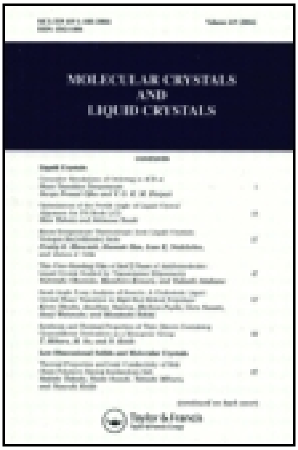

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Trans-1,2-Difluorostilbenes: Promising Materials for High Dielectric Biaxiality Ferroelectric Mixtures

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Trans-1,2-Difluorostilbenes: Promising Materials for High Dielectric Biaxiality Ferroelectric Mixtures

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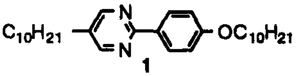
A range of two- and three-ring liquid crystals have been synthesised that incorporate a *trans*-1,2-difluoroethene linking group. Some of the materials have surprisingly low melting points and high smectic C phase stability, and they exhibit the ideal phase sequence for ferroelectric hosts of smectic C to smectic A to nematic. The synthesis was accomplished in a convergent manner through the use of low-temperature lithiations to generate organometallics based on boron and tin. Palladium-catalysed cross-couplings and Michael-type reactions were used to generate the final mesogenic materials. The polar fluoro substituents enable the generation of ferroelectric mixtures with a high dielectric biaxiality which is very important in τV minimum driving schemes. The alkenic linking group in stilbenes normally confers instability, but the difluoro-substituted analogues are stable compounds.

Keywords: liquid crystals; synthesis; smectic C; ferroelectric

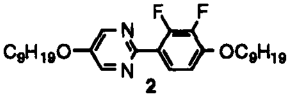
INTRODUCTION

Ferroelectricity in tilted smectic liquid crystals was first discovered by Meyer[1] over 25 years ago. The subsequent invention of the surface-stabilised ferroelectric display device by Clark and Lagerwall in 1980[2] demonstrated many advantages over existing nematic technology, such as extremely short switching times, high capacity for multiplex addressing, wide viewing angle, potential for extremely short switching times, and high multiplexability due to the inherent bistability. All ferroelectric displays have very exacting material requirements, which include good mesomorphic behaviour (a low melting point and a wide smectic C temperature range, and smectic A and nematic phases above for good alignment), chemical and photochemical stability and a low viscosity (for short switching times). There are many other material requirements that need to be tailored for the particular ferroelectric device format, such as spontaneous polarisation (usually quite high for short switching times), tilt angle (usually 22.5° or 45°), birefringence (relatively high for conventional back-lit devices and very low for reflective mode, LCOS devices), and a high dielectric biaxiality (for devices that operate using the τV minimum driving scheme).[3-6]



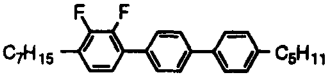
1

C 36.0 S_C 73.0 S_A 77.0 I



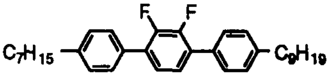
2

C 48.0 S_C 78.0 I



3

C 56.0 S_C 105.5 S_A 131.0 N 136.0 I



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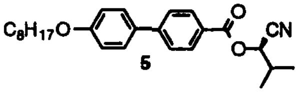
C 49.0 S_C 77.0 S_A 93.0 N 108.5 I



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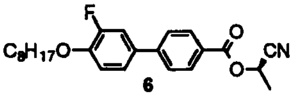
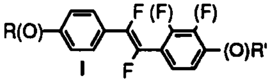


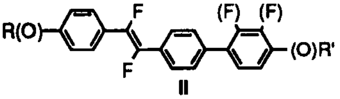
6

In terms of materials, it is 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**)[7-10] which enables the fine-tuning of mesomorphic behaviour and many important physical properties, such as dielectric and optical properties, and particularly the requirement for a low viscosity. Such achiral host mixtures are then doped with a small quantity of a chiral material (*e.g.*, **5** and **6**), which need not be mesogenic, to provide the necessary chirality, which on removal of the macroscopic helical structure generates the ferroelectric properties.

Ferroelectric mixtures based on the *ortho*-difluoroterphenyls (*e.g.*, **4** and **5** have a high dielectric biaxiality and hence make excellent host materials for τV minimum devices.[3,5,7] Dielectric biaxiality (δε) is proportional to the perpendicular dielectric permittivity ($\varepsilon_{\perp}$), and hence a high lateral dipole confers a high δε.



I

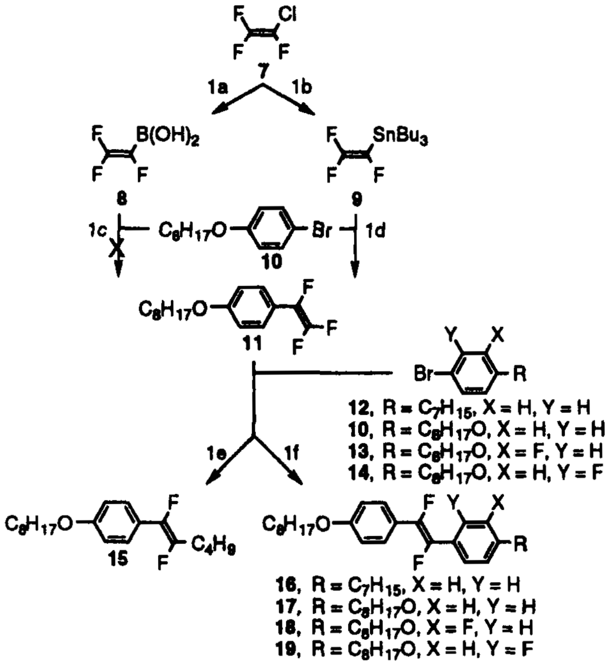


II

The aim of this work was to design and synthesise materials (types **I** and **II**) that combine attributes of high dielectric biaxiality, low viscosity and low melting point with moderately high smectic C phase stability. Two-ring structures would minimise viscosity and melting point, and the difluoroethene linking group was used in order to assess the extent to which the polar fluoro substituents would promote the generation of the tilted smectic C phase, and ultimately evaluate their influence on dielectric biaxiality. Additionally, the *ortho*-difluorophenyl unit has been incorporated into the structures to enhance dielectric biaxiality. Two three-ring analogues have been synthesised to generate very high smectic C phase stability and to broaden the range of materials available for mixtures.

SYNTHESIS

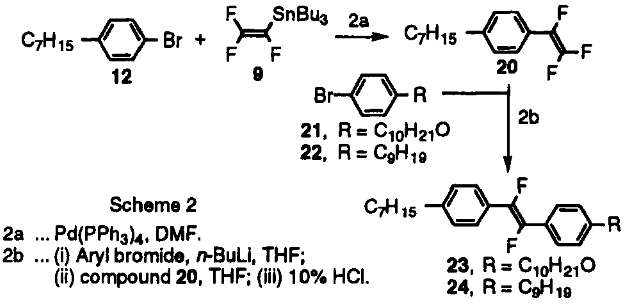
As the required physical properties of liquid crystals become increasingly exacting for the applications of the future, then the required molecular structures are more complex and hence the synthesis is more demanding. A precise combination of structural moieties is required to generate desired physical properties such as ideal mesomorphic behaviour, low viscosity, and tailored optical and dielectric properties, and tilt angle and spontaneous polarisation.



Scheme 1

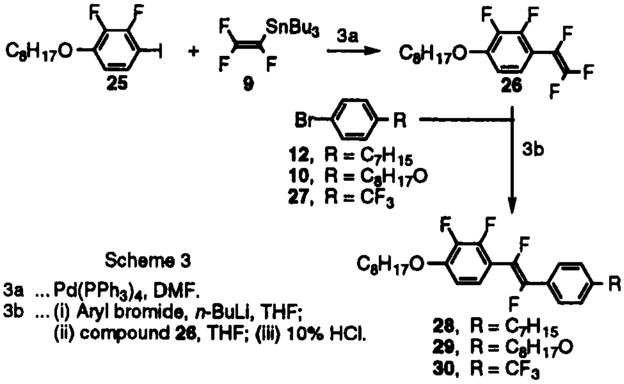
1a ... (i) *sec*-BuLi, EE; (ii) $(MeO)_3B$, EE; (iii) 10% HCl.
1b ... (i) *sec*-BuLi, EE; (ii) Bu_3SnCl, EE; (iii) NH_4Cl, H_2O.
1c ... $Pd(PPh_3)_4$, 2M Na_2CO_3, DME, H_2O.
1d ... $Pd(PPh_3)_4$, DMF.
1e ... (i) Compound **12**, *n*-BuLi, EE; (ii) compound **11**, EE; (iii) 10% HCl.
1f ... (i) Aryl bromide, *n*-BuLi or *tert*-BuLi, THF; (ii) compound **11**, THF; (iii) 10% HCl.

Chlorotrifluoroethene (**7**) was treated with *sec*-BuLi at low temperature to generate the alkenyllithium derivative which was quenched with trimethyl borate to provide trifluoroethenylboronic acid (**8**) as a colourless powder in excellent yield (Scheme 1). Boronic acid **8** was then subjected to a palladium-catalysed cross-coupling reaction with aryl bromide **10** under standard conditions, unfortunately no reaction occurred. The lack of reaction was not really surprising considering the known susceptibility of electron-deficient arylboronic acids to undergo hydrodeboronation. The problem was circumvented by preparing the tributyltin derivative (**9**) from chlorotrifluoroethene (**7**) in a similar manner to that used in the preparation of the boronic acid (**8**). A Stille coupling of the tributyl(trifluoroethenyl)stannane (**9**) provided a good yield of the trifluorostyrene analogue **11**. A Michael-type addition of the aryllithium, prepared from an aryl bromide, to the trifluorostyrene **11** and subsequent elimination of lithium fluoride provided the desired 1,2-difluoroalkenes **16-19**. However, the initial attempt to generate the lithium salt of aryl bromide **12** was carried out in diethyl ether; no aryllithium was generated and a butyl chain, from the butyllithium, was introduced to give compound **15**. Subsequent attempts to generate the lithium salt of aryl bromides were effected successfully in THF, and 1,2-difluoroalkenes **16-19** were generated as expected. Isolation of the desired *trans* isomers of 1,2-difluoroalkenes proved simple by column chromatography.



Scheme 2
2a ... $Pd(PPh_3)_4$, DMF.
2b ... (i) Aryl bromide, *n*-BuLi, THF;
(ii) compound **20**, THF; (iii) 10% HCl.

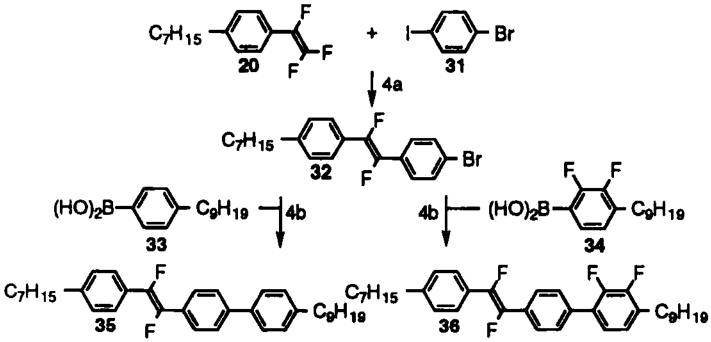
Scheme 2 shows a similar approach to that outlined in Scheme 1, but the trifluorovinyltin compound (**9**) was coupled to an alkyl-substituted aryl bromide (**12**) to generate an alkyl-substituted trifluorostyrene **20** which facilitated the generation of an alkoxy-alkyl-1,2-difluoroalkene (**23**) in 22% yield and a dialkyl example (**24**) in 25% yield. The *ortho*-difluorophenyl class of compound has been most successful in the generation of the smectic C phase. The lateral dipole generated from the two aryl fluoro substituents is sufficiently powerful to promote molecular tilting, yet the steric effect is minimal thereby upholding liquid crystallinity.



Scheme 3
3a ... $Pd(PPh_3)_4$, DMF.
3b ... (i) Aryl bromide, *n*-BuLi, THF;
(ii) compound **26**, THF; (iii) 10% HCl.

Compound **25** (Scheme 3) has been employed in previous work to generate ferroelectric host materials and was used here in a Stille coupling with the trifluorovinyltin **9** to provide the desired *ortho*-difluoro(trifluorovinyl)phenyl system **26** in excellent yield. Three aryl bromides (**12**, **10** and **27**) were then employed in lithiation procedures and Michael-type addition to the styrene **26** to generate three final difluorostilbene mesogens with an *ortho*-difluorophenyl unit (**28**-**30**).

In order to extend the core system for much higher phase stability of the smectic C phase a difluorostilbene with a bromo substituent was targeted to enable subsequent Suzuki couplings to facilitate the introduction of another aryl ring (Scheme 4). The selective lithiation of 1-bromo-4-iodobenzene (**31**) and a subsequent Michael-type addition to the trifluorostyrene **20** generated the bromo-substituted difluorostilbene **32**. Aryl bromide **32** was then employed in separate Suzuki coupling reactions with arylboronic acid **33** and *ortho*-difluorophenylboronic acid **34** to generate two analogous phenyl-substituted 1,2-difluorostilbenes (**35** and **36**) in good yield.

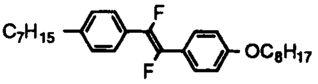


Scheme 4

4a ... (i) Compound **31**, *n*-BuLi, THF; (ii) compound **20**, THF; (iii) 10% HCl.
4b ... $Pd(PPh_3)_4$, 2M Na_2CO_3, DME, H_2O.

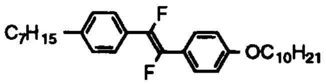
MESOMORPHIC PROPERTIES

Stilbene mesogens with terminal alkyl or alkoxy chains exhibit ordered smectic phases, particularly tilted analogues, but they are photochemically unstable.[11,12] Some difluorostilbenes have also been reported, and these materials are photochemically stable, however, their mesophase morphology was not characterised.[13]



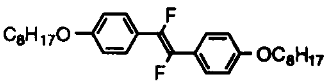
16

C 38.5 S_C 83.5 S_A 89.0 N 110.5 I



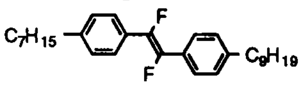
23

C 37.5 S_C 92.5 N 102.0 I



17

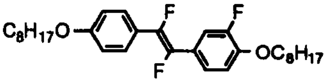
C 88.5 S_C 108.0 N 132.5 I



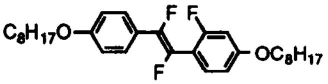
24

C 28.5 (S_C 17.0) S_A 66.5 N 77.0 I

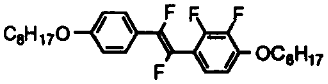
The parent difluorostilbenes reported here (**16**, **17**, **23** and **24**) have low melting points, generally show the smectic C, smectic A and nematic phases, and have remarkably high smectic C phase stability compared with two-ring esters[14] and phenylpyrimidines.[9] As expected, the dialkoxy analogue (**17**) has a high melting point, and the smectic C phase stability is so high as to preclude the generation of a smectic A phase. The dialkyl compound (**24**) has a very low melting point, but the smectic C phase is monotropic. The alkoxy-alkyl analogues (**16** and **23**) show the best compromise of low melting point with remarkably high smectic C phase stability.



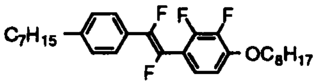
18
C 74.0 S_C 102.5 N 117.0 I



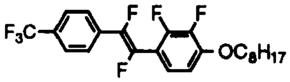
19
C 45.0 N 91.0 I



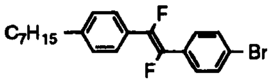
29
C 48.5 S_C 52.5 N 88.0 I



28
C 22.0 S_C 56.0 N 60.5 I

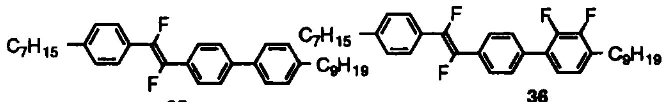


30
C 42.5 S_A 46.5 I



32
C 83.5 S_A 110.0 I

Lateral fluoro substituents in the phenyl rings usually reduce melting point and liquid crystal phase stability. Compared with their parent analogues, compounds **18**, **19**, **28** and **29** all have lower melting points. The outer-edge fluoro substituent of compound **18** might have been expected to promote the exhibition of a smectic A phase, but the smectic C phase stability has been maintained, thus showing the strong tendency towards molecular tilting. The inner-core fluoro substituent of compound **19** has caused the elimination of all smectic phases to give a nematogen over a wide temperature range, this result is a typical effect of such fluoro-substitution.[15] The most interesting result is that the smectic C phase stability of the dialkoxy system (**29**) is actually lower than for the alkoxy-alkyl analogue (**28**); this contrasts markedly with the case seen above (compounds **16** and **17**) and other typical examples,[16] yet the nematic phase stability behaves normally. Terminal trifluoromethyl compounds typically support the smectic A phase, and compound **30** is no exception and would serve to ensure the presence of a smectic A phase in mixtures. Although compound **32** was prepared as an intermediate it exhibits a smectic A phase.



35

C 87.0 S_F 148.0 S_I 151.5 S_C 178.0 S_A 196.5 N 202.0 I

36

C 47.0 S_C 133.5 N 166.0 I

Although compounds **35** and **36** have three rings, they exhibit extremely high smectic C phase stability considering their fluorohydrocarbon construction. In addition to a smectic A phase above the smectic C phase, the parent system (**35**) exhibits underlying, ordered smectic I and Smectic F phases. As is typical, the *ortho*-difluorophenyl unit in compound **36** ensures a low melting point and eliminates the ordered smectic phases, and the smectic phase stability is now reduced to below the limit of molecular tilting to leave the smectic C phase as the sole smectic phase over a very wide temperature range.

CONCLUSIONS

The difluoroethene linking group is most effective in generating the tilted smectic C phase from materials of two-ring construction with relatively short terminal chains. The three-ring analogues exhibit remarkably high smectic C phase stability considering their fluorohydrocarbon construction. Low melting points are found, particularly for the lateral fluoro-substituted examples, where even with three rings the melting point is very low. The difluoroalkene linkage has proved to be photochemically stable which supports previous reports.[13] Thus the materials show great promise as host materials for ferroelectric mixtures, and their physical properties will be reported later by our collaborators at DERA (Malvern).

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