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T. J. Phillips[a]; J. C. Jones[a]
[a] Defence Research Agency, England

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On the refractive indices, polarizabilities and order parameter of a nematic discogenic mixture

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

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The phase diagram of a mixture of the discogens triphenylene hexa-*n*-heptanoate (HET7) and triphenylene hexa-(2-methyl-4-*n*-decyloxy)benzoate is presented. This mixture provides a more accessible nematic temperature range than was previously possible. The refractive indices of one mixture composition are measured and a rather small, negative birefringence found. The two-parameter Haller extrapolation method is used to calculate the molecular polarizability ratio $\Delta\alpha/\bar{\alpha}$. This has a rather small magnitude compared with calamitic mesogens, although the individual polarizabilities are much larger, due to the greater molecular mass of these compounds. The calculated value of $\Delta\alpha/\bar{\alpha}$ is used to give the uniaxial orientational order parameter S, whose value is comparable to those of calamitic examples. Tabulated bond polarizability data are used to predict a value for $\Delta\alpha/\bar{\alpha}$, which is found to be similar to the experimental result.

1. Introduction

A most useful approach to the study of the physical properties of discogens [1] is to exploit the analogy between calamitic (rod-like) and discotic systems to the full. This was facilitated by the discovery of the nematic discotic (N_D) phase [2], enabling the work by Heppke *et al.* [3], Warmadam *et al.* [4], Raghunathan *et al.* [5] and Mourey *et al.* [6]. Recently, we have investigated the effect of short range order upon the dielectric and elastic properties of a nematic discogen [7].

As with calamitic systems, control of phase sequence and desirable transition temperatures are most readily achieved by the use of mixtures. In direct analogy to the case of smectic alignment [8], an overlying nematic phase allows improved alignment of a columnar phase. For example, slow cooling of triphenylene hexa-*n*-octoxybenzoate (H8OBT) from the aligned nematic phase into its columnar phase, gives uniform alignment, in contrast with triphenylene hexa-*n*-heptanoate (HET7), which has no nematic phase and simply gives a focal-conic texture. Here, we present the phase diagram of a triphenylene mixture. The low nematic temperatures of one of the resultant mixtures allows measurement of the refractive indices and the quadrupolar uniaxial long range order parameter S. The results are compared with calamitic examples.

2. Experimental

2.1. *Phase diagram of the mixture*

The two triphenylenes shown in figure 1 were mixed. The first component was DB126 [9] (triphenylene hexa-(2-methyl-4-*n*-decyloxy)benzoate) with phase transitions (±2°C, temperatures obtained on cooling are indicated by square brackets)

$$C_1\,23\,C_2\,67\,C_3\,109[75]\,N_D\,164\,I,$$

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*Author for correspondence.

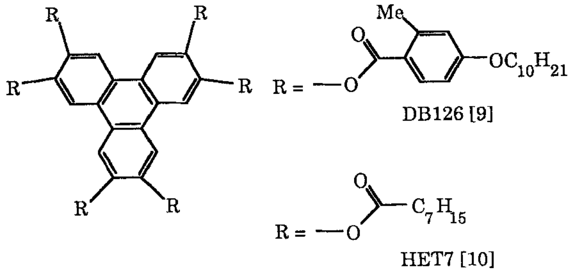

Figure 1. Structures of materials.

and the second component was triphenylene hexa-*n*-heptanoate, HET7 [10], with phase transitions

$$\mathrm{C}\,64\,\mathrm{D_{hd}}\,128{\cdot}5\,\mathrm{I}.$$

The former compound has a single, nematic mesophase, whereas the latter has a single columnar mesophase. Mixtures of various compositions were made by dissolving the two components in ethyl acetate and evaporating off the solvent. The resultant phase diagram, T1, as a function of composition, was then obtained by measuring the phase transitions using differential scanning calorimetry (DSC), thermal optical analysis (TOA) and polarizing optical microscopy, and is shown in figure 2. The diagram consists of two parts: the right-hand part of the diagram has a nematic region with an underlying crystal phase; the left-hand part has a $\mathrm{D_{hd}}$ phase with a crystal phase below. The nematic–isotropic line is linear on the right-hand half of the diagram, extrapolating to a virtual $\mathrm{N_D}\to\mathrm{I}$ transition at ~30°C for HET7. The nematic temperatures for a range of mixtures are considerably lower than for DB126, providing far more useful materials. The 45 wt% DB126 mixture, T1a, has phase transitions

$$\mathrm{C}\,66[40]\,\mathrm{N_D}\,90\,\mathrm{I},$$

and is the mixture used for the rest of this work.

As an attempt was made to use the Schröder–van Laar equation [11]

$$\ln X_A = \frac{\Delta H_A}{R}\left(\frac{1}{T_A} - \frac{1}{T_M}\right), \tag{1}$$

to predict the melting temperature of a mixture of components, where X_A is the mole fraction of component A in the mixture, ΔH_A the melting enthalpy of the component, R the gas constant, T_A the melting temperature of the component, and T_M the melting temperature of the mixture. The Schröder–van Laar prediction for the melting point of T1a, using the measured melting enthalpy of HET7 (21·4 kJ mol^{-1}), is 54°C. In fact, the melting point of T1a is slightly *higher* than that of HET7, showing that the ideal mixture assumption in the derivation of equation (1) is not valid here.

2.2. *Refractive index measurement*

The refractive indices of T1a were measured, to a tolerance of 0·1 per cent, using an Abbé refractometer, with light of wavelength $\lambda_{\mathrm{Na_D}} = 589{\cdot}6\,\mathrm{nm}$. The $\mathrm{N_D}$ phase of the sample was aligned homeotropically between the prisms using a thin layer of rubbed poly-vinyl alcohol (PVA). When the sample was cooled into the crystalline phase, the alignment deteriorated and the refractive indices could no longer be measured. The results are shown plotted versus temperature in figure 3; where $n_{\parallel}$, $n_{\perp}$ and

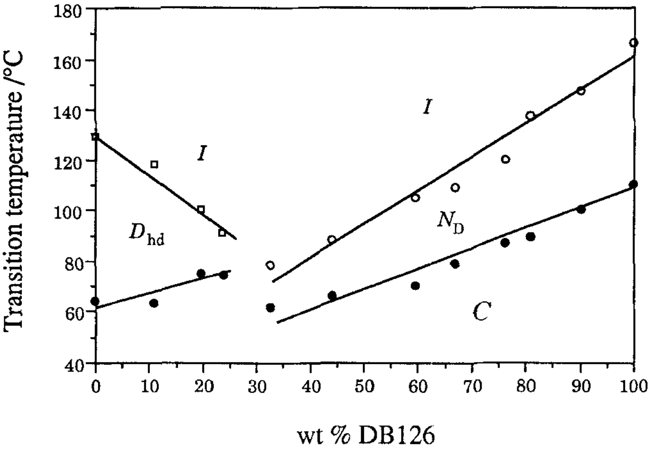

Figure 2. Phase diagram for system T1.

$\bar{n}=\frac{1}{3}(n_{\parallel}+2n_{\perp})$ are the refractive indices parallel and perpendicular to the director and the mean refractive index, respectively. The material clearly has a negative birefringence, $\Delta n=n_{\parallel}-n_{\perp}$, as confirmed by conoscopic measurements [7]. The refractive indices were also measured at several other wavelengths and fitted to the two-parameter Cauchy formula

$$n_{\lambda}=n_{\infty}+\frac{A}{\lambda^2}, \tag{2}$$

where n_{λ} is the refractive index at wavelength λ and n_{∞} is the refractive index at infinite wavelength.

3. Discussion and calculation

3.1. *Refractive indices and polarizability*

The data for $\bar{n}$ in figure 3 are continuous at the N→I transition to within experimental tolerance. Since $\bar{n}$ is given by the Lorenz–Lorentz equation [12]

$$\frac{\bar{n}^2-1}{\bar{n}^2+2}=\frac{N}{3\varepsilon_0}\bar{\alpha}, \tag{3}$$

and the mean molecular polarizability $\bar{\alpha}$ is not expected to change at the transition, this shows that the molecular number density N, and hence the density ρ, is continuous at the transition. This supports the argument that the change in the mean permittivity $\bar{\varepsilon}$ at the transition described previously [7] is purely a dipole correlation effect, and contains no density contribution. In addition, assuming ρ is comparable to calamitic values, $N=\rho N_A/M_m$ will be reduced by a factor of about six because of the increase in the molar mass M_m (compare the molar mass of 5CB, 249×10^{-3} kg mol^{-1}, with that of T1a, 1481×10^{-3} kg mol^{-1}). Now, because $\bar{n}$ has roughly the same value as calamitic examples, this suggests that $\bar{\alpha}$ is about a factor of six greater than for calamitics.

Figure 4 shows the plot of birefringence Δn versus temperature; Δn is found to have a rather small magnitude, about 0·08 at the lowest temperature measurable ($T/T_{NI}=0{\cdot}86$). The permittivity anisotropy at optical frequencies is given by [13]

$$\Delta\varepsilon_{op}=n_{\parallel}^2-n_{\perp}^2=\frac{NhF}{\varepsilon_0}S\Delta\alpha, \tag{4}$$

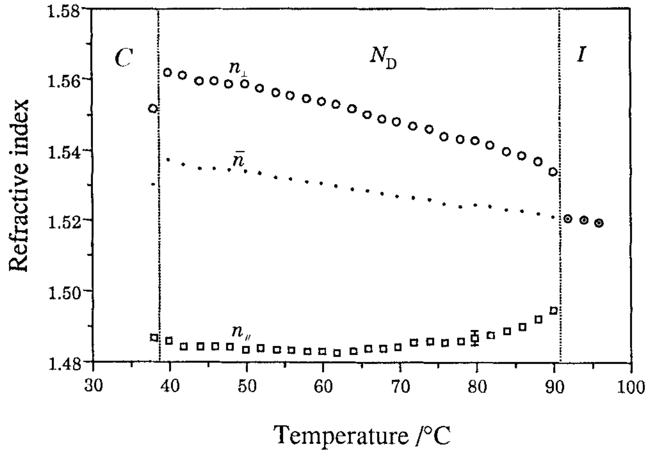

Figure 3. Refractive indices versus temperature for T1a (45 wt%DB126).

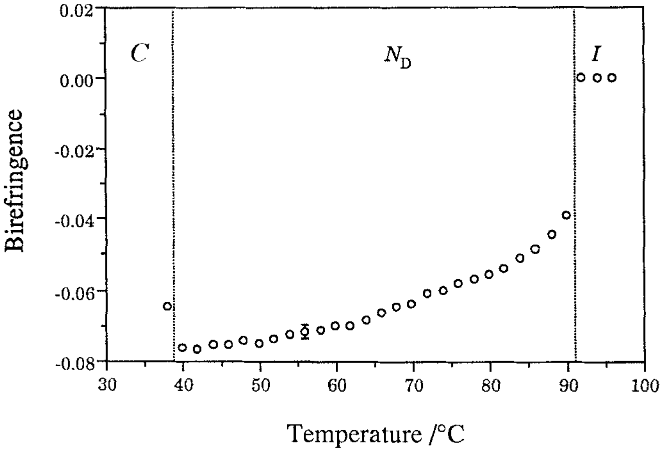

Figure 4. Birefringence versus temperature for T1a (45 wt%DB126).

where h and F are local field factors. (These do not vary much between discogens and calamogens as $\bar{\varepsilon}$ is comparable and the effect of N is small.) As the birefringence of T1a is rather smaller than that of most calamitics, the product $NS\Delta\alpha$ must be rather smaller. Hence because of the reduction in N, $S\Delta\alpha$ must be rather less than six times larger than for a typical calamitic material.

3.2. *Order parameter calculation*

The order parameter S as a function of temperature was determined using the Vuks expression [14]

$$S=\frac{\bar{\alpha}}{\Delta\alpha}\frac{n_{\parallel}^2-n_{\perp}^2}{\bar{n}^2-1}. \tag{5}$$

The ratio $\Delta\alpha/\bar{\alpha}$ was measured using the Haller method [15], to a random tolerance of ~ 1 per cent although a systematic error of the order of 10 per cent may be inherent in this method [16]. In this method the polarizabilities are assumed independent of temperature, and the order parameter to vary as

$$S=(1-HT/T_{\mathrm{NI}})^m, \tag{6}$$

where T is the absolute temperature, T_{NI} is the clearing temperature and H, m are variable parameters. The Haller plot (figure 5) gave the best fit to the data, with values for the parameters $H=0{\cdot}995\pm0{\cdot}001$, $m=0{\cdot}225\pm0{\cdot}001$. The value of $|\Delta\alpha|/\bar{\alpha}$ calculated was $0{\cdot}270\pm0{\cdot}003$ (cf. 5PCH, $\Delta\alpha/\bar{\alpha}=0{\cdot}446$; 5CB, $\Delta\alpha/\bar{\alpha}=0{\cdot}748$ [17]). This is rather a small value considering that the basic triphenylene molecule has three benzene rings oriented in the same plane and implies, as above, that $\bar{\alpha}$ is very large in these molecules. The Cauchy formula (equation (2)) was used to give values for all the refractive indices at infinite wavelength. The ratio $(|\Delta\alpha|/\bar{\alpha})_\infty$ was calculated as above and found equal to $0{\cdot}23\pm0{\cdot}01$. This value is used later to compare with tabulated polarizability data.

The order parameter was calculated from equation (5), using the $\lambda_{\mathrm{Na_D}}$ value for all quantities. The results are shown in figure 6 versus reduced temperature T/T_{NI}, where the experimental results are represented by the filled circles and the solid line is the theoretical Meier–Saupe (M–S) variation (given by equation (6), to within 1 per cent, with $H=0{\cdot}98$, $m=0{\cdot}22$ [12, 18]). The order parameter has a similar value to that measured for calamitics [17], suggesting that the low birefringence is not due to an unusually low S, and rather that $|\Delta\alpha|$ is not sufficiently large to compensate for the large $\bar{\alpha}$. The fact that the value is slightly lower than the M–S prediction may be due to the binary mixture interaction effects elucidated by Palffy-Muhoray *et al.* [19], which predict a lower order parameter in the mixture than in either single component. This theory also predicts a deviation from the M–S temperature-dependence, although the effect seen in these results is probably largely due to short range order affecting the refractive indices.

3.3. *Calculation of molecular polarizabilities*

Here an attempt is made to calculate the molecular polarizability tensor of T1a using the tabulated bond polarizability data given by le Fèvre [20]. To do this, uniaxial ordering of the substituent benzene rings on DB126 and the carbonyl groups is assumed (this makes little difference to the final calculated value). The polarizabilities of

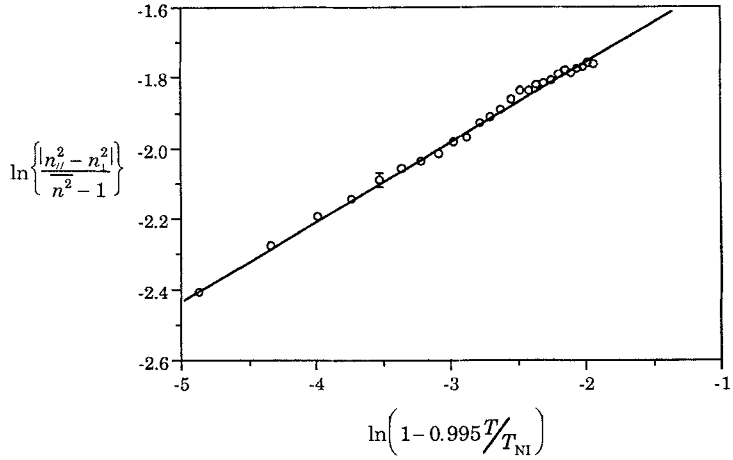

Figure 5. Haller plot of refractive index data, $H=0{\cdot}995$. $y=-1{\cdot}3097+0{\cdot}2245x$, and $r=0{\cdot}9978$.

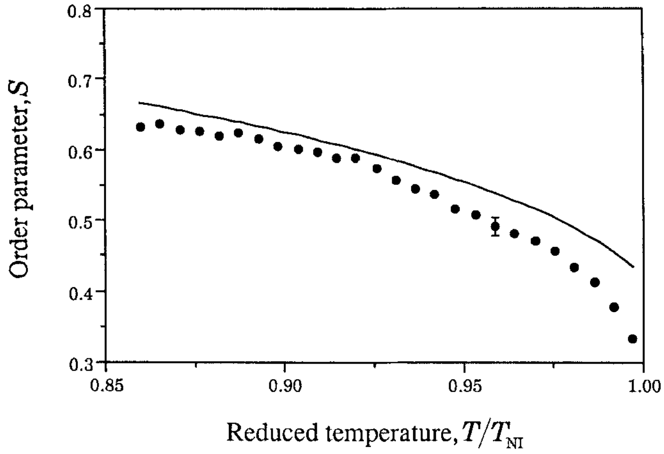

Figure 6. Order parameter versus reduced temperature for the measured value of $|\Delta\alpha|/\bar{\alpha}$. The solid line is the Meier–Saupe prediction. ($|\Delta\alpha|/\bar{\alpha}=0{\cdot}270$).

a single substituent group are calculated, assuming an all-*trans*-conformation for the alkyl chains, and then combined with the core polarizability to give the value for the molecule. The transverse polarizability of the core is expected to be considerably affected by de-localization of the electron cloud. Hückel theory of molecular orbitals [21] could be used to account for this, but is found to give incorrect results unless excessive complications are introduced. Here the effect is calculated approximately in the following simple way: the transverse polarizability of a benzene ring is taken to be due to a spherical electron cloud around a point charge, and the result for a benzene ring pair is achieved by extending one dimension of the cloud in the manner outlined below.

The polarizability of a spherical cloud of charge q surrounding a point charge of equal and opposite magnitude is calculated by a simple semi-classical argument using the restoring force arising when the cloud is distorted a distance x by an external field E. This force is given by

$$F_{\text{res}}=-\frac{q^2}{4\pi\varepsilon_0 x^2}\frac{x^3}{r^3}=-qE, \tag{7}$$

where r is the radius of the cloud. The induced polarization is then

$$p=qx=4\pi\varepsilon_0 r^3 E, \tag{8}$$

and the polarizability

$$\alpha=\frac{\partial p}{\partial E}=4\pi\varepsilon_0 r^3. \tag{9}$$

The measured transverse polarizability of a benzene ring of $12{\cdot}46\times10^{-40}\,\text{F m}^2$ corresponds to a physically reasonable value for r of 2·24 Å. Expanding one of the dimensions of the cloud to $2\times2{\cdot}24=4{\cdot}48$ Å gives a value for $\alpha=25{\cdot}00\times10^{-40}\,\text{F m}^2$ along a benzene ring pair. This method has been found to have a wide applicability (for example, for azobenzene a longitudinal polarizability of $40{\cdot}5\times10^{-40}\,\text{F m}^2$ is obtained, compared with an estimated value from the optical Kerr effect [22] of $38\times10^{-40}\,\text{F m}^2$), and gives values for the triphenylene core which compare fairly well with those in solution [23].

Calculated values of the polarizabilities (all × 10^{-40} F m^2).

	Core		Substituent group		Molecule	
Material	α_s	α_t	α_l	α_t	α_s	α_t
DB126	24·56	56·19	40·94	35·83	239·5	286·5
HET7	24·56	56·19	20·21	18·46	135·3	172·2
T1a					167·6	207·6

We now use the le Fèvre value for the polarizability across a biphenyl group and take a triphenylene core as three such groups at 120° intervals. No double counting of benzene rings is implied by this method, because the above calculation eliminates the charge of the cloud. The calculated polarizabilities are summarized in the table, where the core and complete molecule values α_s and α_t are parallel and transverse to the molecular short axis respectively, and the substituent group values α_l and α_t are along and transverse to the length of the group respectively.

The results for the two molecules are combined using a weighted average (the mole fraction of DB126 is 0·31) to achieve the final values for T1a. The calculated value of $\bar{\alpha}$ is 194×10^{-40} F m^2, which is indeed approximately six times that for *p*-azoxyanisole [12]. The final value for $|\Delta\alpha|/\bar{\alpha}$ is $0{\cdot}21 \pm 0{\cdot}03$ (or $0{\cdot}19 \pm 0{\cdot}03$ using the triphenylene solution values). This compares rather well with the above measured value for this ratio at infinite wavelength of $0{\cdot}23 \pm 0{\cdot}01$, considering the approximate nature of the polarizability calculation.

4. Conclusions

The phase diagram of the triphenylene mixture shows significant depressions of the transition temperatures, providing a far more accessible nematic range. The nematic refractive indices of one mixture have been measured. The material has a negative Δn of rather small magnitude.

The refractive index data have been used to calculate the uniaxial order parameter, S, of the material, using the two-parameter Haller extrapolation method. The order parameter is found to have roughly the expected value, similar to that for calamitics, and indicates that the low birefringence is not due to an unusually low degree of order in the system.

Bond polarizability data have been used to calculate a value for $\Delta\alpha/\bar{\alpha}$. This is compared with the measured value and found to agree rather well. The individual polarizabilities are much larger than calamitic examples, although $|\Delta\alpha|/\bar{\alpha}$ is rather small due to the large isotropic contribution from the substituent chains.

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