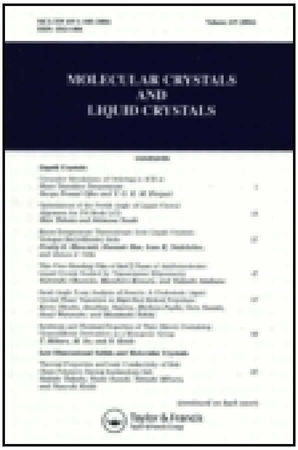

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The Synthesis and Properties of Fluoroterphenyls for High Dielectric Biaxiality Ferroelectric Liquid Crystal Mixtures

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The Synthesis and Properties of Fluoroterphenyls for High Dielectric Biaxiality Ferroelectric Liquid Crystal Mixtures

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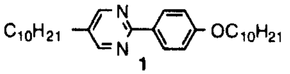
A series of liquid crystalline terphenyls with three strategically located fluoro substituents has been synthesised and evaluated for a range of physical properties. Low temperature metallations were used to prepared arylboronic acids which were employed in selective palladium-catalysed cross-coupling reactions to generate the final liquid crystals. The syntheses are discussed as efficient routes to functional, multi-substituted liquid crystals. The trifluoroterphenyls have low melting points and exhibit the smectic C phase to moderately high temperatures. The melting points, transition temperatures and mesophase morphology are discussed and compared with analogous difluoroterphenyls. The materials have been evaluated for a range of physical properties and enable the formulation of ferroelectric mixtures with a high dielectric biaxiality which is very important in τV minimum driving schemes.

Keywords: liquid crystals; synthesis; smectic C; dielectric biaxiality

INTRODUCTION

When ferroelectricity in tilted smectic liquid crystals was first discovered by Meyer[1] nearly 25 years ago smectic liquid crystals were just a curiosity and undesirable in the context of nematic materials for displays. Accordingly, very few compounds exhibiting the smectic C phase (chiral or achiral) were known. The invention of the surface-stabilised ferroelectric display device by Clark and Lagerwall in 1980[2] demonstrated the potential for extremely short switching times and high multiplexability. The massive commercial potential of this device resulted in intense research into the chemistry and physics of ferroelectric liquid crystals. Initially, ferroelectric liquid crystal materials were based wholly on chiral compounds, but this approach gave many problems such as poor mesomorphic behaviour and a high viscosity. It has become well recognised that the best way of achieving ferroelectricity in liquid crystals is to use a base mixture of achiral compounds (*e.g.*, **1-4**) which enables the fine-tuning of mesomorphic behaviour and many important physical properties, such as birefringence and particularly the requirement for a low viscosity. Such achiral host mixtures are then doped with a chiral material (*e.g.*, **6** and **7**) to provide the necessary chirality, which on removal of the macroscopic helical structure generates the ferroelectric properties. The quantity of chiral dopant should be a low as possible so as not to affect the properties of the host mixture, but must be sufficiently high to provide the necessary spontaneous polarisation.[3,4]



1

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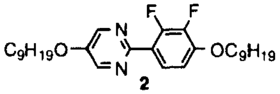

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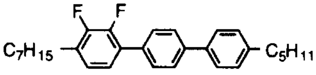
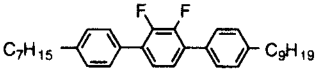


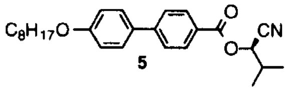
3

C 49.0 S_C 77.0 S_A 93.0 N 108.5 I



4

C 56.0 S_C 105.5 S_A 131.0 N 136.0 I



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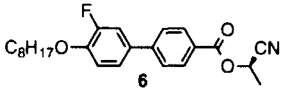
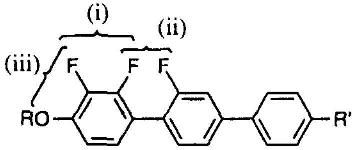


6

Ferroelectric mixtures based on the *ortho*-difluoroterphenyls (*e.g.*, **3** and **4**) have a high dielectric biaxiality and hence show a minimum in their response time-voltage relationship.[5,6] This minimum offers many advantages for ferroelectric devices such as high levels of multiplexability, high contrast ratios, wide viewing angles and short switching times. In such a system, a high dielectric biaxiality ($\delta\varepsilon$) is essential in order to obtain the optimum combination of short switching times (τ) and a low operating voltage (V).

$$\tau_{\min} \propto \frac{\eta\delta\varepsilon}{P_S^2} \qquad V_{\min} \propto \frac{P_S}{\delta\varepsilon}$$

From the equations above, a high spontaneous polarisation (P_S) reduces the switching time (τ), but the required voltage (V) increases. A high $\delta\varepsilon$ reduces V, or enables a higher P_S to be used to maintain V. The higher $\delta\varepsilon$ increases τ, but an increase in P_S would reduce τ to the second power. Thus a higher $\delta\varepsilon$ allows a higher P_S to be used to the benefit of reduced τ, without increasing V. Of course, switching time (τ) can be reduced by employing a low viscosity (η) material, which would perhaps allow a lower P_S to be used which would reduce V. Overall, the best compromise of $\delta\varepsilon$, P_S and η needs to be used so that the minimum in the response time-voltage relationship occurs at the lowest possible voltage and switching time.[3,4]



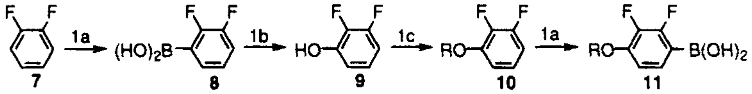
(I)

The important physical parameters discussed above are controlled by the structural nature of the compounds in the ferroelectric mixture. Dielectric biaxiality ($\delta\varepsilon$) is proportional to the perpendicular dielectric permittivity ($\varepsilon_\perp$), and hence a high lateral dipole confers a high $\delta\varepsilon$. The aim of this work is to synthesise and evaluate novel, improved host materials of high dielectric biaxiality. To achieve this aim, three structural features known to give a high lateral dipole have been combined in one molecular architecture (**I**). (i) two *ortho* fluoro substituents fixed on the same side of the molecule,[5,6] (ii) two fluoro substituents in a 2,2' relationship which are known to attract,[7,8] and (iii) a fluoro substituent next to an ether oxygen which are known to give enhanced combined polarity.[5] Overall, it is expected that structure **I** will have all three fluoro substituents and the ether oxygen reinforcing to provide a very high lateral dipole. The arrangement of fluoro substituents should also minimise molecular breadth and provide reasonably high smectic C phase stability.

SYNTHESIS

As the required physical properties of liquid crystals become increasingly exacting for the applications of the future, then the required molecular structures are more complex and hence the synthesis is more demanding.

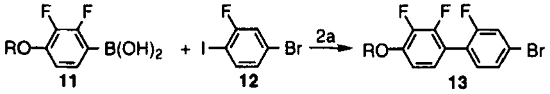
It is difficult, if not impossible, to use conventional electrophilic substitution when the substituents are required in the inner core positions of a multiaryl system because of steric hindrance and probable incompatible directing and activating effects from existing substituents. Accordingly, the only viable synthetic strategy is a convergent one that involves the synthesis of the subunits with the desired substitution pattern and joining them together with a carbon-carbon bond-forming metal-catalysed cross-coupling reaction. The coupling reactions involving boronic acids were established in the synthesis of liquid crystals through the synthesis of the *ortho*-difluoroterphenyls as mentioned above.[5]



Scheme 1

1a ... (i) n-BuLi, THF; (ii) $(MeO)_3B$, THF; (iii) 10% HCl.
1b ... H_2O_2, THF.
1c ... RBr, K_2CO_3, butanone.

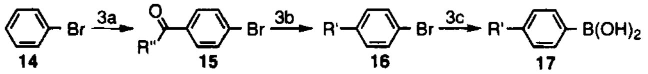
Scheme 1 involves the exploitation of an acidic proton next to the fluoro substituent with butyllithium at –78 °C, the low temperature is essential to prevent elimination of lithium fluoride. Subsequent treatment with trimethyl borate followed by acid hydrolysis yields the boronic acid (**8**). The boronic acid was oxidised to provide the phenol (**9**) which was used in several *O*-alkylation reactions to provide the homologous ethers (**10**). Exploitation of the remaining acidic proton next to a fluoro substituent in the manner described above yields the desired difluorophenylboronic acids **11**. The difluorophenylboronic acids (**11**) were then involved in selective palladium-catalysed cross-coupling reactions with commercially-available 4-bromo-2-fluoro-1-iodobenzene (**12**) to provide the necessary bromo-trifluorobiphenyl intermediates (**13**). The selectivity of the coupling at the more reactive iodo site was efficient only if the reaction temperature was carefully controlled at 65 °C. The various homologues of biphenyl **13** were purified carefully and isolated in yields of around 65% (Scheme 2).



Scheme 2

2a ... $Pd(PPh_3)_4$, 2M Na_2CO_3, DME.

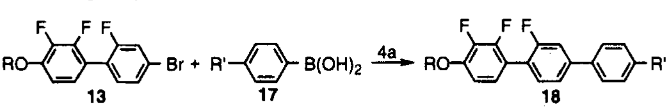
The second coupling reaction required the appropriate alkylphenylboronic acids (**17**), which were prepared from bromobenzene (**14**) through a three-step synthesis (Scheme 3). In each case, a Friedel-Crafts acylation followed by a reduction facilitated the efficient introduction of the alkyl chain.[5] The subsequent exploitation of the bromo substituent with butyllithium and trimethyl borate generated the desired alkylphenylboronic acids (**17**).[9]



Scheme 3

3a ... R''COCl, $AlCl_3$.
3b ... $NH_2NH_2{\bullet}H_2O$, KOH, diethylene glycol.
3c ... (i) n-BuLi, THF; (ii) $(MeO)_3B$, THF; (iii) 10% HCl.

The palladium-catalysed cross-coupling of each homologous alkylphenylboronic acid (**17**) to the purified bromo-trifluorobiphenyl intermediates (**13**) did not involve any selectivity issues, and was carried out under the usual reflux conditions to give excellent yields of the desired liquid crystalline terphenyls (**18**, Scheme 4).



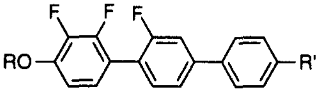
Scheme 4

4a ... $Pd(PPh_3)_4$, 2M Na_2CO_3, DME.

The coupling strategy involving boronic acids **18** in the first selective coupling with isomeric 1-bromo-2-fluoro-4-iodobenzene was attempted, but proved to be much less efficient overall.

MESOMORPHIC BEHAVIOUR

Table 1 Transition temperatures (°C) for some trifluoroterphenyls



Compound			Transition Temperatures (°C)								
No.	R	R'	C		S_C		S_A		N		I
18a	C_4H_9	C_9H_{19}	•	57.7	•	87.0	•	89.1	•	112.9	•
18b	C_6H_{13}	C_5H_{11}	•	43.8	•	(38.1)	-	-	•	112.3	•
18c	C_6H_{13}	C_7H_{15}	•	40.1	•	75.7	-	-	•	111.8	•
18d	C_6H_{13}	C_9H_{19}	•	47.9	•	91.5	-	-	•	109.6	•
18e	C_6H_{13}	$C_{11}H_{23}$	•	51.2	•	95.2	•	98.6	•	106.2	•
18f	C_8H_{17}	C_5H_{11}	•	47.3	•	50.2	-	-	•	110.3	•
18g	C_8H_{17}	C_7H_{15}	•	48.0	•	81.0	-	-	•	108.8	•
18h	C_8H_{17}	C_9H_{19}	•	55.4	•	95.0	-	-	•	107.3	•
18i	$C_{10}H_{21}$	C_5H_{11}	•	56.1	•	(52.1)	-	-	•	102.1	•
18j	$C_{10}H_{21}$	C_7H_{15}	•	56.0	•	83.2	-	-	•	104.5	•
18k	$C_{10}H_{21}$	C_9H_{19}	•	59.6	•	95.9	-	-	•	104.4	•

Table 1 shows the transition temperatures of a series of eleven alkyl-alkoxy-trifluoroterphenyls with a 2,2',3-trifluoro substitution pattern (**18a-k**). The most striking feature of these novel materials is their relatively low melting points (between 40 and 60 °C), far lower than expected when considering their high polarity due to the presence of three fluoro substituents and an alkoxy chain. Reasonably high smectic C phase stability is seen for some homologues, notably those with longer terminal chains. The tendency of the molecules towards tilting is strong relative to the overall smectic phase stability, a fact emphasised by the lack of orthogonal smectic phases. The smectic C phase stabilities of the trifluoroterphenyls depend strongly on the length of the terminal chains, but the nematic phase stabilities are very similar for each homologue combination. Thus, in general, the short-chain homologues have wide nematic temperature ranges and long-chain types have moderately wide smectic C temperature ranges. A long alkyl chain (R') is particularly advantageous for a high smectic C phase stability (compare compounds **18b** and **18e**), whereas a longer alkoxy chain (RO) makes much less difference (compare compounds **18a** and **18k**). Thus, taking account of melting point and smectic C phase stability, compounds **18c**, **18d**, **18e**, **18h** and **19k** appear the most promising host materials for ferroelectric mixtures.

PHYSICAL PROPERTIES

As expected, the dipole value of the trifluoroterphenyls (4.83 D) is higher than that of the *ortho*-difluoroterphenyls (3.57 D). The viscosity values of the trifluoroterphenyls (95 cP) are fairly low and very similar to those of the *ortho*-difluoroterphenyls. These results indicate that the trifluoroterphenyls may aid the generation of high dielectric biaxiality ferroelectric mixtures with short switching times.

Figures of merit, Mt and Mv, have been developed to assess mixtures for their τ_{min} and V_{min} parameters; the product of the two being an overall assessment (Mo) of suitability for use in τV minimum ferroelectric mixtures, the lower the Mo value the more impressive the mixture.[4]

$$\mathrm{Mt} \propto \eta \qquad \mathrm{Mv} \propto \frac{1}{\delta\varepsilon}$$

From the equations above, a low Mt indicates a low viscosity and a low Mv indicates a high dielectric biaxiality. Several of the trifluoroterphenyls (notably **18a**, **18c-e** and **18k**) have been used as components of varying percentages in ferroelectric mixtures for evaluation. Electrooptic switching results depend strongly on the mixture composition. When compared with analogous *ortho*-difluoroterphenyls, some mixtures containing a selection of trifluoroterphenyls show lower Mv and a V_{min} of less than 30 V (due to a higher dielectric biaxiality), similar Mt and a τ_{min} of less than 20 μs (indicating a similar viscosity) at 25 °C.

SUMMARY

Efficient synthetic routes have been developed to generate a wide range of homologous 4-alkoxy-4''-alkyl-2,2',3-trifluoroterphenyls. The materials have surprisingly low melting points and the longer chain homologues exhibit fairly wide smectic C phase temperature ranges with narrow smectic A and nematic phases at higher temperature. The fluoro substituent in the 2' position enhances the lateral dipole without increasing viscosity, and the trifluoroterphenyls enable the formulation of ferroelectric mixtures with low viscosity and high dielectric biaxiality and hence short switching times.

ACKNOWLEDGEMENTS

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