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Cyanoalkyl difluoro-terphenyl-carboxylate chiral dopants

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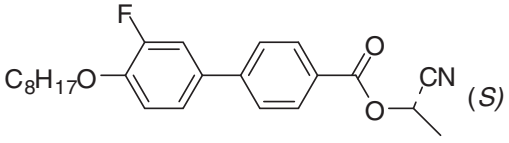
ABSTRACT

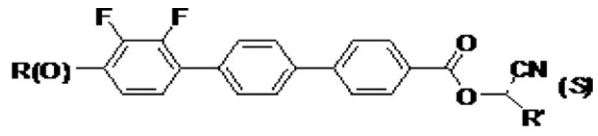
A liquid crystal like difluoroterphenyl chiral dopant was synthesized to match the dimensions of a host chiral dopant mixture. The melting point of the chiral dopants was decreased by increasing the length of the alkyl chain. The melting point of the chiral dopants also decreased when fluorine was on the same ring as the ester i.e. at 2″, 3″ position. These dopants were formulated with terphenyl host mixture and liquid crystal properties were assessed. New dopants, when added to the host mixture, maintain SmA[1] but the SmC[2] phase was reduced markedly. There was a decrease in spontaneous polarisation when fluorine was on the same ring as the ester i.e. at 2″, 3″ position. As the molecular weight of the chiral dopant increased (pentyl→heptyl→nonyl), spontaneous polarisation decreased.

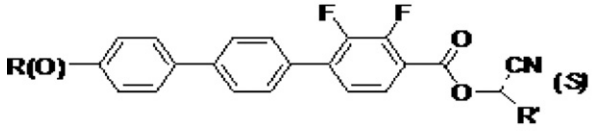
1. Introduction

A chiral dopant (BE80F2N[3]) that has proved to be successful is the octyloxyfluorobiphenyl ester which has a chiral cyanohydrin as the branched asymmetric group.



This molecule, when added to an achiral FLC[4] host mixture (5–12% w/w) provides an FLC mixture with a reasonable compromise of liquid crystalline and electro-optic properties. Enhancement of the dopants' mesogenic properties can be obtained from using a terphenyl [1,2] structure and further improvement may be obtained from increasing the length of the chain attached to the cyanohydrin. The increased chain length may, however also increase polarisation and decrease the pitch length of the material. The study of ferroelectric liquid crystals (FLCs) has fast developed into multidisciplinary field involving physicists, electrical engineers, computer engineers, and chemists. As in nematic technology, the FLC material is not a single component, but a mixture of many compounds. It is best to employ an achiral room temperature 'host' SmC with a broad LC phase temperature range, low viscosity, good stability etc. and to dope this with a chiral material. One example of a chiral dopant is (BE80F2N) which has proven increase in the Ps and decrease in the pitch length. The latter effects result from the restricted rotation caused by lengthening the chain. Syntheses of the longer chain cyanohydrin esters involve a different route, starting from amino acids. The synthetic targets chosen, will examine the effect of the position of the ortho-difluoro substituent and the chain length. The synthetic routes involve directed lithiation and Suzuki palladium catalysed cross coupling of boronic acids with arylhalides as a key component [3]. Target chiral dopants are given below.





Alkyl R = C_5H_{11}, C_7H_{15}, C_9H_{19}

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[1] Smectic A.
[2] Smectic C.
[3] Octyloxyfluorobiphenyl ester.
[4] Ferroelectric liquid crystal.

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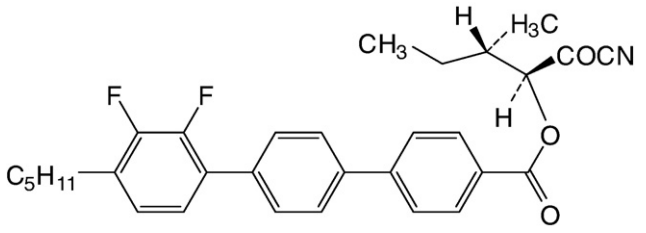
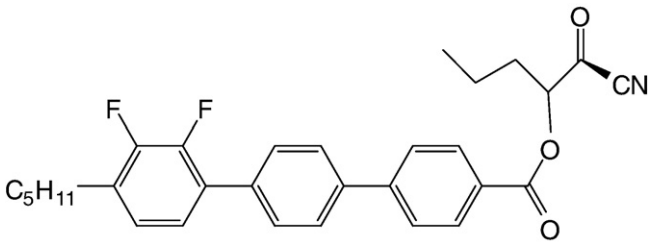


(S)-(−)-1-cyno-2-methylbutyl-4-pentyl-difluoroterphenyl-4′-carboxylate



(S)-(−)-1-cyno-2-methylbutyl-4-pentyl difluoroterphenyl-4′-carboxylate

2. Synthesis details of ferroelectric liquid crystals

The initial aim of this work was to synthesize ortho difluoro substituted materials that possess a central terphenyl core and to incorporate a chiral centre in the terminal chain. Eight materials were prepared, five of which possess fluorine on the alkyl side and the other three on the chiral side. In six dopants a chiral centre was introduced using commercially available (S)-lactamide. L-leucine and L-norvaline were also used to induce a chiral centre in the ortho difluoro-substituted materials to produce two dopants.

2.1. Synthesis schemes

Here are six schemes to elaborate the synthesis of all intermediate compounds as well as dopants. In Fig. 1 synthesis of bromobiphenyl cynohydrin ester is given which is an intermediate compound for the synthesis of 4-heptyl-2,3-difluoro terphenyl nitrile and 4-nonyl-2,3-difluoroterphenyl nitrile [4]. In Fig. 2, synthesis of 4-heptyl-2,3-difluoro terphenyl nitrile (D7), 4-nonyl-2,3-difluoro terphenyl nitrile (D9), 4-pentyl-2″,3″-difluoro terphenyl nitrile (D5R) and 4-heptyl-2″,3″-difluoro terphenyl nitrile (D7R) are presented while Fig. 3 gives the synthesis route for 4-pentyl-2,3-difluoro terphenyl nitrile (D5)[4] and Fig. 4 for 4-nonyl-2″,3″-difluoro terphenyl nitrile (D5R). Figs. 5 [5] and 6 provide the synthesis route for dopants (S)-(−)-1-cyno-pentyl-4-pentyl difluoroterphenyl-4′-carboxylate (D52) and (S)-(−)-1-cyno-2-methylbutyl-4-pentyl difluoroterphenyl-4′-carboxylate (D53) respectively [6].

2.1.1. 4-pentyl-2,3-difluoro terphenyl carbonyl nitrile (D5)

2.1.1.1. Quantities. 4-pentyl-2,3-difluoro terphenyl carbonyl amide (1 g, 12.16 mmol, 473 g/mol), $POCl_3$ (1.33 ml,14.5 mmol,153 g/mol) and dry DMF (27.5 ml).

2.1.1.2. Procedure. Dry DMF was cooled to 0 °C. $POCl_3$ was added slowly by syringe under nitrogen keeping the temperature below 5 °C. It was stirred for 20 min and turned coloured. Pentyl-2,3-difluoro terphenyl carbonyl amide was added in portion and stirred for 20 h at room temperature. The solution was poured in ice and water mixture, swirled around and was placed to settle down. A precipitate was

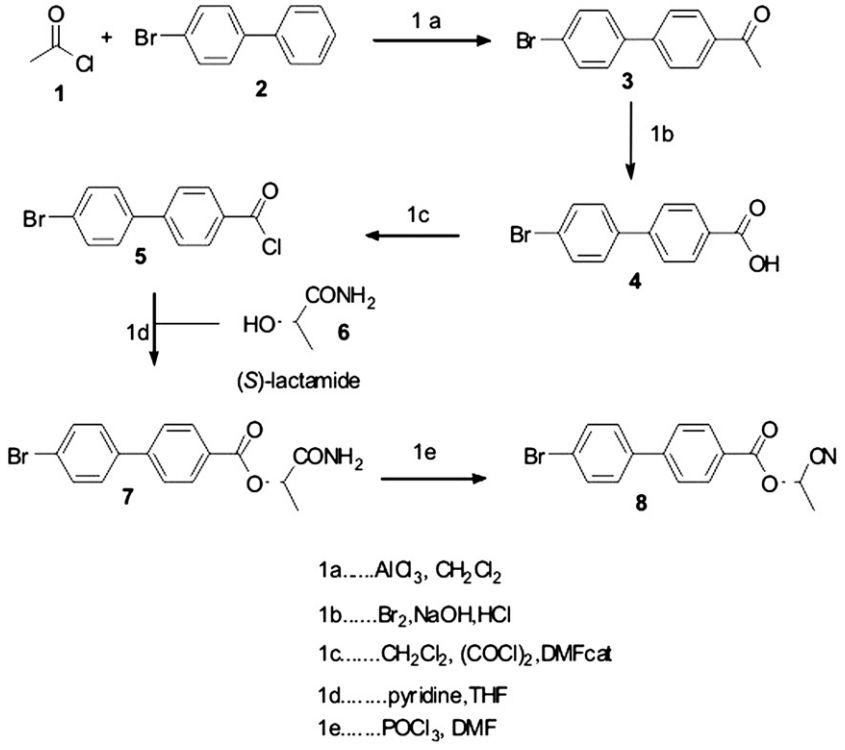


Fig. 1. Synthesis steps of biphenyl cyanohydrin ester.