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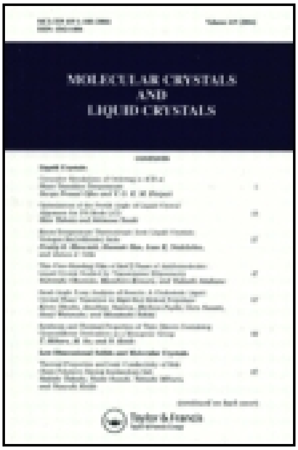

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Synthesis and Evaluation of Some 4,4″-Disubstituted Lateral Fluoro-1,1′:4′,1″-terphenyls

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Synthesis and Evaluation of Some 4,4″-Disubstituted Lateral Fluoro-1,1′:4′,1″-terphenyls†

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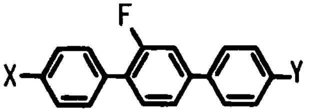
(*Received October 2, 1984*)

A number of laterally fluorinated 4,4″-di-n-alkyl-, 4,4″-di-n-alkoxy- and 4-n-alkyl-4″-n-alkoxy-1,1′:4′,1″-terphenyls of structure (I) have been synthesised, with the lateral fluoro-substituent in the central benzene ring.



(I)

X,Y = n-alkyl or n-alkoxy

The nematic and smectic thermal stabilities for all three series of compounds, have been examined. A typical example is (I), X = n—C_5H_{11}, Y = n—C_3H_7, C—N 50°C and N—I 140.6°C. For the 4,4″-di-n-alkyl-1,1′:4′,1″-terphenyls, the position of the lateral fluoro-substituent with respect to the longest n-alkyl chain is found to be important in determining the smectic behaviour of this class of compound. By using a combination of optical microscopy, X-ray diffraction and miscibility studies, the complex smectic behaviour of the higher homologues of this series has also been investigated. A comparison of the liquid crystal behaviour of the laterally fluorinated terphenyls of structure (I) with their non-fluorinated analogues is also given.

A selected number of these compounds, have been further examined to assess their usefulness as high T_{N-I} additives for multiplexed mixtures used in electro-optic display devices.

INTRODUCTION

There are today many ways in which liquid crystal materials may be used in electro-optic display devices ranging from the well-estab-

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lished, but still most widely used device, the Twisted Nematic Display Device, to newer devices such as Guest-Host Display Devices and the Ferroelectric Device. All these devices of course operate only whilst the material in the display is in the liquid crystal state.

Since the temperature in which display devices now need to operate can extend to 100°C, there is a need to raise the upper temperature limit of commercial liquid crystal mixtures without adversely influencing other properties. Even for mixtures used in the well-established Twisted Nematic Display Device, the upper temperature limit could advantageously be raised still further, and the usual way of attempting to achieve this is by adding suitable high T_{N-I} additives to the mixtures.

The 4-n-alkyl-4″-cyano-1,1′:4′,1″-terphenyls[1] and similar three ring compounds based on this structure are a widely used family of high T_{N-I} additives for Twisted Nematic Display Devices, having both high T_{N-I} values and high birefringence; the latter property is an important facet of liquid crystal materials used in this type of display. However, such materials also have relatively high viscosities, and this is a feature of compounds containing a terminal cyano-substituent. By contrast, corresponding compounds containing a terminally situated n-alkyl group in place of the cyano-group have lower viscosities. Although the 4,4″-di-n-alkyl-1,1′:4′1″-terphenyls are smectogens (see later), we have shown earlier[2] that a laterally-situated substituent, especially a fluoro-substituent, decreases the smectic tendency of a system.

Thus, it was hoped that by combining these two features, i.e., a terminal n-alkyl group in place of a cyano-substituent, and a laterally-situated fluoro-substituent, we would reduce the smectic tendency of the 4-n-alkyl-4″-cyano-1,1′:4′,1″-terphenyls, and produce a fairly high T_{N-I} additive with reasonable viscosity and high birefringence.

As will emerge later in this paper, even though the dialkyl substituted fluoroterphenyls gave reasonable T_{N-I} values, it was necessary, in order to enhance the T_{N-I} value, to synthesise and evaluate a number of the related alkyl-alkoxy and dialkoxy homologues.

RESULTS AND DISCUSSION

In order to evaluate the effect of a lateral fluoro-substituent upon the liquid crystal behaviour of the laterally fluorinated dialkyl terphenyls, a number of the non-fluorinated analogues had to be prepared. Comparison of the m.p.s. and transition temperatures, obtained by optical

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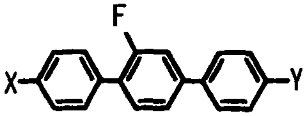
microscopy and verified by DSC, for these compounds is given in Table I. Even though only four pairs of compounds are listed in Table I, the following conclusions can reasonably be drawn. The lateral fluoro-substituent in the terphenyl moiety has:

1. reduced the nematic thermal stability by an average of 55°C (54°C and 56.5°C);
2. greatly reduced the smectic thermal stability of the system (see the first three examples given);
3. reduced the melting point by an average of 136°C (130–142°C).

This shows clearly the advantages of introducing a lateral fluoro-substituent into the terphenyl moiety in order to produce compounds with reasonable T_{N-I} values, low melting points and low smectic tendencies.

Altogether we have prepared twenty-one dialkyl-, nine alkyl-alkoxy-, and five dialkoxy-fluoroterphenyls of structure (I). The m.p.s. and transition temperatures (obtained by optical microscopy and verified by DSC) for these compounds are given in Tables II, III, and IV respectively.



(I)

X,Y = n-alkyl or n-alkoxy

To simplify discussion of these terphenyl compounds, we will first assess the merits of the individual series, i.e., the dialkyl compounds, the alkyl-alkoxy compounds, and the dialkoxy compounds, and then compare the nematic thermal stability across the three series of laterally fluorinated terphenyls. Finally, we will discuss some of the physical properties found for the dialkyl- and alkyl-alkoxy-fluoroterphenyls.

1. The dialkyl compounds

In this series, twenty-one compounds were prepared, with the X group in structure (I) ranging from hydrogen to n-undecyl and the Y group from hydrogen to n-pentyl (Table II).

Two homologous series could be derived from this set of materials and plots of the transition temperatures against the number of carbon atoms in the n-alkyl chains are given in Figures 1 and 2.

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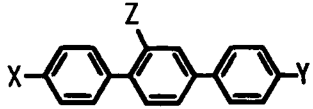
TABLE I

Comparison of the transition temperatures (°C) for the laterally fluorinated and non-fluorinated disubstituted terphenyls of structure (II)



(II)

X	Y	Z	C—S_E, N	S_E—S_B	S_E—S_A	S_B—S_A	S_A—N	S_A—I	N—I
C_5H_{11}	C_3H_7	F	50.0						140.6
C_5H_{11}	C_3H_7	H	180.0	200.0		214.0		218.0	
C_5H_{11}	C_2H_5O	F	98.0						191.5
C_5H_{11}	C_2H_5O	H	234.0		237.0		242.0		248.0
C_4H_9O	C_3H_7	F	92.0						180.0
C_4H_9O	C_3H_7	H	239.0		241.0			249.5	
C_4H_9O	C_2H_5O	F	136.0						226.0
C_4H_9O	C_2H_5O	H	270.0				(268.5)		280.0

( ) monotropic transition

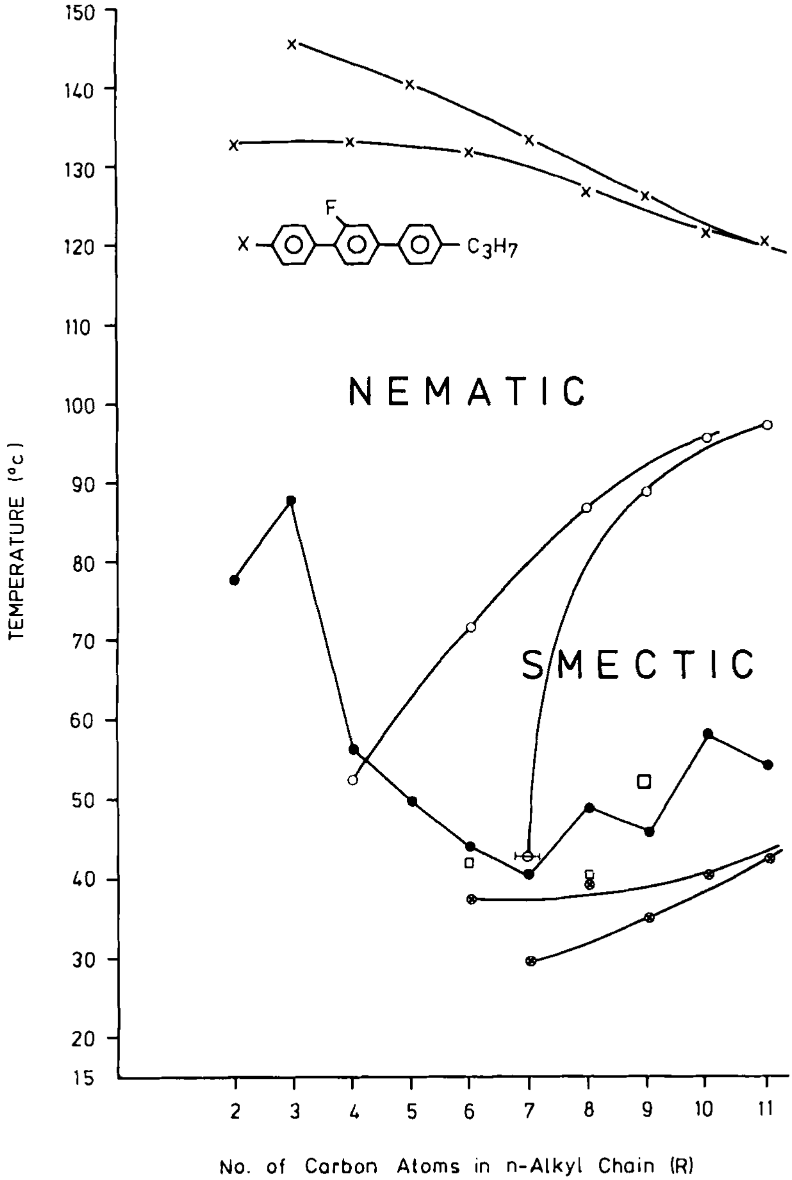


FIGURE 1 Graph of m.p.s. and transition temperatures plotted against the number of carbon atoms in the n-alkyl chain for the 4-n-alkyl-2′-fluoro-4″-n-propyl-1,1′:4′,1″-terphenyls. Key: x N–I; OS_A–N; □S_c–S_A; ⊗ S_B–S_C or S_A; ● C–S or N.

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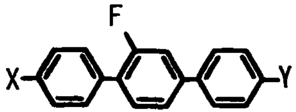
TABLE II

Transition temperatures (°C) for the 4,4″-di-n-alkyl-2′-fluoro-1,1′:4′,1″-terphenyls



X	Y	C—S_B, S_C, S_A, N or I	S_B—S_C	S_B—S_A	S_C—S_A	S_C—N	S_A—N	N—I
H	C_3H_7	75.5						
C_2H_5	CH_3	115.0						138.2
C_3H_7	H	95.0						
C_3H_7	CH_3	114.0						150.5
C_3H_7	C_2H_5	73.5						133.3
C_2H_5	C_3H_7	78.0						133.0
C_3H_7	C_3H_7	88.0						145.7
C_4H_9	C_3H_7	56.5[c]					(52.5)	133.5
C_5H_{11}	C_3H_7	50.0[a]						140.6

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C_6H_{13}	C_3H_7	44.5[a]	(37.5)		(42.0)		71.5	132.0
C_7H_{15}[b]	C_3H_7	40.5	(29.5)			42.5[d]		133.5
C_8H_{17}	C_3H_7	49.0	(39.2)		(40.5)		86.8	127.0
C_9H_{19}	C_3H_7	46.0	(35.0)		52.2		89.0	126.5
$C_{10}H_{21}$	C_3H_7	58.0		(40.5)			95.5	121.7
$C_{11}H_{23}$	C_3H_7	54.5		(42.5)			97.2	120.6
C_5H_{11}	H	71.0						(47.0)
C_5H_{11}	C_2H_5	54.5						127.5
H	C_5H_{11}	83.0						
C_2H_5	C_5H_{11}	64.0					90.0	128.7
C_3H_7	C_5H_{11}	61.0					99.5	141.5
C_4H_9	C_5H_{11}	68.0					106.8	131.2
C_5H_{11}	C_5H_{11}	51.5		62.0			109.5	136.5

( ) Monotropic transition.

[a] Crystal-Crystal transition at 39.0°C.

[b] X-ray diffraction studies have indicated that there could be a S_G or S_J—S_B transition at 18°C for this compound. Further work is being carried out to establish the nature of this monotropic transition.

[c] Crystal-Crystal transition at 54.0°C

[d] This relates to a S_C—S_A—N transition (see text)

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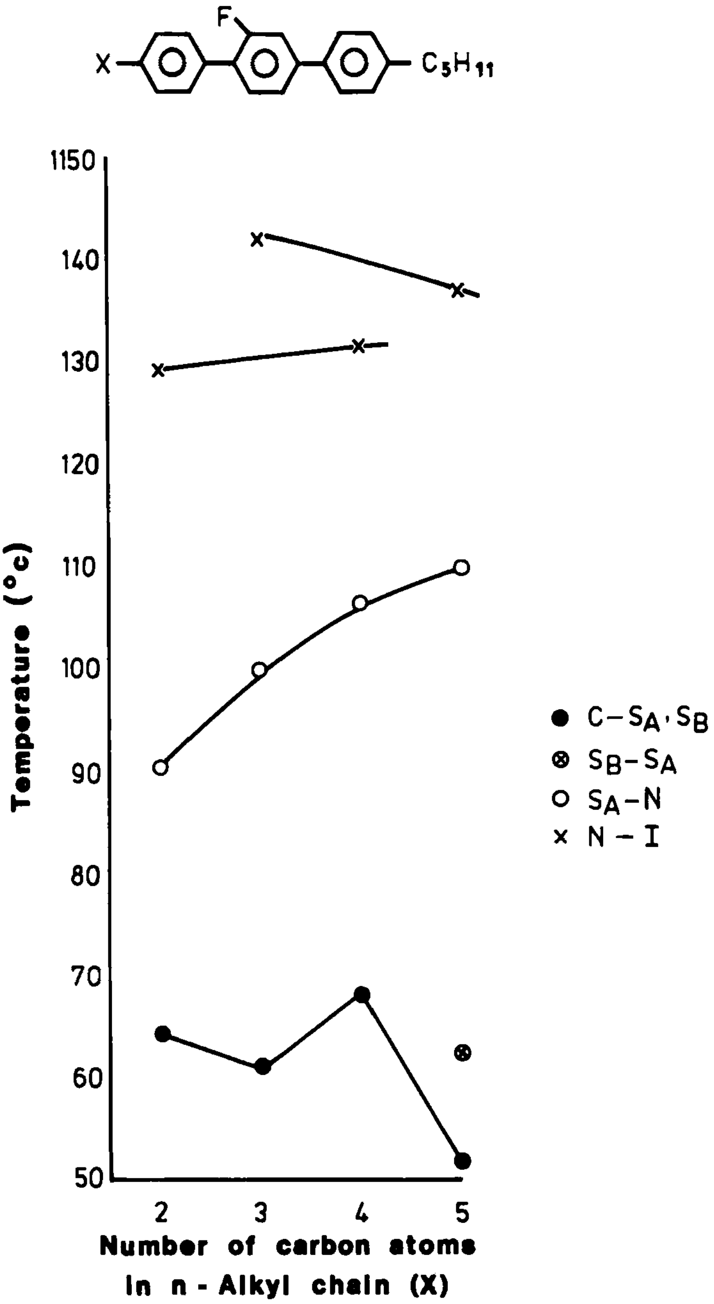

FIGURE 2 Graph of m.p.s. and transition temperatures plotted against the number of carbon atoms in the n-alkyl chain for the 4-n-alkyl-2′-fluoro-4″-n-pentyl-1,1′:4′,1″-terphenyls.

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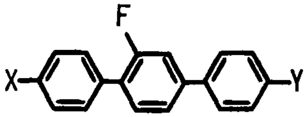
TABLE III

Transition temperatures (°C) for the 4-n-alkyl-4″-n-alkoxy-2′-fluoro-1,1′:4′,1″-terphenyls



X	Y	C—S_E, S_C, N	S_E—S_B	S_B—S_C	S_C—S_A	S_C—S_N	S_A—N	N—I
CH_3O	C_5H_{11}	60.5						177.5
C_2H_5O	C_5H_{11}	88.0						186.0
C_4H_9O	C_3H_7	92.0						180.0
C_4H_9O	C_5H_{11}	65.5				96.5		172.5
C_3H_7	C_4H_9O[a]	103.0			112.5		135.0	183.0
C_5H_{11}	C_2H_5O	98.0						191.5
C_5H_{11}	C_4H_9O	59.5	85.5	86.5	99.5		144.0	176.0
C_8H_{17}	C_2H_5O	107.0						170.5
C_9H_{19}	C_2H_5O	92.0						167.5

[a] Crystal-crystal transition at 78.0°C

In the second homologues series (Figure 2), where Y = n-pentyl and the X group is varied from ethyl to n-pentyl, all the compounds exhibited a smectic A and a nematic phase. In the case of the dipentyl homologue, a smectic B phase was also observed. The T_{N-I} values gave the usual alternation, with the points for the even members falling onto a rising curve, which was situated below a descending curve for the odd members. There was no such alternation for the T_{S_A-N} values, all the points falling onto a smoothly ascending curve.

In the first homologues series (Figure 1), where Y = n-propyl and the X group was varied from ethyl to n-undecyl, the early members exhibit only a nematic phase. However, from the n-hexyl homologue onwards, a variety of additional smectic phases was observed. The T_{N-I} values fall onto two curves; the lower curve for the even members initially rises, before falling gently to meet the steadily descending curve for the odd members. This alternation effect was also observed for the T_{S_A-N} values (contrast the homologues series in Figure 2), with the points for the even and odd members falling onto two separate ascending curves. The highest T_{S_A-N} values were observed for the even members. However, for the n-heptyl homologue, a simple T_{S_A-N} transition was not observed directly by microscopy; a T_{S_C-N} transition appeared to occur. From miscibility studies, it was however

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shown that this compound does have an extremely short range smectic A phase just below the transition to the nematic phase. This clarified the position with regard to the shape of the S_A-N curve for the odd members in this homologues series. The point denoted (⊢●⊣) in Figure 1 and the temperature of 42.5°C in Table II therefore relate to a $S_C \rightarrow S_A \rightarrow N$ transition.

X-ray diffraction results

The transitions for the n-heptyl homologue with Y = C_3H_7 were confirmed by X-ray diffraction. The tilt angle for the S_C phase was 17 ± 1° with a layer spacing of 24.7 Å; the fully extended molecular length for the n-heptyl homologue, measured from space filling models, is 26.4 Å. The true nature of the monotropic phase (S_G or S_J) exhibited by this homologue below the monotropic S_B phase could not be confirmed by X-ray diffraction studies due to alignment problems.

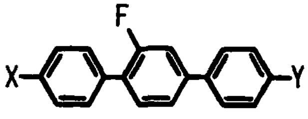
X-ray diffraction measurements have also confirmed the following phase behaviour of a selected number of the dialkylfluoroterphenyls.

X	Y	Phase behaviour	
C_4H_9	C_3H_7	C_1, C_2, N, I	(monotropic S_A)
C_7H_{15}	C_3H_7	C, S_C, N, I	(monotropic S_B and S_G or S_J)
C_9H_{19}	C_3H_7	C, S_C, S_A, N, I	(monotropic S_B)
$C_{10}H_{21}$	C_3H_7	C, S_A, N, I	(monotropic S_B)

The above X-ray diffraction data and the identification of a $T_{S_B-S_A}$ transition for the decyl and undecyl homologues by optical

TABLE IV

Transition temperatures (°C) for the 4,4″-di-n-alkoxy-2′-fluoro-1,1′:4′,1″-terphenyls



X	Y	C_1—C_2	C—S_C, N	S_C—N	N—I
CH_3O	C_2H_5O		165.0		244.3
C_2H_5O	C_4H_9O		140.0		225.5
C_4H_9O	C_2H_5O		136.0		226.0
C_4H_9O	C_4H_9O	118.0	139.0	144.5	222.5
$C_7H_{15}O$	C_2H_5O		125.0		201.5

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microscopy have established a third sequence of alternating transitions in this series involving the monotropic $T_{S_B-S_C}$ and $T_{S_B-S_A}$ values from the hexyl to the undecyl homologues. In this case all the points lay on two concave ascending curves, with the even members giving the highest values.

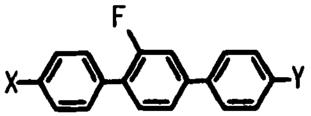
A number of the smectic phases exhibited by individual dialkyl homologues have not yet been established by either X-ray diffraction or miscibility studies; this work will be carried out and presented in a future paper.

One of the most interesting points about the dialkyl terphenyls is illustrated in Table V, where liquid crystal behaviour of a number of isomeric homologues is compared. In all three cases, the nematic thermal stability was not significantly affected by the position of the lateral fluoro-substituent with respect to the longer of the two alkyl chains. However, with regard to the smectic thermal stability, the last two pairs of homologues indicate that this is affected by the relative position of the lateral fluoro-substituent.

Although the number of examples is limited, the results from Table V indicate that the *lower* smectic thermal stability is obtained when the lateral fluoro-substituent point towards the *longer* alkyl chain.

TABLE V

Comparison of the thermal data for isomeric homologues of the 4,4″-di-n-alkyl-2′-fluoro-1,1′:4′,1″-terphenyls



X	Y	Transition temperatures (°C)		
		C—N, S_A	S_A—N	N-I
C_3H_7	C_2H_5	73.5		133.3
C_2H_5	C_3H_7	78.0		133.0
C_5H_{11}	C_3H_7	50.0		140.6
C_3H_7	C_5H_{11}	61.0	99.5	141.5
C_5H_{11}	C_2H_5	54.5		127.5
C_2H_5	C_5H_{11}	64.0	90.0	128.7

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2. Alkyl-alkoxy compounds

In this family, nine compounds were prepared involving variations not only in the relative sizes of X and Y in structure (I), but also the nature of X and Y, i.e., X or Y = alkyl or alkoxy groups (see Table III). This somewhat complicates comparisons of the thermal data for these compounds, since for each pair of X and Y, there will be two equivalent compounds. Thus, the two alkyl-alkoxy equivalents to the dialkyl compound, where Y = n-pentyl and X = n-propyl, will be (a) Y = n-butyoxy and X = n-propyl and (b) Y = n-pentyl and X = ethoxy.

A comparison of the thermal data for the isomeric pairs of alkyl-alkoxy compounds analogous to the dialkyl compounds with pentyl/propyl, propyl/pentyl and pentyl/pentyl groups is given in Table VI. If we assume that the oxygen atom is equivalent to a —CH_2—group, then apparently, as in the dialkyl series, the smectic thermal stability is very low (i.e., the compounds are purely nematic) when the lateral fluoro-substituent points towards the longest chain—see Table VI, examples 1 and 4.

However, in example 3, where the lengths of X and Y are the same, then we see that a new factor is at work, i.e., the position of the lateral fluoro-substituent with respect to the *nature* of the terminal X substituent also influences the smectic thermal stability. In the case where X = n-pentyl, not only do we observe the highest T_{S_A-N} transition in Table VI, but this compound also gives additional three enantiotropic smectic phases, i.e., S_E, S_B, and S_C phases. Thus, when chains at each end are equal in length (alkyl or alkoxy), the lower smectic tendency is observed when the fluoro-substituent points towards the alkoxy group.

In example 2 in Table VI, the first compound listed again shows that when the fluoro-substituent point towards the shorter chain (C_3H_7), a fairly high S_A-N transition is observed. However, when the C_3H_7 group becomes C_2H_5O, and C_4H_9O becomes C_5H_{11}, no smectic phase is observed, emphasising again that orientation of the fluoro-substituent towards the alkoxy group lowers the smectic tendency of the compound.

Whether the nature or the size of the terminal substituent X has the dominant influence upon the smectic thermal stability of these compounds is difficult to assess. However, it is noted that even when one chain is very long and smectic properties might have been expected, e.g., X = C_8H_{17} or C_9H_{19} and Y = C_2H_5O (see Table III), these compounds do *not* exhibit smectic phases and the fluoro-substituent points towards the longer chain. However, with more

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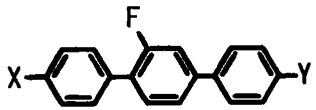
TABLE VI

Comparison of the thermal data for a selected number of 4-n-alkyl-4″-n-alkoxy- and 4-n-alkoxy-4″-n-alkyl-2′-fluoro-1,1′:4′,1″-terphenyls



Equivalent dialkyl compound	X	Y	Transition temperatures (°C)				Other smectic phases
			C—N, S_A, S_C	S_A—N	S_C—N	N—I	
1. C_5H_{11}/C_3H_7	C_5H_{11}	C_2H_5O	98.0			191.5	
	C_4H_9O	C_3H_7	92.0			180.0	
2. C_3H_7/C_5H_{11}	C_3H_7	C_4H_9O	103.0	135.0		183.0	S_C
	C_2H_5O	C_5H_{11}	88.0			186.0	
3. C_5H_{11}/C_5H_{11}	C_5H_{11}	C_4H_9O	59.5	144.0		176.0	S_E, S_B, S_C
	C_4H_9O	C_5H_{11}	65.5		96.5	172.5	
4. C_9H_{19}/C_3H_7	C_9H_{19}	C_2H_5O	92.0			167.5	

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balanced chain lengths for X and Y, orientation of the fluoro-substituent towards the alkoxy group, even when this may be longer than the alkyl chain, appears to have a strong influence in depressing smectic phases.

A number of homologues in this series also gave rise to compounds with relatively high T_{N-I} values with wide nematic ranges. For example (see Table III), when X = methoxy and Y = n-pentyl, the T_{N-I} is 177.5°C, and the nematic range is 117.0°C; for X = n-pentyl and Y = ethoxy, the T_{N-I} is 191.5°C and the nematic range is 93.5°C.

3. Dialkoxy compounds

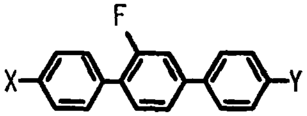
In this series (Table IV), only five compounds were prepared. The most interesting aspects of this series are:

1. the very high T_{N-I} values and wide nematic ranges, e.g., when X = n-butoxy and Y = ethoxy, T_{N-I} is 226.0°C, and the nematic range is 90.0°C;
2. the apparently low incidence of smectic phases in this series.

This could of course be due to the fact that the melting points for these compounds are quite high, so hiding some smectic tendencies. Moreover, a comparison of the liquid crystal behaviours of the alkyl-alkoxy and dialkoxy compounds (see Tables III and IV) is revealing. If we compare compound 40.04 with 5.04, we see that the S_A phase of the latter material has disappeared and 40.04 shows only a S_C phase.

Comparison of the T_{N-I} values for the three series of compounds

A comparison of the effect of the nature and size of the terminal substituents X and Y, in relation to the position of the lateral fluoro-substituent, upon the nematic thermal stability of three individual sets of isomers is given in Table VII. From these results, the expected nematic thermal stability order given below was compiled.



$$R'O/OR \underset{41.9}{>} \begin{matrix} R'/OR \\ R'O/R \end{matrix} \underset{43.0}{>} R'/R$$

R,R' = n-alkyl

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The figures under the two inequalities are the averages of each of the two sets of six differences given in Table VII, and it is interesting to note that these represent an approximate additivity effect on changing any given alkyl group to an alkoxy group of the same length.

Physical properties

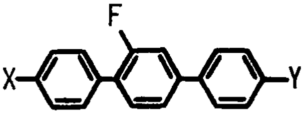
Physical assessments of the dialkyl and alkyl-alkoxy compounds have been carried out at R.S.R.E., Malvern, and some results are given in Table VIII.

The viscosities, extrapolated from data for 20% w/w solutions of the fluoroterphenyls in ZLI 1132 (E. Merck, Darmstadt), for both the dialkyl and alkyl-alkoxy compounds were somewhat higher than would be desirable for a high T_{N-I} additive. However, with regard to solubility of the dialkyl compounds, the results were very good, and as expected, a high value for the birefringence was obtained. A 1:1 mixture containing the heptyl/propyl and dipropyl homologues was used for the Δn measurement; the solubility in a biphenyl host was measured for the butyl/propyl homologue.

From assessment work on the smectic tendencies of these materials in various mixtures (see Table VIII), it was evident that although the

TABLE VII

Comparison of the T_{N-I} values (°C) for a selected number of laterally fluorinated 4,4″-di-n-alkyl-, 4-4″-di-n-alkoxy- and 4-n-alky-4″-n-alkoxy-1,1′:4′,1″-terphenyls



X	Y	T_{N}—I	ΔT_{N-I} values			
C_3H_7	C_5H_{11}	141.5	41.5	44.5		
C_3H_7	C_4H_9O	183.0			42.0	
C_2H_5O	C_5H_{11}	186.0				39.0
C_2H_5O	C_4H_9O	225.0				
C_5H_{11}	C_3H_7	140.6	50.9	39.4		
C_5H_{11}	C_2H_5O	191.5			34.5	
C_4H_9O	C_3H_7	180.0				46.0
C_4H_9O	C_2H_5O	226.0				
C_5H_{11}	C_5H_{11}	136.5	39.5	36.0		
C_5H_{11}	C_4H_9O	176.0			46.5	
C_4H_9O	C_5H_{11}	172.5				50.0
C_4H_9O	C_4H_9O	222.5				

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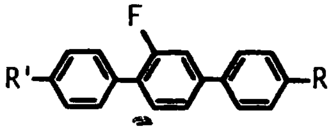
TABLE VIII

Some physical characteristics of the 4,4″-di-n-alkyl- and 4-n-alkyl-4″-n-alkoxy-2′-fluoro-1,1′:4′,1″-terphenyls



	Viscosity (extr) cP		Δn[b]	Solubility[a] (wt %)	
	20°C	0°C	25.8°C	0°C	−20°C
R′/R	40	115	0.239	11–12	≈7
R′/OR	75	300			

Smectic behaviour	wt %	S_A—N (°C)	Comment
(a) $C_7/C_3 + C_3/C_3$	50/50	25.5	
(b) $C_7/C_3 + C_5/C_3$	67/33	21.5	
(b) + 10 wt % C_5/C_5 FDE[c]		≈3	
(b) + 9 wt % K6 (BDH Chemicals Ltd)		84.0	Other biphenyl positive dopants gave smectic phases up to 50°C

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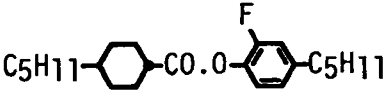
[a] The solubility study was carried out on the C_4H_9/C_3H_7 homologue.

[b] The birefringence was measured for mixtures containing the C_7H_{15}/C_3H_7 and C_3H_7/C_3H_7 homologues (50:50 wt %).

[c]



(FDE)

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T_{S_A-N} values were relatively low when pairs of dialkylfluoroterphenyl homologues were mixed together, on addition of a positive biphenyl dopant, the T_{S_A-N} value increased rapidly. It should be noted however that the dialkylfluoroterphenyl mixture used contained a predominance of the fairly smectic C_7H_{15}/C_3H_7 homologue, and further experiments with mixtures of purely nematic materials would seem desirable.

However, it is well-known that the 4-alkyl-4′-cyanobiphenyls (the K series) themselves have a relatively high smectic tendency. With this is mind, further assessment work is now being carried out on these compounds at E. Merck, Darmstadt, FRG, using less smectogenic positive dopants such as PCH materials. These results were not available at the time this paper was presented.

Further synthetic work on these fluoroterphenyls is being undertaken, and this, together with results of the assessment work being carried out at E. Merck, will be reported in a subsequent paper.

CONCLUSIONS

From our investigations into the liquid crystal behaviour and physical properties of a number of laterally fluorinated and non-fluorinated 4,4″-di-n-alkyl-, 4-4″-di-n-alkoxy- and 4-n-alkyl-4″-n-alkoxy-1,1′:4′,1″-terphenyls, we can reach the following summarising conclusions.

1. The smectic thermal stability of the parent compounds was significantly reduced by the introduction of a lateral fluoro-substituent. This gave rise to a number of compounds exhibiting high T_{N-I} values and wide nematic ranges.
2. The influence on the smectic properties of the orientation of the fluoro-substituent in relation to the size and nature of the terminal groups (alkyl, alkoxy) has been shown to be important. The nematic thermal stability of the compounds was relatively independent of these factors.
3. From the T_{N-I} values of the three different series, the expected terminal group efficiency order for nematic thermal stability was confirmed.
4. The value of these materials as high T_{N-I} additives of high birefringence would be restricted to nematic hosts of fairly low viscosity with which, moreover, the injected smectic phenomenon found to occur with cyanobiphenyl hosts would have to be less pronounced.

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EXPERIMENTAL

Materials

The two reaction pathways used in the preparation of the disubstituted laterally fluorinated terphenyls are given in Figure 3 and 4. Both synthetic schemes start from 4-bromo-2-fluorobiphenyl. The

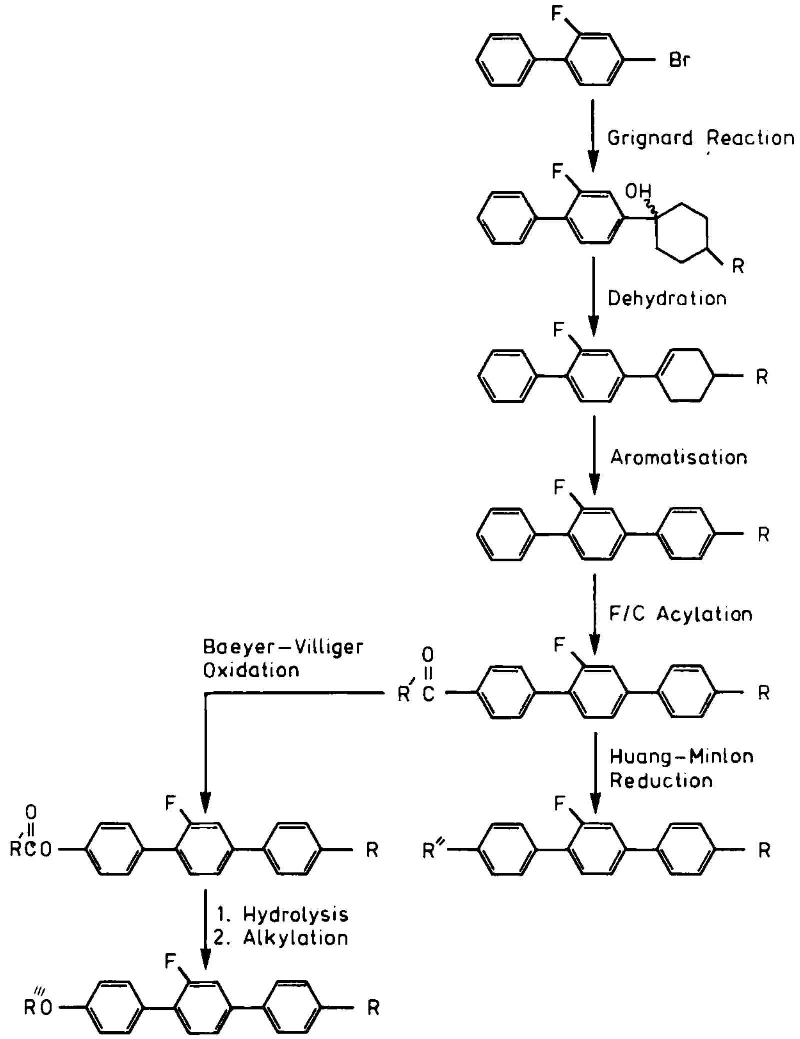

FIGURE 3 Synthetic scheme used originally, mainly for the preparation of the dialkylfluoroterphenyls.

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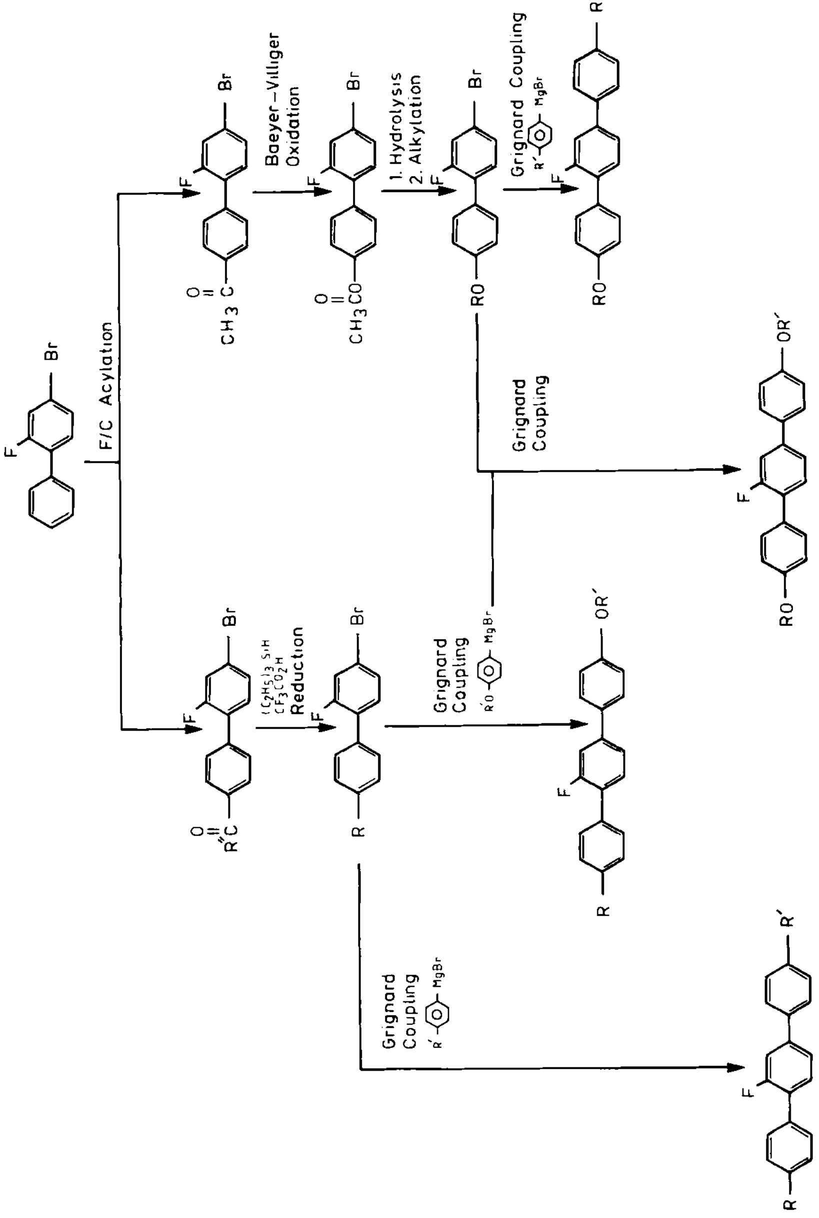

FIGURE 4 Synthetic scheme applicable to the preparation of all three series of compounds.

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synthetic scheme outlined in Figure 3 was the original one used mainly to prepare the dialkylfluoroterphenyls. However, by using the Grignard coupling reaction,[3] a synthetic scheme was later devised (Figure 4) which can be used to prepare all three series of compounds.

It is not appropriate, in a conference paper of this kind, to elaborate the extensive experimental details of the synthetic work; these will appear in another publication.

Physical Measurements

All final products were shown to be pure by various standard techniques (t.l.c., g.l.c., and h.p.l.c.). Structural confirmation for these products (and, where necessary, for any of the intermediates) was obtained by ^1H n.m.r. spectroscopy (Jeol J.N.M. - P.M. × 60 spectrometer), infra-red spectroscopy (Perkins-Elmer 457 grating spectrometer) and mass spectrometry (A.E.I.M.S. 902 mass spectrometer).

The transition temperatures were measured using a Mettler FP5 hot stage and control unit, in conjunction with a Nikon LKe polarising microscope.

The differential scanning calorimetric measurements were carried out using a Perkin-Elmer DSC 2C with data station.

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