beattie, D. R., and Goodby, J. W. (to be published).

[9] Bishop, D. I., Jenner, J., and Sage, I., 1986, *11th International Liquid Crystal Conference*, Berkeley, USA (available from Merck U.K. Ltd.).

[10] Jones, J. C., 1991, Ph.D. Thesis, University of Hull.

[11] Clark, M. G., Raynes, E. P., Smith, R. A., and Tough, R. J. A., 1980, *J. Phys.* D, **13,** 2151.

[12] Saupe, A., 1960, *Z. Naturf.* (*a*), **15,** 815.

[13] Gruler, H., Scheffer, T. J., and Meier, G., 1972, *Z. Naturf.* (*a*), **27,** 966.

[14] Raynes, E. P., 1985, *Molec. Crystals liq. Crystals Lett.*, **1,** 69.

[15] De Jeu, W. H., 1980, *Physical Properties of Liquid Crystals* (Gordon & Breach).

[16] Bone, M. F., Price, A. H., Clark, M. G., and McDonnell, D. G., 1982, in *Liquid Crystalline Ordered Fluids*, Vol. 4, edited by A. C. Griffin and J. F. Johnson (Plenum), p. 799.

[17] Kresse, H., 1983, *Advances in Liquid Crystals*, edited by G. H. Brown (Academic Press), p. 118.

[18] De Jeu, W. H., and Lathouwers, Th. W., 1973, *Molec. Crystals liq. Crystals*, **26,** 235.

[19] Bradshaw, M. J., 1985, Ph.D. Thesis, University of Exeter.

[20] Tsvetkov, V., 1942, *Acta Phys. USSR*, **16,** 132.

[21] Maier, W., and Saupe, A., 1960, *Z. Naturf.* (*a*), **15,** 287.

[22] Poniewerski, A., and Stecki, J., 1982, *Phys. Rev.* A, **25,** 2368.

[23] Haslam, S. D., and Richardson, R. M. (unpublished work).

[24] Sokalski, K., and Ruijgrok, Th. W., 1982, *Physica* (*a*), **113,** 126.

[25] Swift, J., and Andereck, B. S., 1982, *J. Phys., Paris, Lett.*, **43,** 437.

[26] Chandrasekhar, S., 1977, *Liquid Crystals* (Cambridge University Press), Chap. 2, p. 85. Madhusudana, N. V., and Chandrasekhar, S., 1973, *Proceedings of the International Liquid Crystal Conference*, Bangalore, *Pramana*, Suppl. I, p. 57.