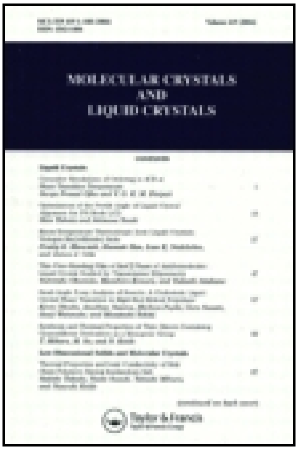

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Some Physical Properties of Nematic Liquid Crystals of Strong Negative Dielectric Anisotropy

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Some Physical Properties of Nematic Liquid Crystals of Strong Negative Dielectric Anisotropy

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The dielectric and elastic constants, birefringence and stability of some new dicyano substituted esters of strong negative dielectric anisotropy have been determined. These measurements were made on single components and ternary mixtures of the esters. This is the first time that such direct measurements on dicyano substituted liquid crystals have been reported. These new esters are suitable components for nematic mixtures of negative dielectric anisotropy, especially for homeotropic nematic displays.

Keywords: nematic liquid crystals, negative dielectric anisotropy, homeotropic nematic displays

INTRODUCTION

Nematic liquid crystals of negative dielectric anisotropy are needed for "guest-host" displays with positive contrast[1,2] and for displays based on the electrically controlled birefringence of nematic layers with homeotropic boundaries.[3-6] A low threshold voltage for these effects is required for battery operation and/or because of CMOS compatibility. Since the threshold voltage is proportional to $(-\Delta\epsilon)^{-1/2}$, a large negative value of $\Delta\epsilon$, the dielectric anisotropy, is desirable.

Until recently the only commercially available nematic mixtures with negative dielectric anisotropy were those (EN18 and EN24) produced by the Chisso corporation.[7] These mixtures contain esters

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with two lateral cyano-groups (ie, benzoate esters of 3-*alkoxy*-6-hydroxy-1,2-benzenedicarbonitrile). The resultant dipole moment is large (*ca.* 7D) and is directed perpendicular to the long axis of these molecules. This gives rise to the large negative value of the dielectric anisotropy of the nematic mixtures (eg, EN18 : $\Delta\epsilon \cong -6$ at 25°). Although the magnitude of the dielectric anisotropy is adequate, both the thermal and photochemical stabilities of nematic mixtures containing these esters are insufficient for their fully satisfactory use in display devices.

Nematic mixtures of negative dielectric anisotropy containing an ethane-compound with two lateral nitrile groups have also been reported.[8] The thermal and photochemical stabilities of these mixtures are expected to be much superior to those of the esters,[7] but as yet no values have been published. The nematic-isotropic transition temperature of this compound (N—I $\cong -55°$) is too low to allow measurements to be made on the pure component.

Some unusually substituted mono-cyano-cyclohexane derivatives of strong negative dielectric anisotropy ($\Delta\epsilon \cong -10$) have been recently described in the literature.[9,10] These compounds appear to be very suitable for guest-host displays.[1,2] However, the very low birefringence of these materials renders them unsuitable for the homeotropic nematic display (HN-display).[5,6]

The physical properties of other compounds containing two cyano-groups in a lateral position reported in the literature[7,8,11] have either not been determined or they have been derived by extrapolation from experiments with mixtures.[11] In such extrapolations large errors may arise from large differences in the particle number densities or from deviations from ideal behaviour.[12,13]

The recently reported benzoate esters of 3-*alkyl*-6-hydroxy-1,2-benzenedicarbonitrile[14] are expected to be more stable than the esters of the analogous 3-*alkoxy*-6-hydroxy-1,2-benzenedicarbonitrile.[7] Many homologues of these esters form enantiotropic nematic phases. This paper reports the physical properties of the nematic phases of some of these esters[14] and the compositions of nematic mixtures suitable for the HN-displays.

RESULTS AND DISCUSSION

Some of the physical properties of the pentyl homologue (5/5) of the 4-*n*-pentyl-2,3-dicyanophenyl 4′-n-alkyl-4-biphenyl-1-carboxylates[14] have been measured directly (ie, in single component samples). The molecular structure and the temperature dependence of the dielectric constants of this ester are depicted in Figure 1. The isotropic dielectric constant (ϵ_i) does not change over the narrow temperature range examined. The dielectric constants parallel ($\epsilon_\parallel$) and perpendicular ($\epsilon_\perp$) to the nematic director of the aligned sample show the temperature dependence normally observed.[12] The dielectric mean ($\bar{\epsilon} = (\epsilon_\parallel + 2\epsilon_\perp)/3$) is inversely proportional to the temperature. The discontinuity in the dielectric mean at the nematic-isotropic transition is

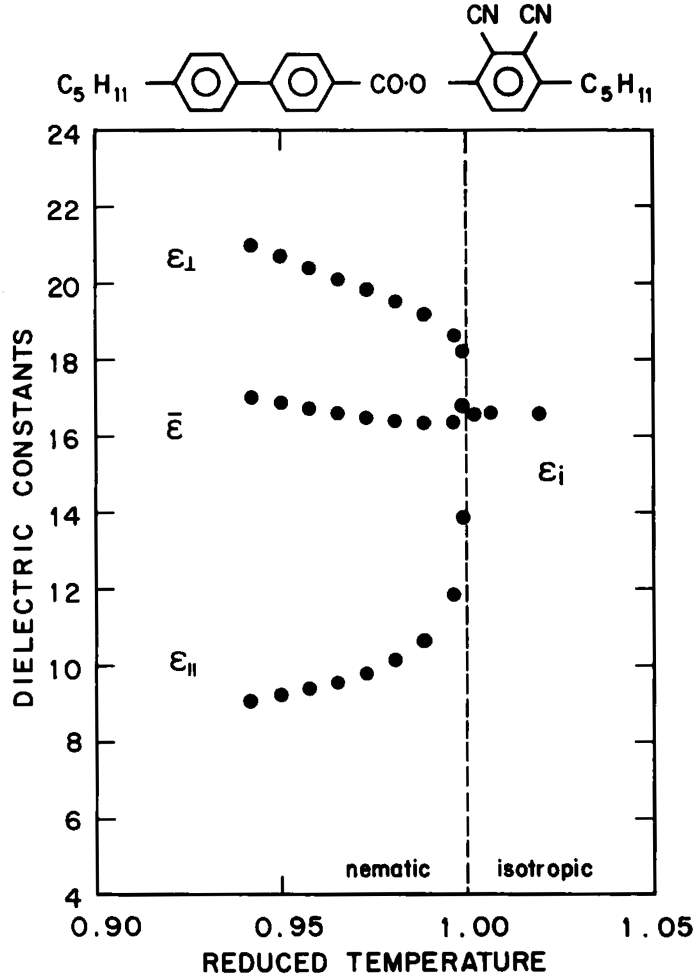


FIGURE 1 Plot of the dielectric constants of the ester against reduced temperature (t_r).

positive as is usually observed.[12] The dielectric anisotropy ($\Delta\epsilon = \epsilon_{\parallel} - \epsilon_{\perp}$) is large and negative (-11.5 at $T/T_{N-I} = 0.95$). The birefringence ($\Delta n = 0.152$, Na_D) and the elastic constants ($k_{11} = 10.5 \times 10^{-12}$ N, $k_{22} = 3.8 \times 10^{-12}$ N and $k_{33} = 14.3 \times 10^{-12}$ N), respectively have been determined at the same reduced temperature ($t_r = T/T_{N-I} = 0.95$).

A ternary mixture of the propyl, pentyl, and heptyl homologues was also prepared (30,40,30 wt %). The temperature range of this mixture (M1) is wider (C—N = 79°; N—I = 111°) than that of the pentyl component (5/5) described above (C—N = 99°; N—I = 112.5°).

The values of the dielectric and elastic constants as well as the diamagnetic anisotropy of the mixture (M1) at various temperatures are collated in Table I. The dielectric constants are plotted against reduced temperature in Figure 2. At the lowest temperature achieved the dielectric anisotropy is -14.

Some of the physical properties of the analogous esters[14] where the benzene ring attached to the alkyl chain in the acid part of the ester has been replaced by a cyclohexane ring have also been investigated. Since all the homologues of these cyclohexane esters are strongly monotropic, it was necessary to prepare a ternary mixture (of similar composition to that of the biphenyl ester mixture M1). The cyclohexane mixture (M2) exhibited an enantiotropic nematic phase (C—N = 73.5°, N—I = 97°).

The dielectric constants determined at $t_r = 0.95$ ($\epsilon_{\parallel} = 10.0$; $\epsilon_{\perp} = 21.0$) and the elastic constants ($k_{11} = 7.5 \times 10^{-12}$ N; $k_{22} = 3.6 \times 10^{-12}$ N; $k_{33} = 11.3 \times 10^{-12}$ N) are very similar to those values obtained for the mixture (M1) of the biphenyl esters, see above and Table I. The birefringence ($\Delta n = 0.095$) and the diamagnetic anisotropy ($\Delta\chi = 6.8 \times 10^{-8}$) are considerable smaller, see above and

TABLE I

Some physical data for the mixture M1

tr	t(°C)	$\epsilon_{\parallel}$	$\epsilon_{\perp}$	$\Delta\chi$ (10^{-8})	k_{11} (10^{-12} N)	k_{22} (10^{-12} N)	k_{33} (10^{-12} N)
0.900	71.9	8.9	22.8	13.9	16.1	5.2	18.3
0.920	79.5	8.9	22.0	13.5	13.5	4.8	15.4
0.950	91.0	9.7	20.7	12.6	9.0	4.0	11.1
0.980	102.5	10.9	19.5	10.5	6.3	3.0	7.8
1.002	111.0	16.5	16.5				
1.007	113.0	16.4	16.4				
1.013	115.0	16.35	16.35				
1.018	117.0	16.3	16.3				
1.026	120.0	16.2	16.2				

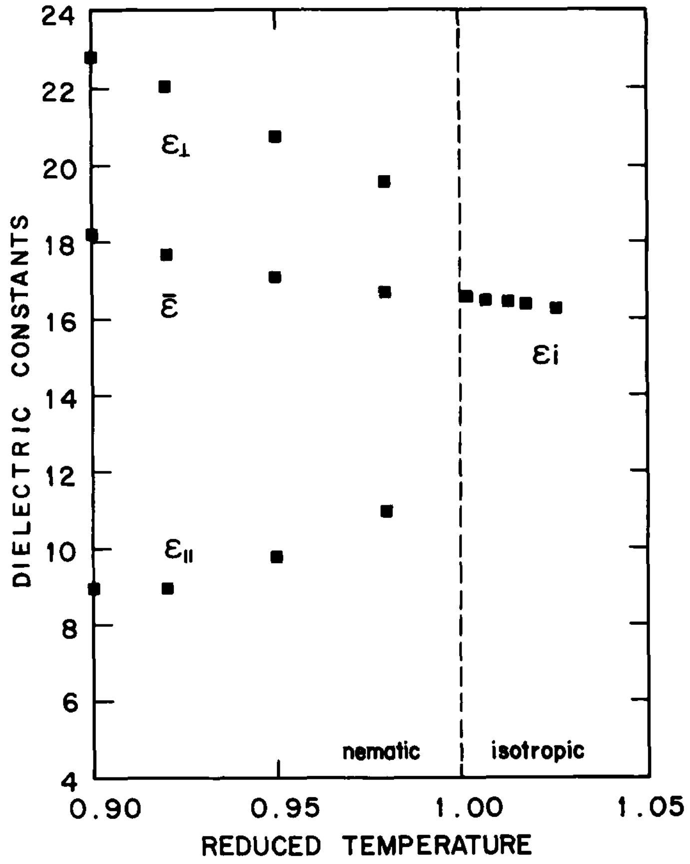


FIGURE 2 Plot of the dielectric constants of the ternary mixture M1 against reduced temperature (t_r).

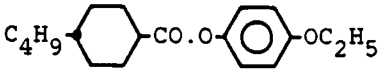
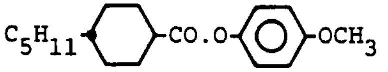
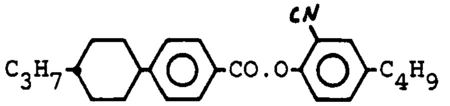
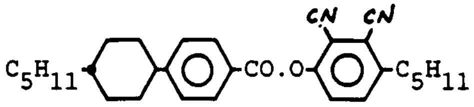
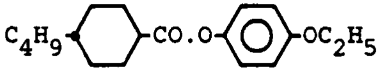
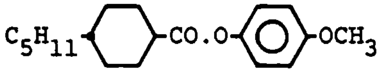
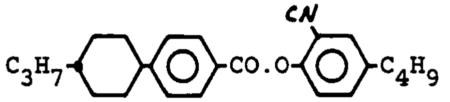
Table I. This is due to the lower number of benzene rings (2) in the cyclohexane esters compared to the biphenyl esters (3).

For the elastic constants of the dicyano compounds studied (as single components or as ternary mixtures) the relationship $k_{33} > k_{11} > k_{22}$ holds. The ratio k_{33}/k_{11} lies in the range 1.1–1.4 and the ratio k_{22}/k_{11} is about 0.4. The latter value is exceptionally low.

A mixture of one of the cyclohexane dicyano esters and four commercially available components was made up (mixture M3), see Table II. A similar mixture (M4) with the same components, but without the dicyano-ester, and almost identical transition temperatures, was also prepared, see Table II. The stability of these mixtures (M3 and

TABLE II

Mixture M3; C—N = 0°; N—I = 62°

	18.6 wt %
	23.4 wt %
	13.9 wt %
	29.8 wt %
	14.3 wt %
Mixture M4; C—N = 0°; N—I = 64.5°	
	23.2 wt %
	29.1 wt %
	10.7 wt %
	37.0 wt %

M4) and that of EN18[7] to ultra-violet light were then determined in HN test cells combined with a polariser-filter (cut-off at 400 nm) (see Figure 3 and the Experimental Section). The increase in conductivity with time of the mixtures M3 and M4 is markedly lower than that of the mixture EN18. Thus if a UV-filter is combined with the circular polariser[5,6] then the mixtures (M3 and M4) described above are observed to be photochemically and thermally stable enough for commercial applications in HN-displays.

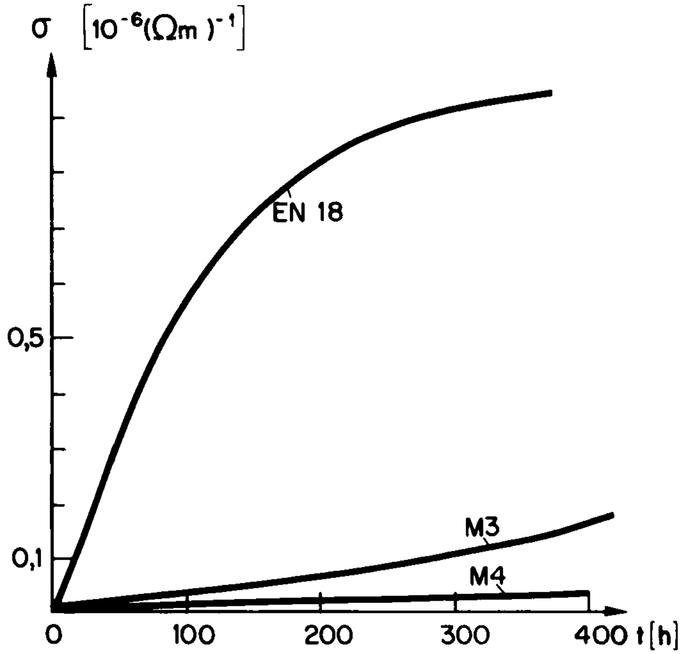


FIGURE 3 Plot of the conductivity (σ) of the mixtures M3, M4 and EN18 against time (t).

Values for some physical properties of nematic mixtures suitable for the HN-display are given in Table III. The mixtures M3 and M4 (compositions given above) fulfill the specifications for the HN-display[5,6] with respect to $-\Delta\epsilon/\epsilon_{\parallel}$, birefringence and the elastic constant ratio (k_{33}/k_{11}). The Freedericksz threshold voltage (Uf) of the mixture M4 is higher than that of M3 (due to the absence of a component of strong negative dielectric anisotropy, see Table II). Some other experimental mixtures (from F. Hoffmann-La Roche, Basle and E.

TABLE III

Some physical data of mixtures for the HN-display

mixture	N—I (°C)	Δn	$\Delta\epsilon$	Uf (V)	$-\Delta\epsilon/\epsilon_{\parallel}$	k_{33}/k_{11}
M4	65.2	0.096	−1.7	2.8	0.49	1.50
M3	62.7	0.094	−3.3	1.9	0.78	1.36
ZLI 2659	83.0	0.075	−2.9	2.1	0.79	1.34
ZLI 2787	70.8	0.073	−3.4	1.8	0.92	1.37
Ro-3086	80.0	0.087	−3.6	2.0	0.88	0.86

Merck, Darmstadt) containing stable components of strong negative dielectric anisotropy also exhibit low Freedericksz thresholds. However the other parameters are not as satisfactory as those of the mixtures M3 and M4 for application in the HN-display. The nematic-isotropic transition temperatures of all of the mixtures are adequate.

EXPERIMENTAL

Transition temperatures

The liquid crystal transition temperatures of the esters[14] and the mixtures (M1–M4) were determined by optical microscopy using a Leitz Orthoplan microscope in conjunction with a Mettler FP52 heating stage and FPS control unit.

UV-stability

The nematic mixtures (M3, M4, and EN18) were placed in identical HN-display test cells.[5,6] Instead of a normal polariser, a polariser-filter (cut-off 400 nm) LC2-82-125 from Sanritsu (Japan) was used. The cells were then exposed to ultra-violet light at room temperature in a Suntest apparatus (Hanau, FRG) and the conductivity measured at periodic intervals.

Physical properties

The other physical properties reported in the text and in Table I were determined using methods previously reported.[15]

CONCLUSION

The physical properties of the nematic phases of some compounds incorporating two lateral cyano-groups have been measured directly for the first time. The nematic phases of dicyano derivatives have strong negative dielectric anisotropy, high birefringence (for the biphenyl type), good UV and thermal stability and exhibit high nematic-isotropic transition temperatures. These derivatives are the most suitable components of high negative dielectric anisotropy for the HN-display yet investigated.

Acknowledgments

The authors thank Dr. M. Schadt of F. Hoffmann-La Roche (Basle) and Dr. B. S. Scheuble of E. Merck (Darmstadt) for the supply of the experimental mixtures of negative dielectric anisotropy (Ro-3086 and ZLI 2659/ZLI 2787 respectively).

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