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The Synthesis and Liquid Crystal Properties of Some Laterally Fluorinated *trans*-Cyclohexane-1-carboxylate and Benzoate Esters

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A large number of laterally fluorinated 4-*n*-alkyl- and -alkoxy-phenyl 4′-*n*-alkyl- and -alkoxy-benzoates and 4-*n*-alkylphenyl *trans*-4′-*n*-alkyl- and -alkoxy-cyclohexane-1-carboxylates were synthesised. In these compounds, the lateral fluoro-substituent was situated in either the phenol or the carboxylic acid moiety of the molecules for the benzoate esters, but only in the phenol moeity for the *trans*-cyclohexane-1-carboxylate esters. The nematic thermal stabilities for the fluorophenyl benzoate and *trans*-cyclohexane-1-carboxylate esters and the fluorobenzoate esters were compared with those for the corresponding non-fluorinated analogues. A nematic thermal efficiency order was derived for the 4-*n*-alkyl-fluorophenyl 4-*n*-alkylbenzoate and *trans*-4-*n*-alkylcyclohexane-1-carboxylate esters, but only in the case of the latter esters, which were extensively examined, was the smectic tendency of the system investigated.

Explanations are given for the observed nematic and smectic thermal stabilities of the titled esters, and some of their physical properties are discussed.

INTRODUCTION

Benzoate esters of structure (I) have found an important use as host nematogens for multiplexing mixtures used in twisted nematic display devices. The preconceived idea that esters are too viscous for use in such display devices has long vanished, and their good electro-optic responses as mixtures with biphenyls, coupled with their ease of synthesis and their photochemical and thermal stabilities, have made the use of benzoate esters widespread.

However, the major disadvantages of these esters are their relatively low

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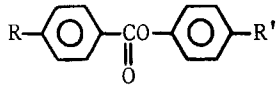
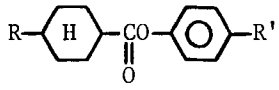
nematic thermal stabilities, and the tendency of smectic phases to be injected in their mixtures with other nematogens.



(I)



(II)

R, R' = n-alkyl or n-alkoxy

This problem was somewhat alleviated by the advent of the *trans*-cyclohexane-1-carboxylates (II), where the left-hand phenyl ring has been replaced by a *trans*-cyclohexane ring. This change in structure gave an increase in the nematic thermal stability but was accompanied by an increase in the melting point.

Lateral substituents usually exert two opposing effects on the thermal stability of the mesophase. Firstly, the substituent changes the molecular polarisability and this may tend to increase the thermal stability of the mesophase. However, the size of the lateral group broadens the molecule, and in doing so, decreases the length/breadth ratio, and hence the mesophase thermal stability. The second of these effects normally predominates, but the destabilising effect on the mesophase is minimised by using a small substituent such as fluorine.

We have therefore prepared a large number of esters in order to investigate the possible advantageous effects of introducing a lateral fluoro-substituent into the esters (I) and (II), where R and R′ can be either *n*-alkyl or *n*-alkoxy.

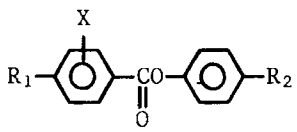
RESULTS AND DISCUSSION

Throughout the following sections, a monotropic transition temperature is denoted by a ( ) bracket around the recorded temperature, whilst a virtual value is signified by a [ ] bracket.

This section can be conveniently sub-divided into two parts.

1 The fluorobenzoate esters

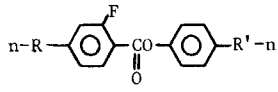
This section covers the esters which have the following general structure:



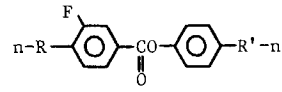
R_1 = n-alkoxy;
R_2 = n-alkoxy, n-alkyl, or cyano;
X = 2-fluoro or 3-fluoro

TABLE I

Thermal Data for the Fluorobenzoate Esters



Code	n-R	n-R'	Transition Temperatures (°C) C-N/C-I	N-I	Enthalpy of Fusion kcal mole^{-1}
F^2MeO.4	CH_3O	C_4H_9	28.4	[-10.0]	-
F^2MeO.5	CH_3O	C_5H_{11}	35.5	[16.5]	5.8
$F^2$40.5	C_4H_9O	C_5H_{11}	49.0	(41.5)	-
$F^2$50.07	$C_5H_{11}O$	$C_7H_{15}O$	46.0	63.9	14.6
$F^2$50.4	$C_5H_{11}O$	C_4H_9	36.0	(16.2)	-
$F^2$50.5	$C_5H_{11}O$	C_5H_{11}	37.5	(33.0)	14.7
$F^2$60.06	*$C_6H_{13}O$	$C_6H_{13}O$	40.0	73.4	13.3
$F^2$60.07	$C_6H_{13}O$	$C_7H_{15}O$	44.0	70.9	-
$F^2$60.5	$C_6H_{13}O$	C_5H_{11}	22.0	43.7	7.9



Code	n-R	n-R'	Transition temperatures (°C) C-N/C-I	S_A-N	N-I
$F^3$60.CN	$C_6H_{13}O$	CN	90.0	-	-
$F^3$40.06	C_4H_9O	$C_6H_{13}O$	72.0	-	(71)
$F^3$60.07	$C_6H_{13}O$	$C_7H_{15}O$	63.0	(56.5)	71.5
F^3MeO.5	†CH_3O	C_5H_{11}	82.0	-	-
$F^3$60.5	$C_6H_{13}O$	C_5H_{11}	66.0	-	-
$F^3$70.5	$C_7H_{15}O$	C_5H_{11}	63.0	-	[35]

* See reference 1

† See reference 2

The melting points and transition temperatures of these esters are listed in Table I. The following conclusions were reached by comparing the melting points and transition temperatures of the fluorobenzoate esters with those of the analogues non-fluorinated benzoate esters.

a) The introduction of a lateral fluoro-substituent into the 2-position of the benzoate esters has had an adverse effect upon the nematic thermal stability. For the dialkoxy compounds, the average decrease was found to be 17° (16.1°–18.6°) whilst for the alkyl-alkoxy compounds, the decrease was even higher, some 24.5° (19.3°–34.5°).

b) The 2-fluorobenzoate esters have lower melting points than their non-fluorinated analogues. A noticeable feature here is the low melting point of 4-*n*-pentylphenyl 4-*n*-hexyloxy-2-fluorobenzoate ($F^2$60.5); this has a melting point of 22°, which is about 15° lower than most of the melting points of the other members of the series.

c) In general, in going from the di-alkoxy esters to the alkoxy-alkyl esters, the melting points and N–I transition temperatures decrease. In fact, in the case of the latter esters, many of the homologues exhibit only a monotropic or virtual nematic phase; the exception was $F^2$60.5 (low melting point).

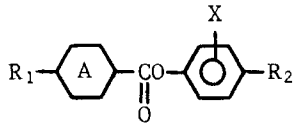
d) The melting points for the 3-fluorobenzoate esters are much higher than those of either the 2-fluorobenzoate esters or their non-fluorinated analogues.

Although the benzoate esters, which give the lowest viscosities, and hence fast rise and decay times, are usually the di-alkyl esters (see Table II), it was thought unprofitable to prepare the di-alkyl 2-fluorobenzoate esters, since this would lower further the already relatively low N–I transition temperatures of the alkoxy-alkyl compounds.

Instead, a large number of 2- and 3-fluorophenyl benzoates and *trans*-cyclohexane-1-carboxylates were synthesised.

2 Fluorophenyl benzoates and the corresponding *trans*-cyclohexane-1-carboxylates

This section covers the esters which have the following general structure:



(III)

R_1 = n-alkyl or n-alkoxy, when  is a phenyl ring;

R_1 = n-alkyl, when  is a *trans*-cyclohexane ring;

R_2 = n-alkyl;

X = 2- or 3-fluoro.

The melting points, transition temperatures, and enthalpies of fusion for the 4-*n*-alkyl-2-fluorophenyl *trans*-4-*n*-alkylcyclohexane-1-carboxylates are listed in Table II; data for the 4-*n*-alkyl-2-fluorophenyl 4-*n*-alkyl- and -alkoxybenzoates are listed in Table III, and for the 4-*n*-alkyl-3-fluorophenyl 4-*n*-alkoxy- and -alkyl-benzoates and 4-*n*-alkyl-3-fluorophenyl *trans*-4-*n*-alkylcyclohexane-1-carboxylates in Table IV.

A substantial number of the 4-*n*-alkyl-2-fluorophenyl *trans*-4-*n*-alkylcyclohexane-1-carboxylates exhibit a room temperature nematic phase—sixteen out of the thirty-eight esters prepared. Only in this series of compounds could a meaningful plot of the N–I transition temperature against the number (*n*) of carbon atoms in the *n*-alkyl chain be drawn. The graphs plotted for the 4-*n*-alkyl-2-fluorophenyl *trans*-4-*n*-heptylcyclohexane-1-carboxylates and the 4-*n*-heptyl-2-fluorophenyl *trans*-4-*n*-alkylcyclohexane-1-carboxylates (Figure 1 and 2 respectively) show the usual odd-even alternation of the N–I transition temperatures: two ascending curves may be drawn through the points for each series, the lower curve for the esters with an even number of

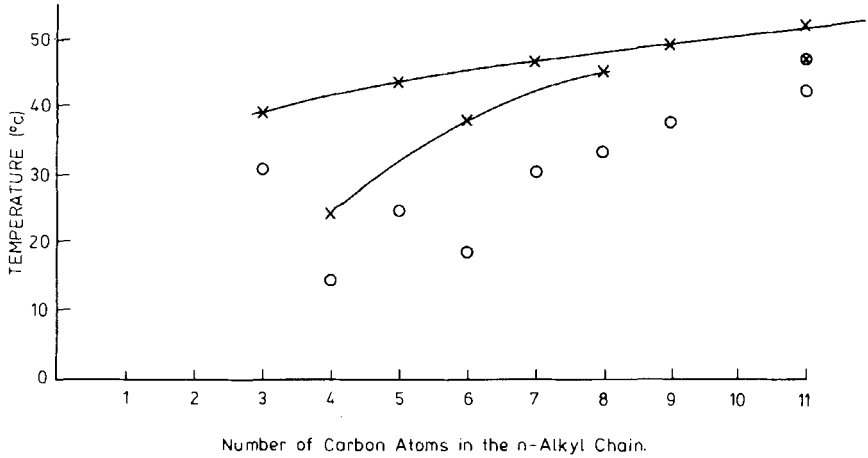
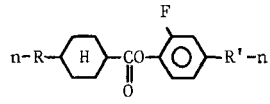


FIGURE 1 Graph of the transition temperature against the number of carbon atoms in the *n*-alkyl chain for the 4-*n*-alkyl-2-fluorophenyl *trans*-4-*n*-heptylcyclohexane-1-carboxylates. ○, crystal-nematic; ×, nematic-isotropic liquid; ⊗, nematic-S_A.

TABLE II

Thermal Data for the 4-*n*-Alkyl-2-fluorophenyl *trans*-4-*n*-Alkyl-cyclohexane-1-carboxylates



Code	n-R	n-R'	Transition temperature (°C) C-N/C-I	N-I	Enthalpy of fusion kcal mole^{-1}
MeH.3F^2	CH_3	C_3H_7	27.0	[-27.0]	7.6
MeH.5F^2	CH_3	C_5H_{11}	13.5	[-36.0]	-
MeH.7F^2	CH_3	C_7H_{15}	18.5	[-24.0]	-
2H.5F^2	C_2H_5	C_5H_{11}	23.5	[-10.0]	-
2H.7F^2	C_2H_5	C_7H_{15}	13.0	(-5.5)	-
3H.3F^2	C_3H_7	C_3H_7	32.5	(19.0)	7.0
3H.5F^2	C_3H_7	C_5H_{11}	36.0	(26.5)	-
3H.7F^2	C_3H_7	C_7H_{15}	27.0	30.3	9.9
4H.3F^2	C_4H_9	C_3H_7	10.5	10.9	-
4H.5F^2	C_4H_9	C_5H_{11}	10.5	23.1	6.4
4H.7F^2	C_4H_9	C_7H_{15}	16.0	26.7	7.7
5H.3F^2	C_5H_{11}	C_3H_7	30.0	30.7	8.3
5H.4F^2	C_5H_{11}	C_4H_9	10.0	23.0	6.9
5H.5F^2	C_5H_{11}	C_5H_{11}	17.5	36.5	8.0
5H.6F^2	C_5H_{11}	C_6H_{13}	10.0	32.8	9.0
5H.7F^2	C_5H_{11}	C_7H_{15}	33.0	41.4	-
5H.8F^2	C_5H_{11}	C_8H_{17}	25.0	39.4	-
5H.9F^2	C_5H_{11}	C_9H_{19}	38.0	43.8	-
6H.3F^2	C_6H_{13}	C_3H_7	22.0	29.6	-
6H.4F^2	C_6H_{13}	C_4H_9	14.0	20.3	-
6H.5F^2	C_6H_{13}	C_5H_{11}	11.5	34.3	7.5
6H.6F^2	C_6H_{13}	C_6H_{13}	11.0	30.7	11.1
6H.7F^2	C_6H_{13}	C_7H_{15}	22.0	38.9	10.2
6H.8F^2	C_6H_{13}	C_8H_{17}	16.0	36.2	-
6H.9F^2	C_6H_{13}	C_9H_{19}	28.5	43.0	-
7H.3F^2	C_7H_{15}	C_3H_7	30.5	39.2	10.8
7H.4F^2	C_7H_{15}	C_4H_9	14.5	24.1	-
7H.5F^2	C_7H_{15}	C_5H_{11}	24.5	43.4	11.0

TABLE II—*continued*

Code	n-R	n-R'	Transition temperature (°C) C-N/C-I	N-I	Enthalpy of fusion kcal mole^{-1}
7H.6F[2]	C_7H_{15}	C_6H_{13}	18.5	37.8	-
7H.7F[2]	C_7H_{15}	C_7H_{15}	30.0	46.4	11.7
7H.8F[2]	C_7H_{15}	C_8H_{17}	33.0	45.0	-
7H.9F[2]	C_7H_{15}	C_9H_{19}	37.0	49.3	-
7H.11F[2]	C_7H_{15}	$C_{11}H_{23}$	42.5*	52.0	-
8H.3F[2]	C_8H_{17}	C_3H_7	21.5	38.5	9.2
8H.5F[2]	C_8H_{17}	C_5H_{11}	23.5	41.0	-
8H.7F[2]	C_8H_{17}	C_7H_{15}	22.5	44.0	-
9H.5F[2]	C_9H_{19}	C_5H_{11}	41.0	47.7	-
9H.7F[2]	C_9H_{19}	C_7H_{15}	34.0	49.3	-

* C-S_A with S_A-N at 47.0°

carbon atoms in the *n*-alkyl chain, and the curves converge as *n* increases. The N–I transition temperatures rise very rapidly for the first few members of the series (see Figure 2), so much so that the very early numbers of the series exhibit only a virtual or monotropic nematic phase. The 4-*n*-undecyl-2-fluorophenyl *trans*-4-*n*-heptylcyclohexane-1-carboxylate is the only ester of this type that we synthesised that exhibits a smectic phase (S_A–N, 47.0°). The smectic tendency of these esters in relation to that of the analogous non-fluorinated *trans*-4-*n*-alkylcyclohexane-1-carboxylates and 4-alkylbenzoates will be discussed later.

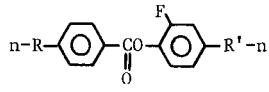
COMPARISON OF THE N-I TRANSITION TEMPERATURES FOR THE VARIOUS ESTER SYSTEMS

1 Esters containing the 2-fluorophenyl moiety

The following conclusions can be drawn by comparing the melting points and N–I transition temperatures of the 4-*n*-alkyl-2-fluorophenyl 4-*n*-alkylbenzoates and *trans*-4-*n*-alkylcyclohexane-1-carboxylates with the corresponding data for the non-fluorinated analogues. It must be remembered however, that due to lack of information about some of the 4-*n*-alkylphenyl *trans*-4-*n*-alkylcyclohexane-1-carboxylates, the comparisons are based on only four or five homologues.

TABLE III

Thermal Data for the 4-*n*-Alkyl-2-fluorophenyl 4-*n*-Alkyl- and -Alkoxy-benzoates



Code	n-R	n-R'	Transition temperatures (°C) C-N/C-I	N-I
40.5F^2	C_4H_9O	C_5H_{11}	44.0	(37.9)
60.5F^2	$C_6H_{13}O$	C_5H_{11}	28.0*	37.0
3.7F^2	C_3H_7	C_7H_{15}	23.0	[-7.0]
4.5F^2	C_4H_9	C_5H_{11}	16.0	[-14.0]
5.5F^2	C_5H_{11}	C_5H_{11}	14.0	(1.2)
5.7F^2	C_5H_{11}	C_7H_{15}	24.0	(4.2)
6.4F^2	C_6H_{13}	C_4H_9	7.0	<-20.0
6.5F^2	C_6H_{13}	C_5H_{11}	19.5	[-5.0]
7.5F^2	C_7H_{15}	C_5H_{11}	19.0	(4.3)

* Enthalpy of fusion = 2.6 kcal mole^{-1}

a) The introduction of a lateral fluoro-substituent into the *trans*-cyclohexane-1-carboxylates lowers the N–I transition temperature by 11° (range: 10.0°–11.5°, five homologues), whilst the introduction into the benzoate system reduces the N–I transition temperature by as much as 25° (range: 22.5°–28.0°, four homologues). Thus the nematic thermal stabilities of the non-fluorinated benzoate esters are much more affected by the introduction of a lateral 2-fluoro-substituent than are those of the non-fluorinated *trans*-cyclohexane-1-carboxylates. In fact, all the 4-*n*-alkyl-2-fluorophenyl 4-*n*-alkylbenzoates exhibit either a virtual or monotropic nematic phase (5.3F^2 shows no mesophase above −20°, the temperature limit of our microscope assembly).

b) Replacement of the left-hand phenyl ring in the benzoate ester of structure (I) by a *trans*-cyclohexane ring, to give ester (II), increases the N–I transition temperature by 18° (range: 11.5°–26.0°, five homologues). This fact can be checked by comparing the N–I transition temperatures of the 4-*n*-alkyl-2-fluorophenyl *trans*-4-*n*-alkylcyclohexane-1-carboxylates with those

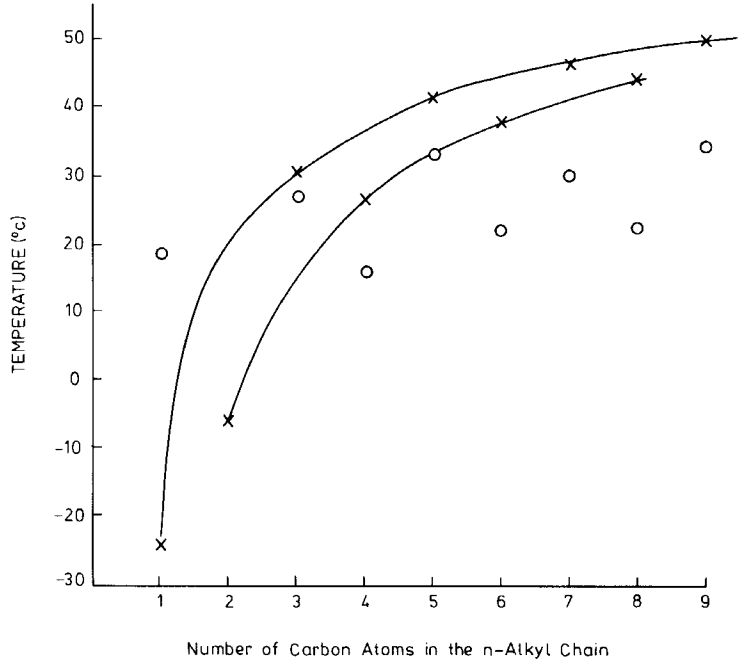


FIGURE 2 Graph of the transition temperature against the number of carbon atoms in the *n*-alkyl chain for the 4-*n*-heptyl-2-fluorphenyl *trans*-4-*n*-alkylcyclohexane-1-carboxylates. ○, crystal-nematic or isotropic liquid; ×, nematic-isotropic liquid.

of the 4-*n*-alkylphenyl 4-*n*-alkylbenzoates. In this case, the cyclohexane esters again have the higher N–I transition temperatures by 10° (range: 0.8°–15.9°, thirteen homologues). When this difference is added to the decrease in the N–I transition temperature caused by introducing the lateral fluoro-substituents into the carboxylate esters, ie, 11°, this makes a total of 21°. This compares well with the above figure of 18° found for a more limited number of homologues.

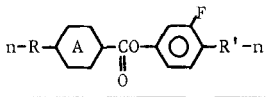
Thus, from the above data, a nematic thermal efficiency order can be complied for the various ester systems studied. The order is:

$$\text{Ester (II)} > \begin{matrix}\text{2-Fluoro-analogue}\\ \text{of Ester (II)}\end{matrix} > \text{Ester (I)} \gg \begin{matrix}\text{2-Fluoro-analogue}\\ \text{of Ester (I)}\end{matrix}$$

The relative positions of the esters (I) and (II) are not of course surprising, since in many other systems, replacement of a benzene ring by a *trans*-cyclohexane ring causes an increase in the nematic thermal stability, especially at relatively low N–I temperatures. The most interesting features of this order are

TABLE IV

Thermal Data for the 4-*n*-Alkyl-3-fluorophenyl 4-*n*-Alkoxy- and -Alkyl-benzoates and the 4-*n*-Alkyl-3-fluorophenyl *trans*-4-*n*-Alkylcyclohexane-1-carboxylates



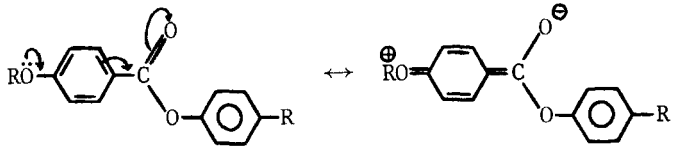
Code	n-R	Ring A	n-R'	Transition temperatures (°C) C-I/C-S_A	S_A-N	S_A-I	N-I
MeO.4F[3]	CH_3O	Benzene	C_4H_9	51.5	-	-	-
6O.5F[3]	$C_6H_{13}O$	Benzene	C_5H_{11}	39.5	-	48.6	-
4.5F[3]	C_4H_9	Benzene	C_5H_{11}	3.0	-	-	<-9.0
5.3F[3]	C_5H_{11}	Benzene	C_3H_7	1.0	-	-	(-8.0)
5.5F[3]	C_5H_{11}	Benzene	C_5H_{11}	15.0	-	-	[0]
3H.5F[3]	C_3H_7	Cyclohexane	C_5H_{11}	26.5	-	-	(9.2)
4H.5F[3]	C_4H_9	Cyclohexane	C_5H_{11}	14.5	(-3.7)	-	(7.4)
5H.3F[3]	C_5H_{11}	Cyclohexane	C_3H_7	33.5	-	-	[14.0]
5H.5F[3]	C_5H_{11}	Cyclohexane	C_5H_{11}	27.5	(18.7)	-	(26.3)
6H.5F[3]	C_6H_{13}	Cyclohexane	C_5H_{11}	29.0	-	(24.7)	-
7H.5F[3]	C_7H_{15}	Cyclohexane	C_5H_{11}	33.5	-	34.4	-

a) the extent to which the introduction of a lateral fluoro-substituent into the benzoate ester system reduces the N–I transition temperature, in comparison with its effect in the *trans*-cyclohexane-1-carboxylates,
and

b) the relative positions of the esters (I) and the 2-fluoro-analogues of ester (II) in the efficiency order.

These observations may be explained by the following arguments. Both Neubert[3] and Dewar[4] have discussed the additional nematic thermal stability when the carbonyl group of an ester linking function is adjacent to a phenyl ring carrying a substituent, particularly one such as alkoxy, compared with the same system in which the ester function is reversed. They explain this in terms ((IV), (V)) of overlap of the π-electrons of the carbonyl moiety with the π-cloud of the phenyl ring. To obtain maximum overlap in this conjugative interaction, the carbonyl moiety of the ester linking group and the phenyl ring should be coplanar. Thus any factor which opposes coplanarity will

reduce the overlap and in turn, both the degree of conjugation and the anisotropy of polarisability. Furthermore, any twist about the ester linking group will principally involve the phenol-moiety carbon-oxygen bond.

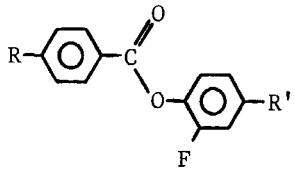


(IV) (V)

In the case of the 2-fluorophenyl benzoate esters, the fluoro-substituent is attached to an aromatic ring. The effect of the fluorine atom, or for that matter any other halogen atom in this situation is that the electron-withdrawing, inductive effect is very strong, and is not overwhelmed by the electron-releasing, resonance effect of the fluorine (halogen) atom. Thus, the small fluoro-substituent will have a relatively high charge density, identical in sign to that carried by the oxygen atom of the carbonyl moiety of the ester linking group. Thus, the repulsion between these two will either cause a reduction in the coplanarity between the carbonyl moiety and the phenyl ring to which it is attached, or twist the two phenyl rings out of plane by rotation about the phenol-moiety carbon-oxygen bond.

In either event, the nematic thermal stability of the benzoate ester molecule will be partially lost in the fluorinated analogue through the loss of conjugation and/or thickening of the molecule.

Alternatively, if this repulsive situation is alleviated by the fluoro-substituent lying on the opposite side of the molecule to the carbonyl function (VI), the molecular breadth is markedly increased. Again, a reduction in N–I transition temperature would be expected, although the molecule is now planar.



(VI)

In the case of the 2-fluorophenyl *trans*-cyclohexane-1-carboxylates, no conjugation can occur between the carbonyl moiety and the cyclohexane ring, although the oxygen atom of the carbonyl group will still of course be negatively charged. Thus for these carboxylate esters, the repulsion between the fluorine atom and the carbonyl group will again result in a twisting effect

and thickening of the molecule, or the adoption of a broader molecular structure similar to (VI).

The increase in nematic thermal stability when the phenyl ring of the non-fluorinated benzoate ester (I) is replaced by a *trans*-cyclohexane ring (ester II) is of course very interesting. This effect has been discussed in general terms in other papers presented at the Kyoto meeting and in the present context, it need only be noted that two factors probably contribute to this situation:

a) in the esters, smaller repulsive interactions may be involved between the oxygen atom of the carbonyl group and the cyclohexane rings of neighbouring molecules;

b) although the cyclohexane ring has a larger volume, this may in effect lead to more efficient packing of the molecules in the nematic melt.

Effect (a) could be even more important in the fluoro-esters, because of the extra negative substituent in the molecule, and so account for the larger decrease in N–I temperature in the benzoate esters compared with the cyclohexane esters. If these ideas are correct, then the ideal case would be when both rings of an ester are cyclohexane rings. Osman[5] has in fact prepared such compounds and the higher nematic-isotropic transition temperatures of the di-propyl and pentyl-propyl esters compared with those of the corresponding *trans*-cyclohexane-1-carboxylates and benzoates (see Table V) lend some support to the above arguments. The smaller decrease in N–I temperature resulting from 2-fluorination of (II) may also suggest that the bulkier cyclohexane ring partly shields the out of plane 2-fluoro-substituent, and that a structure like (VI) is not adopted.

2 Esters containing the 3-fluorophenyl moiety

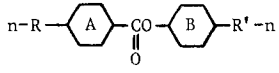
The following conclusions can be drawn by comparing the melting points and transition temperatures of the 4-*n*-alkyl-3-fluorophenyl *trans*-4-*n*-alkylcyclohexane-1-carboxylates with the corresponding 2-fluoro analogues.

a) The re-positioning of the fluorine atom from the 2- to the 3-position has decreased the nematic thermal stability of the system by 15° (range: 10.2°–17.3°, four homologues). The melting points of the esters have increased, and consequently all the 3-fluoro-analogues exhibit either a monotropic or a virtual nematic phase.

b) The 4-*n*-alkyl-3-fluorophenyl *trans*-4-*n*-alkylcyclohexane-1-carboxylates have a greater tendency to form smectic phases than the corresponding 2-fluoro-analogues, eg, 4-*n*-pentyl-3-fluorophenyl *trans*-4-*n*-hexyl- and -heptyl-cyclohexane-1-carboxylates are pure smectogens. The decrease in

TABLE V

Comparison of the N–I transition temperatures of di-alkyl bicyclohexane esters with those of the corresponding *trans*-cyclohexane-1-carboxylates and benzoates



A	B	n-R	n-R'	N-I (°C)
H	H	C_3H_7	C_3H_7	36.6
H	O	C_3H_7	C_3H_7	29.0
O	O	C_3H_7	C_3H_7	(15.0)
H	H	C_5H_{11}	C_3H_7	52.1
H	O	C_5H_{11}	C_3H_7	42.0
O	O	C_5H_{11}	C_3H_7	18.7

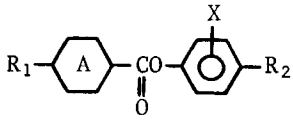
nematic thermal stability, coupled with an enhanced smectic tendency, could be consistent with the molecules being planar (more smectogenic), but broader (less shielding of the 3-fluoro-substituent by the cyclohexane ring).

The melting points and transition temperatures for the 4-*n*-alkyl-3-fluorophenyl 4-*n*-alkylbenzoates were very low and comparable with those found for the 2-fluorophenyl analogues. However, comparisons are difficult to make here because of the smaller number of homologues examined and the magnitude and nature of the transition temperatures.

GENERAL CONCLUSION

By comparing the N–I transition temperatures of the 4-*n*-alkylphenyl 4-*n*-alkylbenzoates and *trans*-4-*n*-alkylcyclohexane-1-carboxylates with their

fluorinated analogues, the following nematic thermal efficiency order has been compiled



A	cyclo		cyclo		benzene		cyclo	benzene ≡ benzene
X	hydrogen	>	2-fluoro	>	hydrogen	>	3-fluoro	> 2-fluoro ≡ 3-fluoro

cyclo = *trans*-cyclohexane ring

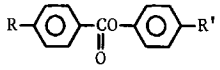
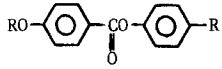
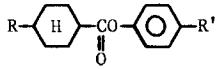
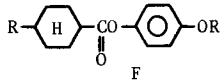
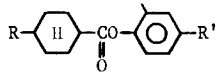
PHYSICAL PROPERTIES

The results of measurements of viscosity, dielectric constant, and birefringence for a selection of the esters are listed in Table VI.

The viscosities of the di-alkyl esters are very similar and much lower than the values obtained for the alkyl-alkoxy esters. In both these series of esters, the lower viscosities are always recorded for the esters containing a cyclohexane ring. Even when a lateral fluoro-substituent is introduced in the case of the 4-*n*-alkyl-2-fluorophenyl *trans*-4-*n*-alkylcyclohexane-1-carboxylates,

TABLE VI

Some properties of the esters measured at 20°C

	Viscosity (cP)	Δn	Δε
	23*	0.13*	0.4*
	65	0.14	0.1
	18	0.07	-0.5
	44	0.08	-1.4
	22	0.07	-0.8

* Extrapolated value

only a slight increase in viscosity is observed. This again illustrates the ability of the cyclohexane ring to shield the fluoro-substituent and reduce its broadening effect.

The birefringence of the cyclohexane carboxylates is very low, about half the value obtained for the benzoate esters. Replacement of one of the alkyl groups in the di-alkyl esters by an alkoxy group only very slightly increases the birefringence.

The dielectric data show that, due to the dipole moment which acts across the long molecular axis for the lateral fluoro-substituent or the terminal oxygen of the alkoxy chain, the fluoro- and alkyl-alkoxy compounds are much more negative than their non-fluorinated or di-alkyl analogues. There is a very marked decrease in $\Delta\varepsilon$ (more negative) for the cyclohexane-1-carboxylates when the right-hand alkyl chain is replaced by an alkoxy chain. Also, both the di-alkyl and alkyl-alkoxy cyclohexane-1-carboxylates are much more negative than the corresponding benzoate esters.

INJECTED SMECTIC TENDENCIES

The relative injected smectic tendencies of the di-substituted phenyl benzoates and phenyl and 2-fluorophenyl *trans*-cyclohexane-1-carboxylates were established by examining the binary phase diagram of each of the di-pentyl analogues with 4-cyano-4′-*n*-nonylbiphenyl. The phase diagram showed that the fluoro-ester (5H.5F^2) has the lowest injected smectic tendency. Whereas at first sight, the non-fluorinated cyclohexane ester (5H.5) has the highest injected smectic tendency of all the esters, if we use the equation $(T_{N-I}-T_{S_A-N})(T_{N-I})^{-1}$, which takes into account the N–I transition temperatures of the esters (see Table VII), then the following injected smectic order is obtained.

$$5.5 > 5H.5 \gg 5H.5F^2$$

TABLE VII

Data for the injected smectic order of the esters

Compound Code	$(T_{N-I}-T_{S_A-N})(T_{N-I})^{-1}$ at 50% ^{w}/w of ester	at 60% ^{w}/w of ester
5H.5F	1.52	1.11
5H.5	0.33	0.18
5.5	0.23	0.15

where

5.5 = 4-*n*-pentylphenyl 4-*n*-pentylbenzoate
5H.5 = 4-*n*-pentylphenyl *trans*-4-*n*-pentylcyclohexane-1-carboxylate
5H.5F^2 = 4-*n*-pentyl-2-fluorophenyl *trans*-4-*n*-pentylcyclohexane-1-carboxylate

This smectic order illustrates once again that the 2-fluorophenyl cyclohexane-1-carboxylates have very little tendency to form smectic phases. The two non-fluorinated esters are very close in their smectic tendencies; from the phase diagram, the smectic tendency of the cyclohexane ester is greater than that of the benzoate ester and this may be related to the fact that 4-*n*-pentylphenyl *trans*-4-*n*-pentylcyclohexane-1-carboxylate does exhibit a smectic phase (S_A–N, 29.0°). However, when the N–I transition temperatures of the esters are taken into account, this smectic tendency is reversed.

EXPERIMENTAL

All the transition temperatures were measured using a Mettler FP5 hot stage and control unit, in conjunction with a Nikon LKE polarising microscope. For low temperature measurements, the Mettler heating stage was cooled by using nitrogen gas, pre-cooled in a copper coil immersed in liquid nitrogen. Throughout this section, virtual transition temperatures are denoted by [ ] and monotropic transition temperatures by ( ).

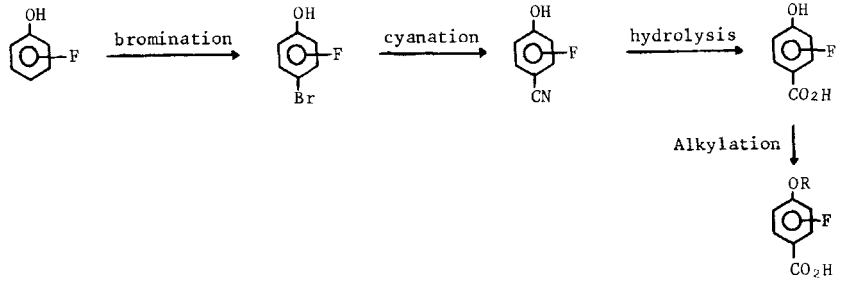
Differential thermal analysis was carried out using a Stanton Redcroft 671 low temperature differential thermal analyser coupled to an Oxford 3000 recorder. The heating and cooling cycle rates were 5° min^{-1}, and the reference material used was alumina. The standard material used to calibrate the measurements was ultra-pure indium wire.

Infrared spectra (KBr disc) were recorded using a Perkin–Elmer 457 Grating Infrared Spectrophotometer, low resolution n.m.r. spectra were obtained using a JEOL JNM–PMX60 N.M.R. Spectrometer (internal standard: tetramethylsilane; solvent: $CDCl_3$), and low resolution mass spectroscopic data were measured using and A.E.I. MS902 Mass Spectrometer.

All gas-liquid chromatograms were recorded on a Pye Unicam 104 Chromatograph coupled to a Columbia Programable Computing Integrator (Supergrator 2), using a column of 10% carbowax 20M on 60–85 mesh Chromosorb W (2 m long, 4mm internal diameter). Thin layer chromatography was carried out using pre-coated silica gel plates ($60F_{254}$, MERCK 5714) using chloroform:petroleum ether (bp 60–80°) (1:1) as the solvent.

Preparation of esters of 2- and 3-fluorobenzoic acids

The following scheme represents the reaction pathway used to prepare the 4-alkoxy-2-fluoro- and 3-fluorobenzoic acids.



The following experimental procedures relate to the preparation of 4-alkoxy-3-fluorobenzoic acids, with appropriate comments on the synthesis of the 4-alkoxy-2-fluorobenzoic acids.

Bromination

A solution of bromine (28.6 g, 0.18 mole) in chloroform (80 cm^3) was added quickly to a stirred solution of 2-fluorophenol (20 g, 0.179 mole) in chloroform (80 cm^3). Thirty seconds after completion of the addition, a solution of sodium hydroxide (21.4 g, 0.54 mole) in water (110 cm^3) was quickly added to destroy the hydrogen bromide formed and hence prevent polybromination. The aqueous layer was removed and acidified with hydrochloric acid (30 cm^3) to liberate the phenol, which was then extracted into ether. The solution was washed with water (2 × 100 cm^3) and dried ($MgSO_4$). The ether was removed and the crude residue distilled under vacuum to give 4-bromo-2-fluorophenol as a colourless liquid (bp 85–88°/8 mm)—single component by g.l.c. The yield was 69%.

The n.m.r. spectrum was complex due to the presence of the fluoro-substituent, and the use of several different solvents, and chemical shift reagents failed to clarify the position. However, mass spectrometry indicated that the product was the mono-brominated compound.

3-Fluorophenol was also brominated using the above procedure. After the product was vacuum distilled (96°/2.8 mm), it was crystallised from petroleum ether (bp 40–60°) to afford a white crystalline solid (61%), mp 71.5–72.5°—single component by g.l.c.

The n.m.r. spectrum was again inconclusive, but the mass spectrum indicated that mono-bromination had occurred.

In both cases therefore, bromination had given a single component, mono-brominated product, but conclusive evidence that the bromo-substituent

TABLE VIII

Melting points, transition temperatures and yields for the 4-*n*-alkoxy-3- and -2-fluorobenzoic acids

		C-I/C-N	N-I	Yield (%)	Lit mp[6]
1.	2-Fluoro acids				
	Methoxy	191-2°	-	62°	-
	Butyloxy	107	-	64	-
	Pentyloxy	104-5	114°	55	-
	Hexyloxy	108	119	61	-
2.	3-Fluoro acids				
	Methoxy	210-211	-	64	211.5°
	Butyloxy	141-142.5	-	43	143.5
	Hexyloxy	128-129	-	57	129.5
	Heptyloxy	124	-	55	124

was in the 4-position was not obtained. However, by analogy with results from similar brominations on other mono-substituted phenols, we were certain that the products were the required 4-bromo-isomers. We decided therefore to carry on with the synthesis, and the liquid crystalline properties of the resulting esters, and in some cases of the acids, together with the agreement of our mps for the acids with the lit. mps in several cases (see Table VIII), finally verified that 4-bromination had occurred.

Cyanation

Copper (I) cyanide (18.8 g, 0.210 mole) was added to a stirred solution of 4-bromo-2-fluorophenol (20 g, 0.105 mole) in 1-methyl-2-pyrrolidinone (100 cm^3). The mixture was then heated at 180° for 2 h. When cooled, the reaction mixture was added to a mixture of iron (III) chloride (16 g, 0.1 mole), water (200 cm^3) and concentrated hydrochloric acid (10 cm^3) and the solution was stirred at 50° for 20 min. The crude produce was then extracted into ether, and the extract washed with water and dried ($MgSO_4$). The ether was then removed.

The above cyanation procedure was also carried out on 4-bromo-3-fluorophenol.

Hydrolysis

Without further purification, the 4-cyano-2-fluorophenol was hydrolysed with sodium hydroxide (15 g) in water (135 cm^3) for 60 h. When cooled, the mixture was acidified with concentrated hydrochloric acid and the product extracted into ether. The carboxylic acid was extracted with saturated aqueous sodium bicarbonate (100 cm^3) and then liberated as the free acid by acidifying the alkaline extract with concentrated hydrochloric acid. The free acid was extracted into ether, and the ether extract washed with water and dried (Na_2SO_4). The ether was then removed and the carboxylic acid crystallised from the minimum amount of water to afford a white crystalline solid (89%), mp 159–160.5°. The infra-red spectrum was consistent with the desired product. ν_{max} (KBr) 3350 (OH str. band), 2800–3100 (acid OH), 1680 (acid C=O) cm^{-1}.

4-Cyano-3-fluorophenol was similarly hydrolysed and the product crystallised from the minimum amount of water to afford the carboxylic acid as a white solid (73%), mp 204–205.5°. The infra-red spectrum was consistent with its structure. ν_{max} (KBr) 3400 (OH str.band), 2800–3100 (acid OH), 1685 (acid C=O) cm^{-1}.

Alkylation

Ethanol (160 cm^3) was added to a solution of potassium hydroxide (4.26 g, 0.076 mole) in water (20 cm^3) and, whilst stirring, 4-hydroxy-3-fluorobenzoic acid (6.0 g, 0.038 mole) was added. The dropwise addition of the appropriate *n*-alkyl bromide (0.041 mole) was followed by heating the mixture under reflux for 23 h. A further amount of potassium hydroxide (1 g) in water (10 cm^3) was now added, and the whole was heated under reflux for a further 2 h. When cooled, the mixture was diluted with water (200 cm^3) and acidified with dilute hydrochloric acid before filtering off the product.

Recrystallisation of the crude products from ethanol gave the 4-*n*-alkoxy-3- and -2-fluorobenzoic acids as white crystalline needles. The melting points, transition temperatures, and % yields for the acids prepared by this method are given in Table VIII.

The infra-red, n.m.r. and mass spectroscopic data for the 4-*n*-hexyloxy-3-fluorobenzoic acid exemplify the 3-fluorobenzoic acids as a whole. ν_{max} (KBr) 2800–3100 (acid OH str.), 1680 (acid C=O str.) cm^{-1}; δ ($CDCl_3$) 0.55–2.10 (11H, m), 4.00 (2H, t, J6.0Hz, $-OCH_2-$), 7.00 (1H, t, J9.0Hz), 7.90 (2H, m), 11.20 (1H, s, $-CO_2H$); $^m/e$ 240 (M^+).

The n.m.r. and mass spectroscopic data for the 4-*n*-hexyloxy-2-fluorobenzoic acid exemplify the 2-fluorobenzoic acids as a whole. δ ($CDCl_3$) 0.6–2.10 (11H, m), 4.00 (2H, t, J6.0Hz, —OCH_2—), 6.60 (2H, m), 8.00 (1H, t, J9.0Hz), 11.05 (1H, s, —COOH); ^{m}/e 240 /M^+).

Preparation of the benzoate esters

The 4-*n*-alkyl- and -alkoxy-phenols and the 4-cyanophenol used to prepare the benzoate esters were supplied by B.D.H. Chemicals, Poole, Dorset, under a Ministry of Defence contract.

The following procedure for the preparation of 4-*n*-pentylphenyl 4-*n*-hexyloxy-2-fluorobenzoate exemplifies the method used.

4-*n*-Hexyloxy-2-fluorobenzoic acid (0.0035 mole) was heated, with exclusion of moisture, with freshly distilled thionyl chloride (10 cm^3) for 1.5 h. The excess of thionyl chloride was then removed by distillation. The residual acid chloride was diluted with dry dichloromethane (10 cm^3) and chilled. Whilst stirring, a chilled solution of 4-*n*-pentylphenol (0.0035 mole) in triethylamine (10 cm^3) and dry dichloromethane (10 cm^3) was added dropwise. After the addition, the stirred mixture was heated under reflux, with the exclusion of moisture, for 2 h.

To the cooled reaction mixture was added a small amount of ether and the precipitated triethylamine hydrochloride was then filtered off. The filtrate was washed with water (50 cm^3) and dried (Na_2SO_4). The ether was removed by vacuum distillation, and the residue dissolved in the minimum amount of a mixture of chloroform (2):petroleum ether [bp 60–80°] (1). This was now chromatographed on a column of silica gel, eluting with chloroform (2): petroleum ether [bp 60–80°] (1).

The fractions containing the ester (identified by t.l.c.) were combined and crystallised several times from ethanol to afford the pure 4-*n*-pentylphenyl 4-*n*-hexyloxy-2-fluorobenzoate as a white crystalline solid.

The purities of all esters were determined by g.l.c.; in all cases the purity was >99%. The melting points and transition temperatures of the esters prepared are listed in Table I. The average yield for the esters was 71% (56–79%).

Preparation of 4-n-alkyl-2- and -3-fluorophenyl 4-n-alkyl- and -alkoxy-benzoates and *trans*-4-n-alkylcyclohexane-1-carboxylates

The 4-*n*-alkyl-2 and -3-fluorophenols and the *trans*-4-*n*-alkylcyclohexane-1-carboxylic acids[7] were synthesised and supplied to Hull University by B.D.H. Chemicals, Poole, Dorset, under a Ministry of Defence contract.

4-Methoxybenzoic acid was obtained from Aldrich, whilst the 4-*n*-butyloxy-

TABLE IX

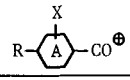
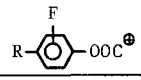
Selected n.m.r. data for the fluoro esters

Compound Code	Aromatic Protons		Aliphatic Protons			
$4.5F^2$	8.13 (d, 2H, J8.0Hz)	7.18 (m, 5H)		2.69 (m, 4H)	1.58 (m, 10H)	0.91 (m, 6H, 2xCH_3)
$60.5F^2$	8.15 (d, 2H, J8.0Hz)	7.09 (m, 5H)	4.04 (t, 2H, J6.0Hz)	2.59 (t, 2H, J7.0Hz)	1.63 (m, 11H)	0.89 (m, 6H, 2xCH_3)
$F^260.06$	8.02 (t, 1H, J8.0Hz)	6.92 (m, 6H)	4.00 (m, 4H)		1.63 (m, 17H)	0.89 (m, 6H, 2xCH_3)
$F^360.5$	7.93 (m, 2H)	7.17 (m, 5H)	4.16 (t, 2H, J6.0Hz)	2.63 (t, 2H, J7.0Hz)	1.63 (m, 15H)	0.87 (m, 6H, 2xCH_3)
$4H.5F^2$		6.96 (m, 3H)			2.01 (m, 26H)	0.86 (m, 6H, 2xCH_3)
$6H.5F^3$		7.03 (m, 3H)			1.96 (m, 29H)	0.89 (m, 6H, 2xCH_3)

Units: ppm (δ)

TABLE X

Selected mass spectroscopic data for the fluoro-esters

Compound Code	 X = H or F	 F = 2- or 3-position
$4.5F^2$	161	-
$60.5F^2$	205	-
$F^260.06$	223	-
$F^360.5$	223	-
$4H.5F^2$	167	209 (very small)
$6H.5F^3$	195	209 (very small)

Ring A = cyclohexane or benzene

and 4-*n*-hexloxybenzoic acids were prepared by the method of Gray and Jones.[6]

The preparation of these esters was carried out by a similar procedure to that used to prepare the fluorobenzoate esters, and g.l.c. on all these esters indicated that they were $>99\%$ pure.

The melting points and transition temperatures for these esters are listed in Tables II, III, and IV. The average yield for these esters was 79% (67–91%).

N.m.r. and mass spectroscopic data for the esters

On very few occasions did the low resolution mass spectroscopic data give a peak for the molecular ion, and instead recorded the fragment R–Ar–CO from the ester. However, the structures of the esters were verified by analysing the mass spectroscopic data in conjunction with the data obtained by n.m.r.

The n.m.r. and mass spectroscopic data for some representative examples of the esters prepared are given in Tables IX and X respectively.

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