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## Liquid Crystals

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## Mesomorphic properties of some laterally fluorinated 4-alkyl,4''-oxoalkyl 1,1':4',1''terphenyls

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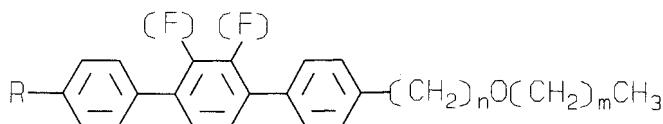
(Received 29th September 1992; accepted 1 December 1992)

The liquid crystalline behaviour and nematic viscosities of a series of laterally fluorinated alkyl-oxoalkyl terphenyls are reported. The mesomorphic behaviour and nematic viscosity can be influenced by the position of the oxygen atom in the oxoalkyl chain as well as the position of lateral fluorination. Compounds have been synthesized that are suitable for use in ferroelectric smectic C ( $S_C^*$ ) mixtures; the switching properties of a four component mixture are also reported.

### 1. Introduction

Materials for ferroelectric smectic C ( $S_C^*$ ) mixtures require host materials with good  $S_C$  ranges. Fluorinated *p*-terphenyls with terminal alkyl and alkoxy chain substituents are well-documented [1-3]. The use of oxygenated chains in liquid crystals has also been described, especially by Kitamura *et al.* [4, 5], who prepared phenylcyclohexanecarboxylates with oxoalkyl substituents. The work of Kitamura *et al.* demonstrated that it was possible to influence the mesomorphic phase behaviour by the position of the oxygen atom in the oxoalkyl chain.

Also, Adams *et al.* [6] demonstrated that terminal polyether substituted materials in ferroelectric  $S_C^*$  mixtures gave lower viscosities than the hydrocarbon analogues. The work reported here investigated the potential use of fluorinated *p*-terphenyls with one terminal alkyl chain and one terminal oxoalkyl chain as  $S_C$  host materials. A series of terphenyls, varying in each, the position of the oxygen atom in the oxoalkyl chain and the position and number of lateral fluorine atoms (see structure 1) was synthesized. Their liquid crystalline phase behaviour and extrapolated nematic viscosities were examined. A mixture was made from the low melting point compounds which exhibited a  $S_C$  phase. The switching time ( $\tau$ ), tilt angle ( $\theta$ ) and spontaneous polarization ( $P_s$ ) for this mixture when doped with a typical chiral dopant were measured.



Structure 1.  $R = C_3H_7 - C_9H_{19}$ ,  $n = 0, 1, 2, 3$ ,  $m = 0, 1, 2, 3$ .

### 2. Experimental

The compounds reported in this paper were synthesized by standard synthetic organic procedures involving for example Friedel Crafts acylation and Huang Minlon reductions [7] and palladium catalysed coupling reactions [7-10]. The synthesis of the various oxoalkyl chain containing intermediates was performed according to the routes detailed in figure 1. Once synthesized, the crude materials were purified by flash

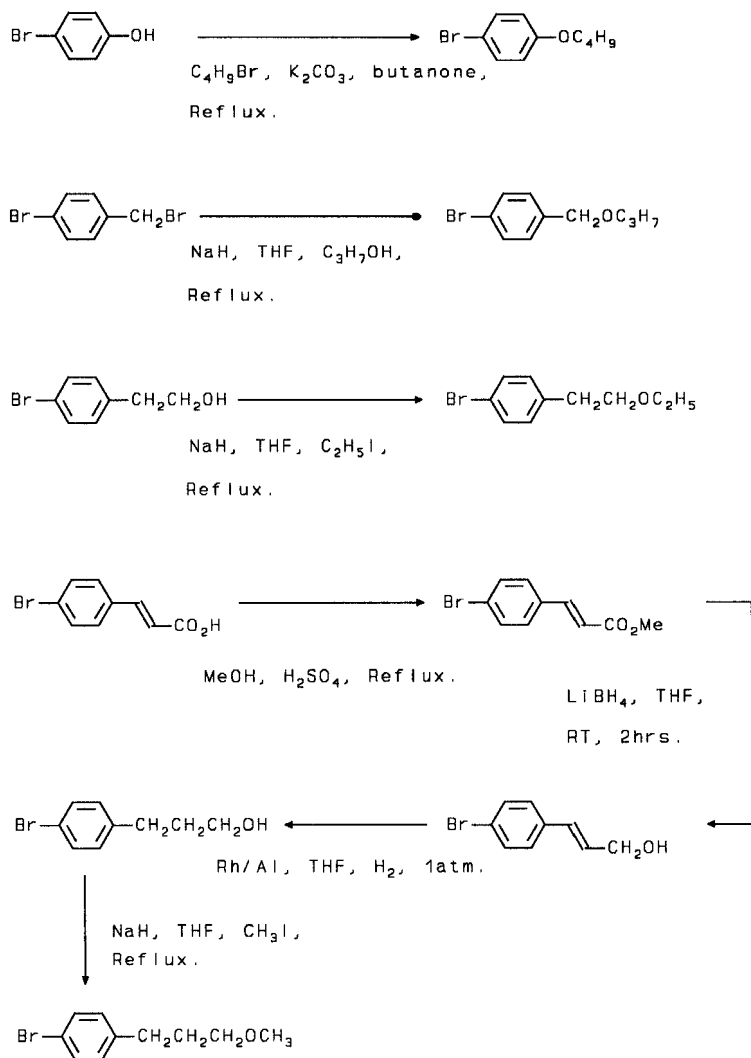


Figure 1. Synthetic routes to 1-oxoalkyl-4-bromobenzenes used in the syntheses of 4-alkyl-4'-oxoalkyl-2',3'- and 2',3'-mono- and difluoro-terphenyls.

column chromatography on Merck 40–63  $\mu\text{m}$  silica gel, using petroleum spirit (bp 40–60°C) as eluant. The materials were then recrystallized to >99.5 per cent purity with varying amounts of petroleum spirit (bp 80–100°C) or *n*-propanol. The materials were analysed by reverse phase high performance liquid chromatography using a Hewlett-Packard 1090 with diode array detector.

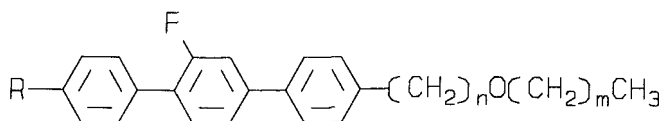
The structure of the compounds was confirmed by  $^1\text{H}$  NMR spectroscopy using a Jeol PMX 60 SI and GC mass spectrometry using a Nermag R10-10S quadrupole instrument. Phase transition temperatures were measured using a Du Pont 1090 differential scanning calorimeter and by polarizing microscopy using a Mettler FP 52 hot stage to control the temperature of the sample. Extrapolated nematic viscosities were measured at 20°C for solutions of 10 per cent of the test compound in a neutral dielectric anisotropy ( $\Delta\epsilon$ ) mixture (ZLI 3086) using a capillary flow viscometer. A four component mixture was prepared and made chiral by addition of a high  $P_s$

cyanohydrin [11,12] dopant at 2 per cent w/w concentration. The electrooptic properties of the mixture were measured by standard techniques [13]. The switching speed was measured at 25°C in a 3.5  $\mu\text{m}$  antiparallel aligned polyimide rubbed cell, at 15 V  $\mu\text{m}^{-1}$ . The molecular tilt angle and spontaneous polarization were measured for a 10  $\mu\text{m}$  antiparallel aligned polyimide rubbed cell at 25°C.

### 3. Results and discussion

#### 3.1. Mesomorphic phase behaviour

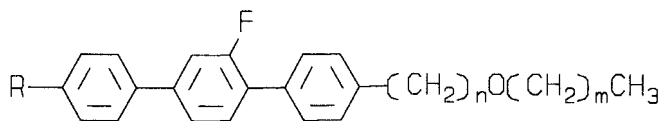
In the examples shown in table 1 the lateral fluorine atom points away (see structure 2) from the oxoalkyl chain. When the oxygen atom in the oxoalkyl chain is an even number of atoms away from the terphenyl core ( $n=1$  or 3), a  $S_C$  phase is observed, but the  $S_C$  phase is not seen when the oxygen atom in the oxoalkyl chain is an odd number of atoms away from the terphenyl core ( $n=0$  or 2). This odd-even effect may be due to the different preferred conformations of the oxoalkyl chains. If the clearing points of these materials are examined, it is seen that in all cases the clearing point is significantly reduced compared to the alkoxy compound ( $n=0$ ). An example of this is compound 2, the clearing point of which is reduced by 60°C, when compared to compound 1. This is in agreement with the work of Kitamura *et al.* [4, 5] who reported the depression of the clearing point in oxoalkylphenylcyclohexane carboxylates in comparison to alkoxyphenylcyclohexane carboxylates. In compounds 2, 3, 4 and 7, where  $n=1$ , a  $S_C$  phase is the only smectic phase observed and its stability increases with increasing alkyl chain length, while the clearing point (N-I) decreases with increasing alkyl chain length. Both these factors are consistent with previously published work [7, 14, 15]. The reduced smectic polymorphism and the low melting points of these compounds make them potentially useful as achiral materials in ferroelectric mixtures.



Structure 2.

Table 1. Transition temperatures (°C) for 4-alkyl-4'-oxoalkyl (or alkyl (see compound 9))-2'-fluoroterphenyls. Type 1 compounds (see structure 2).

Compound	R	n	m	Transition temperatures /°C					
				$\frac{C-}{S_A/S_B/}$ $\frac{S_C/S_E}$	$S_E-S_B$	$\frac{S_B-}{S_C/S_A}$	$\frac{S_C-}{S_A/N}$	$S_A-N$	N-I
1	C <sub>7</sub> H <sub>15</sub>	0	3	67.5	79.2	87		148	166.4
2	C <sub>3</sub> H <sub>7</sub>	1	2	38			(35.2)		106.6
3	C <sub>5</sub> H <sub>11</sub>	1	2	35.1			48.4		108.9
4	C <sub>7</sub> H <sub>15</sub>	1	2	22			54		100
5	C <sub>7</sub> H <sub>15</sub>	2	1	23.4		50.1		90.5	105.1
6	C <sub>7</sub> H <sub>15</sub>	3	0	43.7		44.3	71.6	77.2	124.0
7	C <sub>9</sub> H <sub>19</sub>	1	2	34			63.6		96.0
8	C <sub>9</sub> H <sub>19</sub>	3	0	41.7		45.4	68.2	94.6	118.0
9	C <sub>7</sub> H <sub>15</sub>	n-C <sub>5</sub> H <sub>11</sub>		64.5				113	128.5



Structure 3.

Table 2. Transition temperatures ( $^{\circ}\text{C}$ ) for 4-alkyl-4'-oxoalkyl (or alkyl (see compound 14))-3'-fluoroterphenyls. Type 2 compounds (see structure 3).

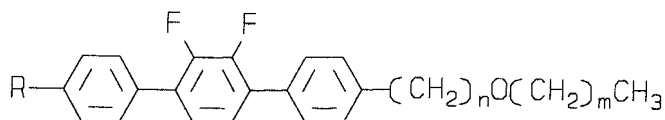
Compound	R	n	m	Transition temperatures / $^{\circ}\text{C}$				
				C-S <sub>B</sub>	S <sub>B</sub> -S <sub>C</sub> / S <sub>A</sub>	S <sub>C</sub> -S <sub>A</sub>	S <sub>A</sub> -N	N-I
10	C <sub>7</sub> H <sub>15</sub>	0	3	50	88.8	107.7	135.9	161.7
11	C <sub>7</sub> H <sub>15</sub>	1	2	40.2	60.1		100.8	104.8
12	C <sub>7</sub> H <sub>15</sub>	2	1	< -20	72.9		104.6	105.3
13	C <sub>7</sub> H <sub>15</sub>	3	0	< -20	71.2		99.3	118.9
14	C <sub>7</sub> H <sub>15</sub>	n-C <sub>5</sub> H <sub>11</sub>		< -20	87.5		123.5	129.4

In type 2 compounds (see structure 3), the lateral fluorine atom points towards the oxoalkyl chain (see table 2). This type of compound shows no odd-even effect as for type 1 compounds and only compound 10, the alkoxy compound, shows an S<sub>C</sub> phase. All the other type 2 compounds show the phase sequence of C-S<sub>B</sub>-S<sub>A</sub>-N-I and have similar clearing points. As with the type 1 compounds, the clearing points are reduced, in comparison to the alkoxy compound [4, 5] and both type 1 and 2 compounds show similar clearing points. Type 2 compounds, in which the polar lateral fluorine atom points in the same direction as the more polar oxoalkyl end group, have a greater tendency to exhibit smectic phases. This feature was also recognized by Chan *et al.* in fluoroterphenyls [7, 14, 15].

In type 3 compounds (see table 3), where there is lateral difluoro substitution (see structure 4), all smectic phases are suppressed, and only a nematic mesophase is present. This is similar to results presented earlier on difluoroterphenyls [1]. Again, as with type 1 and type 2 compounds, the clearing points of all the oxoalkyl compounds are significantly lower than the clearing point of the alkoxy compound, compound 15. In this case, as with type 2 compounds, the phase sequence appears to be dominated by the influence of the lateral fluorine atom rather than the oxoalkyl chain, whereas in type 1 compounds the oxoalkyl chain can be seen to exert some influence on the relative phase stabilities.

### 3.2. Viscosity

Figure 2 shows the viscosity values for the different types of heptyl terphenyls (compounds 1, 4, 5, 6, 10, 11, 12, 15, 16, 17 and 18). For all three types of compound, the pattern of values is similar, tending to a minimum for a given position of the oxygen atom in the oxoalkyl chain. A possible reason for this is that the different position of the oxygen atom in each type of oxoalkyl chain gives the chain a different preferred conformation and orientation with respect to the terphenyl core, and this may affect the viscosity behaviour. Kitamura *et al.* [5] suggest that the lower viscosity of the alkoxyethylene compounds is due to the lower polarizability of the alkoxyethylene group affecting the molecular packing. It can also be seen that, interestingly, the type 3



Structure 4.

Table 3. Transition temperatures ( $^{\circ}\text{C}$ ) for 4-alkyl-4''-oxoalkyl (or alkyl (see compound **19** [16]))-2',3'-difluoroterphenyls. Type 3 compounds (see structure 4).

Compound	R	n	m	Transition temperatures / $^{\circ}\text{C}$	
				C-N	N-I
<b>15</b>	$\text{C}_7\text{H}_{15}$	0	3	48.9	148.9
<b>16</b>	$\text{C}_7\text{H}_{15}$	1	2	57.0	85.0
<b>17</b>	$\text{C}_7\text{H}_{15}$	2	1	30.2	81.1
<b>18</b>	$\text{C}_7\text{H}_{15}$	3	0	58.5	105.2
<b>19</b>	$\text{C}_7\text{H}_{15}$	$n\text{-C}_5\text{H}_{11}$		38.0	114.5

difluorosubstituted compounds have a lower viscosity than either type 1 or 2 compounds, the monofluorosubstituted terphenyls.

### 3.3. Mixture behaviour

A mixture of compounds **2** (26.38 wt%), **3** (30.11 wt%), **4** (37.46 wt%) and **7** (6.05 wt%)—all having structure 2 with  $n=1$  and  $m=2$ —gave the phase sequence shown in table 4. This was slightly modified when 2 wt% of a chiral dopant containing a cyanohydrin chiral group [11, 12] was added to produce a ferroelectric mixture with a  $\text{S}_{\text{C}}^*-\text{N}^*$  transition. The  $\text{S}_{\text{C}}^*-\text{N}^*$  transition for this mixture is  $13^{\circ}\text{C}$  lower than would be predicted by linear extrapolation of the  $\text{S}_{\text{C}}-\text{N}$  transitions for the individual components. This non-ideal behaviour between homologues underlines the unusual behaviour of the smectic C phase stability. Although the  $\text{S}_{\text{C}}^*-\text{N}^*$  temperature is low the response time is unusually slow and may be influenced by the nature of the  $\text{S}_{\text{C}}$  transition to a nematic phase rather than the usual  $\text{S}_{\text{A}}$  phase.

## 4. Conclusions

It has been shown in the above results that the mesomorphic phase behaviour is alkyloxoalkylfluoroterphenyls is influenced by both the position and number of lateral fluoro substituents and the position of the oxygen atom in the oxoalkyl chain. Depending on the position of lateral fluorination, either the lateral fluoro substituted core or the oxoalkyl chain dominates the nature of the phase behaviour. It has also been shown that the viscosity behaviour of these materials tends to a minimum for each type of compound. Mixtures of the low melting point  $\text{S}_{\text{C}}$  materials could be used as ferroelectric  $\text{S}_{\text{C}}^*$  mixture host materials.

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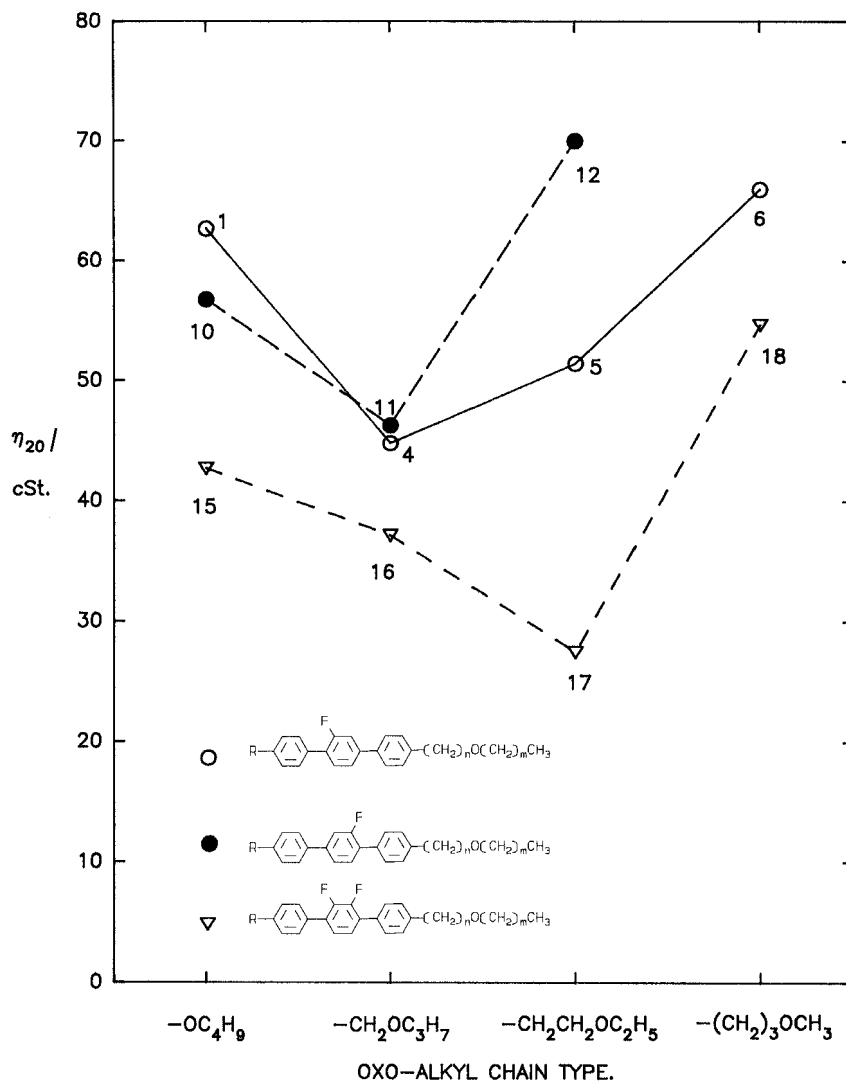


Figure 2. Extrapolated nematic viscosities of selected 4-alkyl-4''-oxoalkyl-2', 3'- and 2',3'-mono- and difluoro-terphenyls at 20°C in a neutral  $\Delta\epsilon$  host mixture (10 wt% solutions). (Each point number corresponds to an individual compound.)

Table 4. Mesomorphic phase behaviour and electrooptic properties of mixtures of selected 4-alkyl-4''-oxoalkyl-2'-fluoroterphenyls.

Mixture	Phase sequence	$P_s/n\text{C cm}^{-2}$	$\theta/^\circ$	Switching time/ $\mu\text{s}$
Eutectic	C 17.9°C S <sub>C</sub> 34.0°C N 104.0°C I	—	—	—
Eutectic + 2 per cent w/w dopant	C 13.0°C S <sub>C</sub> * 35.2°C N* 100.5°C I	+4.1	19.5	280

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