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## Liquid Crystals

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Online publication date: 11 November 2010

**To cite this Article** Chen, Ximin , Chen, Jingkui and Wen, Jianxun(2010) 'Synthesis and mesomorphic properties of 4-cyanophenyl and 4-nitrophenyl 4- n -alkoxytetrafluorobiphenyl-4'-carboxylates', *Liquid Crystals*, 29: 8, 1097 – 1100

**To link to this Article:** DOI: 10.1080/02678290210149577

**URL:** <http://dx.doi.org/10.1080/02678290210149577>

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# Synthesis and mesomorphic properties of 4-cyanophenyl and 4-nitrophenyl 4-*n*-alkoxytetrafluorobiphenyl-4'-carboxylates

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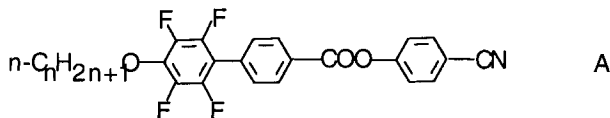
(Received 15 December 2001; accepted 15 March 2002)

Four homologous series of 4-cyanophenyl and 4-nitrophenyl 4-*n*-alkoxytetrafluorobiphenyl-4'-carboxylates have been synthesized. Their mesomorphic properties were measured by polarizing optical microscopy and differential scanning calorimetry. The relationship between the properties and chemical structures of these compounds has been studied; the effects of terminal alkoxy chain length, polarizable end groups and the position of tetrafluorophenylene in the rigid core on mesomorphic behaviour are discussed in detail.

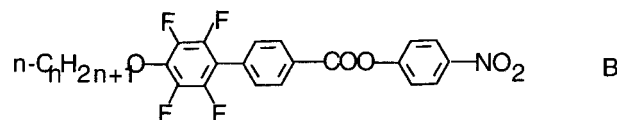
## 1. Introduction

Because the study of new liquid crystalline compounds can stimulate scientific understanding of liquid crystals (LCs) and their device applications, increasing research attention has been paid to laterally fluorinated LCs [1–11]. It is of great interest that fluorine substitutions allow one to modify the mesophase range, as well as other physical properties, such as chemical and thermal stabilities, viscosity and birefringence [12–14]. Up to now, thousands of liquid crystalline compounds with fluoro-substituted phenyl groups have been prepared, including many from this group [11, 15–19].

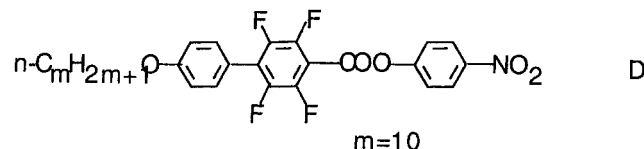
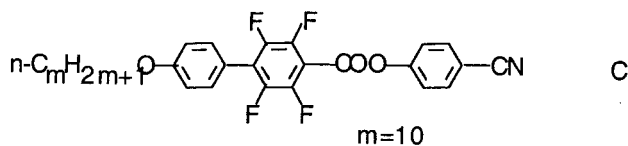
In the search for new high quality liquid crystalline materials much effort has been applied to the synthesis of new compounds with polar end groups and highly fluorinated aromatic substructures. In this paper, we report the synthesis and mesomorphic behaviour of 4-cyanophenyl 4-*n*-alkoxy-2,3,5,6-tetrafluorobiphenyl-4'-carboxylates (compounds **A**) and 4-nitrophenyl 4-*n*-alkoxy-2,3,5,6-tetrafluorobiphenyl-4'-carboxylates (compounds **B**); these series have differing polar end groups.

A<sub>1</sub>: n=7; A<sub>2</sub>: n=8; A<sub>3</sub>: n=9; A<sub>4</sub>: n=10; A<sub>5</sub>: n=12

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B<sub>1</sub>: n=7; B<sub>2</sub>: n=8; B<sub>3</sub>: n=9; B<sub>4</sub>: n=10; B<sub>5</sub>: n=12

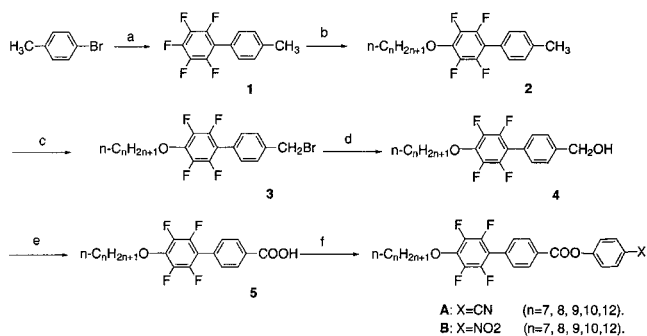
To study the effects produced by the different positions of tetrafluorophenylene in the rigid core, compounds **C** and **D** were also synthesized.



## 2. Synthesis

### 2.1. Series A and B

The preparation of compounds **A** and **B** is outlined in scheme 1, and was based on an esterification reaction with hexafluorobenzene as the starting material. In the first step, 4-pentafluorophenyl toluene (**1**) was prepared from 4-bromotoluene which first reacted with Li to form *p*-toluylithium and then with hexafluorobenzene. The



Conditions and reagents. a: 1 Li/Et<sub>2</sub>O; 2 C<sub>6</sub>F<sub>6</sub>/Et<sub>2</sub>O. b: *n*-C<sub>n</sub>H<sub>2n+1</sub>OH/THF, NaOH, 35–40°C. c: AIBN, NBS, CCl<sub>4</sub>, reflux. d: CaCO<sub>3</sub>/H<sub>2</sub>O, THF, reflux. e: KMnO<sub>4</sub>/Na<sub>2</sub>CO<sub>3</sub>, H<sub>2</sub>O, 1,4-dioxane, reflux. f: *p*-cyanophenol or *p*-nitrophenol, DCCI/PPY, THF.

Scheme 1. Synthesis of compounds **A** and **B**.

nucleophilic substitution reaction between compound **1** and an alkanol in THF with NaOH as base gave compound **2**, which was brominated using NBS and AIBN in anhydrous carbon tetrachloride to produce compound **3**. Subsequently, the 4-*n*-alkoxy-2,3,5,6-tetrafluorobiphenyl-4'-methanol (**4**) was prepared through the hydrolysis of compound **3**. The oxidation of compound **4** using potassium permanganate generated compound **5**. Finally, ester **A** or **B** was obtained by esterification of compound **5** with *p*-cyanophenol or *p*-nitrophenol involving DCCI and PPY in THF.

A description of the synthesis of compound **A<sub>4</sub>** is now given; the remaining **A** and **B** compounds were prepared in the same way. All had satisfactory elemental analysis and spectral data.

*4-Cyanophenyl 4-n-decanoxy-2,3,5,6-tetrafluorobiphenyl-4'-carboxylate (A<sub>4</sub>)*. In a dry 25 ml round-bottomed flask were placed 150 mg (0.35 mmol) of compound **5** (*n* = 10), 95 mg (0.8 mmol) of *p*-cyanophenol, 165 mg (0.8 mmol) of *N,N*-dicyclohexylcarbodiimide (DCCI), 15 mg of PPY and 10 ml of dried THF. The reaction mixture was protected from air and stirred at room temperature for 30 h. After analysis by TLC revealed a complete reaction, the white precipitate was filtered off, the filtrate was washed with water, and then the filtrate solvent was removed. The residue was purified by column chromatography on silical gel using a mixture of light petroleum (b.p. 60–90°C)/ethyl acetate (10/1) as eluent to give a yellow solid. This was recrystallized from acetone/methanol to yield white crystals of compound **A<sub>4</sub>**; yield 163 mg (88.37%). <sup>1</sup>H NMR δ<sub>H</sub> (90 MHz; CCl<sub>4</sub>; TMS): 0.95 (t, 3H, *J* = 7.2 Hz, CH<sub>3</sub>), 1.2–2.1 (m, 16H), 4.30 (t, 2H, *J* = 7.0 Hz, OCH<sub>2</sub>), 7.35 (d, 2H)/7.75 (d, 2H) (AA'BB', *J* = 9.0 Hz, –C<sub>6</sub>H<sub>4</sub>–), 7.60 (d, 2H)/8.25 (d, 2H) (AA'BB', *J* = 9.0 Hz, –C<sub>6</sub>F<sub>4</sub>–C<sub>6</sub>H<sub>4</sub>–) ppm. <sup>19</sup>F NMR δ<sub>F</sub> (60 MHz; CCl<sub>4</sub>; TFA): 66.0 (m, 2F, Farom), 78.0 (m, 2F, Farom) ppm. IR (KBr, cm<sup>-1</sup>): 2940 2860 2240 1736

1601 1502 1495 1410 1280 1264 1218 1185 1070 990 860 560. MS (*m/z*, %): 528 (M<sup>+</sup> + 1, 1.37), 409 (M<sup>+</sup> – 118, 100.00). Elemental analysis for C<sub>30</sub>H<sub>29</sub>NF<sub>4</sub>O<sub>2</sub>: calcd C 68.31, H 5.50, N 2.80, F 14.42; found C 68.32, H 5.53, N 2.67, F 14.42%.

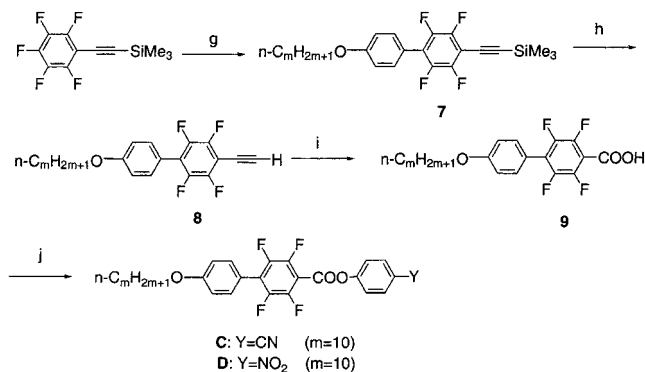
## 2.2. Series **C** and **D**

The preparation of compounds **C** and **D** is outlined in scheme 2. In a previous study [15], we reported the synthesis of intermediates **6**, **7** and **8**. By oxidation of intermediate **8** using KMnO<sub>4</sub>, we easily obtain intermediate **9**. Esterification of compound **9** with *p*-cyanophenol or *p*-nitrophenol, involving DCCI and PPY in THF, gave the desired compounds **C** or **D**. The final products were purified by column chromatography over silica gel (200–400 mesh) using light petroleum (b.p. 60–90°C)/ethyl acetate (10/1) as the eluent, and were recrystallized from acetone/methanol. Their chemical structures and those of the intermediates were identified by elemental analysis and MS, IR and <sup>1</sup>H, <sup>19</sup>F NMR spectroscopy.

## 3. Characterization

The transition temperatures and phase assignments for the final products were determined with an Olympus BH2 polarizing microscope in conjunction with a Mettler FP 52 hot stage and FP 5 control unit; the observed textures were compared with those in the literature [20] to identify the mesomorphic phases. The enthalpies of transitions were investigated by DSC using a Shimadzu DSC 50 calorimeter with a heating/cooling rate of 5°C min<sup>-1</sup>.

IR spectra were recorded on a Shimadzu IR-440 spectrometer. <sup>1</sup>H NMR spectra with TMS as internal standard, and <sup>19</sup>F NMR spectra with trifluoroacetic acid (TFA) as external standard, were recorded on a Varian



Conditions and reagents. g: *p*-*n*-C<sub>10</sub>H<sub>21</sub>–C<sub>6</sub>H<sub>4</sub>–MgBr, THF, reflux. h: CH<sub>3</sub>OH/CH<sub>3</sub>COCH<sub>3</sub>, NaOH/H<sub>2</sub>O, r.t. i: KMnO<sub>4</sub>/Na<sub>2</sub>CO<sub>3</sub>, H<sub>2</sub>O, 1,4-dioxane, reflux. j: *p*-cyanophenol or *p*-nitrophenol, DCCI/PPY, THF.

Scheme 2. Synthesis of compounds **C** and **D**.

EM 360L spectrometer (60 MHz) or FX-90Q spectrometer (90 MHz), respectively. For  $^{19}\text{F}$  NMR spectra, high field is positive. Mass spectra were measured on a Finnigan-4021 spectrometer.

#### 4. Results and discussion

The transition temperatures of compounds **A** and **B** are summarized in table 1; the two series of compounds exhibit similar mesophases. Compounds with a short alkoxy chain exhibit a nematic phase only, while those with a long alkoxy chain show a smectic phase only. However, those compounds with an intermediate length alkoxy chain exhibit both smectic and nematic phases. This is because, with increasing alkoxy chain length, the lateral intermolecular cohesions increase, whereas the terminal attractions decrease. Because of the lengthened alkoxy chain, the separation of the aromatic centres, which are highly polarizable and may carry permanently dipolar substituents, is increased; there should then be a decrease in the strength of terminal intermolecular cohesions. At the same time, the longer alkoxy chain, the larger the lateral intermolecular attractions.

A comparison of the ranges of transition temperatures between compounds **A** and **B** shows that a compound of series **A** tends to have higher melting and clearing points than the compound of series **B** with the same terminal alkoxy chain length. In addition, the transition temperature ranges of compounds **A** are larger than those of compounds **B**. We can conclude that in these two series, when the tetrafluorophenylene is at the side of the core unit in molecule, a CN substituent is better than  $\text{NO}_2$  for the promotion of mesomorphic properties.

In order to study the effect of the position of the tetrafluorophenylene group in the core structure, we list

Table 1. Transition temperatures by polarizing microscopy for compounds **A** and **B**. Cr, crystal; SmA, smectic A phase; N, nematic phase; I, isotropic phase.

Compound	<i>n</i>	Transition temperatures/ $^{\circ}\text{C}$
<b>A</b> <sub>1</sub>	7	Cr 119.5 N 145.8 I 144.8 N 116.2 Recr
<b>A</b> <sub>2</sub>	8	Cr 114.5 N 131.0 I 130.4 N 111.8 Recr
<b>A</b> <sub>3</sub>	9	Cr 115.8 N 132.6 I 132.4 N 111.4 Recr
<b>A</b> <sub>4</sub>	10	Cr 116.7 SmA 124.4 N 136.1 I 135.1 N 123.5 SmA 113.3 Recr
<b>A</b> <sub>5</sub>	12	Cr 114.6 SmA 129.3 I 128.8 SmA 111.7 Recr
<b>B</b> <sub>1</sub>	7	Cr 120.1 N 128.5 I 127.5 N 97.0 Recr
<b>B</b> <sub>2</sub>	8	Cr 119.2 N 126.7 I 124.6 N 88.7 Recr
<b>B</b> <sub>3</sub>	9	Cr 105.5 N 113.1 I 110.7 N 92.1 SmA 84.3 Recr
<b>B</b> <sub>4</sub>	10	Cr 106.7 SmA 112.6 N 121.4 I 119.8 N 110.0 SmA 84.3 Recr
<b>B</b> <sub>5</sub>	12	Cr 103.8 SmA 115.5 I 113.9 SmA 86.1 Recr

Table 2. Transition temperatures by polarizing microscopy for compounds **A**<sub>4</sub>, **B**<sub>4</sub>, **C** and **D**. Cr, crystal; SmA, smectic A phase; N, nematic phase; I, isotropic phase.

Compound	<i>n</i> or <i>m</i>	Transition temperatures/ $^{\circ}\text{C}$
<b>A</b> <sub>4</sub>	10	Cr 116.7 SmA 124.4 N 136.1 I 135.1 N 123.5 SmA 113.3 Recr
<b>B</b> <sub>4</sub>	10	Cr 106.7 SmA 112.6 N 121.4 I 119.8 N 110.0 SmA 84.3 Recr
<b>C</b>	10	Cr 100.0 SmA 111.0 N 149.9 I 147.3 N 120.1 SmA 87.5 Recr
<b>D</b>	10	Cr 80.7 SmA 140.5 N 142.8 I 141.8 N 139.4 SmA 56.0 Recr

the transition temperatures of compounds **A**<sub>4</sub>, **B**<sub>4</sub>, **C** and **D** in table 2. The tetrafluorophenylene in compounds **C** and **D** is at the centre of the core unit, whereas in compounds **A**<sub>4</sub> and **B**<sub>4</sub> it is at the side of the core unit in the molecule. The clearing points of compounds **C** and **D** are higher than those of compounds **A**<sub>4</sub> and **B**<sub>4</sub>, and the melting points lower. So the transition temperature ranges of compounds **C** and **D** are larger than those of compounds **A**<sub>4</sub> and **B**<sub>4</sub>. This indicates that the central tetrafluorophenylene group position favours enlargement of the mesomorphic temperature ranges. Comparing compound **C** with **D**, it can be seen that the clearing point and melting point of **C** are higher than those of **D**, but the transition temperature range of the latter is larger than that of the former. So it can also be concluded that, when the tetrafluorophenylene is at the centre of the core unit, the compounds with the polar  $\text{NO}_2$  group possess better mesomorphic properties than those with the CN group.

#### 5. Conclusions

We have synthesized and studied the properties of four homologous series of 4-cyanophenyl or 4-nitrophenyl 4-*n*-alkoxyl-tetra fluorobiphenyl-4'-carboxylates. With the increase of alkoxy chain length, the tendency to show the nematic phase decreases and the tendency to exhibit smectic properties increases. As far as the effects of polar end groups are concerned, the CN group favours mesomorphic stability when the tetrafluorophenylene group is at the side of the core unit in the molecule, while the  $\text{NO}_2$  group is more effective when the tetrafluorophenylene is at the centre. As to the influence of tetrafluorophenylene group position in the rigid core, the central position is effective for increasing mesomorphic temperature ranges.

The authors gratefully acknowledge the financial support of the National Natural Science Foundation of China.

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