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M. Sasaki [a], K. Takeuchi [a], H. Sat[obar] [a] & H. Takatsu [a]
[a] Dainippon Ink & Chemicals, Inc., 3-35-58, Sakashita, Itabashi, Tokyo, Japan
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Synthesis and Some Properties of 3-Fluoro-4-Cyanophenyl 4′-*n*-alkylbenzoates

M. SASAKI, K. TAKEUCHI, H. SATŌ and H. TAKATSU

Dainippon Ink & Chemicals, Inc., 3-35-58, Sakashita, Itabashi, Tokyo, Japan

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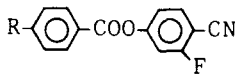
A series of 3-fluoro-4-cyanophenyl 4′-*n*-alkylbenzoates, which show monotropic nematic phases, was prepared and their transition temperatures and melting enthalpies were measured. The 3-fluoro-4-cyanophenyl 4′-*n*-propylbenzoate, 3-chloro-4-cyanophenyl 4′-*n*-propylbenzoate and 4-cyanophenyl 4′-*n*-propylbenzoate were mixed with a nematic mixture (A) of 4-*n*-alkoxyphenyl 4′-*n*-alkylcyclohexane-1′-carboxylates. 3-Fluoro-4-cyanophenyl 4′-*n*-propylbenzoate decreases the N–I transition temperature less, increases the birefringence more, and increases the bulk viscosity less than 3-chloro-4-cyanophenyl 4′-*n*-propylbenzoate, and reduces the threshold voltage to the greatest extent. The dielectric anisotropies of 3-fluoro-4-cyanophenyl 4′-*n*-propylbenzoate and 4-cyanophenyl 4′-*n*-propylbenzoate determined from a series of solutions of the compounds in nematic mixture (A) are 35.9 and 29.6, respectively.

INTRODUCTION

Compounds with a strong positive dielectric anisotropy are very attractive as components of liquid crystal mixtures for TN-LCDs as they reduce the threshold voltage for the displays which can then be driven at lower voltages. 4-Cyanophenyl 4′-*n*-alkylbenzoates[1] have strong positive dielectric anisotropies and have been used as one of the most useful components for TN-LCDs.

The introduction of a 3-chloro group into the 4-cyanophenyl 4′-*n*-alkylbenzoates increases the dipole moment parallel to the molecular long axis. We developed the 3-chloro-4-cyanophenyl 4′-*n*-alkylbenzoates,[2] which do not exhibit mesophases, as dopants to reduce the threshold voltage for TN-LCDs.

The introduction of a 3-fluoro group into 4-cyanophenyl benzoates reduces the linearity of the molecule less and increases the viscosity less than the introduction of a 3-chloro group. Therefore, we have synthesized a new series of 3-fluoro-4-cyanophenyl 4′-*n*-alkylbenzoates of formula (I) in order to achieve nematic compounds with strong positive dielectric anisotropies and in order to compare their properties with those of the 4-cyanophenyl 4′-*n*-alkylbenzoates and 3-chloro-4-cyanophenyl 4′-*n*-alkylbenzoates.



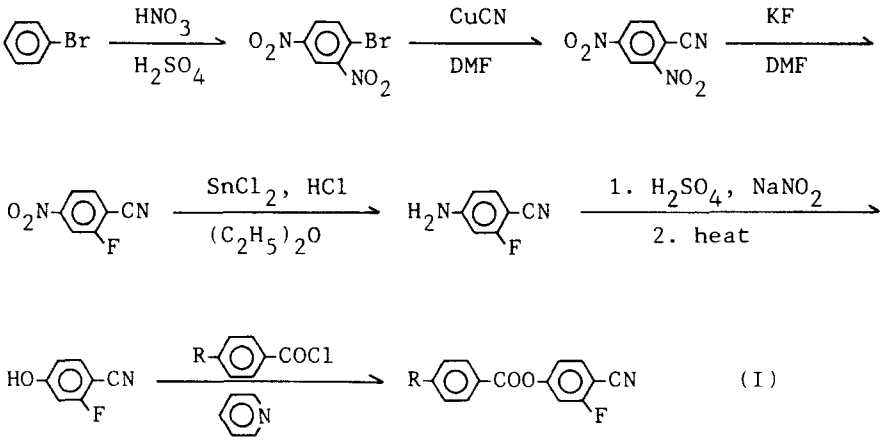
(I)

R= n-alkyl

PREPARATION OF MATERIALS

The 3-fluoro-4-cyanophenyl 4′-*n*-alkylbenzoates were prepared according to the following Scheme I.

The intermediates were purified by recrystallization; the solvents used for recrystallization and the melting points measured are listed in Table I. All of the benzoates of formula (I) were distilled and purified



R= n-alkyl

Scheme I

TABLE I

Solvents for recrystallization and the melting points for the intermediates (scheme I) in the synthesis of the 3-fluoro-4-cyanophenyl 4′-*n*-alkylbenzoates

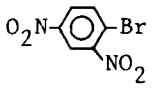
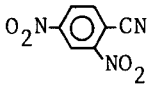
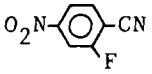
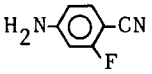
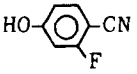
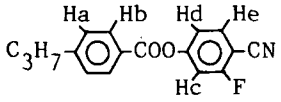
Formula	Solvent for recrystallization	Melting point (°C)
	Ethanol	70.3
	Toluene	103.5
	Methanol	68.7–70.2
	Methanol/Water	103.0–105.0
	Toluene	123.5

TABLE II

^{1}H NMR chemical shifts (relative to TMS in $CDCl_3$) for 3-fluoro-4-cyanophenyl 4′-*n*-propylbenzoate



	δ (ppm)		
CH_3—C	0.90	*t*	3
C—CH_2—C—Ph	1.67	*m*	2
C—C—CH_2—Ph	2.65	*t*	2
Ha, Hc, Hd	7.1–7.4	*d*, *d*, *d*	4
He	7.60	*d*	1
Hb	8.05	*d*	2

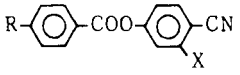
by recrystallization from ethanol, and their purity was tested by high pressure liquid chromatography and gas-liquid chromatography. Each product was identified by NMR spectrometry and mass spectrometry. The NMR values for 3-fluoro-4-cyanophenyl 4′-*n*-propylbenzoate are shown in Table II.

RESULTS AND DISCUSSION

The transition temperatures for the series of 3-fluoro-4-cyanophenyl 4′-*n*-alkylbenzoates, for 3-chloro-4-cyanophenyl 4′-*n*-propylbenzoate and for 4-cyanophenyl 4′-*n*-propylbenzoate were measured by using a polarizing microscope equipped with a heating and cooling stage. The melting enthalpies (ΔH) were measured by differential scanning calorimetry and the melting entropies (ΔS) were calculated from the enthalpies and melting points. These thermal data are listed in Table III. The 3-fluoro-4-cyanophenyl 4′-*n*-alkylbenzoates show monotropic nematic phases and their transition temperatures plotted against the alkyl chain length are shown in Figure 1. The nematic-to-isotropic (N–I) transition temperatures exhibit an odd-even effect, the odd chain lengths being associated with the higher values of around 20 °C and the even chain lengths with the lower values of around 7 °C. The

TABLE III

Transition temperatures, melting enthalpies (ΔH), and melting entropies (ΔS) for the 3-fluoro-4-cyanophenyl 4′-*n*-alkylbenzoates, 3-chloro-4-cyanophenyl 4′-*n*-propylbenzoate and 4-cyanophenyl 4′-*n*-propylbenzoate

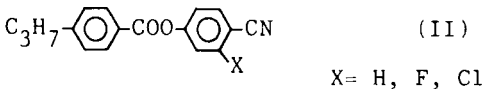


R	X	Transition temp. (°C) C → I	Transition temp. (°C) N ⇌ I	ΔH (kcal/mol) C → I	ΔS (EU) C → I
C_2H_5-	F	77	(6)	3.66	10.5
C_3H_7-	F	70	(18)	5.29	15.4
C_4H_9-	F	14	(7)	—	—
C_5H_{11}-	F	30	(20)	—	—
C_6H_{13}-	F	35	(8)	6.14	19.9
C_7H_{15}-	F	25	(22)	—	—
C_3H_7-	Cl	64	—	4.93	14.6
C_3H_7-	H	102	(53)	5.77	15.4

Values in parenthesis are for monotropic transitions

value of the melting entropy for each 3-halo-4-cyanophenyl 4′-*n*-propylbenzoate of formula (II) remains nearly constant, being about 15 EU. A similar result was obtained for 1-(*trans*-4′-*n*-alkylcyclohexyl)-2-(4″-halobiphenyl-4′-yl)ethanes.[3]

3-Fluoro-4-cyanophenyl 4′-*n*-propylbenzoate, 3-chloro-4-cyanophenyl 4′-*n*-propylbenzoate and 4-cyanophenyl 4′-*n*-propylbenzoate were mixed separately with a mixture (A) consisting of 4-alkoxyphenyl 4′-*n*-alkylcyclohexane-1′-carboxylates,[4] which are suitable for high level multiplexing,[5] in order to determine the influence of the 3-sub-



(II)

X= H, F, Cl

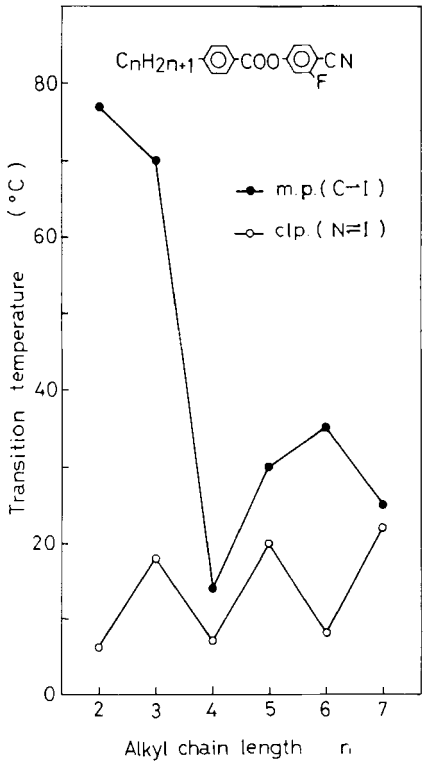
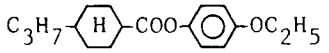
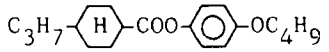
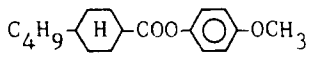


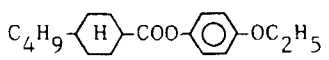
FIGURE 1 Transition temperatures plotted against the alkyl chain length for the 3-fluoro-4-cyanophenyl 4′-*n*-alkylbenzoates.

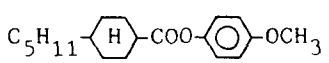
stituent X of formula (II) on the N–I transition temperature, birefringence, bulk viscosity, dielectric constants and threshold voltage. The composition and physical properties of mixture (A) are as follows:
Composition:

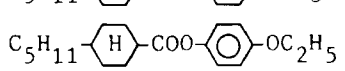
16.7 wt% of 

16.7 wt% of 

16.7 wt% of 

16.7 wt% of 

16.6 wt% of 

16.6 wt% of 

N–I transition temperature:	73.0 °C
Bulk viscosity at 20 °C:	19.9 c.p.
Birefringence at 25 °C:	0.0826

The viscosity measurements were made using a rotating coneplate viscometer at 20 °C. The birefringences were measured by polarizing microscopy using a compensator. The static transmission characteristics of TN-LCDs, for which the cell thickness was 8.0 μm, were measured at 25 °C. The threshold voltage (Vth) is the driving voltage for 10% transmission.

The influence of the addition of each component on the N–I transition temperature, birefringence, bulk viscosity, and threshold voltage of the nematic mixture (A) is shown in Figure 2 and Figure 3. The orders of the N–I transition temperatures, birefringences, bulk viscosities and threshold voltages for the mixtures of compounds of formula (II) and mixture (A) are as follows:

N–I transition temperatures

$$X = H > X = F > X = Cl$$

Birefringences

$$X = H > X = F > X = Cl$$

Bulk viscosities

$$X = Cl > X = F > X = H$$

Threshold voltages

$$X = H > X = Cl > X = F$$

The N–I transition temperatures and birefringences decrease with increase in the volume of the halogeno group X because of the increased breadth of the molecules. The halogeno group of larger volume enhances the bulk viscosity. We have reported[3] that the logarithm of the bulk viscosity increases linearly with increase in the volume of the terminal halogeno group for 1-(*trans*-4′-*n*-alkylcyclohexyl)-2-(4″-halobiphenyl-4′-yl) ethanes. However, a similar relationship is not obtained for the 3-halogeno groups of formula (II). The halogeno group in formula (II) reduces the threshold voltage, and it is interesting that the fluoro group reduces the threshold voltage more than the chloro group in spite of its smaller dipole moment.

The dielectric constants were determined from the capacitance of a parallel-plate capacitor measured empty and then filled with liquid crystal. The dielectric constants for a series of solutions of 3-fluoro-4-cyanophenyl 4′-*n*-propylbenzoate and 4-cyanophenyl 4′-*n*-pro-

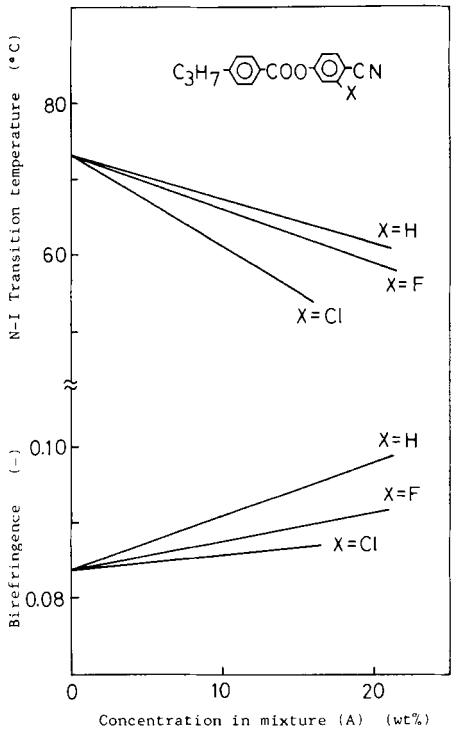


FIGURE 2 The transition temperatures and birefringences for a series of solutions of the 3-substituted 4-cyano-phenyl 4′-*n*-propylbenzoates in mixture (A)—(see text).

pylbenzoate in mixture (A) are plotted against concentration in Figure 4 and Figure 5, respectively. The dielectric constants determined from extrapolation in Figure 4 and Figure 5 are listed in Table IV.

The dielectric constant parallel to the optical axis ($\epsilon_{\parallel}$), perpendicular to the optical axis ($\epsilon_{\perp}$) and the dielectric anisotropy ($\Delta\epsilon$) for 3-fluoro-4-cyanophenyl 4′-*n*-propylbenzoate are larger than those for 4-cyanophenyl 4′-*n*-propylbenzoate. The value of $\Delta\epsilon/\epsilon_{\perp}$ for 3-fluoro-4-cyanophenyl 4′-*n*-propylbenzoate is smaller than that for the 4-cyanophenyl 4′-*n*-propylbenzoate. The introduction of 3-fluoro group into 4-cyanophenyl 4′-*n*-propylbenzoate enhances the dielectric anisotropy and reduces the value of $\Delta\epsilon/\epsilon_{\perp}$.

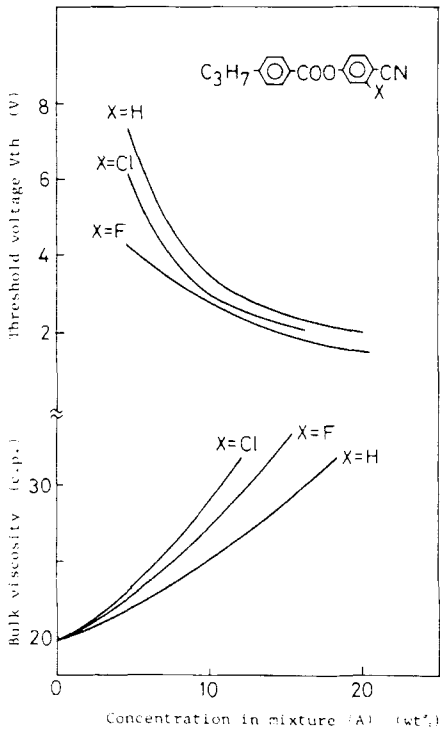


FIGURE 3 The threshold voltages and bulk viscosities for a series of solutions of the 3-substituted 4-cyanophenyl 4′-*n*-propylbenzoates in mixture (A)—(see text).

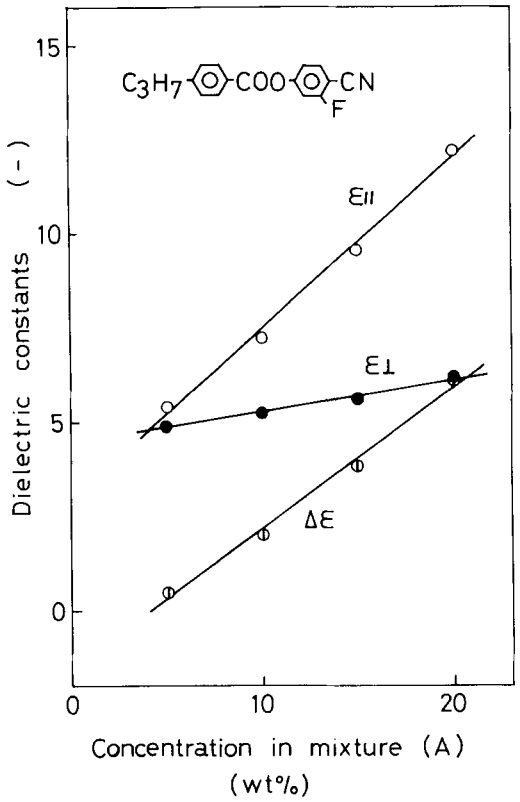


FIGURE 4 The dielectric constants for a series of solutions of the 3-fluoro-4-cyanophenyl 4′-*n*-propylbenzoate in mixture (A)—(see text).

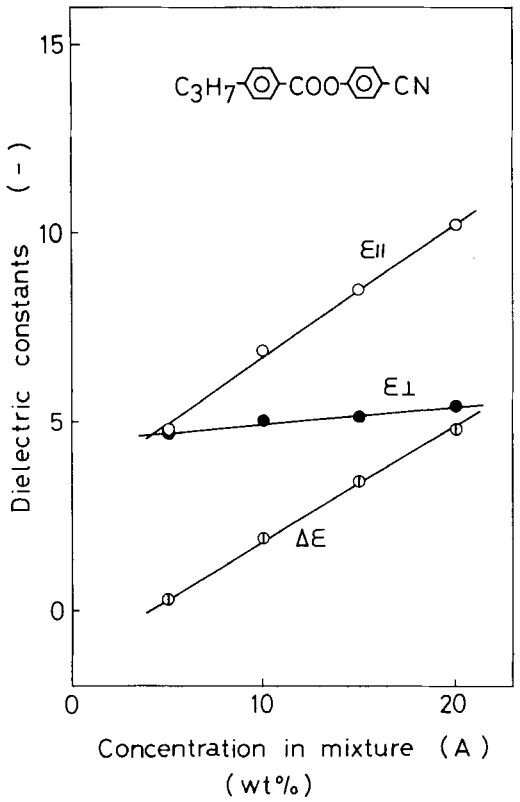
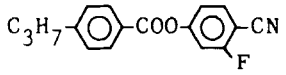
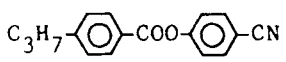


FIGURE 5 The dielectric constants for a series of solutions of 4-cyanophenyl 4′-*n*-propylbenzoate in mixture (A)—(see text).

TABLE IV

Dielectric constants for 3-fluoro-4-cyanophenyl 4′-*n*-propylbenzoate and 4-cyanophenyl 4′-*n*-propylbenzoate

Formula	Dielectric constants			
	$\epsilon_{\parallel}$	$\epsilon_{\perp}$	$\Delta\epsilon$	$\Delta\epsilon/\epsilon_{\perp}$
	48.9	13.0	35.9	2.76
	38.7	9.1	29.6	3.25

Acknowledgment

The authors would like to thank Miss T. Kanoh for the determinations of the melting enthalpies and entropies.

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3. H. Takatsu, K. Takeuchi, and H. Sato, *Mol. Cryst. Liq. Cryst.*, **100**, 345 (1983).
4. D. Demus, H. -J. Deutcher, F. Kuschel, and H. Schubert, *DOS No.* 24 29 093 (1975).
5. K. Toriyama, T. Nakagomi, H. Sato, Y. Fujita, K. Morita, and Y. Arai, *US Patent* 4,372,871 (1983).