Determination and Analysis of the Physical Properties of a New Class of Polar Nematic Liquid Crystals

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We have measured the physical properties of three homologues of a new class of polar nematic liquid crystals having no molecular association. On the basis of mean field and continuum theories an analysis of the physical properties has been performed. The advantageous application of this class of compounds (substituted aromatic ketones) in liquid crystal displays – especially in the highly multiplexed twisted nematic display – is outlined and an example of a simple practical mixture is given.

Introduction

Polar nematic liquid crystals whose molecules incorporate a terminal group with a large dipole moment (e.g., a cyano-group) exhibit a high degree of molecular association [1, 2]. As this fact is not taken into account in the simple theories of the nematic phase [3–6] these theories are incapable of predicting with any accuracy the physical properties of a liquid crystal of a given molecular structure.

In the course of our investigations [7–11] of novel nematic liquid crystals for application in twisted nematic displays [12] with multiplexed addressing [13, 14] we have synthesised polar nematic compounds **1** (n-alkyl-4-(trans-4-n-alkyl-cyclohexyl)phenyl ketones) which exhibit a very small or no degree of association. It is the purpose of this paper to describe the macroscopic physical properties of these new liquid crystals and to relate them by means of theoretical considerations to their molecular structure.

In addition it will be demonstrated that the dielectric and elastic properties of these nematic liquid crystals can be exploited to improve the steepness of the contrast curve (brightness-voltage characteristic) of the twisted nematic display. A steep characteristic is required to achieve good contrast [15] and wide viewing angles at high multiplexing rates.

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Experimental

The compounds investigated were synthesised and their structures verified by literature methods [16, 17]. The purity of the compounds was checked by GLC and found to be ≧ 99.9%. Standard methods and devices were also used for the determination of the phase transitions [18].

For the measurement of the refractive indices a Zeiss Abbé refractometer model B was used with the illumination provided by either a sodium spectral light source (0.589 µm) or a HeNe-laser (0.633 µm). The temperature was regulated by a Lauda K2R thermostat and read by a Pt-100 resistance temperature sensor and a Fluke 2180A Digital Thermometer. The measurement was performed in the transmission mode. In the nematic phase a uniformly oriented layer of the liquid crystal was provided at the plane of refraction by a thin (about 100 Å) layer of SiO obliquely evaporated [19] onto the surface of the measuring prism. A sheet of polaroid, appropriately oriented and inserted between eye and ocular, was used to discriminate between the ordinary and extraordinary light rays which have polarization directions perpendicular to each other.

The methods used to determine the diamagnetic anisotropy [20], the elastic constants [18, 21, 22], and the rotational viscosity [23] have already been described in detail.

Automated digitally controlled set-ups were developed for the measurement of the density and the dielectric constants. The microcomputers (Apple II e) were interfaced [24] in the first case to an

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A. Paar DMA 50 density meter equipped with a DMA 601 HT microcell (which requires only 0.3 cm^3 of the liquid to be measured). In the second case a special, precise capacitance meter [25] was applied to measure simultaneously the capacitance values of liquid crystal condensors with uniform orientations parallel and perpendicular, respectively, to the measuring electric field. The capacitors were immersed directly in the temperature controlling bath. The value of the temperature was taken in the vicinity of the sample by a Pt 100 resistance temperature sensor and controlled by the microcomputer and a thermostat (Lauda K2R). Various temperature intervals were chosen for the density measurements. Intervals of 0.05 °C were used within a range of ± 2 °C of the nematic-isotropic phase transition and outside of this range intervals of 0.5 °C were used. After each temperature change it was waited until the thermal equilibrium had been reached before accepting the new values. In the case of the dielectric constants, temperature intervals of 1 °C were used.

During the experiments the data were stored on a Winchester hard disk (Symbiotic Computers 5 MByte). For the numerical analysis and the generation of plots the data were transfered via a Super Serial-RS232 interface link [26] to a VAX 11/780 minicomputer.

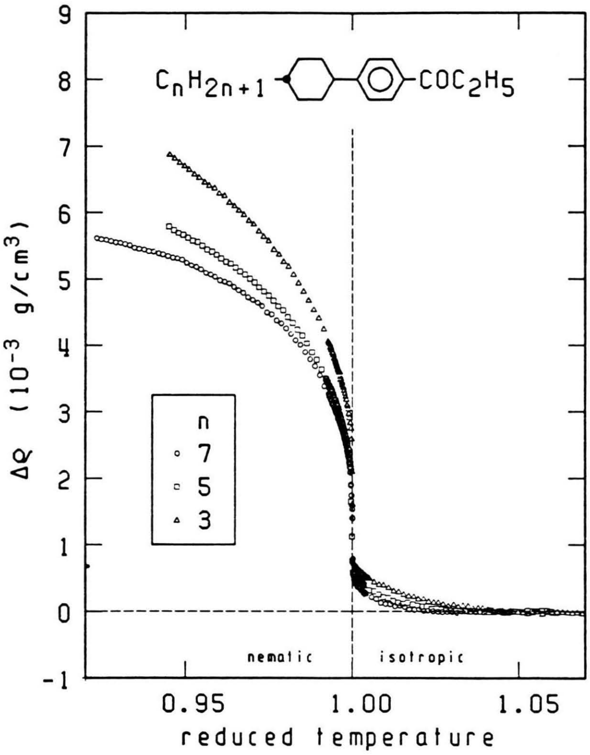
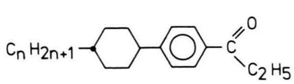


Fig. 1. The density difference $\Delta\varrho$ as a function of reduced temperature for ketones **1** (n = 3, 5, 7).

The accuracy of the experimental values are estimated as follows: temperature values ± 0.1 °C; density values $\pm 5 \cdot 10^{-5}$ g/cm^3; diamagnetic anisotropy ± 2%; refractive indices $\pm 3 \cdot 10^{-4}$; dielectric constants ± 0.5%; elastic constants ± 5%; and rotational viscosity ± 5%.

Table 1. Physical data for the ketones **1** of structure



Property	$n = 3$	$n = 5$	$n = 7$
T_{CN} (°C)	49.2	56.6	52.2
T_{NI} (°C)	57.0	69.0	72.7
T_{lin} (°C)	70.0	80.0	80.0
M (g/mol)	258.4	286.5	314.5
ϱ_0 (g/cm^3)	0.99530 $\pm 4 \cdot 10^{-5}$	0.98343 $\pm 6 \cdot 10^{-5}$	0.97429 $\pm 8 \cdot 10^{-5}$
ϱ_1 (10^{-4} g/cm^3)	-7.115 $\pm 4 \cdot 10^{-3}$	-7.181 $\pm 7 \cdot 10^{-3}$	-7.360 $\pm 8 \cdot 10^{-3}$
$\Delta\varrho_{NI}$ (10^{-3} g/cm^3)	2.0	1.6	1.6
$\Delta\varrho_{NI}$ (10^{-3} g/cm^3) (PCH-n)	5.5	3.7	3.4

Results

The molecular structure of the investigated ketones **1** is shown in Table 1. The melting points (T_{CN}) and the nematic-isotropic transition temperatures (T_{NI}) of the ketones **1** are also recorded in Table 1.

The density of the three ketones was measured over the temperature range from 40 °C–90 °C. The lower value depended on the supercoolability of the individual compound. As for simple organic liquids [27] the temperature dependence of the density in the isotropic phase can be approximated by the linear function $\varrho_{lin} = \varrho_0 + \varrho_1$ $(T - 273.2°)$ provided that T is greater than T_{lin} where T_{lin} is a

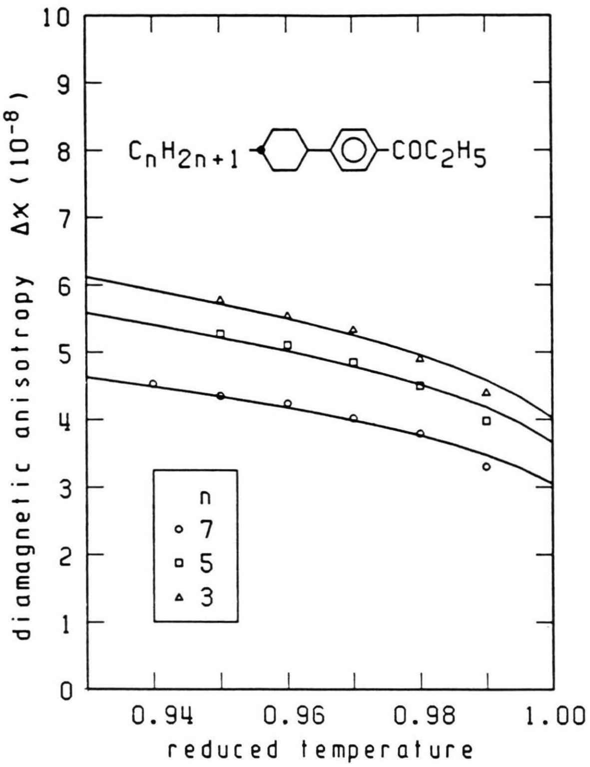


Fig. 2. The diamagnetic anisotropy $\Delta\chi$ as a function of reduced temperature for ketones **1** ($n = 2, 5, 7$).

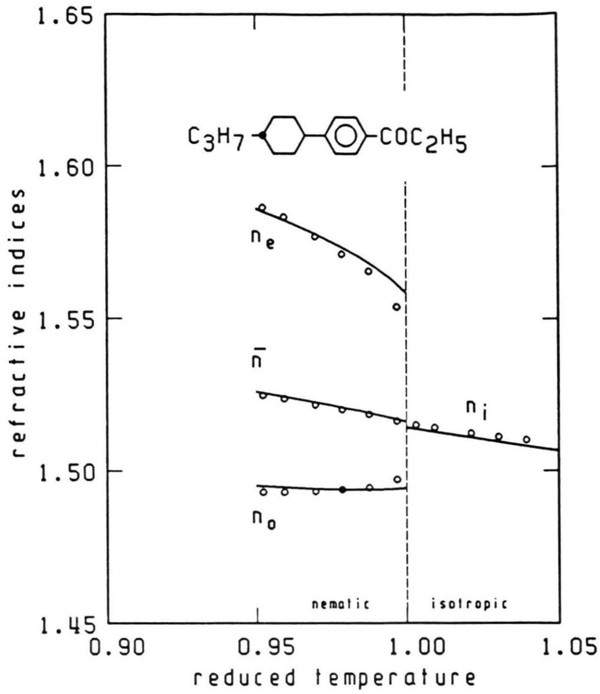


Fig. 3. The refractive indices n_e, n_0, $\bar{n}$, ($\bar{n} = (\overline{n^2})^{1/2}$) and n_i as a function of reduced temperature for compounds **1** ($n = 3$) for a wavelength of 0.589 µm. The solid line is theoretical fit.

temperature above T_{NI} at which pretransitional effects can be assumed to be absent. Values for the parameters ϱ_0, ϱ_1, T_{lin} and T_{NI} are listed in Table 1. It is seen that ϱ_0 and ϱ_1 differ only slightly for the three homologues. In Fig. 1 $\Delta\varrho$ ($\Delta\varrho = \varrho - \varrho_{lin}$) is shown as a function of the reduced temperature $t_r = T/T_{NI}$ (T in K).

The temperature dependence of the diamagnetic anisotropy $\Delta\chi$ is depicted in Figure 2. The temperature dependence of the refractive indices for sodium light (0.589 µm) is shown in Figs. 3–5 and in Figs. 6–8 for the light of a HeNe-laser (0.633 µm). The dielectric constants ($\varepsilon_\parallel$ and $\varepsilon_\perp$), the dielectric mean ($\bar{\varepsilon} = (\varepsilon_\parallel + 2\varepsilon_\perp)/3$) in the nematic phase, and the isotropic dielectric constant ε_i are plotted in Figs. 9–11 as functions of reduced temperature. $\varepsilon_\parallel$ is the dielectric constant with the electric field parallel to the optic axis and $\varepsilon_\perp$ that perpendicular. The points shown are static values measured at 1 kHz. The temperature dependence of the elastic constants of splay deformation (k_{11}) and of twist deformation (k_{22}) is shown in Fig. 12 and Figure 13. The ratio of k_{33} (bend elastic constant) to k_{11} is plotted as a function of reduced temperature in Figure 14.

Discussion and Analysis

Density

The largest contribution to the temperature dependence of the density is the linear dependence mentioned above. In Fig. 1 the difference ($\Delta\varrho$) between the experimentally determined density and the density obtained from the straight line fit are plotted against the reduced temperature t_r. Three factors are responsible for the observed density difference $\Delta\varrho(t_r)$. Firstly, a small pretransitional change in the density is observed just above T_{NI}*.

* A fit of this behaviour in terms of a second order phase transition [3, 4] results in parameter values with rather large errors. This may be due to the smallness of the pretransitional effect and the overlying effect of the much greater first order transition due to the nematic-isotropic transition.

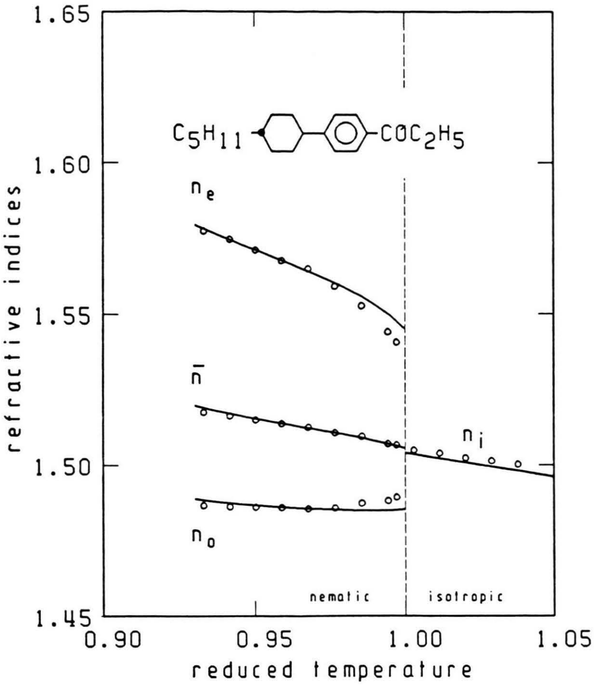


Fig. 4. The refractive indices n_e, n_0, $\bar{n}$, and n_i as a function of reduced temperature for ketones **1** ($n = 5$) for a wavelength of 0.589 μm. The solid line is a theoretical fit.

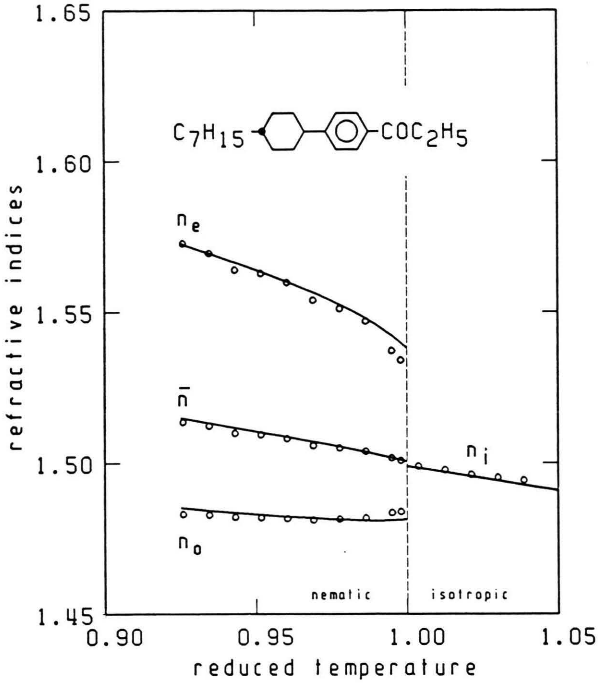


Fig. 5. The refractive indices n_e, n_0, $\bar{n}$, and n_i as a function of reduced temperature for ketones **1** ($n = 7$) for a wavelength of 0.589 μm. The solid line is a theoretical fit.

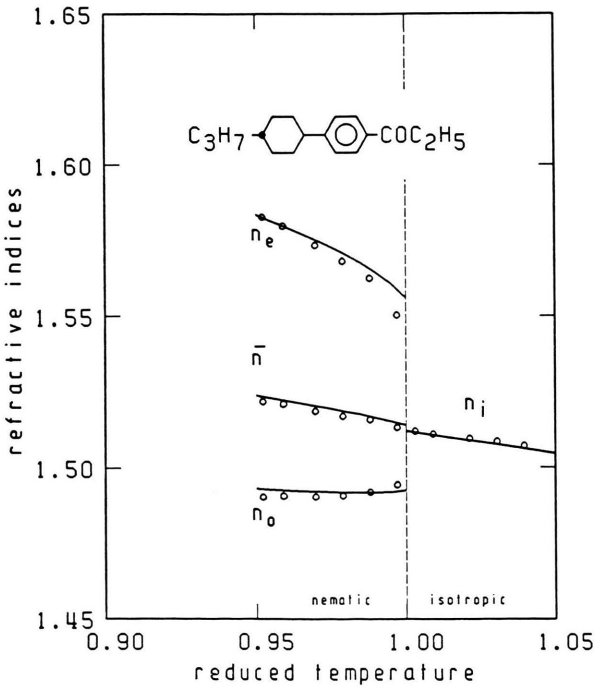


Fig. 6. The refractive indices n_e, n_0, $\bar{n}$, and n_i as a function of reduced temperature for ketones **1** ($n = 3$) for a wavelength of 0.633 μm. The solid line is a theoretical fit.

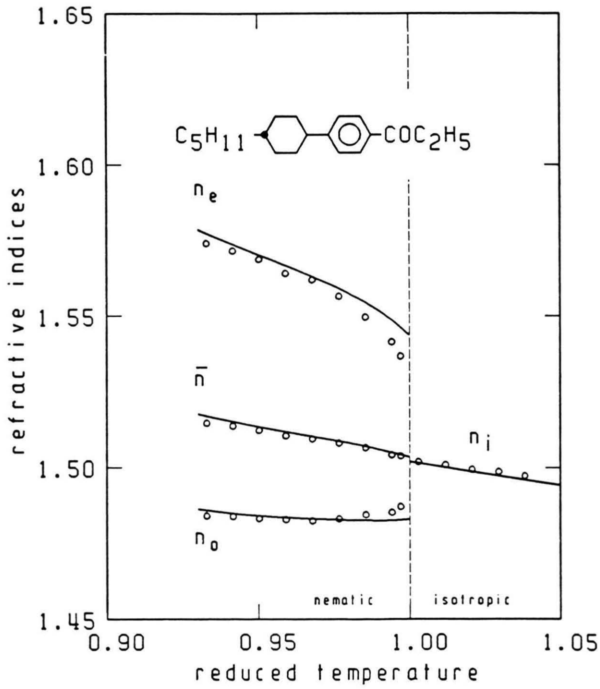


Fig. 7. The refractive indices n_e, n_0, $\bar{n}$, and n_i as a function of reduced temperature for ketones **1** ($n = 5$) for a wavelength of 0.633 μm. The solid line is a theoretical fit.

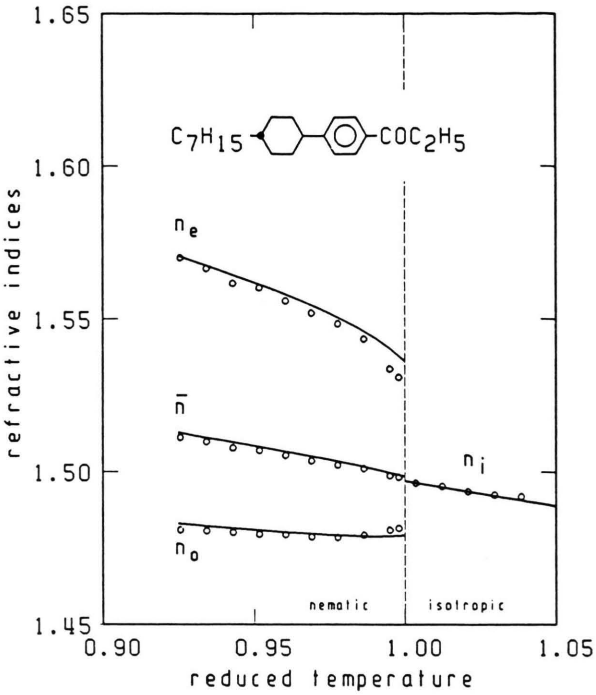


Fig. 8. The refractive indices n_e, n_0, $\bar{n}$, and n_i as a function of reduced temperature for ketones **1** ($n = 7$) for a wavelength of 0.633 μm. The solid line is a theoretical fit.

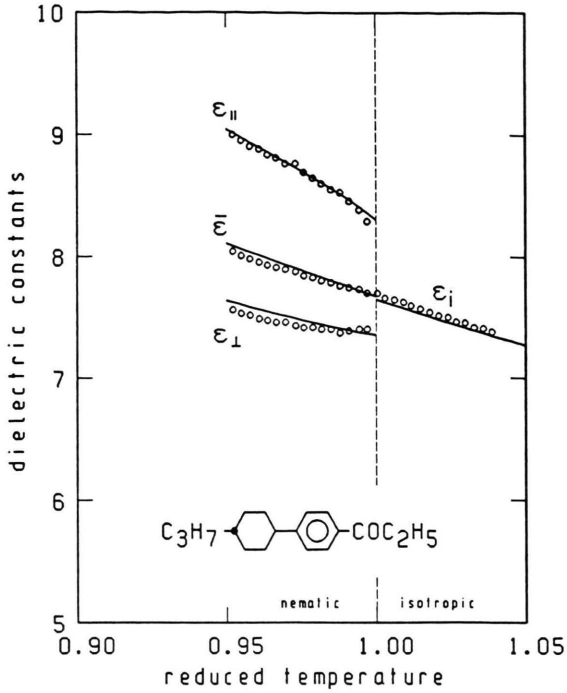


Fig. 9. The dielectric constants $\varepsilon_{\parallel}$, $\varepsilon_{\perp}$, $\bar{\varepsilon}$ ($\bar{\varepsilon} = (\varepsilon_{\parallel} + 2\varepsilon_{\perp})/3$), and ε_i as a function of reduced temperature for ketones **1** ($n = 3$). The solid line is a theoretical fit.

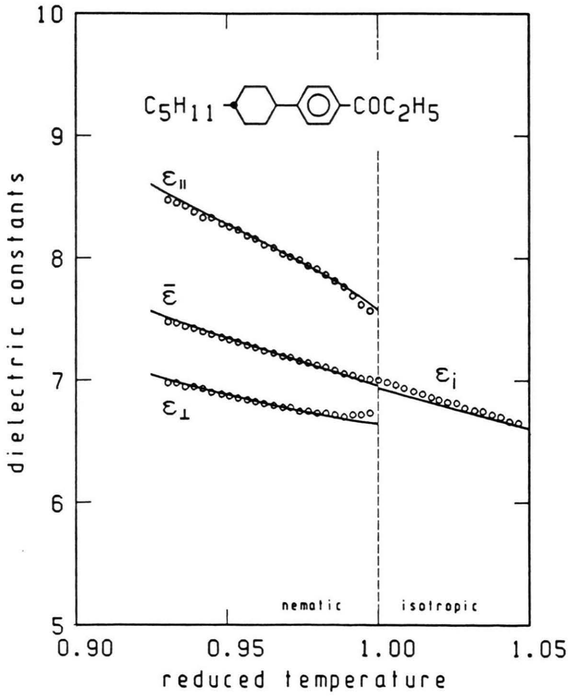


Fig. 10. The dielectric constants $\varepsilon_{\parallel}$, $\varepsilon_{\perp}$, $\bar{\varepsilon}$, and ε_i as a function of reduced temperature for ketones **1** ($n = 5$). The solid line is a theoretical fit.

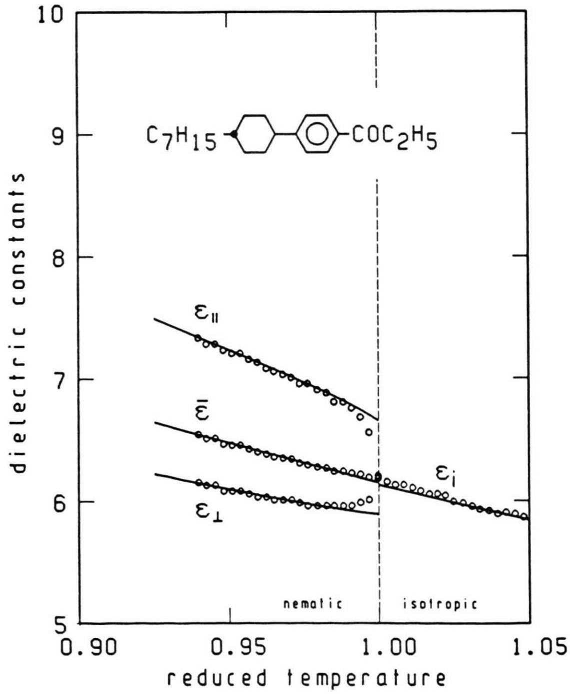


Fig. 11. The dielectric constants $\varepsilon_{\parallel}$, $\varepsilon_{\perp}$, $\bar{\varepsilon}$, and ε_i as a function of reduced temperature for ketones **1** ($n = 7$). The solid line is a theoretical fit.

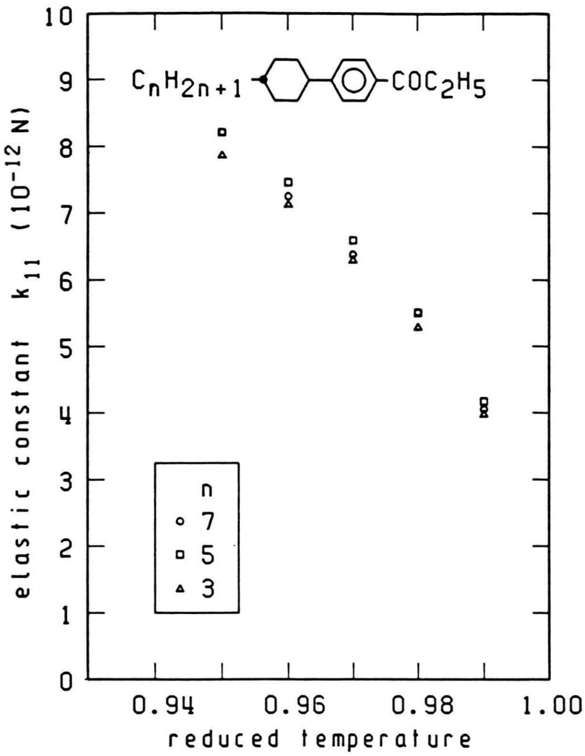


Fig. 12. The elastic constant of splay deformation k_{11} as a function of reduced temperature for ketones **1** ($n = 3, 5, 7$).

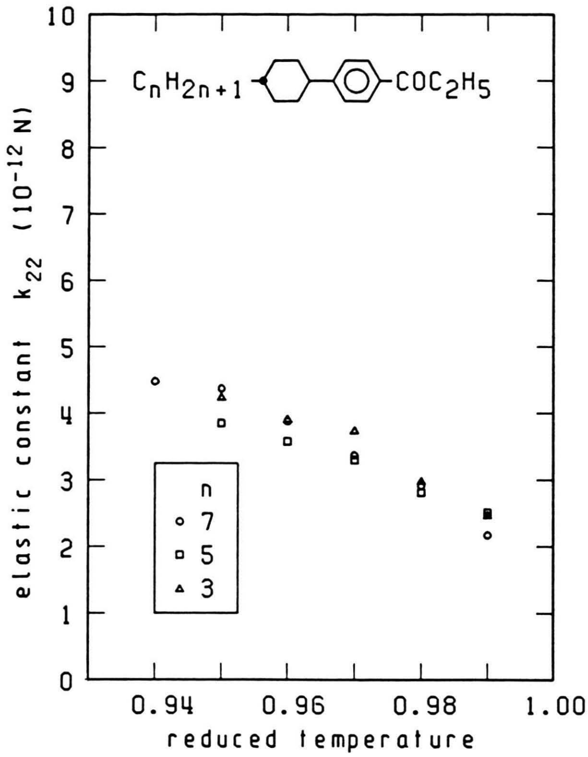


Fig. 13. The elastic constant of twist deformation k_{22} as a function of reduced temperature for ketones **1** ($n = 3, 5, 7$).

The second contribution is the discrete discontinuity $\Delta\varrho_{NI}$ at the nematic-isotropic phase transition. The values for $\Delta\varrho_{NI}$ given in Table 1 are about 2–3 times smaller than those found for polar nematic compounds with a terminal cyano-group and, in addition, are less dependent on the chain length. For reference $\Delta\varrho(t_r)$ of the equivalent PCH homologues [28] with a cyano-group in place of a ketone group, is depicted in Fig.15 and their $\Delta\varrho_{NI}$ values are listed in Table 1. We assume that the molecular association of the molecular dipoles attributable to the terminal cyano-groups [18] is responsible for the larger discontinuities. The third contribution to the density difference $\Delta\varrho(t_r)$ is due to the temperature dependence of the nematic order parameter. This temperature dependence is strongest for the $n = 3$ homologue and increasing with chain length (see Figure 1).

Order Parameter

The Maier-Saupe mean field theory [3, 4] has been used to obtain an analysis of the macroscopic properties of the nematic phases of the compounds under investigation. The theory assumes a cylindrical symmetry of the molecules and a $(1/V)^2$ dependence of the intermolecular interaction strength (V is the mean molecular volume). A consequence of this theory is that a single order parameter S is obtained on a universal temperature scale τ defined as

$$\tau = t_r (V^{nem}/V^{nem}_{NI})^2 . \quad (1)$$

Here t_r is the reduced temperature defined above, V^{nem} is the mean molecular volume in the nematic phase and V^{nem}_{NI} is the mean molecular volume at T_{NI}. $V^{nem} = (N^{nem})^{-1} = \varrho^{nem} L/M$, where N is the particle number density, M the molecular mass, and L is Avogadro's number ($6.0220 \cdot 10^{23}$ cm^{-1}). Equation (1) can be reformulated as follows:

$$\tau = t_r (\varrho^{nem}_{NI}/\varrho^{nem})^2 . \quad (2)$$

Thus the universal temperature scale τ can be related to the reduced temperature scale t_r by using (2), if the density $\varrho^{nem}(t_r)$ is known. The order parameters of the ketones **1** ($n = 3, 5, 7$) have been

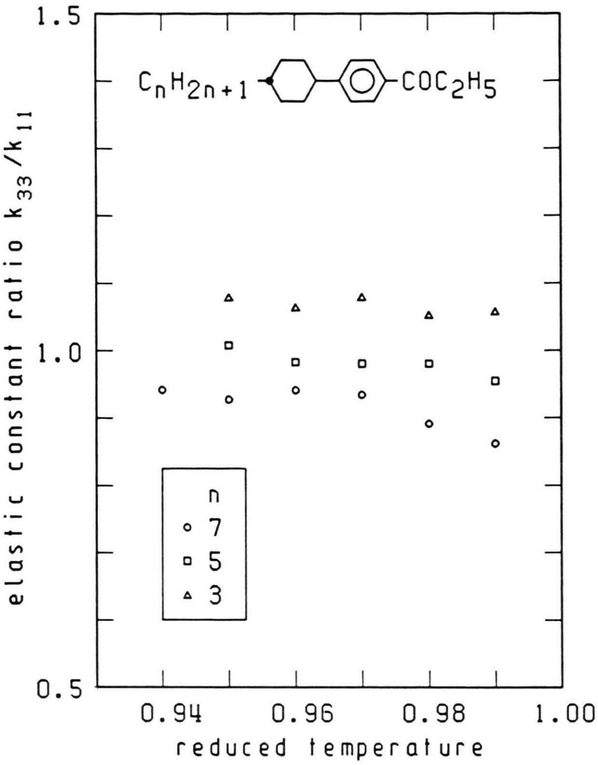


Fig. 14. The ratio of the elastic constants of bend and splay deformation k_{33}/k_{11} as a function of reduced temperature for ketones **1** ($n = 3, 5, 7$).

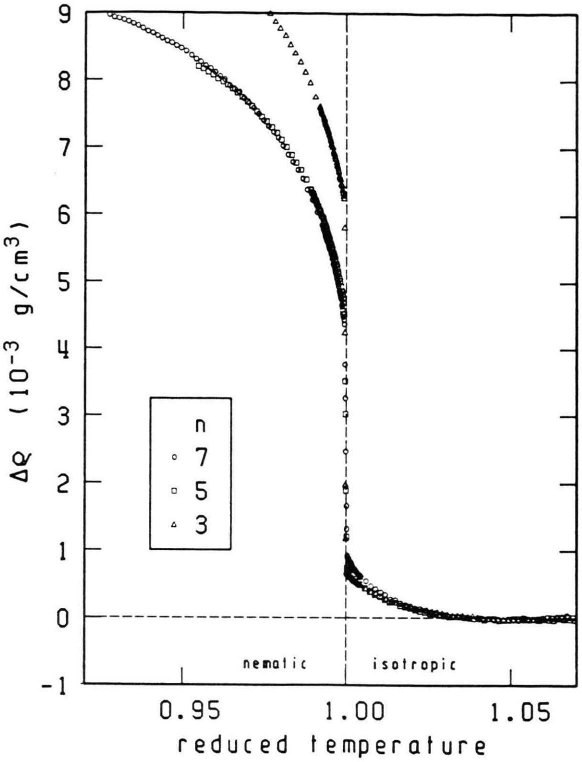


Fig. 15. The density difference $\Delta\varrho$ as a function of reduced temperature for PCH-n ($n = 3, 5, 7$).

calculated using the Maier-Saupe theory [3, 4, 29] and plotted against temperature in Figure 16. Within experimental error, the order parameter of the homologues are equal at the same t_r. Considerably lower values of the order parameter are obtained if the temperature dependence of the density is neglected (solid line in Figure 16). This indicates than an accurate determination of the mean field order parameter requires that the temperature dependence of the density is taken into account. Accurate order parameter values are needed if the macroscopic properties of nematic liquid crystals are to be predicted with reliability.

Diamagnetic Anisotropy

The following Zvetkow relationship [30] relates the macroscopic diamagnetic anisotropy $\Delta\chi$ to the molecular diamagnetic anisotropy $\Delta\chi_{\text{molec}}$:

$$\Delta\chi = \Delta\chi_{\text{molec}}\, NS, \tag{3}$$

or in terms of the molar diamagnetic anisotropy $\Delta\chi_{\text{mol}}$ ($\Delta\chi_{\text{mol}} = L\Delta\chi_{\text{molec}}$) and using $N = \varrho L/M$:

$$\Delta\chi = \Delta\chi_{\text{mol}}\, \varrho S/M. \tag{4}$$

A least squares fit of the experimental $\Delta\chi$ and ϱ according to (4) and the order parameter (Fig. 16) gives the $\Delta\chi_{\text{mol}}$ values listed in Table 2. The fit curves are given in Fig. 2 (solid lines). The variation with chain length is smaller than the experimental error. The mean value for the ketones **1** ($n = 3, 5, 7$) is $25.2 \cdot 10^{-6}$ cm^3/mol. A literature value could not be found.

Close to T_{NI} a deviation between the theoretical and experimental temperature dependence is observed, which may be due to the second order phase transition.

Table 2. Molecular properties of the molecules

Property	$n=3$	$n=5$	$n=7$
$\Delta\chi_{mol}$ (10^{-6} cm^3/mol)			
fitted values	25.3	26.1	24.2
α (10^{-24} cm^3, 0.589 µm)			
fitted values	32.3	36.0	39.8
calculated values	31.6	35.3	38.9
α (10^{-24} cm^3, 0.633 µm)			
fitted values	32.2	35.9	39.6
$\Delta\alpha$ (10^{-24} cm^3, 0.589 µm)			
fitted values	11.3	12.0	12.7
$\Delta\alpha$ (10^{-24} cm^3, 0.633 µm)			
fitted values	11.3	12.2	12.7
α_∞ (10^{-24} cm^3, ∞ µm)			
calculated from Clausius-Mossotti equation (9)	34.3	38.3	42.2
μ (D)			
fitted values	3.02	3.10	3.03
literature value (acetophenone)	2.96	2.96	2.96
β (°)			
fitted values	50.0	49.7	49.9
literature value (acetophenone)	48	48	48

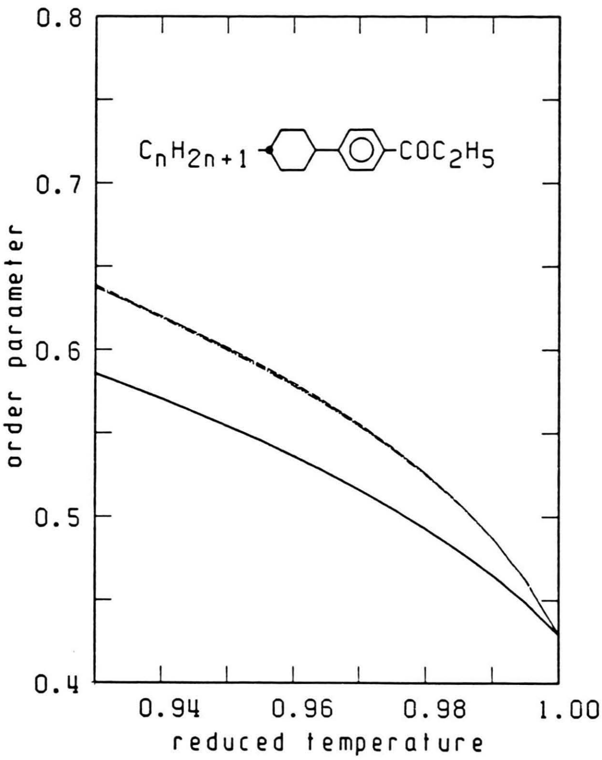


Fig. 16. The order parameter as a function of reduced temperature for ketones **1** ($n = 3, 5, 7$; dashed lines). The solid line is without the temperature dependence of the density.

Dielectric Constants

For simple non-associating isotropic liquids Onsager [31] has derived the formula

$$\varepsilon = 1 + 4\pi N\, h(\varepsilon)\, F(\varepsilon, \varepsilon_\infty) \left\{ \alpha_\infty + \frac{F(\varepsilon, \varepsilon_\infty)\, \mu^2}{3kT} \right\} \tag{6}$$

for the dielectric constant, where

$$h = 3\varepsilon/(2\varepsilon + 1) \tag{7}$$

and

$$F = 1/3\,(\varepsilon_\infty + 2)(2\varepsilon + 1)/(\varepsilon_\infty + 2) \tag{8}$$

are internal field factors, ε_∞ and α_∞ are the limiting values for infinite wavelength of n^2 and of α (the molecular polarisability), and μ is the dipole moment. Using the Clausius-Mossotti [32] equation

$$\frac{\varepsilon_\infty - 1}{\varepsilon_\infty + 2} = \frac{4\pi N}{3}\alpha_\infty . \tag{9}$$

α_∞ can be related to ε_∞:

Inserting (7), (8), and (9) into (6) and rearranging leads to

$$\mu^2 = \frac{9kT}{4\pi N}\, \frac{(\varepsilon - \varepsilon_\infty)(2\varepsilon + \varepsilon_\infty)}{\varepsilon(\varepsilon_\infty + 2)^2} . \tag{10}$$

Equation (10) is generally referred to as the Onsager equation [32]. $\varepsilon_\infty = 1.05\, n^2$ is usually assumed [33]. Replacing in (10) the molecular dipole moment by the effective dipole moment ($\mu_{eff}^2 = g\,\mu^2$) one obtains the Kirkwood-Fröhlich equation [32]. The factor g (correlation factor) indicates a correlation of the molecular dipoles in cases of $g \neq 1$. In the case of strong molecular correlation the designation "association" is often used. The g factor can be calculated provided the dielectric constant, the dipole moment, the refractive index and the density are known. In the case of the ketones under discussion g equals 1 within experimental error ($\pm$ 0.05) for the temperature range under investigation, and therefore practically no dipolar correlation is present. Nematic liquid crystals with a terminal cyano group have values of g as low as 0.4 [1].

The theory of Maier and Meier [6, 7] for the principal dielectric constants of the nematic phase, derived for nematic liquids of small dielectric anisotropy, assumes that in the nematic phase $\bar{\varepsilon} = (\varepsilon_\parallel + 2\varepsilon_\perp)/3$ and $\overline{n^2} = (n_e^2 + 2n_0^2)/3$ are the isotropic equivalents to ε and n^2 of the isotropic phase. Therefore (6)–(10) have to be modified such that now ε, ε_∞, and n^2 are replaced by $\bar{\varepsilon}$, $\bar{\varepsilon}_\infty$, and $\overline{n^2}$. In order to check this assumption, fits for compounds **1** ($n = 3, 5, 7$) have been performed in the isotropic and nematic phase with only the dipole moment as a fit parameter. The other quantities ($N = \varrho L/M$ and α) have been determined experimentally. The fit curves are shown in Figs. 9 to 11 (solid lines). The temperature dependence of experiment and theory is nearly the same. However, the discontinuity at T_{NI} is too small to be verified by experiment. The fitted values of the dipole moments are in good accordance with the tabulated value of acetophenone (2.96 D [34]), which has approximately the same polar structure as the ketones **1**.

Utilizing the theory of Maier and Meier [6, 7] for the principal dielectric constants, the equation

$$\varepsilon_{\parallel,\perp} = \bar{\varepsilon} + 4\pi N h(\bar{\varepsilon}) F(\bar{\varepsilon}, \varepsilon_\infty) S \cdot \left\{\alpha_{\parallel,\perp} \Delta\alpha + b_{\parallel,\perp} \frac{F(\bar{\varepsilon}, \bar{\varepsilon}_\infty)\mu^2}{3kT}(3\cos^2(\beta) - 1)\right\}. \quad (11)$$

can be derived, which holds for nematic liquids of small dielectric anisotropy.

Here $\Delta\alpha$ is the anisotropy of the molecular polarisability and β is the dipole angle with respect to the long molecular axis. The factors a and b have the values: $a_\parallel = 2/3$, $a_\perp = -1/3$, $b_\parallel = 1$, and $b_\perp = 1/2$, respectively. The internal field factors now depend on $\bar{\varepsilon}$ and $\bar{\varepsilon}_\infty$. From (11) the following relationship is derived:

$$\Delta\varepsilon = 4\pi N h(\bar{\varepsilon}) F(\bar{\varepsilon}, \bar{\varepsilon}_\infty) S \cdot \left\{\Delta\alpha + \frac{F(\bar{\varepsilon}, \bar{\varepsilon}_\infty)\mu^2}{2kT}(3\cos^2(\beta) - 1)\right\}. \quad (12)$$

Calculations of $\varepsilon_\parallel$ and $\varepsilon_\perp$ were carried out with β as a fit parameter and taking μ from the first fit and $\Delta\alpha$ from the fit of the refractive indices at 0.589 µm (see next chapter). Since the contribution of $\Delta\alpha$ to the dielectric constants is small (about 5%) the extrapolation to infinite wavelength has been neglected. The results are shown in Figs. 9–11 (solid lines). The values of β (listed in Table 2) agree well with that of acetophenone ($\beta = 48°$) given by Minkin et al. [35].

Refractive Indices

The formulas discussed in the previous section can be modified to be applicable for optical properties as well. At optical frequencies the dipole term and the ionic contribution to the polarisability can be neglected. Therefore $\varepsilon = \varepsilon_\infty = n^2$ and $\bar{\varepsilon} = \bar{\varepsilon}_\infty = \overline{n^2}$. A straight forward derivation with $h(n^2) F(n^2, n^2) = 1/3(n^2 + 2)$ leads to

$$n^2 = 1 + 4/3\pi N(n^2 + 2) \quad (13)$$

and

$$n_{e,0}^2 = n^2 + 4/3\pi N(n^2 + 2) S a_{\parallel,\perp} \Delta\alpha, \quad (14)$$

where $a_\parallel$ and $a_\perp$ have the same values as defined above. Equations (13) and (14) can be rearranged to become

$$\frac{n^2 - 1}{n^2 + 2} = \frac{4\pi N}{3}\alpha, \quad (15)$$

and

$$\frac{n_{e,0}^2 - 1}{\overline{n^2} + 2} = \frac{4}{3}\pi N S a_{\parallel,\perp} \Delta\alpha. \quad (16)$$

Equation (15) is known as the Lorentz-Lorenz equation [32] which relates the molecular polarisability α to the refractive index n. For isotropic organic liquids with small, normal dispersion this relationship holds exactly. An equation similar to (16) has been derived by Vuks [36] for molecular crystals. From the relationship (16) the equation

$$\Delta\alpha = \frac{9}{4\pi N} \frac{n_e^2 - n_0^2}{n_e^2 + n_0^2 + 6} \frac{1}{S} \quad (17)$$

is derived, which relates the molecular anisotropic polarisability $\Delta\alpha$ to the refractive indices.

A fit of the experimental values of the refractive indices (n_e, n_0, n_i) measured for the wavelengths of 0.589 µm and 0.633 µm was calculated according to (13) and (14). The resulting curves are given as solid lines in Figs 3–8 and the fit values for $\Delta\alpha$ are listed in Table 2. It is clear that $\bar{n}$ (corretly designated as $(\overline{n^2})^{1/2}$) is the nematic continuation of n_i, where the discontinuity at T_{NI} (verified by the experimental data) stems from the density. The temperature dependence of the theoretical curves are in good agreement with experiment, except very close to T_{NI}.

Display applications

The application of the twisted nematic effect in large-area, high-information-content displays places

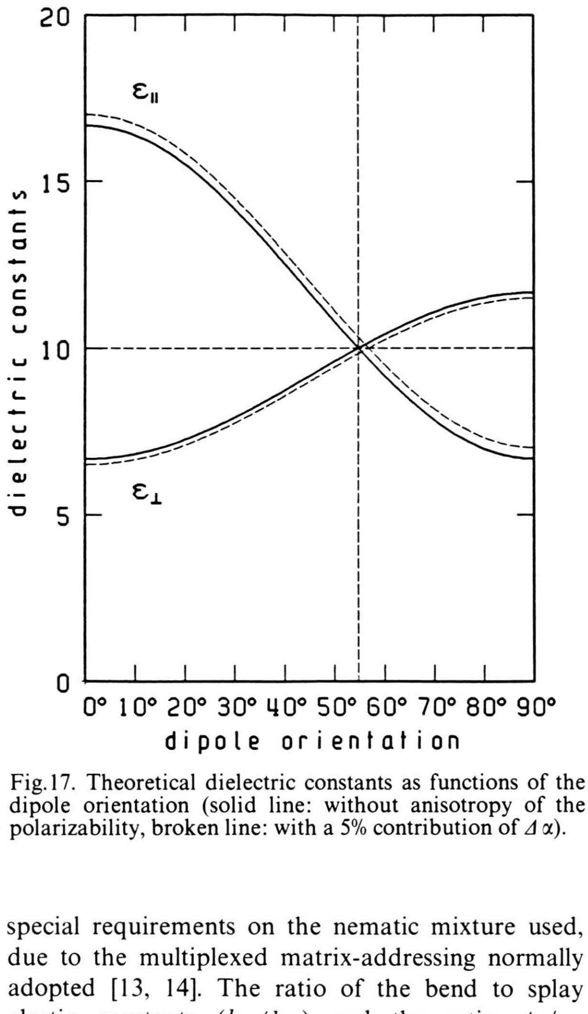


Fig. 17. Theoretical dielectric constants as functions of the dipole orientation (solid line: without anisotropy of the polarizability, broken line: with a 5% contribution of $\Delta\alpha$).

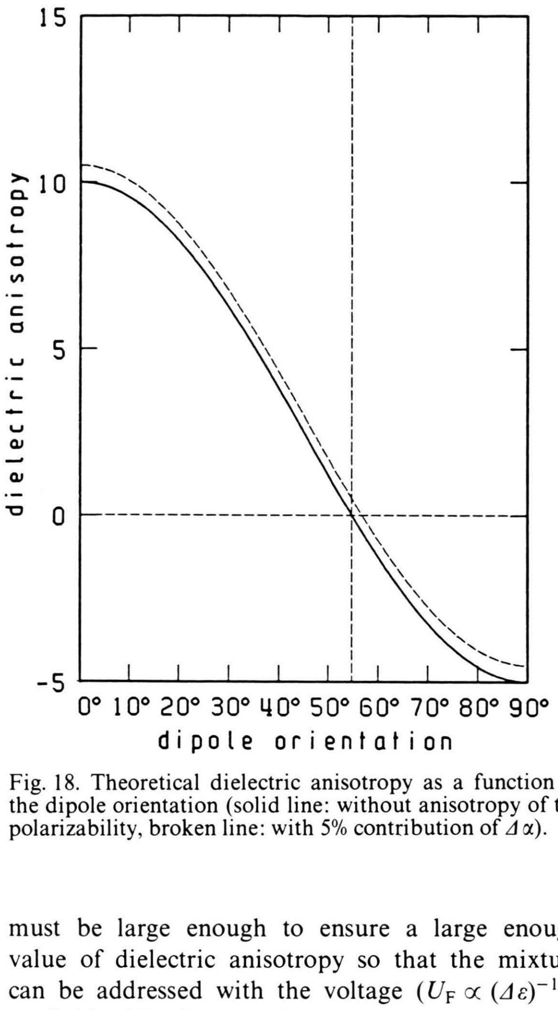


Fig. 18. Theoretical dielectric anisotropy as a function of the dipole orientation (solid line: without anisotropy of the polarizability, broken line: with 5% contribution of $\Delta\alpha$).

special requirements on the nematic mixture used, due to the multiplexed matrix-addressing normally adopted [13, 14]. The ratio of the bend to splay elastic constants (k_{33}/k_{11}) and the ratio $\Delta\varepsilon/\varepsilon_\perp$ should be both as low as possible [15]. New liquid crystals have been developed over the last few years with a low elastic constant ratio ($k_{33}/k_{11} = 0.7$) but the lowest value of $\Delta\varepsilon/\varepsilon_\perp$ achieved (ca. 1.4) is still relatively high. On the basis of our calculations using the Maier and Meier theory [6, 7] which is valid for the ketones **1**, a means to further lower $\Delta\varepsilon/\varepsilon_\perp$ is available. In Fig. 17 (solid lines) the dependence of $\varepsilon_\parallel$ and $\varepsilon_\perp$ on the dipole orientation β is shown for $\Delta\alpha = 0$ and $\bar{\varepsilon} = 10$. A corresponding curve for $\Delta\varepsilon$ is depicted in Figure 18. The broken line is valid for the case, where the contribution of the polarisability anisotropy is 5% of that of the dipole term (which is approximately the case for ketones **1**). The ratio $\Delta\varepsilon/\varepsilon_\perp$ decreases as the angle β nears the crossover angle (54.7°, and 56.8°, respectively). According to equation (12) the dipole momentum μ must be large enough to ensure a large enough value of dielectric anisotropy so that the mixture can be addressed with the voltage ($U_F \propto (\Delta\varepsilon)^{-1/2}$) available. The ketones **1** possess an advantageous $\beta \cong 50°$ which results in a low value of $\Delta\varepsilon/\varepsilon_\perp$ of 0.2–0.4. As $\Delta\varepsilon$ is positive and lies in the range of ($1 \sim 2$), these compounds are suitable as major components of nematic mixture designed for multiplexed applications.

Another property of considerable importance which must be considered, is the rotational viscosity γ_1, as this has a large influence on the rise and decay times of the twisted nematic effect. We have, therefore, measured the rotational viscosity of an equimolar, ternary mixture of the ketones **1** ($n = 3$, 5, 7). This is plotted against temperature in Fig. 19 along with that of a corresponding mixture of the commercially available PCHs [28] (with a cyano-group in place of the keto group). The rotational viscosity of the ternary mixture is only marginally higher than that of the corresponding cyano-com-

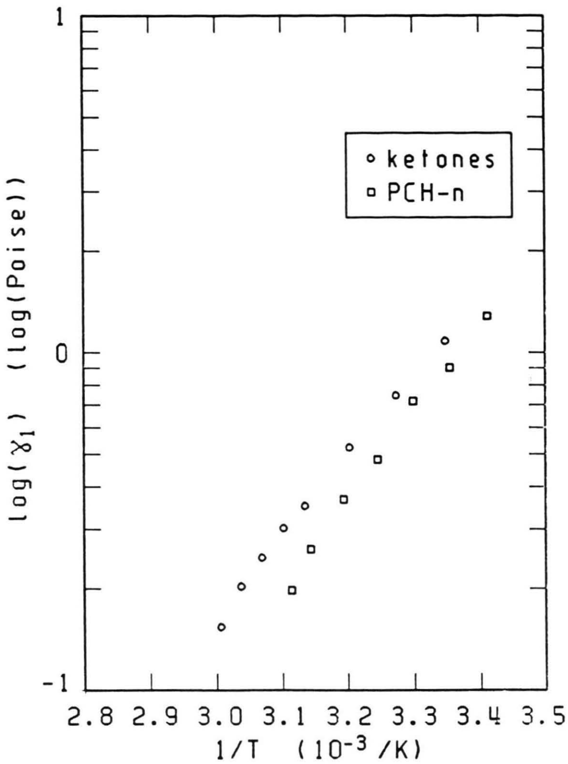


Fig. 19. Logarithm of the rotational viscosities γ_1 of a ternary equimolar mixture of ketones **1** ($n = 3, 5, 7$) and of a eutectic mixture of PCH-n ($n = 3, 5, 7$) as functions of $1/T$ (Arrhenius-plot).

pounds and at lower temperatures (below room temperature) the viscosity of the ketones may be lower.

A nematic mixture suitable for commercial TN cells with a high degree of multiplexed addressing has been prepared (see Table 3) containing a high proportion of the ketones **1** (0.28 mol% of each homologue $n = 3, 5, 7$). In order to increase the clearing point (see Table 4) an analogous compound **2** (X = cyclohexane, see Table 4) containing an additional ester (–CO · O–) linkage between the benzene and cyclohexane rings was added (0.08 mol%). A fifth component (4-cyano-3-fluorophenyl-4-heptylbenzoate [7, 10], 0.08 mol%) of high dielectric anisotropy ($\Delta\varepsilon \approx 50$) was used to increase the $\Delta\varepsilon$ of the mixture. The physical properties of this mixture at a fixed temperature (20 °C) are listed in Table 3.

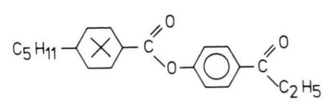
The simple nematic mixture described above exhibits a much lower value of $\Delta\varepsilon/\varepsilon_\perp$ and a somewhat higher value of k_{33}/k_{11} compared to the

Table 3. Physical properties of the nematic mixture.

T_{NC} (°C)	– 25.0
T_{NI} (°C)	64.6
n_e (0.589 µm)	1.602
n_0 (0.589 µm)	1.492
Δn (0.589 µm)	0.110
$\varepsilon_\parallel$	13.6
$\varepsilon_\perp$	7.7
$\Delta\varepsilon$	5.9
$\Delta\varepsilon/\varepsilon_\perp$	0.77
$\Delta\chi$ (10^{-8})	6.2
k_{11} (10^{-12} N)	11.6
k_{33} (10^{-12} N)	12.0
k_{33}/k_{11}	1.03
U_F (V)	1.48
$U_{10\%}$ (V)	2.00
$U_{50\%}/U_{10\%}$	1.13
$U_{50\%}/U_F$	1.53
τ_{on}* (ms)	120
τ_{off}* (ms)	70

* Obtained from measurements of a display cell of 9 µm spacing and an on-voltage of 4.5 V.

Table 4. Physical properties of the compounds **2** ($t_r = 0.96$) of the structure



Property\X	Benzene	Cyclohexane
T_{CN} (°C)	75.4	84.9
T_{NS_A} (°C)	–	74.5
T_{NI} (°C)	86.0	105.8
n_e (0.589 µm)	1.634	–
n_0 (0.589 µm)	1.499	–
Δn (0.589 µm)	0.135	–
$\varepsilon_\parallel$	18.1	7.6
$\varepsilon_\perp$	8.9	6.7
$\Delta\varepsilon$	9.2	0.9
ε_i ($t_r = 1$)	10.8	6.7
$\Delta\chi$ (10^{-8})	12.0	4.9
k_{11} (10^{-12} N)	10.1	7.2
k_{22} (10^{-12} N)	4.3	4.1
k_{33} (10^{-12} N)	8.5	7.6
k_{33}/k_{11}	0.85	1.06

equivalent values of multicomponent, commercially available nematic mixtures designed for a high degree of multiplexed addressing (e.g. ZLI 2728 and ZLI 2889 from E. Merck) with equal threshold voltages. However, the steepness of the corresponding contrast curves (represented by the value of the ratio $U_{50\%}/U_F$) are better. Attempts have not as yet been made to produce an optimised mixture based on the ketones under investigation.

The data for another keto ester **2** (X = benzene) are also given in Table 4. The melting points (T_{CN}) and clearing points (T_{NI}) of both esters are high. The cyclohexane ester also exhibits a monotropic smectic phase (S_A). The elastic constant ratio $k_{33}k_{11}$ and the dielectric ratio $\Delta\varepsilon/\varepsilon_\perp$ are low for both esters. The high birefringence and dielectric anisotropy of the *benzoate* keto ester **2** (X = benzene) render this compound a very useful component for nematic mixtures. The higher degree of conjugation and polarisability of the benzoate keto esters are responsible for these high values (as well as for the much higher diamagnetic anisotropy) compared to the cyclohexane keto ester.

Conclusion

We have investigated the physical properties of a new class of nematic aromatic ketones. It has been established that for this class of compounds the simple mean field theories for nematic liquid crystals are valid. Thus the molecular properties of the ketones can be directly related to their macroscopic physical properties. These ketones and similar keto esters have been shown to be advantageous for use in the twisted nematic display with a high degree of multiplexed addressing.

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