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# Synthesis and characterization of novel fluorinated bistolane-type liquid crystals

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Three series of fluorinated bistolane-type liquid crystals have been synthesized. Their mesomorphic properties were studied by optical polarizing microscopy and DSC. These compounds exhibit only a broad nematic phase with high clearing points, wide phase transition temperatures and low melting points. The effects of lateral fluoro-substitution and the introduction of the tetrafluorophenylene moiety are discussed in detail.

## 1. Introduction

Liquid crystals (LCs) with large birefringence are potentially useful for incorporation into electro-optic devices including various display configurations. We are particularly interested in synthesizing new liquid crystals with large birefringence [1, 2] for applications in flat panel liquid crystal displays that operate by a reflecting or scattering mechanism [3, 4]. From the single band model, the $\Delta n$ of a liquid crystalline compound is determined mainly by its molecular conjugation, differential oscillator strength and order parameter. Molecules that contain high polarizability groups with high electron density, such as benzene rings or acetylene linking groups, will therefore have high optical anisotropy [5]. Some diphenyl-diacetylene LCs have been reported in the literature [5–8], but their melting points are extraordinarily high ($>200$°C) or their phase transition temperature ranges are extremely narrow [9]. Fluorinated LC compounds [10, 11] are known for their modest dielectric anisotropy and low viscosity. In this paper, we report synthesis processes and mesomorphic properties for three series of bistolane LCs containing lateral fluoro-substituents. The synthesis schemes are described in § 2. Detailed structure–property relationships for these compounds are discussed in § 3.

## 2. Experimental

### 2.1. *Characterization techniques*

The structures of intermediates and final compounds were eclucidated by spectral methods. IR spectra were determined on a PE-983G spectrometer using the KBr disc method. $^1$H NMR spectra, with TMS as the internal standard and $CDCl_3$ as the solvent, were run on an FX-90Q (90 MHz) spectrometer. $^{19}$F NMR spectra, with trifluoroacetic acid (TFA) as external standard and $CDCl_3$ as the solvent, were recorded on a Varian EM 360L (56.4 MHz) spectrometer (high field positive). MS spectra were measured with a Finnigan 4021 Spectroscope. The phase transition temperatures of the target compounds were measured visually by optical microscopy using a polarizing Olympus PM-6 microscope fitted with a Mettler FP-80 heating stage and an FP-82 control unit, and by differential scanning calorimetry (DSC, Shimadzu DSC-50 calorimeter with a data system) with heating and cooling rates of 5°C $\min^{-1}$. The transition temperatures shown in this paper are the peak values of the transition on DSC traces. Phase identification was made by comparing the observed textures with those reported in the literature [12, 13].

### 2.2. *Synthesis of fluoro-substituted bistolanes*

The scheme illustrates the procedures used to synthesize the target compounds. The 4-*n*-alkoxyphenylacetylene and 4-*n*-alkoxy-2,3,5,6-tetrafluorophenylacetylene compounds were prepared by reported methods [14, 15]. Compound **1** was prepared from 4-*n*-pentoxyphenylacetylene and 3,5-difluoro-1-iodobenzene used $Pd(PPh_3)_2Cl_2$ and CuI as catalyst.

Compound **1** reacted with iodine at the presence of BuLi as base to give compound **2**. By the coupling reaction of 4-*n*-pentoxyphenyl acetylene with 4-iodoaniline using $Pd(PPh_3)_2Cl_2$ as catalyst compound **3** was obtained. Oxidation by $NaNO_2$ in conc. HCl and addition of KI at 0°C affored compound **4**. The target compounds **A**, **B** and **C** could be obtained by the coupling reaction of compounds **2** or **4** with 4-*n*-alkoxyphenylacetylenes and

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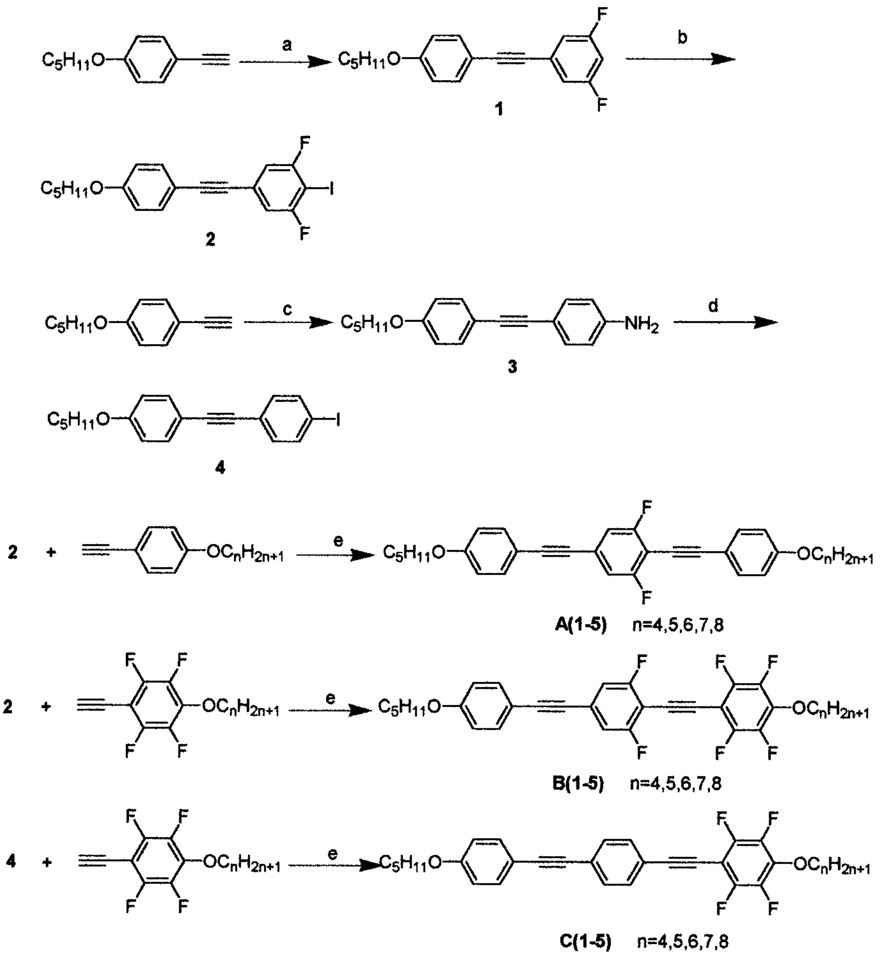

Conditions and Reagents: (a) 3,5-difluoro-1-iodobenzene, $Pd(PPh_3)_2Cl_2$, CuI, $Et_3N$. (b) $^nBuLi$, $I_2$, −78°C-r.t. (c) 4-iodoaniline, $Pd(PPh_3)_2Cl_2$, CuI, $Et_3N$. (d) $NaNO_2$, con.HCl, KI, THF. (e) $Pd(PPh_3)_2Cl_2$, CuI, $Et_3N$.

Scheme. Synthesis of laterally fluorosubstituted bistolane compounds.

4-*n*-alkoxy-2,3,5,6-tetrafluorophenylacetylenes, respectively, using $Pd(PPh_3)_2Cl_2$ as catalyst. All final compounds were purified by chromatography on silica gel with petroleum ether (b.p. 60–90°C)/dichloromethane (8:1) as eluent, and were recrystallized from petroleum ether.

### 2.2.1. *Synthesis of 4-n-pentoxy-3′,5′-difluorotolane (1)*

In a 250 ml dry three-necked flask equipped with a magnetic stirring bar, a nitrogen inlet and a bubbler, were placed 4-*n*-pentoxyphenylacetylene (5.0 g, 26.6 mmol), 3,5-difluoro-1-iodobenzene (5.32 g, 22.2 mmol), $Pd(PPh_3)_2Cl_2$ (0.2 g, 0.29 mmol) and CuI (0.1 g). The reaction system was filled with dry nitrogen, and 100 ml of anhydrous triethylamine was added under nitrogen. The resulting mixture was stirred at 30–40°C for 24 h; the whole process was tracked by TLC and revealed a complete reaction. The precipitate was then filtered off and extracted with ether. The filtrate was washed with water, and dried over anhydrous sodium sulphate. The solvent was removed under vacuum and the residue purified by column chromatography on silica gel using petroleum ether (b.p. 60–90°C)/dichloromethane (4:1) as eluent to give pale yellow crystals. The product was recrystallized from petroleum ether to give white flaky crystals; yield 7.23 g (91%). $\delta_H$ 7.56–7.18 (m, 7H), 4.01 (t, 2H, $J = 5.4$ Hz), 1.90–1.34 (m, 6H), 1.02 (t, 3H, $J = 3.7$ Hz) ppm; $\delta_F$ 32.6 (m, 2F) ppm.

### 2.2.2. *Synthesis of 4-n-pentoxy-3′,5′-difluorotolane (2)*

Compound **1** (7.32 g, 24.1 mmol) was dissolved in THF (84 ml) and cooled to −78°C. $^nBuLi$ (2M, 13.3 ml) was added dropwise with stirring and the mixture was further stirred at −78°C for 1.5 h. Iodine (6.73 g) dissolved in THF (56 ml) was then added dropwise, and the reaction mixture allowed to reach room temperature and stirred for 10 h. Portions of saturated aqueous ammonium chloride were added to heat the reaction. The organic materials was extracted into ether and dried over anhydrous sodium sulphate. The solvent was removed under vacuum and the crude product purified by column chromatography on silica gel using petroleum ether (b.p. 60–90°C) as eluent to give white crystals; yield 5.8 g (57%). $\delta_H$ 7.48–6.82 (m, 6H), 3.98 (t, 2H, $J = 5.5$ Hz), 2.01–1.27 (m, 6H), 0.95 (t, 3H, $J = 3.6$ Hz) ppm; $\delta_F$ 16.5 (m, 2F) ppm.

### 2.2.3. *Synthesis of 4-n-pentoxy-4′-aminotolane (3)*

Compound **3** was prepared by a procedure similar to that used for compound **1**; yield 5.84 g, (79%). $\delta_H$ 7.42–6.61 (m, 8H), 3.88 (t, 2H, $J = 5.5$ Hz), 3.61 (br, 2H), 1.79–1.27 (m, 6H), 0.86 (t, 3H, $J = 3.7$ Hz) ppm.

### 2.2.4. *Synthesis of 4-n-pentoxy-4′-iodotolane (4)*

Compound **3** (2.8 g, 10.04 mmol) was dissolved in THF (15 ml) and cooled to 0°C; a mixture of conc. HCl (5.5 ml) and 40 wt% aqueous sodium nitrite (6.1 ml) was then added. The solution was stirred at 0°C for 30 min and then treated with 6M aqueous KI (17.3 ml). The resulting mixture was stirred at 0°C for 3 h, treated with saturated aqueous sodium thiosulphate (20 ml) and shaken with *n*-hexane. The *n*-hexane solution was washed with water and saturated brine, and dried over anhydrous sodium sulphate. After the solvent was removed under vacuum, the crude product was purified by column chromatography on silica gel using petroleum ether (b.p. 60–90°C) as eluent to give white crystals; yield 1.8 g (50%). $\delta_H$ 7.63–7.72 (m, 8H), 3.87 (t, 2H, $J = 5.4$ Hz), 1.17–1.79 (m, 6H), 0.86 (t, 3H, $J = 3.8$ Hz) ppm.

### 2.2.5. *Synthesis of bistolanes with fluorosubstituent A(1–5), B(1–5), C(1–5)*

The target compounds **A**(**1**–**5**), **B**(**1**–**5**) and **C**(**1**–**5**) were all prepared by coupling of the 4-*n*-alkoxyphenylacetylene or 4-*n*-alkoxy-2,3,5,6-tetrafluorophenylacetylene with compounds **2** and **4** respectively, using procedures synthetic similar to those given for compound **1**. All of the new target compounds had satisfactory elemental analysis and appropriate $^1$H and $^{19}$F NMR, IR and MS spectral data.

## 3. Results and discussion

### 3.1. *Effect of terminal alkoxy chain length*

The phase transition temperatures of the compounds in series **A**, **B** and **C** are listed in the table and figures 1–3. All the compounds give an enantiotropic nematic phase.

Table. Phase transition temperatures of series **A**, **B**, and **C** compounds. Cr = crystal, N = nematic phase, I = isotropic liquid, Recr = recrystallization.

| Compound | *n* | Transition temperature/°C |
|---|---|---|
| **A1** | 4 | Cr 115.0 N 214.3 I 212.6 N 110.1 Recr |
| **A2** | 5 | Cr 103.9 N 203.1 I 201.5 N 93.0 Recr |
| **A3** | 6 | Cr 90.2 N 193.4 I 192.0 N 87.3 Recr |
| **A4** | 7 | Cr 97.8 N 195.4 I 194.1 N 89.4 Recr |
| **A5** | 8 | Cr 94.5 N 191.5 I 190.1 N 82.2 Recr |
| **B1** | 4 | Cr 109.4 N 201.1 I 199.6 N 102.7 Recr |
| **B2** | 5 | Cr 102.5 N 191.8 I 190.5 N 95.4 Recr |
| **B3** | 6 | Cr 101.1 N 186.7 I 185.4 N 95.6 Recr |
| **B4** | 7 | Cr 99.3 N 179.5 I 178.5 N 93.0 Recr |
| **B5** | 8 | Cr 101.8 N 176.1 I 174.4 N 94.8 Recr |
| **C1** | 4 | Cr 82.5 N 211.0 I 209.8 N 74.4 Recr |
| **C2** | 5 | Cr 70.2 N 196.8 I 194.6 N 53.9 Recr |
| **C3** | 6 | Cr 70.8 N 196.4 I 195.0 N 62.1 Recr |
| **C4** | 7 | Cr 91.1 N 188.7 I 187.5 N 66.9 Recr |
| **C5** | 8 | Cr 101.4 N 184.5 I 183.4 N 87.0 Recr |

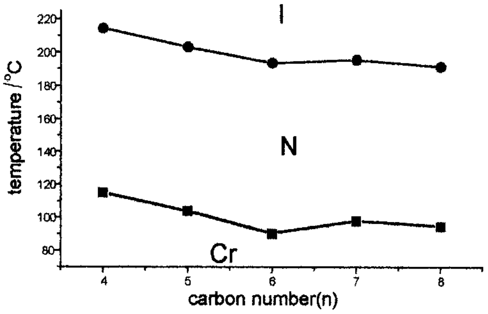

Figure 1. Melting and isotropization temperatures of compounds **A**.

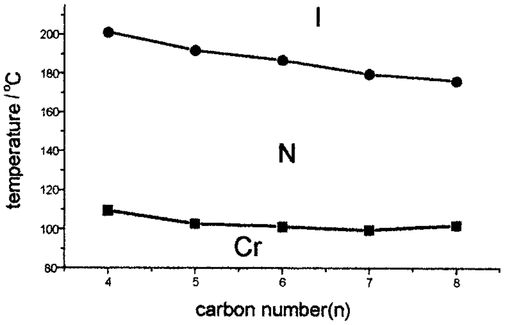

Figure 2. Melting and isotropization temperatures of compounds **B**.

Compounds **A1**–**5** possess the same mesogenic core. The only difference among them is the length of the terminal alkoxy group at one end. In general, these compounds give very high clearing points ranging from 191 to 214°C. Each compound also has a very wide

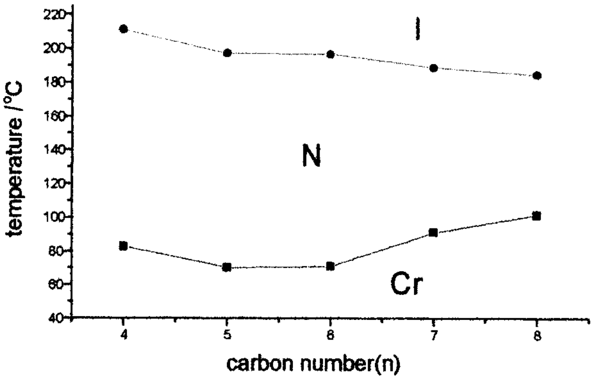

Figure 3. Melting and isotropization temperatures of the compounds **C**.

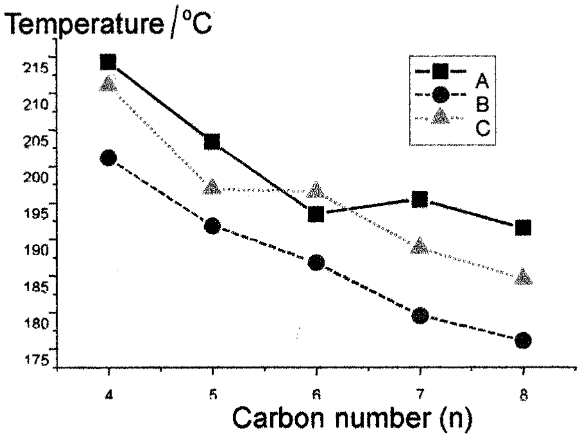

Figure 4. Clearing points of the three series of compounds **A**, **B**, **C**.

nematic phase range (>97°C). Figure 1 gives a plot of the phase transition temperature versus carbon number (*n*) of the terminal alkoxy group and demonstrates that both melting and clearing points decrease gradually with increasing *n*.

Compounds **B1**–**5**, have a tetrafluorophenyl group. This series also exhibits high clearing points ranging from 176–201°C. Each compound exhibits a wide temperature range nematic phase (>74°C). Figure 2 gives a plot of the phase transition temperatures versus the carbon number of the end alkoxyl group, demonstrating that both the melting and clearing points decrease gradually with increase of *n*.

Compounds **C1**–**5**, have no fluorosubstituents in the middle phenyl ring. They have very high clearing points, in the range 184–211°C. Each compound has a very wide temperature range nematic phase (>83°C). Figure 3 demonstrates that clearing points decrease with increasing *n* while the melting points decrease gradually at first and then increase.

### 3.2. *Effect of the lateral fluorosubstituents*

The table summarizes transition temperatures for the three series of compounds **A**, **B** and **C**, while figure 4 gives a combined plot of the clearing points of the compounds versus the carbon number (*n*) of the end alkoxyl group. All the compounds exhibit an enantiotropic nematic phase. From the table and figure 4, we find that the lateral fluorosubstituents have a great influence on the mesomorphic properties of the liquid crystals. With the same *n* in the three series the melting points of compounds **B** are lowest, those of compounds **C** highest. Clearing points are in the order: compounds **A** > compounds **C** > compounds **B**.

Bistolane-type liquid crystals have a large degree of conjugation, and high thermal stability. When fluorine atoms are introduced into this structure, they interact each other or with a hydrogen atom because of its great electronegativity. The repulsion between the fluorine and hydrogen atoms, or between fluorine atoms, will result in a twisting effect and thickening of the molecule, or to the adoption of a broader molecule structure [16]; the nematic thermal stability thus decreases gradually with increase of carbon number. The introduction of the tetrafluorophenylene moiety decreases melting and clearing points as a result of the lateral fluorosubstituents in the side phenyl ring.

## 4. Conclusion

Three series of laterally substituted bistolane LCs were synthesized and characterized. All the bistolanes display enantiotropic nematic phases. The terminal alkoxyl groups have a profound effect on the phase transition temperature of the bistolanes; clearing points decrease as the alkoxy chain length increases. The tetrafluorophenylene moiety plays an important role in lowering the melting points. These bistolanes liquid crystals could find useful application in LC displays.

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