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Development of novel chiral dopants to be used in ferroelectric liquid crystal system

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ABSTRACT

The study of chiral dopant and its application in liquid crystal system is one of the largest area of research in fluids leading to technological application in the field of display devices. Chiral dopant when mixed with achiral host mixture forms ferroelectric liquid crystal to be used in surface stabilised liquid crystal devices.
4-(pentyl, heptyl, nonyl)-2, 3 difluoro terphenyl nitriles and (S)-(−)-1-cyno-2-methylbutyl-4-pentyl-difluoroterphenyl-4′-carboxylate were synthesised and mixed with achiral host mixture HM1 with the percentage of 3 and 7. Ferroelectric properties of synthesised FLC[1] were studied.

1. Introduction

The aim of research was to develop room temperature and stable ferroelectric liquid crystals to be used in surface stabilised ferroelectric liquid crystal (SSFLC) devices. Previously 2 ring cyanohydrin dopant was used to make ferroelectric liquid crystal mixture with dialkyl difluoro terphenyl host mixture [1]. This FLC mixture has high melting point and large reduction in SmC[2] phase stability produced by dopant so there was a need for improved chiral dopant. Hence in the current project a third ring was added to dopant to make it 3 ring cyanohydin dopant. The chiral 'dopant' needs not have ferroelectric properties but it should not cause a large reduction in the SmC phase stability or to raise the melting point markedly. The resulting ferroelectric liquid crystal mixture comprising of small percentage of chiral dopant and major percentage of achiral host mixture should change its phase from I[3] → N[4]* → SmA[5]* → SmC* phase sequence and the N* pitch length should be >4 times the cell gap. The SmC* pitch length should be greater than the cell gap. Spontaneous polarisation of ferroelectric liquid crystal should be high, around 20–25 nC-cm^{-2} and the tilt angle, 22.5°. The tilt angle would not vary over the operating temperature of the device.

2. Experimental

The initial aims of this work were to synthesise ortho difluoro substituted materials that possess a central terphenyl core and incorporate chiral centre in the terminal chain.

Initially synthetic route to synthesis 4-(pentyl, heptyl, nonyl)-2, 3 difluoro terphenyl nitriles used convergent approach by using coupling reaction but yield was low and optical polarity was lost so switched to a conservative approach i.e. attaching chiral centre at the final steps. Synthesis schemes for 4-(pentyl, heptyl, nonyl)-2, 3 difluoro terphenyl nitriles and (S)-(−)-1-cyno-2-methylbutyl-4-pentyl-difluoroterphenyl-4′-carboxylate are described in research paper by Z.N. Kayani et.al. [2]. Synthesis of 4-(heptyl, nonyl)-2, 3 difluoro terphenyl nitriles and (S)-(−)-1-cyno-2-methylbutyl-4-pentyl-difluoroterphenyl-4′-carboxylate used convergent approach while for synthesis of 4-pentyl-2, 3 difluoro terphenyl nitriles conservative approach was used.

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[1] Ferroelectric liquid crystal.
[2] Smectic C.
[3] Isotropic.
[4] Nematic.
[5] Smectic A.

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2.1. Synthesis details of all intermediates and final products

Synthesis of Biphenyl cynohydrin ester

Quantities, procedure, yield and elemental analysis of all intermediates and **Biphenyl cynohydrin ester** can be found in some other paper by Z. N. Kayani et.al. [3].

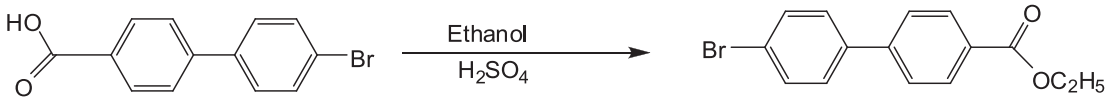
4-heptyl-2, 3-difluoro terphenyl carbonyl nitrile (11a)

Quantities, procedure, yield and elemental analysis of **4-heptyl-2, 3-difluoro terphenyl carbonyl nitrile** can be found in some other paper by Z. N. Kayani et.al. [2].

4-nanoyl-2, 3-difluoro terphenyl carbonyl nitrile (11b)

Quantities, procedure, yield and elemental analysis of **4-nonyl-2, 3-difluoro terphenyl carbonyl nitrile** can be found in some other paper by Z. N. Kayani et.al. [2].

Ethyl-4′-bromobiphenyl-4-carboxylate (23)

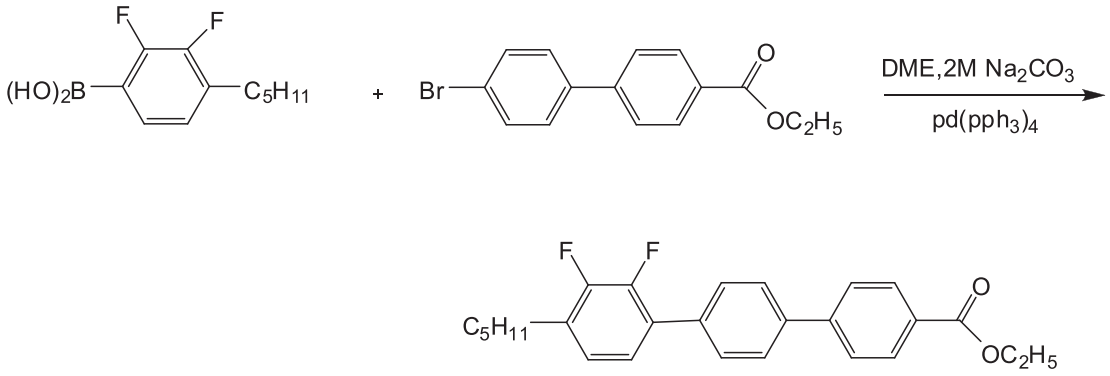


Quantities and procedure

4-bromobiphenyl-4′-carboxylic acid (64.18 g, 230 mmol, 278 g/mol) was stirred with ethanol (46 g/mol, 500 ml) on an oil bath at temperature 130 °C under reflux. Then few drops of sulphuric acid were added in it and was stirred for 10 h. When whole carboxlic acid dissolved, it was filtered off to get dry product. Dry product was washed with enough cool ethanol to wash out traces of acid. Then the dry product was put in desiccators over night.

Yield (30.82 g, 43.79%); M.P. 74.8–75.5 [4].m/z 306 (M^+), 278, 261, 153 (100%), 76; δ_H (400 MHz; $CDCl_3$) 1.42 (3H, t, J 7.1, Me), 4.40 (1H, q, J 7, C**H**Me), 7.49 (2H, d, J 8.6), 7.59 (2H, d, J 8.61), 7.62 (2H, d, J8.61), 8.11 (2H, d, J8.61), δ_C (100.5; $CDCl_3$) 14.36, 61.07, 122.52, 126.81, 128.85, 130.18, 132.07, 138.94, 144.20, 166.38 (CO);

4-pentyl-2, 3-difluoro terphenyl-4′-ethyl ester (25):

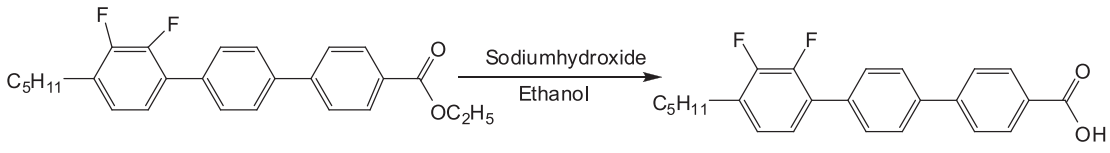


Quantities and procedure

Pentyl diflouroboronic acid (15.62 g, 50.98 mmol, 228 g/mol), Ethyl-4′-bromobiphenyl-4-carboxylate (12 g, 39.22 mmol, 306 g/mol), tetrakis (triphenylphosphine) palladium (0) (0.46 g, 0.1961 mmol, 1156 g/mol), 1, 2-dimethoxyethene (255 ml) and sodium carbonate (2 M, 255 ml). The experimental procedure was as described for the preparation of compound (14 a) in the research paper of Z. N. Kayani et.al. [3].

Yield (12.57 g, 78.56%); M.P. 73.2 °C (from EtOH). **Elemental analysis:** (Found: C, 76.69; H, 6.41.calc. for $C_{26}H_{26}F_2O_2$: C, 76.45; H, 6.42%); m/z 408 (M^+,100%), 363, 351, 335, 323, 277, 165, 153; transitions/°C SmA* 165.9 (11.64 J/g) I; IR (KBr) υ_{max}/cm^{-1} 2929 (CH), 1710 (COvs), 1458, 1275, 1178, 1119, 1100, 863, 835, 812, 774, 703; δ_H (400 MHz; $CDCl_3$) 0.92 (3H, t, J7.1, Me), 1.35–1.39 (4H, m), 1.42 (3H, t, J7.1) 1.66 (2H, quint, J7.7, $ArCH_2C\underline{\mathbf{H}}_2$), 2.70 (2H, t, J8.1, $ArCH_2$), 4.41 (1H, q, J 7.1, CHMe), 7.02 (1H, ddd, J 6.7, 6.5, 1.5), 7.16 (1H, ddd, J 6.9,6.2,1.6,1), 7.64 (2H, dd, J 8.4, 1.5), 7.70 (2H, d, J 2.6), 7.72 (2H, d, J 2.6), 8.13 (2H, d, J 8.6); δ_F (376; $CDCl_3$) −143.30 (1 F, dd, $J_{F,F}$ 20.81, $J_{F,H}$ 6.9), −143.88 (1 F, dd, $J_{F,F}$ 18.5, $J_{F,H}$ 6.9); δ_C (100.5;$CDCl_3$) 13.99, 19.01, 22.45, 28.77, 29.71, 31.44, 57.77(**C**HMe), 117.59 (CN), 124.11 (dd, $J_{C,F}$3.1, 2.3), 124.88 (dd, $J_{C,F}$4.6, 4.5), 127.1, 127.2, 127.4, 127.6, 129.4, 129.5, 130.6, 131.3, 131.5, 135.2 (d, $J_{C,F}$ 2.3), 139, 146.09, 164.57 (CO);

4-pentyl-2, 3-difluoro terphenyl-4′-carboxylic acid (26):



Quantities and procedure

Sodium hydroxide (2.46 g, 61.57 mmol, 40 g/mol) dissolved in 10 ml of water and 200 ml of ethanol was put in 4-pentyl-2,3-difluoro terphenyl-4′-ethyl ester (12.56 g, 30.78 mmol, 408 g/mol). The stirred mixture was heated under reflux (ca. 110 °C) for 1 h. It solidified.