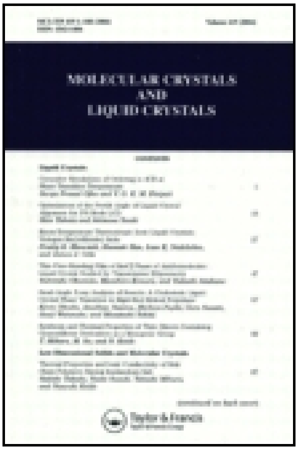

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The Synthesis and Properties of Fluorinated Quinoline Liquid Crystals

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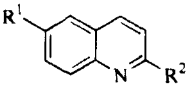
The synthesis and transition temperatures of a series of novel liquid crystalline quinolines is described. Palladium-catalysed coupling of arylboronic acids to 6-bromoquinolines is used to create 6-alkyl-2-arylquinolines in which the phenyl ring is fluorinated at the 2′ and 2′,3′-position. The fluoro-substituents give rise to low melting liquid crystals with a wide-range SmA phase. The Chichibabin reaction is employed to synthesise 6-alkyl-2-arylquinolines but fluoro-substitution is limited to the 3′-position. These compounds are low melting with broad SmC temperature ranges and SmA and N phases. When a fluoro substituent is attached directly to the quinoline nucleus and on the same side as the nitrogen atom the dielectric biaxiality will be increased and the smectic phase range is greater than for those in which the aryl substituents are fluorinated.

Keywords: ferroelectric; fluorinated quinoline; smectic

INTRODUCTION

In order to optimise the performance of ferroelectric mixtures in electro-optic devices increased dielectric biaxiality[1] plays a fundamental role. This can be achieved by employing compounds with a large transverse dipole moment giving rise to a large negative $\Delta\varepsilon$. This has been achieved by attaching highly electronegative substituents such as F or CN laterally to a mesogenic core. The alternative approach is to include a heteroatom such as nitrogen within the core, and this has the obvious advantage of not increasing the molecular width, thus enhancing mesogenicity and minimising viscosity.

2,6-Disubstituted quinolines **1** have the correct attributes to achieve a high negative $\Delta\varepsilon$ namely a broad mesogenic core and a transverse dipole created by the nitrogen atom. In order to enhance the liquid crystal properties of the quinoline nucleus fluoro substituents have been included in these novel materials. It is now well known[2] that the introduction of fluoro substituents tends to decrease melting point, enhance smectic character and, if the fluoro substituents are in alignment with the nitrogen atom, will increase dielectric biaxiality.



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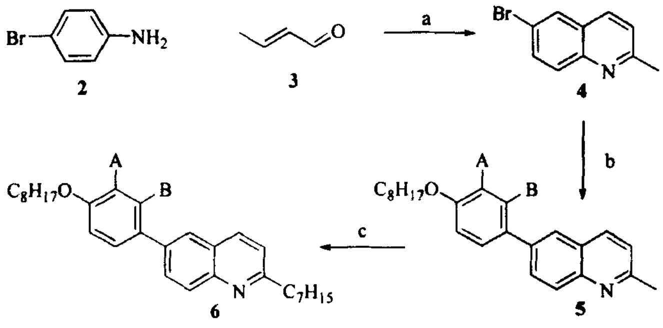
Quinoline liquid crystals have been known[2-8] for over ten years and yet interest in them has been quite limited despite their potential as useful materials. Compounds **1** where R^1 = CN, R^2 = aryl show a broad nematic range and, where R^1/R^2 is aryl/alkyl broad smectic ranges have been observed. This paper describes the synthesis and properties of a series of quinolines in which alkoxyphenyl substituents at the 2- and 6-positions are substituted with lateral fluoro substuents. A novel quinoline is also prepared in which a fluoro substituent is attached directly to the heterocyclic ring at the 6-position.

SYNTHESIS AND LIQUID CRYSTAL PROPERTIES

A convenient route to the 6-aryl-2-heptylquinolines **6** is outined in SCHEME 1. The key intermediate is 6-bromo-2-methylquinoline **4** which was prepared by a modified Skraup (or Doebner-Miller) reaction. In this process acid catalysed condensation of crotonaldehyde **3** with 4-bromoaniline **2** gave the methylquinoline **4** which was isolated as a zinc complex. Washing of the complex with ethanol gave a purple solid from which the pure quinoline was decomplexed by treatment with ammonia. This avoids the tedious steam distillation associated with the usual procedure.



a ... (i) 6M HCl, (ii) $ZnCl_2$, (iii) NH_3
b ... arylboronic acid, 1,2-dimethoxyethane, 2M Na_2CO_3, $Pd(PPh_3)_4$
c ... (i) n-butyllithium or lithiumdiisopropylamide, THF
(ii) 1-bromohexane

SCHEME 1 Synthesis of 6-aryl-2-heptylquinolines **6**

The 6-aryl substituents were introduced by the highly versatile[2,9] palladium(0) cataysed coupling of an arylboronic acid to the bromoquinoline **4**. The protons of 2-methylquinolines are acidic and so lithiation of **5** followed by addition of 1-bromohexane gave the required 6-aryl-2-heptylquinoline **6**.

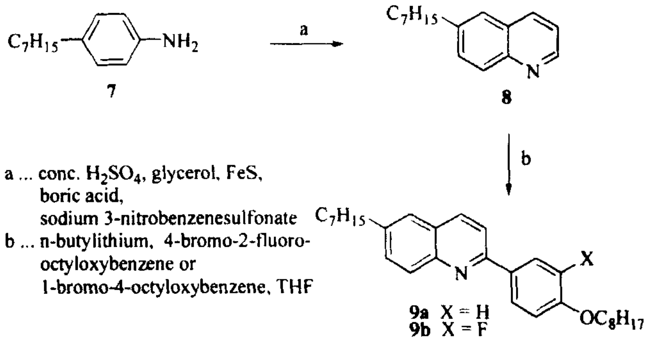
The transition temperatures for compound **6** is shown in TABLE 1.

TABLE 1 Transition temperatures for 6-aryl-2-heptylquinolines **6**

Compound	A,B	Crys		SmA		I
6a	H,H	•	101.9	•	125.6	•
6b	H,F	•	40.6	•	69.3	•
6c	F,F	•	42.4	•	73.7	•

The introduction of fluoro-substituents **6b**,**6c** dramatically reduces the melting point (by 60 °C) compared to the unfluorinated compound with a similar reduction in the clearing point of the SmA phase.

2-Aryl-6-heptylquinolines **9** were synthesised using the route shown in SCHEME 2 which has been previously reported[8] for the preparation of the unfluorinated quinoline **9a**. 6-Heptylquinoline **8** was prepared *via* a Skraup synthesis and this was added to the lithium salt of the appropriate octyloxybenzene at low temperature (Chichibabin reaction). It was found that this reaction was unsuccessful if there was a fluoro-substituent *ortho* to the anionic centre. *Ortho* fluoro-aryllithium salts are stable at low temperature, but a higher temperature is required before the Chichibabin reaction occurs in this case. Hence the lithium salt decomposed by the elimination of LiF to produce benzynes which gave rise to an intractable mixture.



SCHEME 2 Synthesis of 2-aryl-6-heptylquinolines **9**

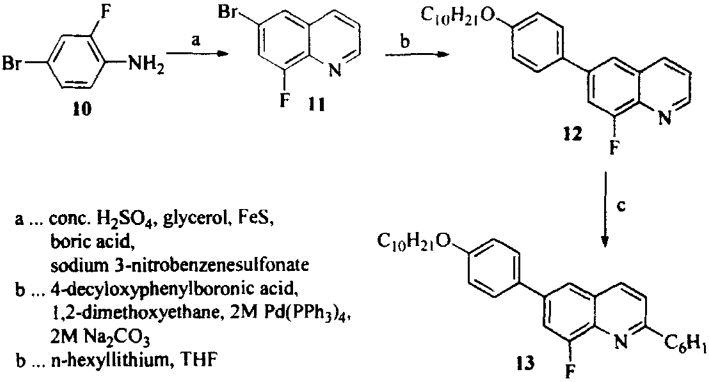
The transition temperatures shown in TABLE 2 show the same marked depression of melting point when a fluoro-substituent is added. The most remarkable difference between compounds **9** and **6** is in the change of phase behaviour. 6-Arylquinolines **6** show only SmA whereas the 2-isomer **9** possesses the ideal ferroelectric host phase sequence of SmC-SmA-N.

TABLE 2 Transition temperatures for 2-aryl-6-heptylquinolines **9**

Cpd.	X	Crys		Sm C		Sm A		N		I
9a	H	•	70	•	109	•	117	•	120	•
9b	F	•	46.5	•	82.5	•	95.6	•	97.4	•

The compounds **6** and **9** show that the addition of fluorino substituents yield compounds with good mesomorphic properties for use in ferroelectric mixtures. However, due to the free rotation of the phenyl rings, any enhancement of dielectric biaxialty may be small. The fluoro substituents could align mainly with the nitrogen thus enhancing $\Delta\varepsilon$ or mostly opposite which would have a delitereous effect. In order to overcome this doubt, a compound was synthesised in which the fluoro-substituent was attached directly to the quinoline nucleus and on the same side as the nitrogen atom. In this case there is no doubt that dielectric biaxiality is increased. The synthetic procedure shown in SCHEME 3 used 4-bromo-2-fluoroanaline **10** in the Skraup synthesis to give 6-bromo-8-fluoroquinoline **11** which was coupled to 4-decyloxyphenylboronic acid. A Chichibabin type reaction using hexyllithium afforded the 8-fluoroquinoline **13**.

The transition temperatures can best be compared with those of compounds **6a** and **6b** . The 8-fluoroquinoline **13** has a lowered melting point similar to that of **6b** but in the case of compound **13** the SmA-I transition is depressed by only 33 °C as opposed to 56 °C for **6b** which is fluorinated on the phenyl ring. This can be expained by the presence of interannular twist in compound **6b** which is absent in **13**.



a ... conc. H_2SO_4, glycerol, FeS, boric acid, sodium 3-nitrobenzenesulfonate

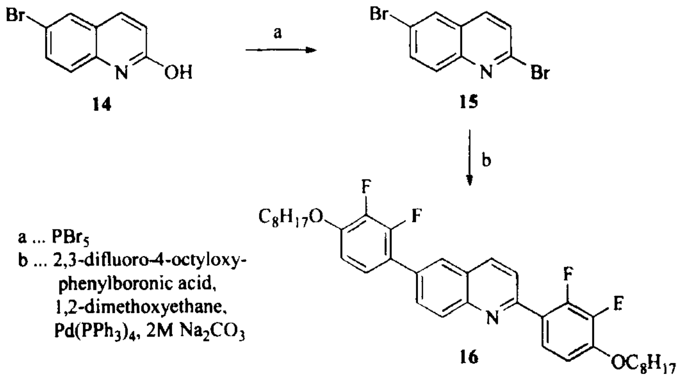
b ... 4-decyloxyphenylboronic acid, 1,2-dimethoxyethane, 2M $Pd(PPh_3)_4$, 2M Na_2CO_3

b ... n-hexyllithium, THF

Crys 49.2 SmA 92.4 I

SCHEME 3 Synthesis of 6-aryl-2-fluoro-2-hexylquinoline **13**

A diarylquinoline **16** was synthesised as outlined in SCHEME 4 which required a double palladium-catalysed coupling of 2,3-difluoro-4-octyloxyphenyl-boronic acid to the dibromoquinoline **15** which was prepared from the corresponding 2-hydroxyquinoline **14** by treatment with phosphorus pentabromide. Despite the presence of a four ring system with two alkoxy chains and five other electronegative atoms the melting point is quite low and there is a wide smectic C range.



14

15

16

a ... PBr_5
b ... 2,3-difluoro-4-octyloxyphenylboronic acid,
1,2-dimethoxyethane,
$Pd(PPh_3)_4$, 2M Na_2CO_3

Crys 136.2 SmC 178.7 SmA 189.6 I

SCHEME 4 Synthesis of 2,6-bis(2,3-difluoro-4-octyloxyphenyl)quinoline

SUMMARY

Synthetic routes to liquid crystalline quinolines have been developed in which fluoroaromatic rings are attached at the 2- and/or the 6-positions **6**, **9**, **13**, **16**. The 2-arylquinolines are low melting with a wide SmA range and the 6-arylquinoline is also low melting and possesses a SmC-SmA-N phase sequence. Both types will be useful components of ferroelctric host mixtures and the dielectric biaxiality is certainly increased when the fluoro substituent is attached to the quinoline ring as in compound **13**. Additionally the depression of phase transition caused by the fluoro substituent is considerably less than for compounds **6** and **9**. Therefore it is envisaged that further examples of this type will be needed to determine their true potential.

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