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Synthesis and Some Properties of 3,4-difluorophenyl Trans-4′-substituted cyclohexane-1′-carboxylates

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A series of 3,4-difluorophenyl *trans*-4′-substituted cyclohexane-1′-carboxylates, which show nematic phases, was prepared and their transition temperatures, enthalpies and entropies were measured. 3,4-Difluorophenyl and 4-fluorophenyl *trans*-4′-*n*-pentylcyclohexane-1′-carboxylates were mixed separately with a nematic mixture A consisting of *trans*-4-*n*-alkyl-1-(4′-cyanophenyl)cyclohexanes. 3,4-Difluorophenyl *trans*-4′-*n*-pentylcyclohexane-1′-carboxylate reduces the threshold voltage more, decreases the N-I transition temperature more, reduces the bulk viscosity less and decreases the birefringence more than 4-fluorophenyl *trans*-4′-*n*-pentylcyclohexane-1′-carboxylate. 3,4-Difluorophenyl, 4-fluorophenyl, 3-fluorophenyl and phenyl *trans*-4′-{ β-(trans-4″-*n*-propylcyclohexyl)-1″}ethylcyclohexane-1′-carboxylates were mixed separately with a mixture B consisting of 4-*n*-alkoxyphenyl *trans*-4′-*n*-alkylcyclohexane-1′-carboxylates and *trans*-4-*n*-alkyl-1-(4′-cyanophenyl)cyclohexanes. The 3,4-difluorophenyl *trans*-4′-{ β-(*trans*-4″-*n*-propylcyclohexyl)-1″} ethylcyclohexane-1′-carboxylate increases the threshold voltage of mixture B to the least extent. The dielectric constants parallel to the optical axis (ϵ_{11}) and perpendicular to the optical axis ($\epsilon_{\perp}$) for a mixture C consisting of 3,4-difluorophenyl *trans*-4′-substituted cyclohexane-1′-carboxylates are 10.0 and 6.3, respectively.

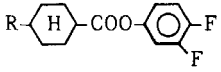
INTRODUCTION

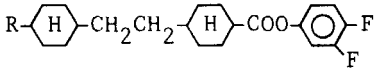
The threshold voltage is one of the important parameters for TN-LCDs. A low threshold voltage enables a TN-LCD to be driven by a

lower power. Compounds with a strong positive dielectric anisotropy are useful components to reduce the threshold voltage. The introduction of a cyano group at the terminus of the long molecular axis increases the dielectric anisotropy. 4-Cyanophenyl 4′-*n*-alkylbenzoates[1] have a strong positive dielectric anisotropy and have been used as most useful components of mixtures for TN-LCDs. However, these nematic compounds including cyano groups are viscous and increase the response time for the TN-LCDs.

4-*n*-Alkoxyphenyl 4′-*n*-alkylcyclohexane-1′-carboxylates[2], which show a negative dielectric anisotropy of about −1.5, are of low viscosity, have high clearing points and are suitable for high level multiplexed TN-LCDs[3]. Some useful nematic compounds containing fluoro groups, whose electron attracting properties can control the dielectric anisotropy, have been developed[4–6]. The introduction of a 3-fluoro substituent into the 4-cyanophenyl 4′-*n*-alkylbenzoates has an impressive effect in reducing the threshold voltages[7].

We have now synthesized a new series of 3,4-difluorophenyl *trans*-4′-substituted cylohexane-1′-carboxylates of formulae (I), (II) and (III) in order to achieve a nematic compound of positive dielectric anisotropy and low viscosity, and to establish the effect of fluoro substituents on mesomorphic and physical properties by comparing there compounds with other fluorinated nematic compounds.


(I)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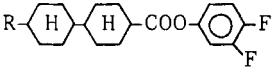
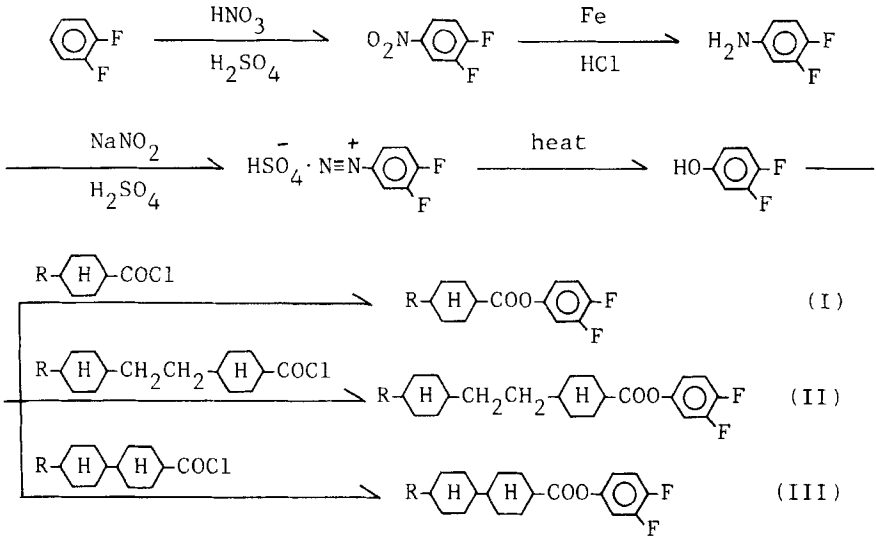

(III)

PREPARATION OF MATERIALS

The 3,4-difluorophenyl 4′-substituted cyclohexane-1′-carboxylates were prepared from *o*-difluorobenzene according to the following

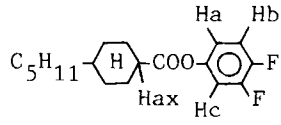
scheme:

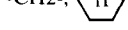


The products (I) were distilled and purified by recrystallization from methanol. The products (II) and (III) were purified by chromatography on silica gel, eluting with a mixture of hexane and benzene,

TABLE I

^{1}H NMR chemical shifts (relative to TMS in $CDCl_3$) for 3,4-difluorophenyl *trans*-4′-*n*-pentylcyclohexane-1′-carboxylate

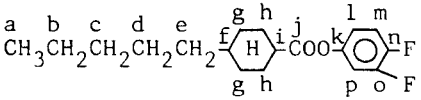


	δ (ppm)		
CH_3-	0.88	t	3
-CH2-, 	1.26~2.33	m	17
Hax	2.43	m	1
Ha, Hb, Hc	6.6~7.3	m	3

followed by recrystallization from ethanol. Each product was identified by ^1H NMR spectrometry, ^{13}C NMR spectrometry and mass spectrometry. The ^1H NMR and $^{13}C\{^1H\}$ NMR chemical shifts for 3,4-difluorophenyl *trans*-4′-*n*-pentylcyclohexane-1′-carboxylate are shown in Table I and Table II, respectively.

TABLE II

$^{13}C\{^1H\}$ NMR chemical shifts (relative to TMS in $CDCl_3$) for 3,4-difluorophenyl trans-4′-*n*-pentylcyclohexane-1′-carboxylate



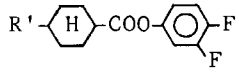
	δ(ppm)		$^nJ_{CF}$(Hz)
Ca	14.1	s	
Cb	22.9	s	
Cc	26.7	s	
Cd	32.4	s	
Ce	37.3	s	
Cf	37.6	s	
Cg	28.9	s	
Ch	32.8	s	
Ci	44.0	s	
Cj	176.9	s	
Ck	146.7	d, d	$^3J_{CF} = 8.5$, $^4J_{CF} = 3.7$
Cl	117.5	m	
Cm	117.1	d	$^2J_{CF} = 25$
Cn	148.2	d, d	$^1J_{CF} = 250$, $^2J_{CF} = 12.5$
Co	151.1	d, d	$^1J_{CF} = 250$, $^2J_{CF} = 12.5$
Cp	111.6	d	$^2J_{CF} = 20$

RESULTS AND DISCUSSION

The transition temperatures for a series of 3,4-difluorophenyl *trans*-4′-substituted cyclohexane-1′-carboxylates were measured using a polarizing microscope equiped with a heating and cooling stage. The transition enthalpies (ΔH) were measured by differential scanning calorimetry and the transition entropies (ΔS) were calculated from the transition enthalpies and transition temperatures. These thermal data are listed in Table III. The three 3,4-difluorophenyl *trans*-4′-*n*-alkylcyclohexane-1′-carboxylates exhibit monotropic nematic phases.

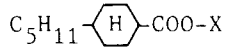
TABLE III

Transition temperatures, enthalpies (ΔH) and entropies ΔS) for the 3,4-difluorophenyl *trans*-4′-substituted cyclohexane-1′-carboxylates

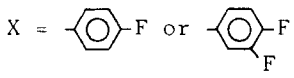


R′	Transition temp. (°C)		ΔH (kcal/mol)		ΔS (EU)	
	C-I	N-I	C-I		C-I	
C_2H_5-	19	—	—		—	
C_3H_7-	32	—	7.40		24.3	
C_4H_9-	25	(−26	6.95		23.3	
C_5H_{11}-	37	(−15	7.78		25.1	
C_6H_{13}-	38	—	8.25		26.5	
C_7H_{15}-	49	(4	9.58		29.7	
	C-N	N-I	C-N	N-I	C-N	N-I
C_3H_7-H-CH_2CH_2-	56	132	7.46	0.197	22.7	0.485
C_3H_7-H-	57	153	8.29	0.190	25.1	0.446

The N-I transition temperature (−15°C) of the 3,4-difluorophenyl *trans*-4′-*n*-pentylcyclohexane-1′-carboxylate is 38°C lower than that (23°C) of 4-fluorophenyl *trans*-4′-*n*-pentylcyclohexane-1′-carboxylate[4].



(IV)



Two compounds of formula (IV) were mixed separately with a mixture A consisting of *trans*-4-*n*-alkyl-1-(4′-cyanophenyl) cyclohexanes[8] in order to assess the influence of the 3-fluoro substituent in formula (IV) on the N-I transition temperature, threshold voltage, bulk viscosity, birefringence and dielectric anisotropy. The

composition and physical properties of mixture A are as follows:

Composition: 40 wt% of C_3H_7-(H)-(O)-CN

30 wt% of C_5H_{11}-(H)-(O)-CN

30 wt% of C_7H_{15}-(H)-(O)-CN

N-I transition temperature: 51.0°C
Bulk viscosity at 20°C: 21.4 c.p.
Birefringence at 25°C: 0.118

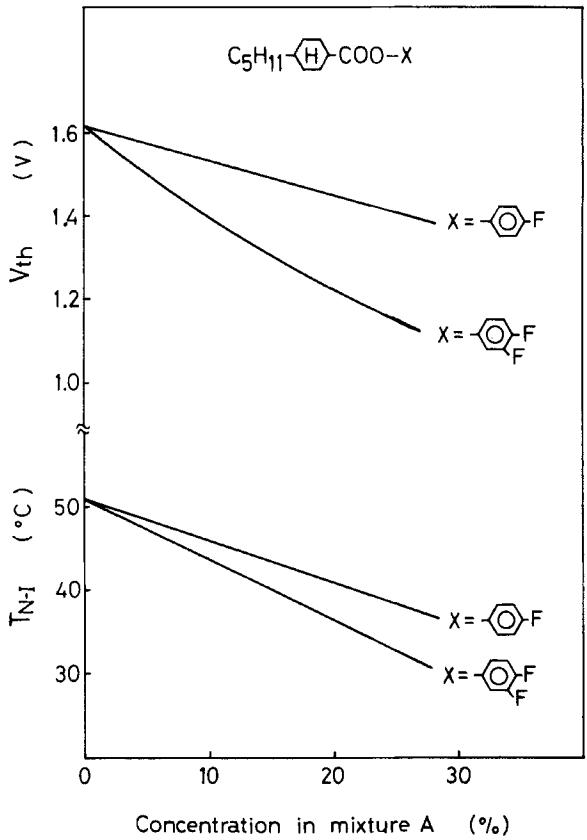


FIGURE 1 The N-I transition temperatures ($T_{N\text{-}I}$) and threshold voltages (Vth) for a series of solutions of 3,4-difluorophenyl and 4-fluorophenyl *trans*-4′-*n*-pentylcyclohexane-1′-carboxylates in mixture A—(see text).

The viscosity measurements were made using a rotating coneplate viscometer at 20°C. The birefringences were measured at 25°C 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 drive voltage to achieve 10% transmission.

The influence of the addition of each compound of formula (IV) on the N-I transition temperature and threshold voltage is shown in Figure 1. The 3,4-difluorophenyl ester of formula (IV) reduces the threshold voltage and decreases the N-I transition temperature more than the 4-fluorophenyl ester. Figure 2 shows the relationships between the threshold voltages and N-I transition temperatures for a series of solutions in mixture A. Two linear relationships between the threshold voltages and the N-I transition temperatures are obtained. The gradient for the 3,4-difluorophenyl *trans*-4′-*n*-pentylcyclohexane-

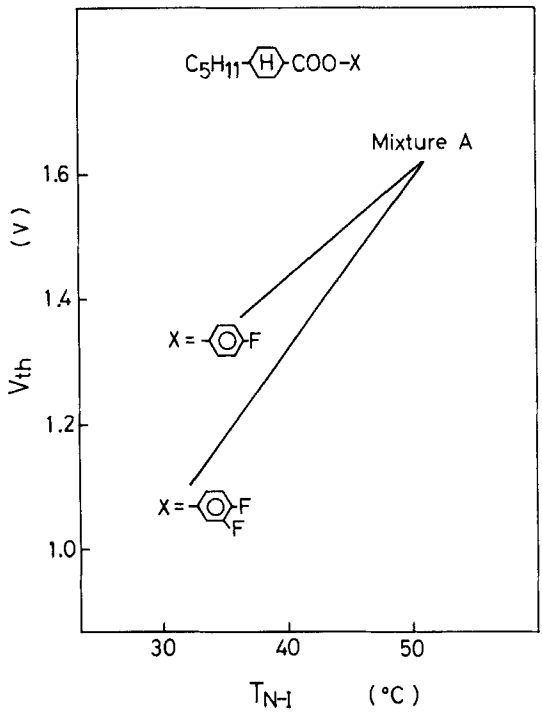
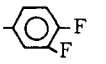


FIGURE 2 The relationships between the threshold voltages (Vth) and N-I transition temperatures ($T_{N\text{-}I}$) for a series of solutions of 3,4-difluorophenyl and 4-fluorophenyl *trans*-4′-*n*-pentylcyclohexane-1′-carboxylates in mixture A—(see text).

1′-carboxylate is larger than that for the 4-fluorophenyl *trans*-4′-*n*-pentylcyclohexane-1′-carboxylate. The introduction of 3-fluoro substituent reduces the threshold voltage effectively.

Figure 3 shows the influence on the bulk viscosity (η), birefringence (Δn) and dielectric anisotropy ($\Delta\epsilon$). The addition of the 3,4-difluorophenyl ester

(X= )

slightly reduces the bulk viscosity of mixture A though the effect in

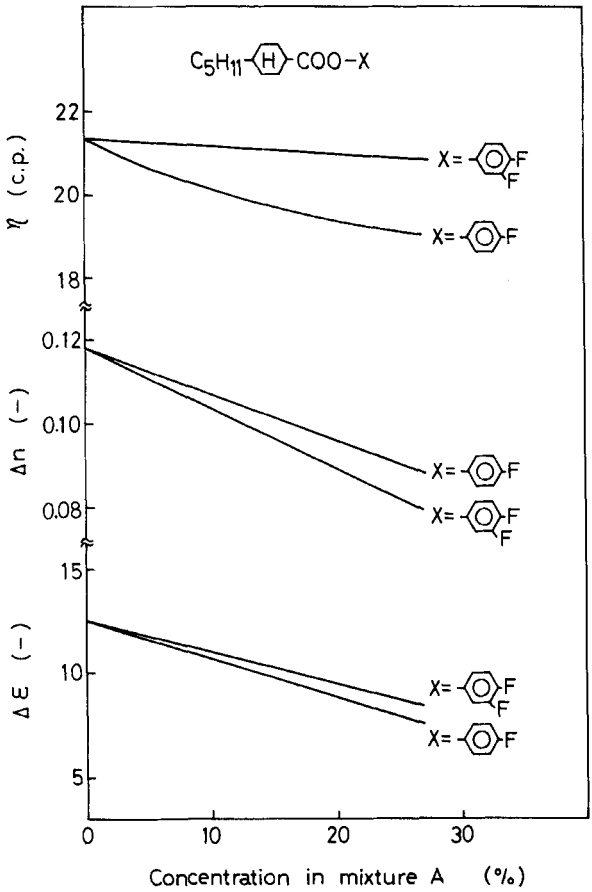
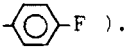


FIGURE 3 The bulk viscosities (η), birefringences (Δn) and dielectric anisotropies ($\Delta\epsilon$) for a series of solutions of 3,4-difluorophenyl and 4-fluorophenyl *trans*-4′-*n*-pentylcyclohexane-1′-carboxylates in mixture A—(see text).

reducing the bulk viscosity is smaller than that for the 4-fluorophenyl ester

(X= ).

Comparison of the 3,4-difluorophenyl ester and the 4-fluorophenyl ester of formula (IV) in Figure 3 shows that the introduction of 3-fluoro substituent into 4-fluorophenyl *trans*-4′-*n*-pentylcyclohexane-1′-carboxylate increases the bulk viscosity, reduces the birefringence and increases the dielectric anisotropy a little.

The transition temperatures and transition entropies (ΔS) for four *trans*-4-{ *β*-(*trans*-4′-*n*-propylcyclohexyl)-1′} ethylcyclohexane-1-

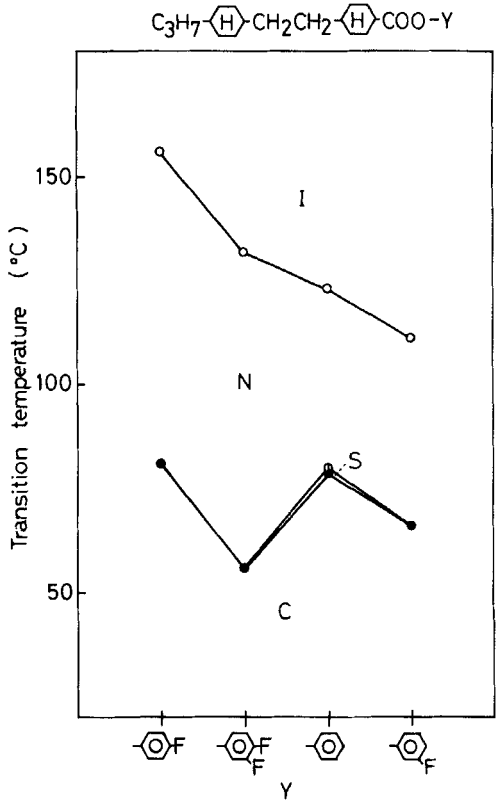
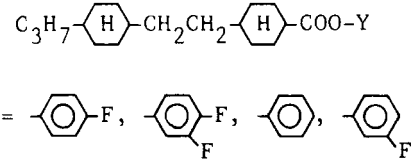


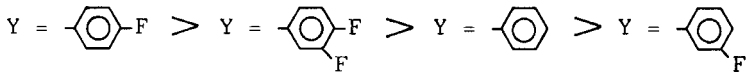
FIGURE 4 The transition temperatures for 4-fluorophenyl, 3,4-difluorophenyl, 3-fluorophenyl and phenyl *trans*-4′-{ *β*-(*trans*-4″-*n*-propylcyclohexyl)-1″}ethylcyclohexane-1′carboxylates

carboxylates of formula (V) are compared in Figure 4 and Figure 5, respectively.



(V)

The order of the N-I transition temperatures for the esters of formula (V) is the following:



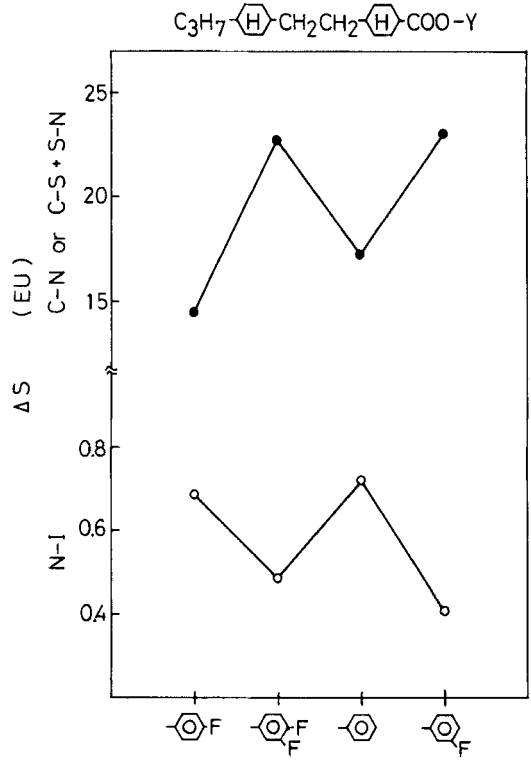
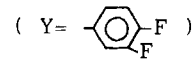
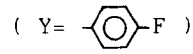


FIGURE 5 The transition entropies (ΔS) for 4-fluorophenyl, 3,4-difluorophenyl, 3-fluorophenyl and phenyl *trans*-4″-{ β-(*trans*-4″-*n*-propylcyclohexyl)-1″}ethyl-cyclohexane-1′-carboxylates.

The 4-fluoro substituent increases the N-I transition temperature , but the 3-fluoro substituent, which increases the breadth of molecule, decreases the N-I transition temperature. The 3,4-difluorophenyl ester

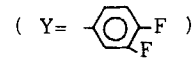


has the lowest melting point of the four esters. Figure 5 shows that the 4-fluorophenyl ester

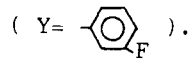


has similar values for the N-I transition entropy and the C-N or C-S + S-N transition entropy to the phenyl ester

and the 3,4-fluorophenyl ester



has a similar value for N-I transition entropy and the C-N transition entropy to the 3-fluorophenyl ester



The 3-fluoro substituent increases the C-N or C-S + S-N transition entropy and decreases the N-I transition entropy. The 4-fluoro substituent does not change the transition entropy for the compounds of formula (V).

The four compounds of formula (V) were mixed separately with a mixture B consisting of 4-*n*-alkoxyphenyl *trans*-4′-*n*-alkylcyclohexane-1′-carboxylates and *trans*-4-*n*-alkyl-1-(4′-cyanophenyl)cyclohexanes. The composition and physical properties of the host mixture B are given in a previous paper[6]. Figure 6 shows the N-I transition temperatures and threshold voltages for a series of solutions of each compound of formula (V) in mixture B. The order of the threshold voltages for the mixtures of compounds of formula (V) and mixture B

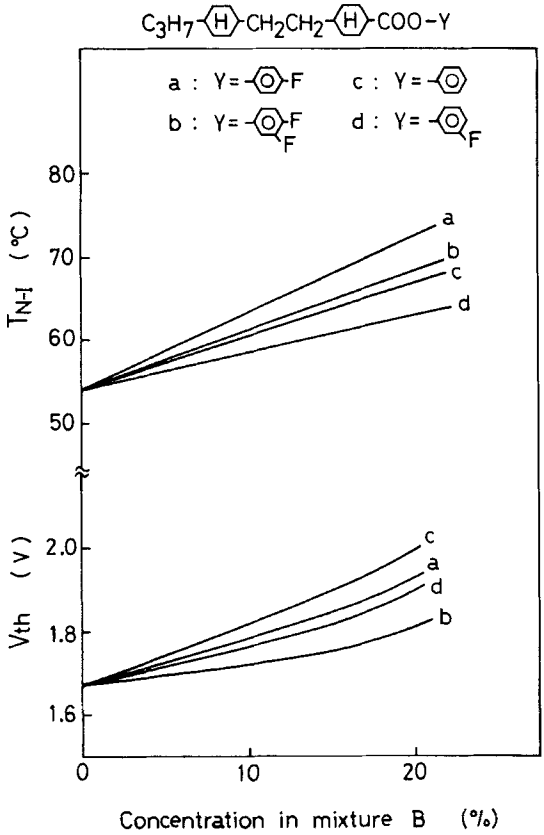
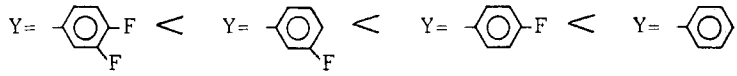


FIGURE 6 The N-I transition temperatures ($T_{N\text{-}I}$) and threshold voltages (Vth) for a series of solutions of 4-fluorophenyl, 3,4-difluorophenyl, 3-fluorophenyl and phenyl *trans*-4′-{ β-(*trans*-4″-*n*-propylcyclohexyl)-1″}ethylcyclohexane-1′-carboxylates in mixture B—(see text).

is the following:



Both of the 3- and 4-fluoro substituents reduce the increase in threshold voltage with concentration relative to the phenyl ester. The 3-fluoro substituent reduces the increase in threshold voltage more than the 4-fluoro substituent, though the 3-fluoro substituent increases the N-I transition temperature less than the 4-fluoro substitu-

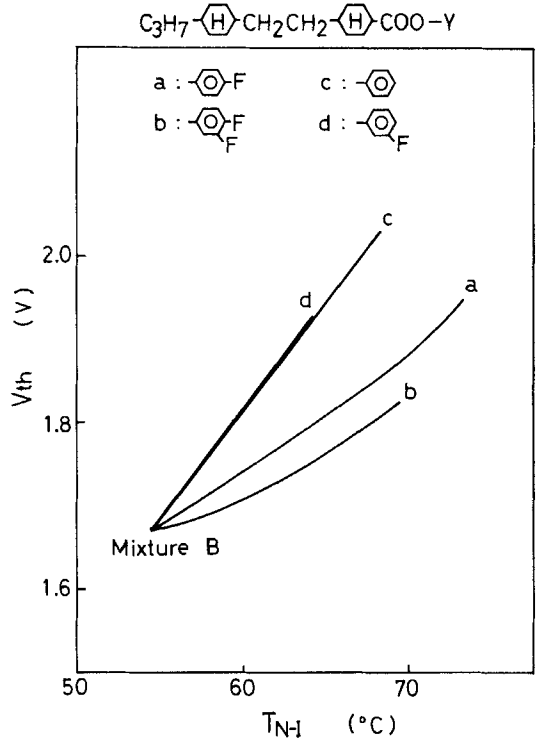


FIGURE 7 The relationships between the threshold voltages (Vth) and N-I transition temperatures ($T_{N\text{-}I}$) for a series of solutions of 4-fluorophenyl, 3,4-fluorophenyl, 3-fluorophenyl and phenyl *trans*-4′-{ β-(*trans*-4″-*n*-propylcyclohexyl)-1″}ethylcyclohexane-1′-carboxylates in mixture B—(see text).

ent. Figure 7 shows the relationships between the threshold voltages and N-I transition temperatures for a series of solutions in mixture B. The addition of a compound to increase the N-I transition temperature increases the threshold voltage. The 3,4-difluorophenyl ester

(Y= -(⬡)-F
F)

as a compound to increase the N-I transition temperature, increases the threshold voltage to the least extent, followed by the 4-fluorophenyl ester

(Y= -(⬡)-F).

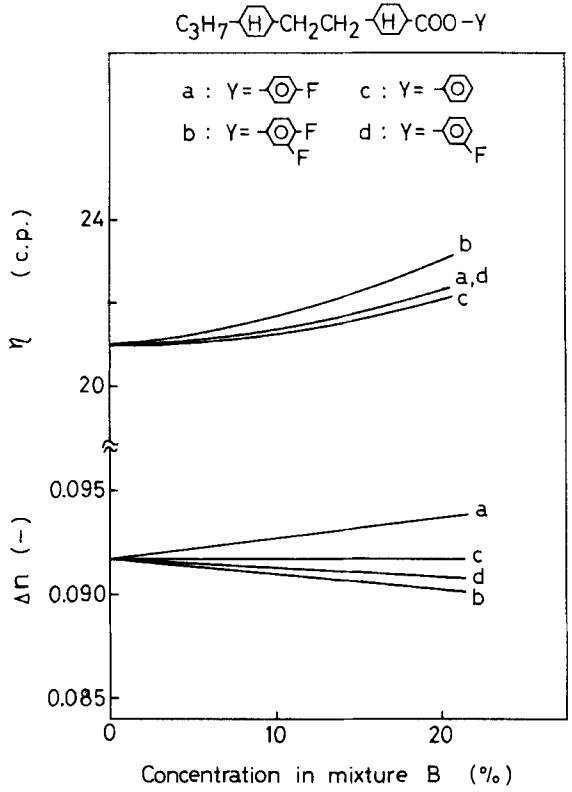
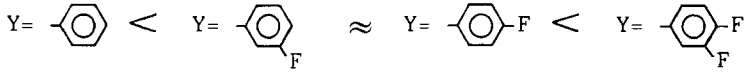


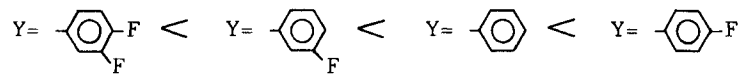
FIGURE 8 The bulk viscosities (η) and birefringences (Δn) for a series of solutions of 4-fluorophenyl, 3, 4-difluorophenyl, 3-fluorophenyl and phenyl *trans*-4′-{ *β*-(*trans*-4″-*n*-propylcyclohexyl)-1″}ethylcyclohexane-1′-carboxylates in mixture B—(see text).

The influence of the addition of each compound on the bulk viscosity and birefringence of mixture B is shown in Figure 8. The orders of the bulk viscosities and birefringences for the mixtures of compounds of formula (V) and mixture B are as follows:

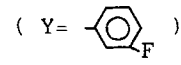
Bulk viscosities:



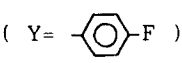
Birefringences:



The introduction of the fluoro substituents increases the bulk viscosities a little. The 3-fluorophenyl ester

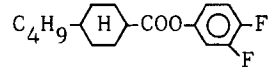


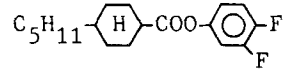
increases the bulk viscosity to the same extent as the 4-fluorophenyl ester

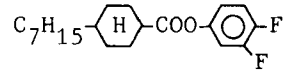


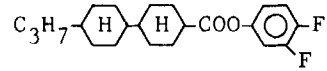
The compounds containing the 3-fluoro substituent decrease the birefringence of mixture B and the 4-fluorophenyl ester increases it. The introduction of the 3-fluoro substituent decreases the birefringence because the 3-fluoro substituent reduces the linearity of the molecule.

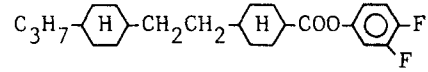
We also prepared a mixture C consisting of compounds (I), (II) and (III) in order to investigate the dielectric constants for the 3,4-difluorophenyl esters. The composition and physical properties for mixture C are as follows:

Composition: 15 wt% of 

40 wt% of 

15 wt% of 

15 wt% of 

15 wt% of 

Nematic temperature range:	14~29°C
Bulk viscosity:	21.6 c.p. at 20°C, 18.7 c.p. at 25°C
Birefingence at 25°C:	0.042
Threshold voltage:	1.08 V
Dielectric constants at 25°C:	$\epsilon_{11} = 10.0$, $\epsilon_{\perp} = 6.3$, $\Delta\epsilon = 3.7$

The dielectric constants were determined from the capacitance of a parallel-plate capacitor measured empty and then filled with liquid crystal. The mixture C has a weak positive dielectric anisotropy and a low value (0.59) of $\Delta\epsilon/\epsilon_{\perp}$. Mixture C has a higher dielectric anisotropy and a lower threshold voltage than a mixture [4] of 4-fluorophenyl 4′-*n*-alkylcyclohexane-1′-carboxylates which has the same N-I transition temperature (29°C) as mixture C.

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